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Development of new methodologies for the measurement of radionuclides by gamma-ray spectrometry using detectors

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**DEVELOPMENT OF NEW METHODOLOGIES FOR THE
MEASUREMENT OF RADIONUCLIDES BY GAMMA-RAY
SPECTROMETRY USING GE DETECTORS**

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This Thesis is presented to fulfil the requirements of the Official PhD programme in Industrial and Environmental Science and Technology of the University of Huelva and to obtain the title of DOCTOR.

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DECLARE: that the Doctoral Thesis called "Development of new methodologies for the measurement of radionuclides by gamma-ray spectrometry using Ge detectors", has been carried out by Mr. ALEJANDRO BARBA LOBO in the Department of Integrated Sciences of the University of Huelva under their supervision, to obtain the title of Doctor of the University of Huelva

Huelva, December 2022

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RESUMEN

El impacto ambiental causado por contaminantes, como radionucleidos, liberados a través de diferentes fuentes de contaminación, es actualmente un tema de preocupación general, lo cual hace que los controles de los niveles de radiactividad sean más exhaustivos. Además, el riesgo radiológico potencial causado por la exposición a la radiación también es un tema que ha cobrado mayor importancia en las últimas décadas. Esto hace que tengan que aplicarse regulaciones estrictas en general a los diferentes lugares de trabajo y materiales de construcción, y para ello el análisis de radionucleidos es fundamental para evaluar los riesgos radiológicos asociados a las actividades humanas. Por tanto, esta Tesis tiene como objetivo desarrollar nuevas metodologías para determinar radionucleidos tanto naturales como artificiales mediante espectrometría gamma para una amplia variedad de matrices y geometrías.

Para ello, se ha desarrollado un método nuevo y exhaustivo de calibración para obtener la eficiencia de pico de absorción total (*FEPE*) para muestras volumétricas en el caso de geometrías cilíndricas, para cada energía de emisión gamma (E_γ), como una función del espesor (h), densidad aparente (ρ) y composición de la matriz, para un detector de HPGe de rango extendido (XtRa). Los patrones certificados de calibración seleccionados contienen solamente radionucleidos naturales pertenecientes a las series del ^{238}U y ^{232}Th , así como ^{40}K ; códigos RGU-1, RGTh-1 y RGK-1 del Organismo Internacional de Energía Atómica (IAEA). Para detectores de tipo pozo, se ha desarrollado también una metodología novedosa para la calibración en eficiencia, la cual está basada en la obtención de una función general de *FEPE*, variando la densidad aparente y composición de los patrones de calibración, manteniendo h constante. Para ello, se usaron el RGU-1, RGTh-1, KCl, PbS y carbón activado.

Para medir de una forma apropiada *FEPE* para muestras problema cuya composición química y densidad aparente fueran muy diferentes a las de las muestras de calibración, se necesitaron las correcciones debidas a efectos de autoabsorción. Para ello, se usó el factor de corrección por autoabsorción (f_a), el cual hace necesario obtener una función general para el coeficiente de atenuación másico. Para calcular f_a , fue también necesario usar modelos de corrección por autoabsorción.

En algunos casos, las correcciones debidas a efectos verdaderos de suma por coincidencias (TCS) fueron esenciales para el cálculo de *FEPE*. Para ello, se ha abordado un nuevo método para corregir efectos TCS, variando la distancia muestra-detector (d), encontrándose un valor de d para el cual la función obtenida de *FEPE* proporcionó el mejor ajuste para las *FEPEs* experimentales corregidas. Todas las metodologías desarrolladas para el cálculo de *FEPE* fueron sometidas a validaciones tanto externas como internas haciéndose uso de materiales certificados y no certificados, respectivamente. Además, la validez de las correcciones de efectos de autoabsorción proporcionadas por los modelos de Cutshall y Appleby fueron analizadas en profundidad.

Se ha llevado a cabo una metodología nueva y general para la calibración en eficiencia de detectores coaxiales de Ge para la medida de radionucleidos usando diferentes geometrías de filtros de aerosoles atmosféricos. Para ello, se escogieron el RGU-1, RGTh-1 y RGK-1, permitiéndonos reproducir la misma geometría de deposición de la materia particulada. Asimismo, para filtros cuya superficie fueran relativamente grandes, éstos se cortaron en diversos trozos y fueron colocados uno encima del otro. Esto hace que sea más fácil conseguir la misma geometría que la resultante de doblar un filtro problema para medirse. Después, se validó la función general de *FEPE* dependiente de E_γ , encontrada para cada tipo de filtro.

Asimismo, se ha desarrollado una metodología novedosa y precisa para medir los descendientes de corta semivida del ^{222}Rn y ^{220}Rn (^{214}Pb y ^{214}Bi , y ^{212}Pb y ^{212}Bi , respectivamente), para lo cual se empleó un captador de muy alto volumen. Esta metodología se aplicó a la estimación de tiempos de residencia de aerosoles usándose los cocientes de actividades del $^{214}\text{Pb}/^{222}\text{Rn}$ y $^{212}\text{Bi}/^{212}\text{Pb}$, y para la obtención de factores de equilibrio, consiguiéndose resultados consistentes. La consistencia y reproducibilidad de la metodología fueron comprobadas para diferentes duraciones de muestreo y recuento. En el caso del ^{212}Bi y ^{214}Bi , se encontraron los tiempos totales para poder ser medidos con precisión.

ABSTRACT

The environmental impact caused by pollutants, like radionuclides, released from different pollution sources, is currently of general concern, making controls for radioactivity levels be more exhaustive. Moreover, the potential radiological risk caused by the exposure to radiation is also an issue that has become more important in the last decades. This makes strict regulations have to be generally applied to different working places and building materials, and for that the analysis of radionuclides is essential to assess the radiological risks associated to the human activities. Therefore, this Thesis aims to develop new methodologies to determine both natural and artificial radionuclides by gamma-ray spectrometry for a wide variety of sample matrices and geometries.

For this, a new and comprehensive calibration method to obtain the full-energy peak efficiency (*FEPE*) for volume samples in the case of cylindrical geometries, at each gamma emission energy (E_γ), as a function of the thickness (h), apparent density (ρ) and matrix composition has been developed for an extended range (XtRa) HPGe detector. The selected certified calibration standards contain only natural radionuclides belonging to the ^{238}U series and ^{232}Th series as well as ^{40}K ; codes RGU-1, RGTh-1 and RGK-1 from the International Atomic Energy Agency (IAEA). For well-type detectors, a novel methodology for the efficiency calibration has also been developed, based on obtaining a general *FEPE* function varying the apparent density and composition of the calibration standards, keeping h constant. For this, RGU-1, RGTh-1, KCl, PbS and activated carbon were used.

To properly obtain the *FEPE* for problem samples whose chemical compositions and apparent densities were very different from those related to calibration samples, corrections due to self-absorption effects were needed. For this, the self-absorption correction factor (f_a) was used, which made necessary to obtain a general function for the mass attenuation coefficient. To calculate f_a , it was also necessary to use self-absorption correction models.

In some cases, the corrections due to true coincidence summing (TCS) effects were found to be essential for the *FEPE* calculation. For this, a novel method to correct the TCS effects has been addressed, varying the sample-detector distance (d), finding a d for which the obtained *FEPE* function provided the best fit for the corrected experimental *FEPE*s. All the methodologies developed to calculate the *FEPE* were subjected to both internal and external validations by using several certified and non-certified materials, respectively. Moreover, the validity of the self-absorption effect corrections provided by the Cutshall, and Appleby models were analyzed in depth.

A new and general methodology for efficiency calibration of coaxial Ge detectors has been accomplished for the measurement of radionuclides using different geometries of atmospheric aerosol filters. For this, RGU-1, RGTh-1 and RGK-1 were chosen, allowing us to reproduce the same particulate matter deposition geometry. Furthermore, for filters whose surfaces were relatively large, they were cut in several pieces and placed one on top of the other. This makes easier to achieve the same geometry as that resulting from folding a problem filter to be measured. Then, the general *FEPE* function depending on E_γ , found for each filter type, was validated.

In addition, a new and precise methodology to measure the ^{222}Rn and ^{220}Rn short-lived daughters (^{214}Pb and ^{214}Bi , and ^{212}Pb and ^{212}Bi , respectively) has been developed, where a very high-volume sampler was used. This methodology was applied to estimate aerosol residence times using the $^{214}\text{Pb}/^{222}\text{Rn}$ and $^{212}\text{Bi}/^{212}\text{Pb}$ activity ratios, and to obtain equilibrium factors, achieving consistent results. The consistency and reproducibility of the methodology were tested for different sampling and counting times. In the case of the ^{212}Bi and ^{214}Bi , the total times for their precise measurement were found.

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Chapter 1: Introduction

1.1. BACKGROUND AND MOTIVATION

In the last decades, the environmental damage generated by the releases of radioelements (also named as radionuclides) and the radiological risk related to ionizing radiations have become an issue of general concern. Nowadays, exhaustive controls for radioactivity levels and exposure to radiation present in different working places such as mining, fertilizer and pigment industries, waste landfills, etc., must be applied according to the established radiological regulations (Chambers, 2015; European Commission, 1983). The previous sample types usually contain relatively high concentrations of radionuclides which makes necessary to consider them as NORM (Naturally Occurring Radioactive Material) or TENORM (Technologically Enhanced NORM) and, therefore, a careful control of their potential radiological impact is required. In the case of the building materials, they are also currently subjected to strict regulations for their radiological risk assessment, allowing us to know parameters of interest such as the activity concentration index (European Commission, 1983), the radium-equivalent activity (Ravisankar et al., 2012), and the external and internal radiation hazards (Szabó et al., 2013).

The analysis of radionuclide concentrations and radiation exposure is also usually carried out for the particulate matter (PM) present in atmospheric aerosols. This is very useful to keep an air quality control and because of their direct relationship with human health impact due to the radiation emitted by the radionuclides after the PM inhalation, which may affect different body organs, causing severe health problems (Macias-Verde et al., 2021; Yu et al., 2006). In order to collect the PM, different types of air samplers are selected according to the PM size, where PM_{2.5} and PM₁₀ are widely employed (Dueñas et al., 2009; Ordúz et al., 2012). During the sampling, the PM is deposited onto the atmospheric filters chosen for each sampler type, where there is a wide variety of atmospheric filter types depending on their dimensions and geometry.

For the assessment of the radiation exposure in the case of atmospheric aerosols, the equilibrium factors (F_{eq}) of radon isotopes (^{222}Rn (radon, half-life = 3.8 days) and ^{220}Rn (thoron, half-life = 56 s)), which belong to the ^{238}U series and ^{232}Th series, respectively, are very useful to be known since they are related to internal dose rate. The F_{eq} depend on the concentrations of the radon isotopes as well as the concentrations of their respective short-lived progenies (Nader, 2019), which makes the F_{eq} determinations be complicated because of the relatively short half-lives of the radon and thoron progenies (1-10 h and 3-27 min, respectively). The F_{eq} of the radon and thoron can be defined as the ratio of the measured PAEC and the PAEC when all radon decay products are in secular equilibrium with radon and thoron, respectively, where the PAEC is the potential alpha energy concentration of their progenies (UNSCEAR, 2000; Vargas et al., 2016). Furthermore, the radon and thoron progenies are also very useful to estimate the residence times (T_r) of atmospheric aerosols, allowing us to know the time that the radionuclides present in the aerosols last to be deposited on the surface of a specific region. Therefore, T_r can provide us the time during which the probability to inhale those radionuclides, that are attached to the atmospheric aerosol particles, is higher in that region.

These previous motivations are ones of the many reasons why the determination of radionuclides has been studied for last decades in several study fields related to the environmental sciences. They can be employed for multiple applications such as the calculation of external and internal dose rates (Balakrishnan et al., 2021), the trace of atmospheric process (Abdo et al., 2021), the estimation of aerosol residence times (Baskaran and Shaw, 2001), the classification of materials as NORM according to their concentrations of radionuclides (Barba-Lobo et al., 2022b), etc. Consequently, the proper determination of radionuclides contained in industrial and environmental samples is essential to be studied in depth for a wide range of chemical compositions, apparent densities and geometries.

The radionuclides are unstable forms of chemical elements that have an excess of nuclear energy and decay to another radionuclide (daughter radionuclide) or to a stable isotope. In the decay process, a particle (alpha ($^4\text{He}^{2+}$), positron or electron, or photon) is ejected from the atomic nucleus according to the type of radiation emitted (α , β (β^+ or β^-) or γ , respectively). The natural radionuclides that are widely studied because of their numerous applications within environmental sciences and many other study fields are those belonging to the ^{238}U series and ^{232}Th series, as well as ^{40}K , while in the case of the artificial radionuclides, there are several ones of interest such as ^{241}Am , ^{152}Eu , $^{137, 134}\text{Cs}$, ^{133}Ba and $^{60, 57}\text{Co}$. Their respective decay modes and schemes can be consulted in (DDEP, 2017). Therefore, depending on the radiation emitted by the radionuclides, it is necessary to select a radiometric technique by which it is possible to measure them.

The alpha-particle spectrometry is the radiometric technique based on the detection of the α -particle radiation, and it is characterized by being a destructive technique due to the need for applying a radiochemical method (Pérez-Moreno et al., 2019), which allows us to separate the different isotopes of interest prior their respective measurements. In the case of the β -particle radiation, the techniques based on liquid scintillation counting (LSC) or Cherenkov radiation are usually employed (Mosqueda, 2009), for which it is also necessary to make use of a previous radiochemical method to extract the desired beta emitters. However, for the measurement of γ -ray radiation by gamma-ray spectrometry, only a relatively simple physical pretreatment of the sample is required, making it a non-destructive technique, and without needing to separate the radioisotopes of interest. When applying gamma-ray spectrometry for the determinations of radionuclides, Ge detectors are generally used because of their relatively good energy resolution in comparison with other gamma detector types such as NaI(Tl) or LaBr₃(Ce), whose energy resolution are low and medium, respectively. The energy resolution is very useful in order to be able to properly distinguish different full-energy peaks formed in the gamma spectra that are very closed to each other.

For an accurate measurement of radionuclides by gamma-ray spectrometry, the full-energy peak efficiency (*FEPE*) obtention needs to be carefully addressed. The *FEPE* can be defined as the ratio of the net counts of a full-energy peak and the number of photons coming out from the sample that are emitted at the energy E_γ , where E_γ is the centroid of that full-energy peak (Bolívar, 1995). The methodologies for the *FEPE* calculation, that have been developed from about 1980 to 2000, are generally based on varying E_γ for punctual gamma sources or volume sources with fixed thicknesses (Bolívar et al., 1996; Debertain and Helmer, 1988; Gilmore and Hemingway, 1995). In the last two decades, the number of works on obtaining the *FEPE* by using simulation codes such as Geant or Geant4 (Laborie et al., 2000; Quintana and Montes, 2014), DETEFF (Díaz and Vargas, 2010), EFFTRAN (Vidmar et al., 2011), PENELOPE (Peyres and García-Toraño, 2007), LabSOCS (Suárez-Navarro et al., 2020) and MCNP (Maurotto et al., 2009) is increasing. In addition, for the great majority of the methods experimentally developed for volume samples, an efficiency calibration is carried out for each sample matrix type, which increases the costs and time consumption.

The *FEPE* also needs to be properly obtained for samples whose chemical compositions and apparent densities are very different from those related to the calibration samples since the *FEPE* depends on the sample matrix type. These dissimilarities are due to the so-called self-absorption effects of the photons emitted from the different layers of the volume samples (Carrazana et al., 2010). Consequently, to transform the *FEPE* referred to the calibration sample (ε_c) to that related to any problem sample (ε_p), it is necessary to apply the self-absorption effect correction factor (f_a). The self-absorption effects mainly depend on four variables: the energy (E_γ), and the thickness (h), apparent density (ρ) and mass attenuation coefficient (η) of the analyzed sample. The η depends on the E_γ and the chemical composition of the sample. The sample η depends, in turn, on each mass attenuation coefficient (η_i) of each chemical element (i) present in the sample, which are related to each other by

an equation (Pérez-Moreno et al., 2002). Since η_i decreases as E_γ increases, the self-absorption effects are more relevant as E_γ decreases, making the corrections given by the f_a factor be essential for low energies, that is, $E_\gamma < 150$ keV (Eke and Boztosun, 2014; San Miguel et al., 2002). For this reason, ^{234}Th and ^{210}Pb as well as ^{241}Am and ^{57}Co are relatively more difficult to be properly measured in the case of the natural and artificial radionuclides, respectively, since their E_γ with the highest gamma emission probabilities are 63.3 keV, 46.5 keV, 59.5 keV and 122.1 keV, respectively.

When obtaining the *FEPE* varying E_γ , there is another problem that is necessary to address for the *FEPE* calculation, which is the presence of true coincidence summing (TCS) effects for certain E_γ belonging to different radionuclides such as ^{214}Bi , ^{208}Tl , ^{152}Eu , $^{137, 134}\text{Cs}$ and $^{60, 57}\text{Co}$. The TCS effects take place when at least two photons with different E_γ are simultaneously emitted, and the electronics connected to the gamma-ray detector is not able to distinguish between them. Nowadays, for volume samples, the use of the simulation codes previously mentioned has become generalized to correct TCS effects (Ahmed, 2019; Laborie et al., 2002; Zhu et al., 2009) since it is relatively complicated to experimentally correct TCS effects due to the numerous factors involved in this correction type such as the sample-detector distance, the chemical composition and apparent density of the sample, etc. However, their usage requires a relatively high computational cost as well as the need for characterizing the gamma-ray detectors, which makes the detector be inoperative during the characterization process, where this procedure also implies relatively high costs. Therefore, accurate methodologies to experimentally correct TCS effects would be a very proper alternative option.

1.2. OBJECTIVES

Considering everything previously mentioned, the main objective of this Thesis was to develop new methodologies for the measurement of natural and artificial radionuclides by gamma-ray spectrometry.

To achieve the main objective, the following specific objectives were established:

1. To develop new methodologies to calibrate in efficiency different Ge detector types for volume samples varying the sample mass (or thickness) and fixing the energy, obtaining a semiempirical efficiency function.
2. To properly correct self-absorption effects for a wide range of sample matrixes, apparent densities, geometries and energies by using an analytical correction function.
3. To experimentally correct true coincidence summing effects when calibrating in efficiency varying the energy for different sample types, obtaining a general and analytical efficiency function.
4. To develop new methodologies to determine radionuclides present in atmospheric aerosols by using different atmospheric filter types.
5. To develop new methodologies to precisely determine short-lived radionuclides in atmospheric aerosol in order to estimate the radon and thoron equilibrium factors and the aerosol residence times.

1.3. OUTLINE

This manuscript is organized into four chapters. The first chapter introduces the research developed in this Doctoral Thesis, where the background and motivation are included to provide an overview of

previous works and a justification of the objectives pursued, respectively. The main objectives as well as the structure of the Thesis are also presented.

The second chapter shows a general description of all methodologies employed in this Thesis for the determinations of radionuclides for a wide variety of sample matrices, geometries and energies. This also provides a general methodology to determine radionuclides for any sample matrix type. In addition, the experimental set up, that is, the materials and types of detectors and air samplers employed in order to develop the methodologies are also shown.

The third chapter of this Thesis presents the results and discussions, which are divided into six subchapters. Each one of these subchapters corresponds to a complete copy of the published scientific paper, in accordance with the Regulation of PhD studies from the University of Huelva, article 35, 2nd section, chapter IV. The six subchapters are the following ones:

The subchapter 3.1 develops an upgraded lab-based method to determine natural γ -ray emitters in NORM samples by using Ge detectors. This subchapter is focused on the development of an exhaustive calibration method for a XtRa detector, obtaining the full-energy peak efficiency (*FEPE*), for each gamma emission energy, as a function of the thickness, apparent density and matrix composition of the cylindrical sample. For this, certified calibration standards containing only natural radionuclides belonging to the ^{238}U - and ^{232}Th -series as well as ^{40}K (codes RGU-1, RGTh-1 and RGK-1 from the International Atomic Energy Agency (IAEA)) were selected. This study was published in Journal of the International Measurement Confederation (Measurement), where the short reference used for this study in the Thesis is Barba-Lobo et al., 2021a.

The subchapter 3.2 shows a general methodology to determine natural radionuclides by well-type HPGe detectors. For this, a novel methodology is developed, based on obtaining a general function for the full-energy peak efficiency (*FEPE*) versus the sample apparent density and composition, keeping the sample height constant. To obtain the general *FEPE* function, a comprehensive calibration in efficiency is accomplished using numerous mixtures of certified standards provided by IAEA (RGU-1 and RGTh-1) with activated carbon and PbS. In addition, KCl is used in the case of ^{40}K , where its K concentration is varied by dissolving it with acids. This study was published in Journal of the International Measurement Confederation (Measurement), where the short reference employed is Barba-Lobo et al., 2021b.

The subchapter 3.3 is focused on obtaining a general function for determining mass attenuation coefficients to correct self-absorption effects in samples measured by gamma spectrometry. For this, it is necessary to fit the tabulated values of the mass attenuation coefficients versus gamma energy in the range of 20 keV–2000 keV for each chemical element. This is the energy range for the majority of gamma emissions of natural radionuclides. Once those fittings for each chemical element, Z , from 1 (H) to 92 (U) are done, the parameters, that resulted from those fittings, are fitted versus the atomic number, Z . This work was published in Radiation Physics and Chemistry (Radiat. Phys. Chem.), where the short reference used is Barba-Lobo et al., 2021c.

The subchapter 3.4 addresses a practical and general methodology for efficiency calibration of coaxial Ge detectors. For this, a general function is obtained for the full-energy peak efficiency (*FEPE*) by gamma-ray spectrometry using coaxial Ge detectors. Then, the experimental *FEPE* values, obtained fixing the energy, E_γ , are fitted varying the thickness, h , of cylindrical standards. The parameters resulted from these fittings are fitted, in turn, versus E_γ , obtaining a general efficiency function, $\varepsilon_c(E_\gamma, h)$. Then, to correct TCS effects, a recalibration of the detector is carried out by varying the sample-detector distance, d , resulting the efficiency function $\varepsilon_c(E_\gamma, h, d)$, where this practical method is also employed to correct high self-absorptions and high dead times. This study was published in Journal

of the International Measurement Confederation (Measurement), using Barba-Lobo et al., 2022a as the short reference.

The subchapter 3.5 reports a new efficiency calibration methodology for different atmospheric filter geometries by using coaxial Ge detectors. For this, granular certified reference materials (CRM) containing only natural radionuclides (^{238}U -series, ^{232}Th -series and ^{40}K) are selected. Several granular solid CRMs are chosen allowing us to reproduce the same PM deposition geometry and to assure the homogeneity of the CRMs added to atmospheric filters with different geometries. Furthermore, for filters whose surfaces are relatively large, they were cut in several pieces and placed one on top of the other, achieving the same geometry than the PM deposited onto the filter. Then, a general *FEPE* function is found for each filter type. This research article was submitted to Air Quality, Atmosphere and Health (currently in first review).

The subchapter 3.6 addresses a methodology to determine ^{212}Pb , ^{212}Bi , ^{214}Pb and ^{214}Bi in atmospheric aerosols; application to precisely obtain aerosol residence times and Rn-daughters' equilibrium factors. For this, ^{222}Rn and ^{220}Rn are measured using a radon monitoring system, while their respective progenies are collected in an atmospheric filter using an ASS-500 sampler and measured by gamma-ray spectrometry. This methodology is applied to estimate aerosol residence times using the $^{214}\text{Pb}/^{222}\text{Rn}$ and $^{212}\text{Bi}/^{212}\text{Pb}$ activity ratios, and to obtain equilibrium factors. Furthermore, the methodology consistency and validity range were studied with time elapsed between sampling end and counting start, and the sampling durations, finding the optimum times to precisely determine ^{212}Pb , ^{212}Bi , ^{214}Pb and ^{214}Bi . This research article was submitted to Journal of Hazardous Materials (currently in second review).

The fourth chapter shows the main conclusions resulting from this Thesis, as well as the future lines of research. In addition, a list of all references used in this study is included at the end of this chapter.

Chapter 2: Methods and materials

2.1. METHODOLOGY DEVELOPED FOR EFFICIENCY CALIBRATION OF GAMMA DETECTORS

To generally proceed with the efficiency calibration by gamma-ray spectrometry, the *FEPE* is obtained for samples whose concentrations of radionuclides are known, which makes active CRMs be a very proper option, allowing us to quickly obtain the *FEPE* for the calibration sample (ε_c). The *FEPE* is calculated for each gamma emission energy (E_γ) of interest, selecting E_γ with the highest gamma emission probabilities (P_γ), achieving relatively high counting rates, and for which interference terms (I) can be neglected. Given that NORM samples are of especial interest for the radiological risk assessment in many different working places, as previously explained in Chapter 1.1, it is very recommendable to choose natural radionuclides for the calibration, such as those belonging to the ^{238}U series, ^{232}Th series as well as ^{40}K .

The experimental *FEPE* for the calibration sample can be determined at each E_γ as follows:

$$\varepsilon_c(E_\gamma, m_c) = \frac{G - B - F - I}{P_\gamma m_c a_c t} e^{\lambda \Delta t'} = \frac{N}{P_\gamma m_c a_c t} e^{\lambda \Delta t'} \quad (\text{Eq. 2.1.1})$$

where G, B, F, I and N are the total number (gross) of counts, the Compton continuum, the background due to environmental conditions in the laboratory, the interference term and the net counts, respectively, which all of them are referred to the same full-energy peak of interest. Then, P_γ is the gamma emission probability, a_c and m_c are the activity concentration and mass of the calibration sample, respectively, E_γ is the gamma emission energy (the centroid of the full-energy peak of interest), t is the counting time, λ is the decay constant of the radionuclide measured and $\Delta t'$ is the time elapsed between the reference date of the CRM and the counting start, where $e^{\lambda \Delta t'} \approx 1$ for long-lived radionuclides.

By using propagation of uncertainties in Eq. 2.1.1, it is possible to obtain the uncertainty associated to $\varepsilon_c(E_\gamma, m_c)$, which can be written as follows:

$$\sigma(\varepsilon_c) = \varepsilon_c \sqrt{\frac{N' + 2B + t^2 \sigma(f)^2}{(N' - ft)^2} + \frac{\sigma(P_\gamma)}{P_\gamma} + \frac{\sigma(m_c)}{m_c} + \frac{\sigma(a_c)}{a_c}} \quad (\text{Eq. 2.1.2})$$

where $N' = G - B$, f is the background (in cps), and $\sigma(P_\gamma)$, $\sigma(m_c)$, $\sigma(a_c)$ and $\sigma(f)$ are the uncertainties at 1 sigma level (68% of confidence interval) of P_γ , m_c , a_c and f , respectively. Note that in Eq. 2.1.2, the contributions of the interference term (I) and the decay constant (λ) were not considered because of being neglected when $I \sim 0$ and $e^{\lambda \Delta t'} \approx 1$, respectively, which usually occurs when selecting long-lived radionuclides, whose gamma emission energies are free of interferences, for the efficiency calibration.

In the case of varying mass (or thickness) of the sample when calibrating in efficiency, $\sigma(P_\gamma)$ and $\sigma(a_c)$ can be removed from Eq. 2.1.2 because of being systematic uncertainties.

Once the *FEPE* is calculated for each selected E_γ , it is necessary to determine the *FEPE* for any other sample (named as problem sample), allowing us to know the concentrations of radionuclides in any problem sample. The problem and calibration samples can be very dissimilar from each other considering their chemical compositions and apparent densities, which causes differences for the attenuation of photons coming out from layers at the same height for both samples. This makes essential to correct ε_c by the self-absorption correction factor (f_a), obtaining the *FEPE* for the problem sample (ε_p) as follows:

$$\varepsilon_p = f_a \varepsilon_c \quad (\text{Eq. 2.1.3})$$

In order to know the f_a factor, it is necessary to apply a self-absorption correction model.

In the case of coaxial detectors, e.g., XtRa detector, the Cutshall model (Cutshall et al., 1983) is usually employed. To apply this correction model, the geometry of the sample container must be of the cylindrical type, and the trajectory of the photons coming out from the sample needs to be parallel to the coaxial axis of the detector. This correction model is detailed in Chapter 3.1. The f_a equation, that allows us to apply the self-absorption correction by using this model, is the following one:

$$f_a = \frac{\eta_c \rho_c (1 - \exp(-\eta_p \rho_p h))}{\eta_p \rho_p (1 - \exp(-\eta_c \rho_c h))} \quad (\text{Eq. 2.1.4})$$

where η_c (η_p) and ρ_c (ρ_p) are the mass attenuation coefficient and the apparent density for the calibration (problem) sample, respectively, h is the sample thickness which is the same for the calibration and problem samples, which is due to the need for the calibration and problem samples to have the same geometry.

When using well-type detectors, the Appleby model (Appleby et al., 1992) is one of the most chosen corrections. For the usage of this model, the geometry of the sample container is required to be cylindrical, and the trajectory of the photons coming out from the sample needs to be parallel to the radial axis of the sample container. This correction model is widely studied in Chapter 3.2. For this case, f_a is written as follows:

$$f_a = 2 \exp(-kx^2) [(kx^2)^{-1} \sinh(kx^2) - (kx^2)^{-2} (\cosh(kx^2) - 1)] \quad (\text{Eq. 2.1.5})$$

where k is the geometric parameter characterizing the dimensions of the sample, which is given by $k = (\pi r H)^{-1}$, where r and H are the radius and thickness of the sample container used for the efficiency calibration procedure, respectively, and $x = m_p \eta_p$, where m_p is the problem sample mass.

Note that in Eq. 2.1.5, the correction provided by the Appleby model only depends on the mass attenuation coefficient and apparent density (or mass) of the problem sample. This fact can be explained considering that Eq. 2.1.5 is correcting the differences of attenuation effects in comparison with the case for which the sample mass (or density) tends to be zero. For this, when calibrating a well-type detector, ε_c shown in Eq. 2.1.3 must be written as ε_0 since it is the *FEPE* when the sample mass tends to be zero.

Therefore, the mass attenuation coefficient (η) needs to be accurately determined for the analyzed samples. The η depends on E_γ and the sample chemical composition, where for the η determination, it is also necessary to the mass attenuation coefficient η_i of chemical element (i) contained in the sample, being the relationship between η and η_i established by the Bragg's additivity law:

$$\eta(\text{cm}^2 \text{g}^{-1}) = \sum_i x_i \eta_i \quad (\text{Eq. 2.1.6})$$

where x_i is the proportion of each chemical element present in the sample.

Consequently, a general function for the η_i covering a wide range for E_γ and atomic number (Z) is essential to properly correct self-absorption effects. This objective is studied in depth in Chapter 3.3. The accurate calculation of η requires a multielemental analysis of samples in order to know the major

elements contained in them. This can be achieved applying a characterization technique like X-ray fluorescence (XRF), which is offered by the General Services of the University of Huelva, and whose cost is relatively affordable.

As previously explained in Chapter 1.1, there is another correction necessary to apply to ε_c , which is related to the true coincidence summing (TCS) effects. Note that when the efficiency calibration is carried out fixing each E_γ of interest, the TCS effect corrections are not needed since the correction would be the same for both the calibration and problem samples at each specific E_γ . Therefore, corrections due to TCS effects would be only necessary when varying E_γ . This correction type is fully discussed in Chapter 3.4. To proceed with this correction type, a recalibration in efficiency of the detector is carried out varying the sample-detector distance (d) and, therefore, achieving a correction factor, f_s , that depends on E_γ and d . Furthermore, note that it is possible that f_s depends on the calibration sample matrix type for the same E_γ and d . This occurs when one of the energies involved in the TCS effect belongs to the low energy range (< 150 keV), where the self-absorption effects are more relevant. Therefore, for this case, f_s would have a significant dependence on the chemical composition and apparent density of the calibration sample. Because of the method applied to correct TCS effects varying d , another factor is involved for the ε_c correction, which is f_g . In this case, f_g would be due to the different geometry conditions when recalibrating in efficiency compared with those present when calibrating at $d = 0$, that is, just above the detector window.

Considering all previous correction types, Eq. 2.1.3 can be rewritten as follows:

$$\varepsilon_p(E_\gamma, m_c, d, \eta_p) = f_g f_s f_a \varepsilon_c(E_\gamma, m_c) \quad (\text{Eq. 2.1.7})$$

Then, regarding the efficiency calibration carried out for atmospheric filters, the experimental *FEPE* for each E_γ of interest can be calculated by means of Eq. 2.1.1, as previously explained for the other sample types. For this, granular solid CRMs need to be added and very well spread onto each filter type, achieving the homogeneity of this certified material throughout the filter surface. In addition, when adding the CRMs, it is necessary to cover the same regions than those covered by the particulate matter (PM) when depositing onto the problem filters, achieving to reproduce the same PM deposition geometry.

In the case of the filters whose dimensions are relatively large, they are cut in several pieces which are placed one piece on top of the other, getting the same geometry than that achieved when measuring these filter types. If cutting the filters in several pieces, the CRMs need to be added to each single piece, also covering the same regions than those covered by the PM when depositing. In Chapter 3.5, the development of new efficiency methodologies by using different types of atmospheric filters is detailed.

When preparing the filters, it is recommendable to vacuum laminate them since this avoids that the geometrical conditions change over time and makes the filter thickness can be neglected. This latter reason allows us to neglect, in turn, the self-absorption effect corrections in the case of the filters as can be noted if considering Eq. 2.1.4, that is, $f_a \sim 1$. In addition, when selecting the radionuclides to proceed with the efficiency calibration, it is important to choose the same than those pursued when measuring the problem filters. This is important in order to avoid using the TCS effect corrections since if the radionuclides employed in the efficiency calibration and those present in the problem filters are the same, the correction provided by f_s is cancelled. Furthermore, given that the filter thickness can be neglected, $f_a \sim 1$, and therefore, f_s is the same at a fixed E_γ for both the calibration and problem filters, which further proves the non-contribution of f_s .

2.2. MATERIALS AND PRETREATMENT

To carry out the efficiency calibration in the case XtRa detector, standards provided by the IAEA, whose codes are RGU-1, RGTh-1 and RGK-1, were used, which are certified reference materials (CRMs) and contain natural radionuclides from the ^{238}U series, ^{232}Th series, and ^{40}K , respectively. Their certified activity concentrations are $4940(15) \text{ Bq kg}^{-1}$, $3250(45) \text{ Bq kg}^{-1}$, and $14000(200) \text{ Bq kg}^{-1}$, respectively, where their uncertainties, that are shown between parenthesis, are given at 1 sigma level. The RGU-1 and RGTh-1 standards were prepared by the Canada Centre for Mineral and Energy Technology by dilution of a uranium ore BL-5 (7.09% U) and a thorium ore OKA-2 (2.89% Th, $219 \mu\text{g U g}^{-1}$) with floated silica powder of similar grain size distribution, respectively, and no evidence of inhomogeneity was detected after mixing and bottling. Therefore, for both standards there is no disequilibrium problem, confirming that all radionuclides contained in them are in radioactive equilibrium (IAEA, 1987a; IAEA, 1987b). Regarding the RGK-1, it was produced from high purity (99.8%) potassium sulphate provided by the Merck Company. The ^{40}K concentration and its uncertainty were obtained from repeated measurements performed at the IAEA Laboratories in Seibersdorf and the results confirmed the value certified by Merck (IAEA, 2020).

In the case of the well-type detector calibration, RGU-1 and RGTh-1 were also used, selecting high purity KCl for the efficiency calibration done for ^{40}K , where its reference activity concentration was obtained by the relationship established by the IAEA, that is, 1% of natural K $\rightarrow 313 \text{ Bq kg}^{-1}$ of ^{40}K . In addition, for the calibration of this detector, activated carbon and high purity PbS samples were also employed for the mixtures with the RGU-1 and RGTh-1 standards.

To remove the humidity existing in the calibration and problem samples, they are dried at 65°C by using a drying oven, trade RAYPA (see Fig. 2.2.1a), until constant weight. The dried samples are milled by an agate mortar (see Fig. 2.2.1b) and then, well homogenized. A good homogenization is important to apply the self-absorption corrections since the mass attenuation coefficient of the sample (η) is assumed to be the same for the entire sample. Furthermore, the proper homogenization is also essential to assure the concentration of each radionuclide is the same regardless of the sample aliquot selected for its measurement.

Once the samples are homogenized, they are inserted inside the containers chosen for their measurements and then, compacted until reaching the desired thickness. The sample holders chosen for the calibrations of the XtRa and well-type detectors were cylindrical polypropylene containers (see Figs. 2.2.1c and 2.2.1d, respectively), whose heights and radii are $60.0(2) \text{ mm}$ and $17.7(2) \text{ mm}$ (XtRa detector), and $35.0(2) \text{ mm}$ and $6.70(10) \text{ mm}$ (well-type detector), respectively.



Figure 2.2.1. Drying oven (a) and agate mortar (b) used for the pretreatment of samples measured by gamma-ray spectrometry, and container types chosen for the efficiency calibration of the XtRa (c) and well-type (d) detectors.

In the case of the atmospheric filters used to carry out the XtRa efficiency calibration, they were selected according to the filters employed by the great majority of the laboratories for the particulate matter analysis. The filters chosen in our case (see Fig. 2.2.2) were quartz fiber filters characterized

by having different geometries and dimensions: rectangular filters (20 x 25 cm²), circular filters (diameters = 47 mm, 150 mm), slotted filters (13.6 x 14.3 cm²), and square polypropylene filters (44 x 44 cm²). Let us call these filters as R, C-47, C-150, SL and SQ, respectively, to easily identified them.

Each filter type is used to collect the atmospheric PM by using different air sampler types depending on the aerodynamic diameter (*ad*) of the particles. In our case, the filter C-150 is employed when using PM_{1.0} and PM_{2.5} samplers, while the filter R is chosen for the PM₁₀ sampler. In the case of the filters SL, they are selected when using a cascade impactor, which is very useful since it allows us to classify the PM present in atmospheric aerosols as a function of the *ad* of the particles (Aba et al., 2020; Kwon et al., 2003). This sampler can provide us information about the affinity existing between the different pollutants present in the atmospheric aerosols and the size of the aerosol particles. Then, in the case of the filter SQ, it is chosen for very high-volume air aerosol samplers, model ASS-500.

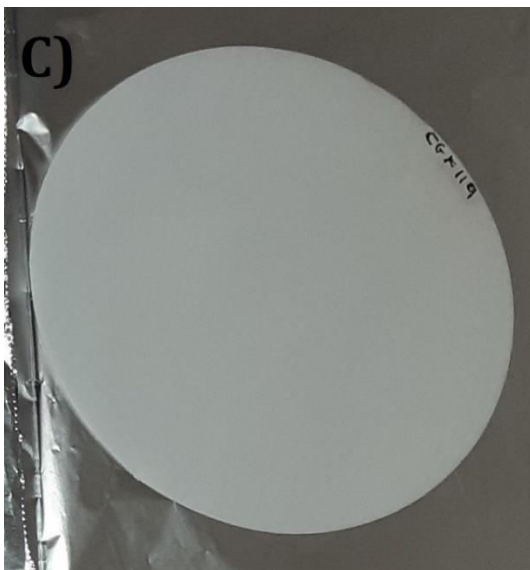
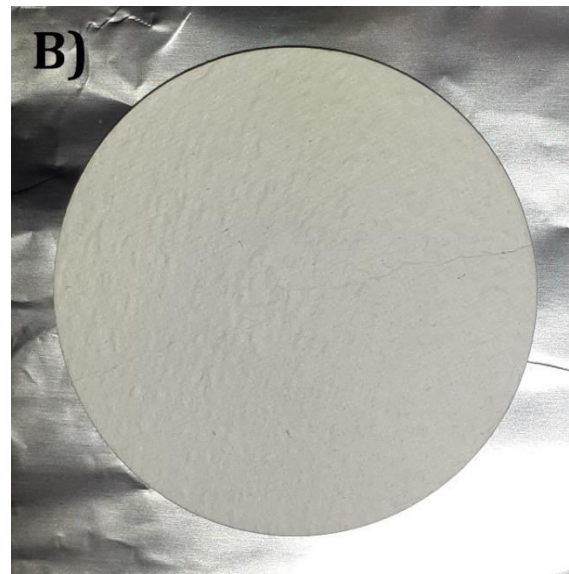
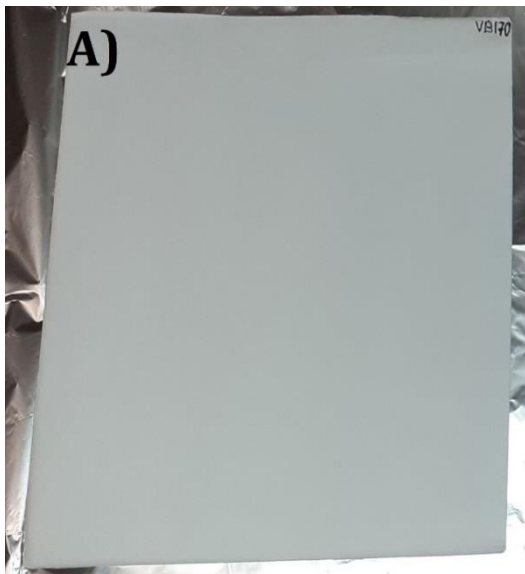




Figure 2.2.2. Atmospheric filters chosen for the XtRa efficiency calibration: R (a), C-47 (b), C-150 (c), SL (d) and SQ (e).

2.3. MEASUREMENT INSTRUMENTATION

2.3.1. Gamma-ray spectrometers: XtRa and well-type Ge detectors

To carry out this study, an extended range high purity germanium detector (XtRa) was employed (see Fig. 2.3.1.1). This spectrometric system also incorporates a device that introduces evaporated nitrogen from the Dewar into the shield, displacing the air initially contained and, consequently, the radon present in it. The XtRa detector has a relative efficiency of 38.4% at 1332 keV (^{60}Co) in relation to a 3"×3" NaI (Tl) detector, a full width at half maximum (FWHM) of 1.74 keV and 0.88 keV at 1332 keV (^{60}Co) and 122 keV (^{57}Co), respectively, and a peak-to-Compton ratio of 67.5:1.

For this study, a well-type HPGe detector (model GCW3023) was also employed (see Fig. 2.3.1.1), where HPGe means high purity germanium. This detector has a relative efficiency of 34.8% in relation to a NaI (Tl) detector with an active area of 3" x 3", as well as a full width at half-maximum (FWHM) of 1.33 keV at 122 keV (^{57}Co) and 2.04 keV at 1332 keV (^{60}Co), and a peak/Compton ratio of 56.2/1. Besides, it has a well depth of 40 mm and an active volume of 180 cm³.

Both detectors were shielded with 10 cm thick Pb. In order to avoid interferences from Pb X-ray, 2 mm thick layers of Cu were placed between the Pb shields and the detectors.

In the case of the well-type detector, it is connected to an anti-Compton system (see Fig. 2.3.1.1) which is used in this study. This system consists of seven NaI (Tl) detectors polarized with a bias voltage of 1000 V, which are connected between them, and they are placed around the well-type detector to properly reduce the Compton continuum, where one of the NaI (Tl) detectors is placed just above the well-type detector. It is necessary to clarify that this system is called "anti-Compton" system, however its function is to eliminate all particles detected in coincidence. In the case of the photons, either photoelectric effect or Compton scattering occur, where the second phenomenon has

higher probability to occur for the great majority of the photons. For this reason, this system is called anti-Compton system.

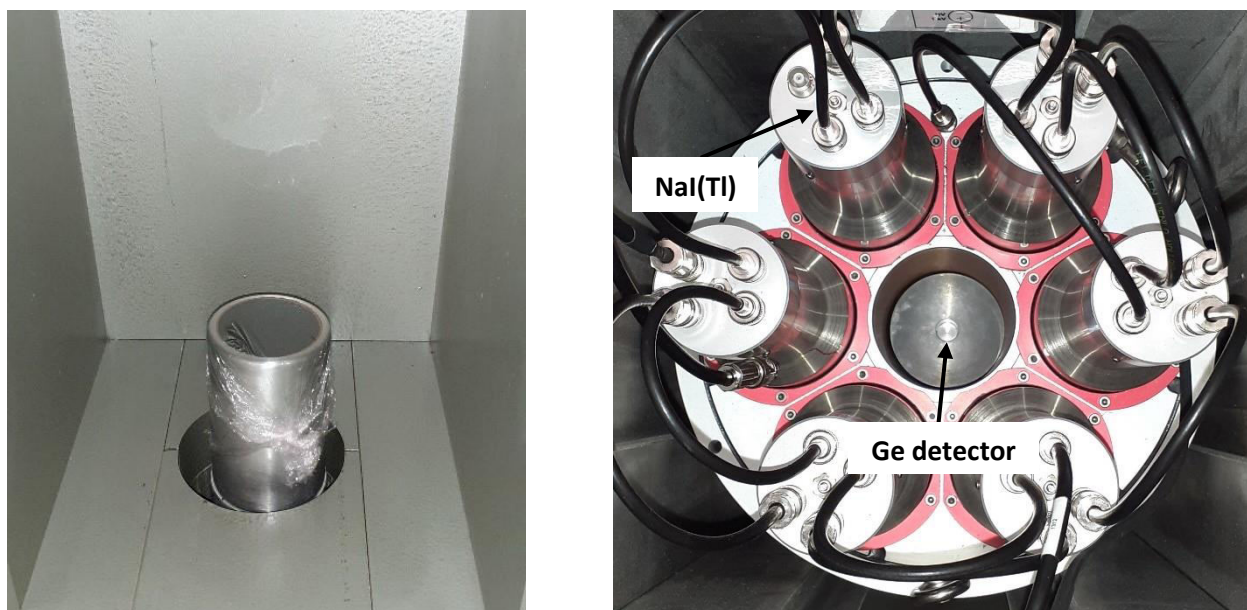


Figure 2.3.1.1. Gamma detectors used in this study: XtRa detector (on the left) and well-type detector (on the right) connected to the anti-Compton system which consists of seven NaI(Tl) detectors.

For both the XtRa and well-type detectors, conventional electronic chains, that is, preamplifier, amplifier, analogic-to-digital converter (ADC) and multichannel analyzer (MCA) are connected to them to obtain the gamma spectra by the Genie 2000 software. This software belongs to Canberra Industries, and it is one of the packages most used for the analysis as well as for the data acquisition in gamma spectrometry, demonstrating the reliability of this software (Suárez-Navarro et al., 2018; Zhu et al., 2009). To analyze the gamma spectra, this software employs algorithms which can be consulted in Canberra Industries, 2004.

Then, regarding the necessary environment conditions in the laboratory in order to carry out the different methodologies proposed in this Thesis, they are the following ones: 1. The detectors and shielding should contain the minimum concentrations of radioactive impurities; 2. The temperature inside the laboratory need to be approximately 20 °C; and 3. The ^{222}Rn concentrations need to be as low as possible in indoor air, being its daily average concentration about 10 Bq m^{-3} .

2.3.2. Very high-volume air aerosol sampler: ASS-500 sampler

In order to be able to carry out samplings spending a sampling duration as short as possible, it is recommendable to make use of a very high-volume air aerosol sampler, model ASS-500 (Valkovic, 2000). This sampler allows us to reach air flows ranged about $500 \text{ m}^3 \text{ h}^{-1}$ and $600 \text{ m}^3 \text{ h}^{-1}$. Furthermore, this last type of sampler is very recommendable to reduce the minimum detectable activity concentration (*mda*), since it is inversely proportional to the air flow, which makes possible to get *mda* values about $1 \text{ } \mu\text{Bq m}^{-3}$. This sampler type allows us to properly determine short-lived radionuclides by gamma-ray spectrometry, such as the short-lived progenies of radon and thoron, that is, ^{214}Pb and ^{214}Bi , and ^{212}Pb and ^{212}Bi , respectively. In Chapter 3.6, a comprehensive study on the determination of these radionuclides can be found. The filters SQ are employed to collect the PM, which is placed inside the ASS-500 sampler by means of a tray (see Fig. 2.3.2.1).



Figure 2.3.2.1. Very high-volume air aerosol sampler, model ASS-500 (on the left), and tray used to place filter SQ inside the air sampler (on the right).

2.3.3. Measurement of atmospheric radon and thoron: ARMON system

The measured activity concentrations of ^{212}Pb and ^{214}Pb are compared to their respective parents (thoron and radon), and the initial activities of ^{222}Rn and ^{220}Rn at the beginning of collection are measured. A measurement system, which was settled at the same place chosen to carry out the samplings, was utilized in order to determine the concentration levels of radon and thoron existing at the beginning of each sampling. This system is based on Atmospheric Radon Monitoring (ARMON), which is comprised of a semiconductor detector inside a 20 L spherical detection volume, with a potential difference of 8000 V between sphere's the inner layer of the sphere and a Passivated Implanted Planar Silicon (PIPS) detector. In this system, the Si detector detects α -particles resulting from ^{216}Po and ^{218}Po decays, from the thoron and radon, respectively. The detector has a $1\text{ }\mu\text{m}$ filter which is placed at sphere entrance to trap all thoron and radon daughters, which are generated before entering this sphere. The ARMON system calibration was carried out by Vargas et al. (2015). The *mda* were about 50 mBq m^{-3} and 200 mBq m^{-3} for thoron and radon, respectively.

Chapter 3: Results and discussion

Subchapter 3.1.: An upgraded lab-based method to determine natural γ -ray emitters in NORM samples by using Ge detectors

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3.1. An upgraded lab-based method to determine natural γ -ray emitters in NORM samples by using Ge detectors

Abstract

The regulation existing on NORM activities requires the accurate and quick measurement of natural radionuclides in a wide range of matrices by gamma spectrometry. The aim of this work has been to develop a comprehensive and accurate methodology to determine natural long-lived radionuclides (^{210}Pb , $^{228,226}\text{Ra}$, $^{234,228}\text{Th}$ and ^{40}K) by gamma spectrometry with Ge detectors in NORM samples. An exhaustive calibration method to obtain the full-energy peak efficiency (*FEPE*), for each gamma emission energy, as a function of the thickness, apparent density and matrix composition of the cylindrical sample, has been developed. The selected certified calibration standards contain only natural radionuclides belonging to the ^{238}U - and ^{232}Th -series as well as ^{40}K (codes RGU-1, RGTh-1 and RGK-1 from IAEA). Then, the obtained *FEPE* curves were validated using Genie 2000 simulations and Certified Reference Materials, for which the self-attenuation corrections were considered. Finally, a study on ^{222}Rn losses was done for several samples.

Keywords: Gamma spectrometry; Ge detectors; Efficiency calibration; NORM; Self-attenuation; ^{222}Rn losses.

3.1.1. Introduction

In many problems related to the field of environmental radioactivity, the determination of long-lived gamma-ray emitting radionuclides such as $^{234, 228}\text{Th}$, $^{228, 226}\text{Ra}$, ^{210}Pb and ^{40}K is needed, in a wide variety of samples with different compositions and densities, as well as their geometry due to the available amount of sample is variable.

There are many industries (e.g., fertilizers, TiO_2 pigments, oil extraction, production of metals, mining) that generate intermediate materials, final products and wastes containing natural radionuclides at significant concentrations, and therefore they have to be considered as NORM (Naturally Occurring Radioactive Material) or TENORM (Technologically Enhanced NORM). The control of their potential radiological impact requires accurate methods for the measurement of natural radionuclides in industrial and environmental samples in a wide range of matrices with very different apparent densities, compositions and amount of sample, which requires different measuring geometries (thickness of sample) (Barbero et al., 2014; Gázquez et al., 2014; Spasic-Jokic et al., 2013).

The Radiation Physics and Environment Group of the University of Huelva (Spain) has led many studies on radiological assessments of chemical NORM industries where a wide range of gamma-ray spectrometry measurements of TENORM samples is needed. TENORM samples contain ^{238}U - and ^{232}Th -series radionuclides, which are not in secular equilibrium, and therefore the separate measurement of ^{238}U (via ^{234}Th), $^{230, 228}\text{Th}$, $^{228, 226}\text{Ra}$, ^{210}Pb and ^{40}K radionuclides is essential. The issue related to the secular disequilibrium is very important to be analyzed since there are many types of samples such as phosphogypsum materials, industrial wastes (like scales) and waters that present a clear disequilibrium between the radionuclides belonging to the ^{238}U - and ^{232}Th -series. The most common disequilibrium cases usually occur between ^{238}U and ^{226}Ra as well as between ^{226}Ra and ^{222}Rn . (See Abdualhadi, 2016; Almayahi et al., 2012; Michalik et al., 2018 for further information about studies on secular disequilibrium).

Nowadays, NORM samples are being very important because society is more committed to environmental sustainability. Among the samples of interest are industrial wastes, which are studied to evaluate their radiotoxicity levels, ensuring that they are within the limits allowed to guarantee the safety of the workers who are exposed to the radiation from these wastes. Besides that, other samples such as waters, which are used to irrigate farm products, are analyzed to assure that they are suitable for consumption (further information about NORM samples can be found in Contreras et al., 2014; Mantero et al., 2015).

On the other hand, exposure to NORM samples can lead to health problems when they have high levels of radioactivity. For this, lately radiological regulations for construction require the measurement of radioactive NORM building materials to calculate parameters, such as the activity concentration index (European Commission, 1983), radium-equivalent activity (Ravisankar et al., 2012), or the external radiation hazard (Szabó et al., 2013). These radiological parameters require the measurement of ^{226}Ra , ^{232}Th and ^{40}K , where ^{226}Ra and ^{232}Th are easier to be determined if they are in secular equilibrium with ^{214}Pb (or ^{214}Bi) and ^{228}Ac , respectively. (See Krieger, 2013 for further information on contamination caused by NORM samples).

Regarding the ^{226}Ra , ^{232}Th and ^{40}K determinations, gamma spectrometry with high purity germanium (HPGe) detectors is the most useful radiometric technique. This kind of detectors must be calibrated with a reference sample that has the same geometry than the one used for the real samples. For that, this study is focused on finding, for every gamma emission of interest, a general efficiency function obtained for the calibration matrix and depending on the sample thickness for a cylindrical geometry. Regarding the specific ranges, it is necessary that the radius of that geometry is smaller than the one of the detectors. On the other hand, those radionuclides previously mentioned can be determined by medium resolution detectors, for example, CeBr_3 detectors. However, in contrast to the HPGe detectors, the activity concentration calculations carried out using medium resolution detectors have very high uncertainties due to their lower resolution (Androulakaki et al., 2020; Ji et al., 2018; Peyres et al., 2017; Tsabaris et al., 2019). Consequently, the radionuclide determinations can be accomplished in a more accurate way using HPGe detectors.

On the other hand, nowadays the calibration of detectors by using MCNP, GEANT4, PENELOPE or FLUKA simulation codes has become generalized (Agarwal et al., 2011; Ahmed, 2019; Eleftheriou et al., 2013; Maidana et al., 2016; Quintana et al., 2018). However, for this, it is necessary to carry out the “characterization” of the detector parameters, which implies a very expensive process developed by the manufacturer, being the detector inoperative and out of the laboratory during several months. Considering this problem as well as all the previous ones, this work is focused on obtaining the full-energy peak efficiency (*FEPE*) for a detection system with a HPGe detector for the certified calibration matrix (ε_c), which depends on the peak energy of interest, and the sample thickness in cylindrical geometry (h), covering the range of energies for natural radionuclides (from 46.5 keV to 1764.5 keV). The efficiency curve found for the calibration sample (ε_c), must be corrected due to the different gamma self-attenuation between the calibration and problem samples. Besides, a study on the “sensitivity” of the method has also been carried out as a function of the parameters for which the measurement is accomplished.

3.1.2. Materials and methods

In order to carry out this study, an extended range high purity germanium detector (XtRa) was employed. This spectrometric system also incorporates a device that introduces evaporated nitrogen

from the Dewar into the shield, displacing the air initially contained and, consequently, the radon present in it. The XtRa detector has a relative efficiency of 38.4 % in relation to a 3"×3" NaI (TI) detector, a full width at half maximum (FWHM) of 1.74 keV and 0.88 keV at 1332 keV and 122 keV, respectively, and a peak-to-Compton ratio of 67.5:1. Then, regarding the necessary environment conditions in the laboratory in order to carry out the methodology proposed in this study, they are the following: 1. The detectors and shielding should contain the minimum concentrations of radioactive impurities; 2. The temperature inside the laboratory need to be approximately 20 °C; and 3. The ^{222}Rn concentrations need to be as low as possible in indoor air, being the daily average concentration about 10 Bq m^{-3} .

On the other hand, a conventional electronic chain is connected to the HPGe detector to obtain the gamma spectra by the Genie 2000 software. This software belongs to Canberra Industries and it is one of the packages most used for the analysis as well as for the data acquisition in gamma spectrometry, demonstrating the reliability of this software (Suárez-Navarro et al., 2018; Zhu et al., 2009). In order to analyze the gamma spectra, this software employs algorithms which can be consulted in Canberra Industries, 2004.

To determine the experimental efficiencies, standards provided by the IAEA (RGU-1, RGTh-1 and RGK-1) have been used, which are Certified Reference Materials (CRM) and contain natural radionuclides from ^{238}U -series, ^{232}Th -series, and ^{40}K , whose certified activity concentrations were $4940 \pm 15 \text{ Bq kg}^{-1}$, $3250 \pm 45 \text{ Bq kg}^{-1}$, and $14000 \pm 200 \text{ Bq kg}^{-1}$, respectively, being the uncertainties given at one sigma level. The RGU-1 and RGTh-1 standards were prepared by the Canada Centre for Mineral and Energy Technology by dilution of a uranium ore BL-5 (7.09 % U) and a thorium ore OKA-2 (2.89 % Th, $219 \mu\text{g U g}^{-1}$) with floated silica powder of similar grain size distribution, respectively, and no evidence of inhomogeneity was detected after mixing and bottling. Therefore, for both standards there is no disequilibrium problem, confirming that all the radionuclides contained in them are in radioactive equilibrium (IAEA, 1987a; IAEA, 1987b). Regarding the RGK-1, it was produced from high purity (99.8 %) potassium sulphate provided by the Merck Company. The ^{40}K concentration and its uncertainty were obtained from repeated measurements performed at the IAEA Laboratories in Seibersdorf and the results confirmed the value certified by Merck (IAEA, 1987b).

Once the most intense gamma emissions of these standards were selected, an apparent density of $1.63 \pm 0.02 \text{ g cm}^{-3}$ was obtained after compacting them until reaching the chosen thickness values (from 5 to 50 mm and from 5 to 45 mm with intervals of 5 mm in the cases of RGTh-1 and RGK-1, and RGU-1 standards, respectively). Then, the experimental *FEPE* values at the different selected gamma energies and thicknesses were calculated. The experimental *FEPE* values calculated in the calibration standard matrices as well as the gamma emission probabilities related to the selected energies were shown in Tables A.1 and A.2 (both in Supplementary Material-A). After the experimental *FEPE* calculations, the simplest empirical *FEPE* function depending on the thickness was obtained for each selected energy. Finally, the efficiency calculated in the standard matrices (ϵ_c) must be determined in the problem sample (also called as real sample) matrices. For this, the so-called self-attenuation factor (f) needs to be employed, which depends on the chemical compositions, thickness of the real sample (h , which is also called as the sample height) and apparent densities of both the standard and the real sample, obtaining the efficiency in the real sample matrix (ϵ).

The validation of the efficiency curves was done by means of samples whose concentrations of natural radionuclides were known. Furthermore, the methodology proposed in this study has been validated using CRMs which were employed in Inter-Comparison exercises. In this kind of exercise, it is necessary to follow a protocol in order to prepare the samples before measuring them. Regarding the reference values resulted from the Inter-Comparison exercises, they are obtained considering all the

calculations provided by each laboratory and taking a mean value of them (see Wiedner et al., 2018 for further information on Inter-Comparison exercises). On the other hand, a study on ^{222}Rn losses in certified materials, such as phosphogypsum materials and dissolved RGU-1 standard, was carried out calculating the ^{226}Ra activity concentration by using either the gamma emissions of the ^{222}Rn daughters, that is, ^{214}Pb and ^{214}Bi , or its gamma emission of 186 keV, subtracting the interference from ^{235}U .

3.1.3. Results and discussion

3.1.3.1. Full-Energy Peak Efficiency (FEPE) curves for the calibration matrix

The experimental *FEPEs* obtained in the calibration sample matrices (ε_c^{exp}) have been calculated by the following equation:

$$\varepsilon_c^{exp}(E_\gamma, h) = \varepsilon_c^{exp}(E_\gamma, m_c) = \frac{G - B - F - I}{P_\gamma a m_c t} \quad (\text{Eq. 3.1.1})$$

where G , B , F , and I are the total number (gross) of counts for the full-energy peak of interest, the Compton continuum, the background due to environmental conditions in the laboratory and the interference term, respectively. Then, P_γ is the probability of gamma emission (taken from DDEP, 2017), a , m_c and h are the activity concentration, mass and height of the standard, respectively, used in the calibration procedure, E_γ is the gamma emission and t is the measurement time. It has been considered that $I \sim 0$, this being one of the requirements in the gamma emission selection. Besides, it is necessary to clarify that the *FEPE* given by Eq. 3.1.1 is an apparent full-energy peak efficiency since the true coincidence-summing corrections have not been included. Thus, from now on, let us call the apparent *FEPE* as *FEPE* in order to abbreviate the name of this type of efficiency.

Firstly, the *FEPE* function depending on the height for each gamma emission was obtained. The mass/ height ratio in the preparation of the standards was constant (about $7.5/5.0 = 1.50 \text{ g mm}^{-1}$), obtaining a constant apparent density, ρ_c , of about 1.63 g cm^{-3} ($\rho_c = m_c/\pi r^2 h$), being r the radius of cylindrical geometry of the standards.

In Tables A.1 and A.2, it is possible to see that the uncertainties given at 1 sigma level for the experimental efficiencies ranged from 1% to 3%, where the uncertainty related to the counting rate was the greatest contribution to the efficiency uncertainties. Besides, the uncertainty associated to the sample height, $\sigma(h)$, was also taken. However, considering $\sigma(h) = 0.2 \text{ mm}$ (heights measured using a high precision caliper), $\sigma(h)$ can be completely neglected compared with the one related to the counting rate.

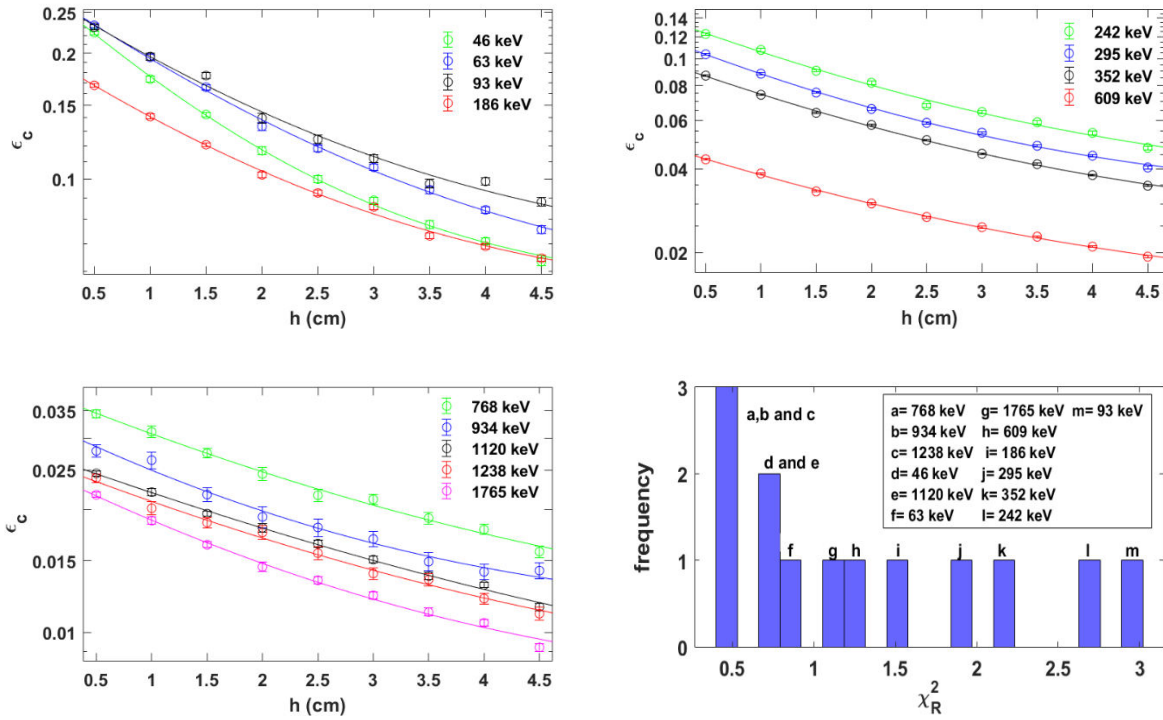


Figure 3.1.1. Experimental ϵ_c values versus height for RGU-1 standard fixing E_γ and histogram of reduced chi-square values (critical χ_R^2 is 2.1 at 0.05 of significance level (α) and 6 degrees of freedom (ν)) obtained after fittings.

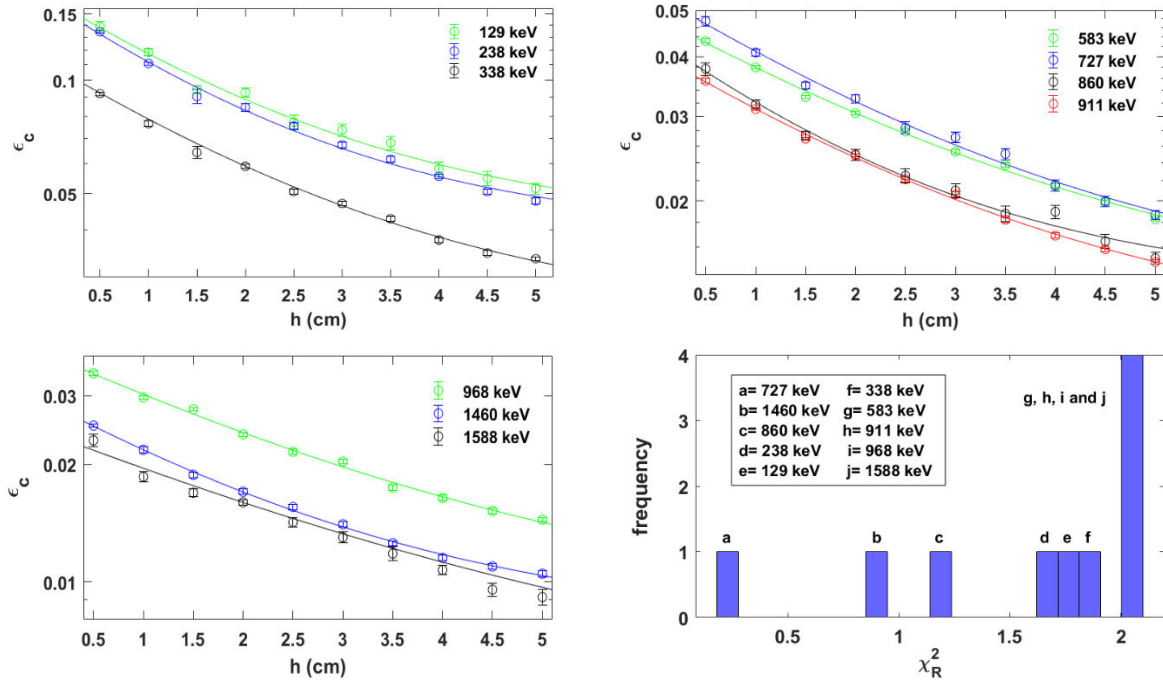


Figure 3.1.2. Experimental ϵ_c values against height for RGTh-1 and RGK-1 standards fixing E_γ and histogram of reduced chi-square values (critical χ_R^2 is 2.01 at 0.05 of significance level (α) and 7 degrees of freedom (ν)) obtained after fittings.

On the other hand, in the case of the RGU-1 standard, it is known that the activity ratio $^{235}\text{U}/^{238}\text{U} = 0.046$, $P_\gamma(^{226}\text{Ra}) = 0.0351(6)$ and $P_\gamma(^{235}\text{U}) = 0.572(5)$ at 186 keV. Therefore, when the secular equilibrium between ^{238}U and ^{226}Ra is considered, an equivalent probability at this energy of $P_\gamma(^{226}\text{Ra} + ^{235}\text{U}) = 0.0614(6)$ can be taken.

In Figs. 1 and 2, the experimental *FEPEs* versus h values in logarithmic scale were shown, observing that the majority of the curves are parallels, except for low energy emissions such as 46 keV and 63 keV, increasing the deviation as the energy decreases and finding the maximum deviation for 46 keV (^{210}Pb). This occurs because of the significant differences between self-attenuation corrections provided at low and high energies (> 150 keV), since within the high energy zone the self-attenuation effects are less relevant than the ones corresponding to the low energy zone. The corrections due to the different self-attenuation effects in the case of the calibration standards compared with the one related to the real samples will be studied in Section 3.1.3.2.

There are some singular cases at 129 keV, 583 keV, 609 keV, 768 keV, 934 keV, 1120 keV and 1238 keV since the *FEPE* values for these energies are lower than the expected ones, being 583 keV, 609 keV and 1120 keV one of the most employed energies in order to determine ^{226}Ra (609 keV and 1120 keV) and ^{228}Th (583 keV). This fact can be explained due to the significant true coincidence summing effects (TCS) existing for those three gamma emissions (see Barba-Lobo et al., 2021b; Gilmore and Hemingway, 1995; Venegas-Argumedo and Montero-Cabrera, 2015), and this corroborates that for natural radionuclides is better to calibrate fixing the energy. As it is well known, the TCS effects decrease as the sample height increases (distance detector-sample), which are observed in Figs. 1 and 2, where it is possible to realize that the efficiency values for 583 keV, 609 keV and 1120 keV are closer than the expected ones as the sample height increases. This occurs in this way because as the sample height increases, the absolute efficiency (ε_{ab}) decreases occasioning a diminution of the TCS effects, since ε_{ab} and the TCS effects are related to each other (see Debertin and Helmer, 1988 for further information about the relationship between ε_{ab} and TCS effects). However, the TCS effects are not a problem in our calibration procedure, since it has been carried out varying the height and fixing the energy. Consequently, the fact that the 583 keV, 609 keV and 1120 keV and all the other energies mentioned in this paragraph present TCS effects does not affect the quality of our activity concentration calculations.

The best fitting for ε_c will be an asymptotic exponential function as follows:

$$\varepsilon_c(E_\gamma, h) = ar_1 \exp(ar_2 h) + ar_3 \quad (\text{Eq. 3.1.2})$$

where ar_1 , ar_2 and ar_3 are parameters obtained after fitting the experimental *FEPEs* versus h , being h the sample height. The fittings given by Eq. 3.1.2 were compared statistically by finding their confidence intervals with the method described in MATLAB, 2021. Besides, note that in Eq. 3.1.2 the efficiency value is $ar_1 + ar_3$ or ar_3 when h is relatively small or large, respectively, as it is expected from the *FEPE* behavior for the particular range of h (from 0.5 to 5 cm). The ar_2 parameter must be negative since the efficiency decreases as h increases.

The fittings provided by Eq. 3.1.2 (continuous lines in Figs. 3.1.1 and 3.1.2) are in very good agreement with the experimental data, obtaining values for the reduced chi-square (χ_R^2) which are lower than the critical value (2.1 or 2.01 in the cases of Figs. 3.1.1 and 3.1.2, respectively) at 0.05 of significance level for the majority of the cases (see histograms in Figs. 3.1.1 and 3.1.2) (Bevington and Keith, 1969).

Tables A.3 and A.4 (both in Supplementary Material-A) show the values of the ar_1 , ar_2 and ar_3 parameters obtained after fitting experimental efficiencies which have been calculated in the calibration matrix of RGU-1 and RGTh-1 and RGK-1, respectively. The uncertainties of these parameters (calculated at one sigma level) were ranged from 1-3%, 5-7% and 4-6% for ar_1 , ar_2 and ar_3 , respectively, in the case of RGU-1 standard while these values were ranged from 1-4%, 4-7% and 4-6% for ar_1 , ar_2 and ar_3 , respectively, in the cases of RGTh-1 and RGK-1 standards. Regarding these uncertainties, it is interesting to realize that the relative uncertainty associated with ar_2 is usually higher than the ones related to the other parameters. On the other hand, regarding the relative average residues, $\langle Res \rangle$, obtained at each energy (Tables A.3 and A.4) are very useful to evaluate the $FEPE$ relative uncertainty obtained from the fitting functions. These $\langle Res \rangle$ values ranged from 0.8% (352 keV) to 3.9% (129 keV), confirming the very good fittings obtained for $FEPE$.

Regarding the calculation of experimental efficiency values in the calibration matrices, we have considered that it would be appropriate to compare these values with the ones calculated by Genie 2000 simulations. This comparison was made to check the validity of the algorithm used by this software, being possible at the same time to verify that the calculations of these experimental efficiencies were carried out correctly. Thus, some energies have been selected in order to make this comparison (63 keV, 352 keV, 609 keV and 1120 keV in the case of the RGU-1 standard and 238 keV, 583 keV, 911 keV and 1460 keV in the cases of RGTh-1 and RGK-1 standards). Then, the z_{score} values were calculated for each height and finally it has been averaged over all these values, obtaining an average z_{score} value ($\langle z_{score} \rangle$) for each energy, where the expression used to calculate each z_{score} value has been as follows:

$$z_{score} = \frac{|a_1 - a_2|}{\sqrt{\sigma(a_1)^2 + \sigma(a_2)^2}} \quad (\text{Eq. 3.1.3})$$

where a_1 and a_2 are the two compared values and $\sigma(a_1)$ and $\sigma(a_2)$ their respective uncertainties calculated at one sigma level.

As can be seen in Tables A.5 and A.6 (both in Supplementary Material-A), the large majority of the z_{score} values obtained for each height were below 1 for the calculations carried out in the RGU-1, RGTh-1 and RGK-1 calibration matrices. In addition, all the $\langle z_{score} \rangle$ values were below 0.5 for the three calibration matrices, so the algorithm used by Genie 2000 to calculate the efficiency values works correctly and it has also been verified that the calculations of the experimental efficiencies have been carried out correctly.

3.1.3.1.1. $FEPE$ fittings versus height ($E_\gamma = \text{constant}$); comparison with other studies

In this Section, the reasons for the selection of the fitting function given by Eq. 3.1.2 have been analyzed. Previous works (Jodłowski, 2006; Montes et al., 2019; Pérez-Moreno et al., 2002; Suárez-Navarro, 2020) were carried out to assess the $FEPE$ varying h and fixing E_γ but using a pure exponential function as:

$$\varepsilon_c(E_\gamma, h) = br_1 \exp(br_2 h) \quad (\text{Eq. 3.1.4})$$

where br_1 and br_2 are the parameters used to fit the experimental efficiencies.

Some of the most intense gamma energies covering the full energy range were selected, these being 63 keV, 352 keV, 911 keV and 1460 keV (belonging to ^{234}Th , ^{214}Pb , ^{228}Ac and ^{40}K , respectively). The fittings obtained by Eqs. 3.1.2 and 3.1.4 were shown in Fig. 3.1.3.

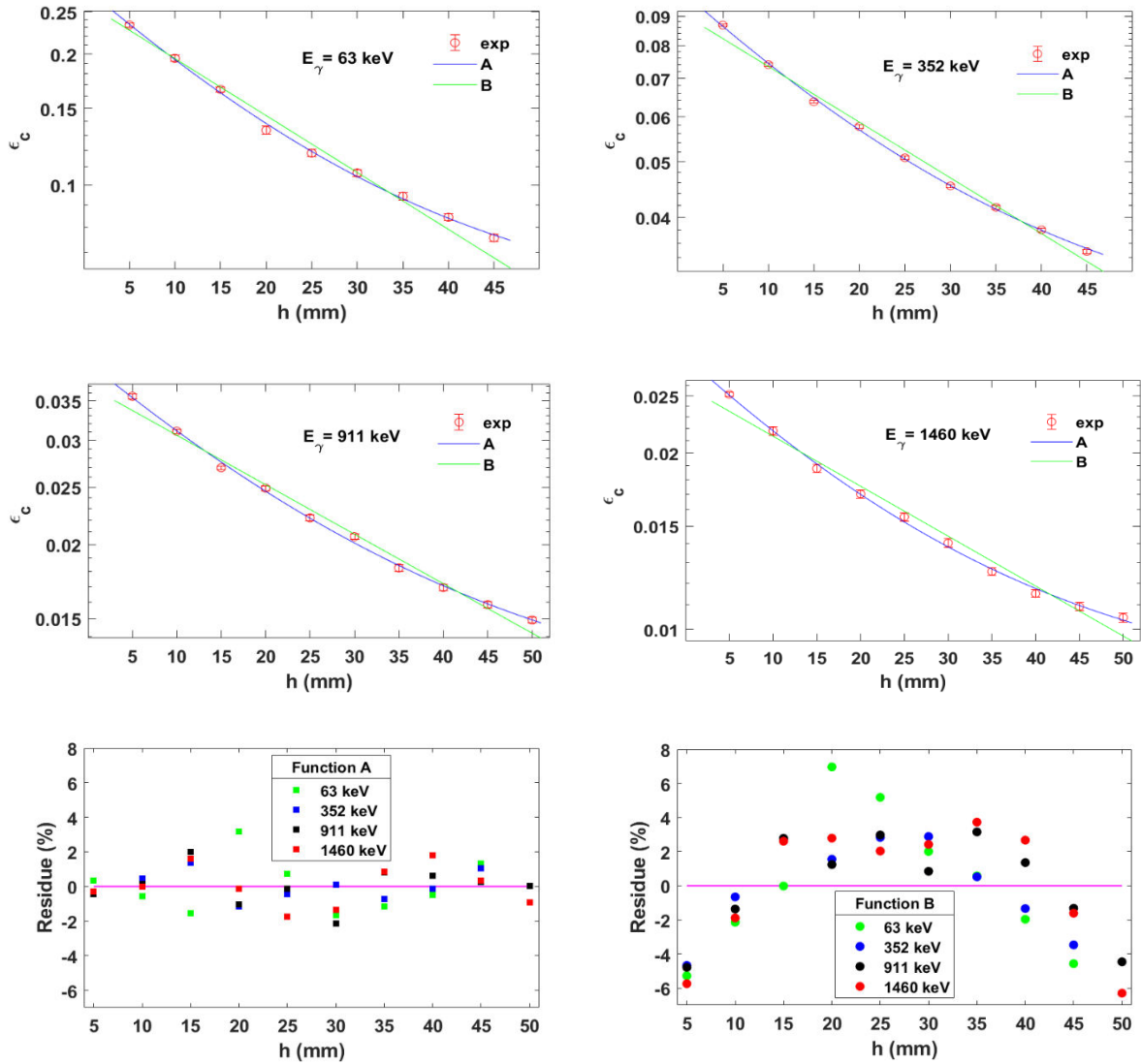


Figure 3.1.3. Comparison between fittings of the experimental efficiencies versus height, where fittings carried out by two function types and their respective relative residues have been shown: A (used in this work) and B (used in previous works).

It is easy to realize that the pure exponential function (function B in Fig. 3.1.3) does not fit properly to the experimental data, especially for the extreme heights, that is, at 5 mm and at 45 or 50 mm. However, our function (A in Fig. 3.1.3) agrees very well with the experimental efficiencies since they continue behaving as an asymptotic function even though the efficiency has been represented using logarithmic scale.

Table A.7 (in Supplementary Material-A) shows the parameters resulted from the fittings carried out by function B as well as the $\langle Res \rangle$ and χ_R^2 values obtained after fitting by both functions. The total relative average residue, $\langle Res \rangle_T$, for the fittings done by function B was 3.4%, while the one obtained by function A was 1.2%. Furthermore, the χ_R^2 values obtained for function B were very much higher than the critical tabulated one (χ_R^2 is 1.94 at 0.05 of confidence level (α) and 8 degrees

of freedom (ν)), while the χ_R^2 values obtained for function A were close or smaller than the tabulated ones (see Table A.7). Therefore, it has been proven that function A (used in this study) works much better than function B (used in previous works) and, consequently, for this reason, function A was chosen.

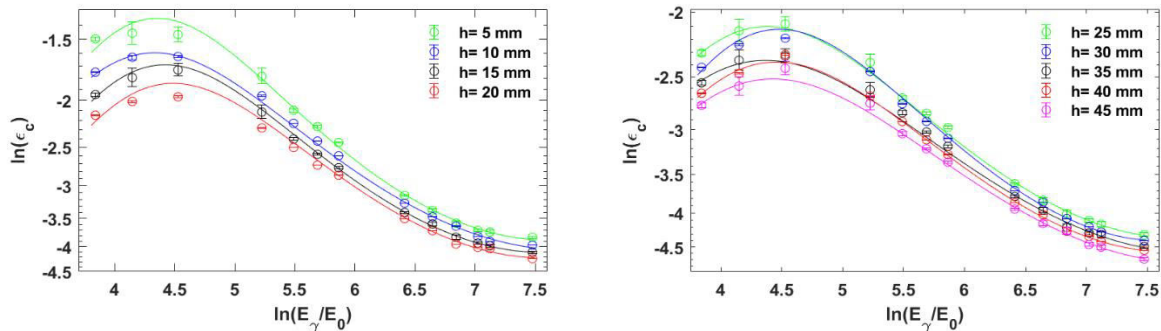
3.1.3.1.2. FEPE versus energy ($h = \text{constant}$) compared to FEPE versus height ($E_\gamma = \text{constant}$)

In this Section, we justify the reasons why an efficiency calibration method in which the height is varied and the energy is fixed for the different natural radionuclides has been selected. For this, the *FEPEs* obtained by our function (*FEPE* vs height) have been compared with the ones obtained using the most common fitting functions resulted from the *FEPE* versus energy. Thus, the function selected was (Bolívar et al., 1996; El-Daoushy and García-Tenorio, 1995; Gilmore and Hemingway, 1995; Martínez-Ruiz et al., 2007; Zare et al., 2016):

$$\varepsilon_c(E_\gamma, h) = \exp\left(\sum_{i=1}^4 cr_i \ln(E_\gamma/E_0)^{i-1}\right) \quad (\text{Eq. 3.1.5})$$

where cr_i are the parameters resulted from the fittings by the cubic polynomial function, whose values are shown in Table A.8 (in Supplementary Material-A) and $E_0 = 1$ keV. Thus, Eq. 3.1.4 will be called “function C”.

The gamma emissions corresponding to the radionuclides that belong to ^{238}U -series (radionuclides contained in RGU-1) were selected for this comparison, since these energies are uniformly distributed throughout the range of low and high energies. In Fig. 3.1.4 it is possible to see the graphics of the experimental efficiency fittings done by the logarithm of function C for an energy range that goes from 46.5 keV to 1764.5 keV and for heights ranged from 5 mm to 45 mm. In these graphics, the experimental efficiency values tend to deviate somewhat from the expected values. This occurs because when calibration in efficiency is carried out varying the energy, the TCS effects are more relevant, so the efficiency values usually deviate from the ones given by the fitting function in this type of calibration. This requires corrections due to the TCS effects. However, doing the calibration in efficiency varying the height and fixing the energy, it is not necessary to take this type of problem into account.



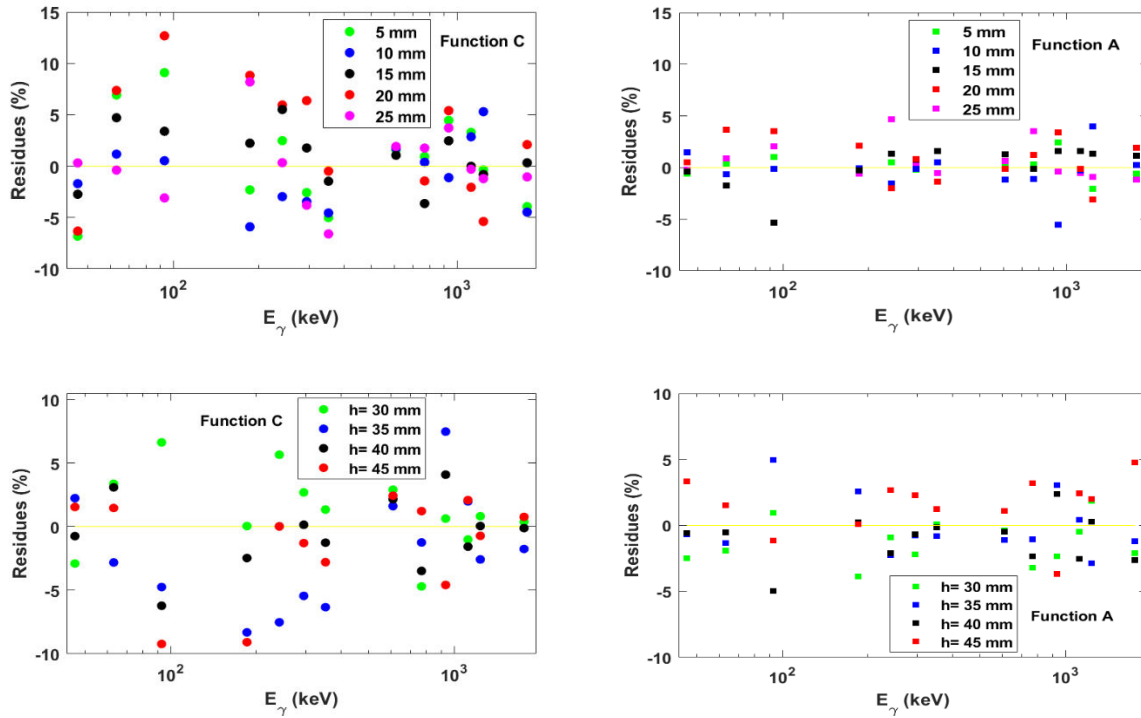


Figure 3.1.4. Fittings of *FEPE* versus energy carried out by function C. Besides, the residues resulted from the fittings done using function C (left column) were compared with the ones obtained by using function A (right column).

On the other hand, it is interesting to note that when a calibration in efficiency varying E_γ is done, the uncertainties related to the emission probability, $\sigma(P_\gamma)$, must be considered. This occurs in this way because applying this calibration method, E_γ is varied and, consequently, $\sigma(P_\gamma)$ is not possible to be considered as a systematic uncertainty. This implies that for this calibration method, the uncertainties of the experimental efficiencies are much higher than the ones obtained when a calibration varying h is carried out. Thus, the relative values of $\sigma(P_\gamma)$ ranged from 0.2% (for 352 keV (^{214}Pb)) up to 9% (for 93 keV (^{234}Th)).

The relative residues are very useful to assess the goodness of the fitting functions. Thus, as can be seen in Fig. 3.1.4, after fitting by function C, the obtained residues were much higher than the ones obtained by function A for all the chosen E_γ and h values (1-6% and 0-3%, respectively). Table A.8 shows the $\langle \text{Res} \rangle$ values at each h value for both functions A and C. Note that for all the h values, $\langle \text{Res} \rangle$ values were about double in the case of the function C in comparison with the ones obtained by function A, getting a $\langle \text{Res} \rangle_T$ value of 4.5% and 2.2%, respectively. Therefore, it is possible to conclude that the function proposed in this work (function A) provided much better results of the *FEPE* fittings in comparison with the ones provided by the traditional function used in the majority of studies (function C). It is necessary to emphasize that this is possible in the case of NORM samples because the assessment of the activity of each radionuclide in the sample is done with reference to the activity of the same radionuclide in the calibration source. When this type of relative measurement is not possible, the efficiencies corrected due to TCS effects, which depend smoothly on energy, should be fitted as a function of energy for the calculation of the *FEPE* for the energies of interest.

3.1.3.2. FEPE curves for real samples; corrections due to self-attenuation effects

The measurement of real samples requires to include corrections because the self-attenuation of the gamma radiation in the real sample matrix is different from the one corresponding to calibration samples. In order to carry out this correction, it is necessary to introduce the so-called self-attenuation correction factor (f), which is defined as the ratio of the number of photons coming out from the real sample and the number of photons coming out from the standard that are recorded in the full-energy peak (Barba-Lobo et al., 2021c; Bonczyk, 2018; Guerra, 2018; San Miguel et al., 2002; Xhixha-Kaçeli et al., 2013). Thus, the self-attenuation factor would be expressed mathematically like this:

$$f = N/N_c = \varepsilon/\varepsilon_c \quad (\text{Eq. 3.1.6})$$

where N_c and N are the number of photons detected in the peak from the calibration and real samples (both with the same activity), respectively, and ε_c and ε are the efficiencies calculated in the calibration and real matrices, respectively.

According to Cutshall et al. (1983); Debertin and Helmer, 1988, assuming cylindrical geometry, only the photons parallel to the symmetry axis are detected, and the activity is homogenously distributed in the sample, the number of detected photons (N) can be calculated as:

$$N = N_0 \frac{1 - \exp(-\eta\rho h)}{\eta\rho h} \quad (\text{Eq. 3.1.7})$$

where N_0 is the number of photons detected from the sample without attenuation, and ρ , η , h are the density, the mass attenuation coefficient and the sample height for the measuring geometry, respectively. It is necessary to clarify that in Eq. 3.1.7 the non-coaxial photons are also considered, being the only approach that the real distance travelled by the detected oblique photons is replaced by the parallel one. Due to the angle between the photon trajectory and the coaxial axis of the detector is very small, the difference between both the real and coaxial distances will be negligible.

If we consider the same measuring geometry for both calibration and problem samples, the self-attenuation factor (Eq. 3.1.6) can be written by:

$$f = N/N_c = \frac{\eta_c \rho_c (1 - \exp(-\eta\rho h))}{\eta\rho(1 - \exp(-\eta_c \rho_c h))} = f(E_\gamma, h, x_i) \quad (\text{Eq. 3.1.8})$$

where h and E_γ are the real sample height and the energy for which the self-attenuation correction factor is calculated, and x_i is the proportion of each chemical element (i) in both the real and calibration samples, since their mass attenuation coefficients depend on their chemical compositions. It is necessary to clarify that in Eq. 3.1.8, the heights of the calibration and real samples are considered the same, that is, h .

Therefore, the efficiency calculated for the real sample (ε) will be given by:

$$\varepsilon = f(E_\gamma, h, x_i) \varepsilon_c(E_\gamma, h) \quad (\text{Eq. 3.1.9})$$

where $\varepsilon_c(E_\gamma, h)$ and $f(E_\gamma, h, x_i)$ are the efficiency in the calibration matrix and the self-attenuation correction factor, respectively.

The average mass attenuation coefficient for each energy and composition can be calculated by using the so-called Bragg's law as follows:

$$\langle \eta \rangle = \sum_i x_i \eta_i \quad (\text{Eq. 3.1.10})$$

where x_i and η_i are the proportion and the mass attenuation coefficient of each chemical element at a specific energy, respectively (η_i values taken from NIST, 2004a). Alternatively, the mass or the linear attenuation coefficients for any element, compound or mixture can be directly evaluated using Barba-Lobo et al. (2021c); XCOM, 2004.

3.1.3.3. Calculations of the minimum detectable activity concentrations for NORM samples

In this Section, it has been carried out a study on the dependence of the minimum detectable activity concentration (*mda*) on the type of sample, height sample and energy. The *mda* is defined as the minimum concentration that a sample needs to have in order to be detected over a background with a significance level (α , this being equal to 0.05 in our case). The *mda* can be calculated by the following equation:

$$mda = \frac{LLD}{\varepsilon m P_\gamma t} \quad (\text{Eq. 3.1.11})$$

where *LLD*, ε , *m* and P_γ are the lower limit of detection, the efficiency calculated in the real sample matrix, the real sample mass and the emission probability, respectively, referred to a specific energy and *t* is the counting time. The equation that defines *LLD* considers the existence or absence of interferences in gamma emissions (equations taken from Bolívar, 1995; Currie, 1968).

The interference term (*I*) is often neglected for most chosen gamma emissions. However, in this Section the gamma emission of 186 keV has been analyzed, which belongs to ²²⁶Ra, in the cases where ²²⁶Ra and ²³⁸U are and are not in secular equilibrium. In the latter case, the interference between ²²⁶Ra and ²³⁵U (*I*_{235U}) must be considered, and it is given by the following equation:

$$I_{235U} = A_{235U} P_\gamma(^{235}\text{U}) \varepsilon_{186\text{keV}} t = 0.0263 A_{238U} \varepsilon_{186\text{keV}} t \quad (\text{Eq. 3.1.12})$$

where A_{235U} , A_{238U} are ²³⁵U and ²³⁸U activities, respectively, $P_\gamma(^{235}\text{U})$ is the emission probability of ²³⁵U at 186 keV, $\varepsilon_{186\text{keV}}$ the efficiency calculated in the real sample matrix at 186 keV and *t* is the counting time.

In Eq. 3.1.12, $A_{235U} = 0.046 A_{238U}$ has been considered (Agha et al., 2011). Besides that, if secular equilibrium between ²³⁴Th and ²³⁸U is also considered, it would be possible to write $A_{238U} = A_{234\text{Th}}$, and since $A_{234\text{Th}}$ can be calculated using ²³⁴Th (63 keV), the interference *I*_{235U} can be determined.

Thus, the *mda* behavior was analyzed for different selected NORM samples: RGU-1, RGTh-1 and RGK-1 standards, phosphogypsum samples provided by IAEA (IAEA-434) and used in the CSN/CIEMAT Inter-comparison carried out in 2008 (CSN-PG), as well as two scales named Scale-

1 and Scale-2. Regarding CSN and CIEMAT, they are the acronyms for the Spanish Nuclear Safety Council (“Consejo de Seguridad Nuclear”) and the Centre for Energy, Environment and Technology Research (“Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas”), respectively.

Firstly, it has been shown the comparison between the *mda* behavior fixing the sample and varying the sample height ($h = 10, 25$ and 45 mm), that is, an internal comparison. The samples chosen for this case were the three standards: RGU-1, RGTh-1 y RGK-1. Then, it has been made an external comparison between the *mda* values obtained considering different samples for the same height ($h = 25$ mm), which has been carried out for the three standards as well as the other samples mentioned above (phosphogypsum and scale samples). The energy emissions chosen to make both types of comparisons were: 46.54 keV, 63.29 keV, 185.96 keV, 295.22 keV, 351.93 keV, 609.31 keV, 1120.29 keV (RGU-1 case), 238.63 keV, 338.42 keV, 583.19 keV, 911.16 keV (RGTh-1 case) and 1460.83 keV (RGK-1 case).

In both comparison types, a common counting time of 172,800 seconds was established, that is, two days. Regarding the apparent densities of each real sample, they are as follows: 0.71 g cm^{-3} (IAEA-434), 1.27 g cm^{-3} (CSN-PG), 1.32 g cm^{-3} (Scale-1) and 1.00 g cm^{-3} (Scale-2).

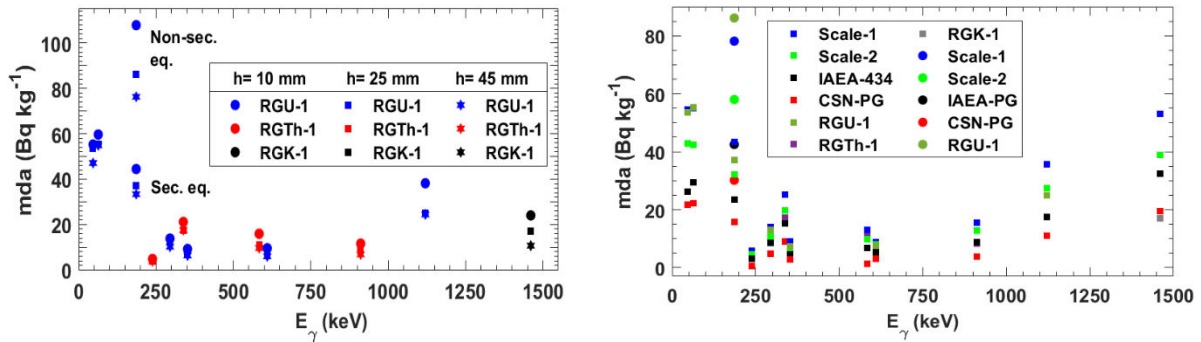


Figure 3.1.5. (Left side) *mda* values obtained by fixing the sample type and varying the height (Non-sec. eq.: Non-secular equilibrium, Sec. eq.: Secular equilibrium at 186 keV); (Right side) *mda* values fixing the sample height ($h = 25$ mm) and varying the sample type (Non-sec. eq. (circles), Sec. eq. (squares)).

In Fig. 3.1.5 (left side), the *mda* values clearly decrease as the standard height (mass) increases, which is consistent because *mda* is inversely proportional to the sample mass. This *mda* behavior was the same for the great majority of the radionuclides contained in each standard. On the other hand, regarding the two cases corresponding to ^{226}Ra (with and without secular equilibrium between ^{226}Ra and ^{238}U), *mda* values were higher in all cases when secular equilibrium was not considered. This is also consistent because in the case of not considering secular equilibrium, the interference term (Eq. 3.1.12) must be taken into account and, consequently, *mda* value increases.

Then, in Fig. 3.1.5 (right side), it can be seen what happens when different sample types are analyzed for the same height. Thus, the *mda* has a clear dependence on the properties of the analyzed samples, where the activity and density are the two factors that mainly contribute to the *mda* value. Regarding the activity, the *mda* specifically depends on the activity of ^{226}Ra and ^{228}Th , since if the Compton continuum at energies belonging to their daughters (^{214}Bi (1765 keV) and ^{208}Tl (2615 keV), respectively) is relatively large, the Compton continuum and, consequently, the *mda* value will also be relatively large for all the other energies. In the cases of radionuclides belonging to the ^{238}U -series, the *mda* behavior was very similar for all these radionuclides, being in the majority of the cases the highest *mda* value corresponding to the Scale-1 sample and followed by RGU-1, Scale-2, PG-IAEA

and PG-CSN. On the other hand, for the cases corresponding to the radionuclides belonging to the ^{232}Th -series, there is a clear distribution of the mda values for the energies of 238 keV and 338 keV, with the largest value being obtained for Scale-1 and followed by Scale-2, RGTh-1, PG-IAEA and PG-CSN.

Finally, regarding the values corresponding to the ^{40}K mda , the highest mda value is the one obtained for Scale-1 and followed by Scale-2, PG-IAEA, PG-CSN and RGK-1. In this case, it has been observed that the mda value of RGK-1 standard was the smallest. This is reasonable since the RGK-1 standard has a relatively small Compton continuum at 1460 keV and given that the mda is related to the Compton continuum counts, it is completely consistent that the mda value for this standard was less than the one obtained for the other samples. In the case of the RGK-1 standard, it has been verified that the number of counts belonging to the full-energy peak is 2 or 3 orders of magnitude higher than the one related to the Compton continuum.

3.1.3.4. Validations of the efficiency calibration methodology for NORM samples

Two kinds of validations have been considered: 1. External and 2. Internal (consistency test) validations. The first kind has been done using CRM samples, while the second one using uncertified samples, verifying that the activity concentration value of a specific radionuclide is very similar regardless of the E_γ and h values chosen to carry out its determination, that is, the second type of validation is a consistency test of the methodology proposed in this study.

In addition, note that the ^{226}Ra activity concentration ($a_{226\text{Ra}}$) can be calculated considering non-secular equilibrium between ^{226}Ra and ^{238}U . At 186 keV ($^{226}\text{Ra} + ^{235}\text{U}$ emissions), for NORM samples where $^{235}\text{U}/^{238}\text{U}$ activity ratio is 0.046, $a_{226\text{Ra}}$ is given by the equation:

$$a_{226\text{Ra}} = \frac{G - B - F - I_{235\text{U}}}{P_\gamma(226\text{Ra}) \varepsilon_{186\text{keV}} m t} = \frac{G - B - ft}{0.0351 m \varepsilon_{186\text{keV}} t} - 0.75 a_{234\text{Th}} \quad (\text{Eq. 3.1.13})$$

where G and B are the gross and the Compton continuum of the 186 keV peak, respectively, $I_{235\text{U}}$ is the interference term previously defined in Eq. 3.1.12 and $P_\gamma(^{226}\text{Ra})$ is the ^{226}Ra emission probability at 186 keV. Then, F and f are the environmental background expressed in counts and counts per second, respectively. On the other hand, $\varepsilon_{186\text{keV}}$ is the efficiency calculated in the real sample matrix at 186 keV, t is the counting time, m is the sample mass and $a_{234\text{Th}}$ is the activity concentration for ^{234}Th . In Eq. 3.1.13 it has been considered that ^{238}U and ^{234}Th are in secular equilibrium.

3.1.3.4.1. External validation

The following certified NORM samples: IAEA-326 (Soil), IAEA-434, CSN-PG and K_2CO_3 , were selected because of their different apparent densities and chemical compositions, whose densities (heights) are as follows: 1.21 g cm $^{-3}$ (25.1 mm), 0.70 g cm $^{-3}$ (7.6 mm), 1.27 g cm $^{-3}$ (15.4 mm) and 1.13 g cm $^{-3}$ (9.1 mm), respectively.

Table 3.1.1

External validation for several NORM samples (IAEA-326, IAEA-434, CSN-PG and K_2CO_3 , where in the case of K_2CO_3 sample, the calculated ^{40}K activity concentration has been 17462(478) Bq kg $^{-1}$ and the reference value was 17800(255) Bq kg $^{-1}$, obtaining a z_{score} value of -0.6).

RN	E_γ (keV)	IAEA-326			IAEA-434			CSN-PG		
		a (Bq kg ⁻¹)	Reference (Bq kg ⁻¹)	z_{score}	a (Bq kg ⁻¹)	Reference (Bq kg ⁻¹)	z_{score}	a (Bq kg ⁻¹)	Reference (Bq kg ⁻¹)	z_{score}
²³⁴ Th	63.29	28(3)	29.4(1.7)	-1.4	156(38)	120(6)	0.9	38(14)	48.6(1.2)	-0.7
²²⁶ Ra	185.96 (Non-sec. eq.)	40(3)		1.5	766(61)		-0.2	614(37)		-0.5
	185.96 (Sec. eq.)	34(3)		0.4	498(40)		-5.6	363(31)	634(13)	-8.2
²¹⁴ Pb	295.22	30.6(9)	33(3)	-0.6	664(24)	780(31)	-3.0	536(17)	580(13)	-2.1
	351.93	31.0(8)		-0.5	648(20)		-3.6	555(15)		-1.3
²¹⁴ Bi	609.31	30.8(8)		-0.6	631(21)		-4.0	535(16)		0.1
	1120.29	30.8(1.7)		-0.5	611(46)		-3.1	557(29)	533(13)	0.7
²¹⁰ Pb	46.54	38(2)	53(5)	-2.7	745(39)	680(29)	1.3	738(31)	781(15)	-1.4
²²⁸ Ac	338.42	42(7)	40(2)	0.2						
	911.16	40.3(1.3)		0.1						
²¹² Pb	238.63	37.8(9)	39.1(1.7)	-0.7						
²⁰⁸ Tl	583.19	37.4(1.1)		-0.9						
⁴⁰ K	1460.83	592(13)	580(28)	0.4						

In Table 3.1.1, the obtained $|z_{score}|$ values can be found, being below 2 in general, i.e., there was no significant differences between our measured and the reference values. In the case of the two phosphogypsum samples, the z_{score} values were very good for ²³⁴Th and ²¹⁰Pb, while the z_{score} values for ²²⁶Ra daughters were very bad in general. This happens because the phosphogypsum samples have a considerable percentage of ²²²Rn losses from their grains, and they were measured immediately after their preparations, so ²²²Rn was not in secular equilibrium with ²²⁶Ra. However, if the ²²⁶Ra activity concentration is determined by its gamma emission of 186 keV, a very good z_{score} value is obtained. Later, in Section 3.1.3.5, the analysis of the ²²²Rn losses in phosphogypsum samples will be analyzed.

3.1.3.4.2. Internal validation

The following NORM samples were chosen, where the followed choice criteria were the same than the ones considered in the first validation type: Scale-1, Scale-2, Tionite and Ilmenite, whose densities (heights) are as follows: 1.32 g cm⁻³ (12.2 mm), 1.00 g cm⁻³ (13.9 mm), 1.21 g cm⁻³ (12.5 mm) and 3.00 g cm⁻³ (18.0 mm), respectively.

Table 3.1.2

Internal validation for several NORM samples (Scale-1, Scale-2, Tionite and Ilmenite).

RN	E_γ (keV)	Scale-1	Scale-2	Tionite	Ilmenite
		a (Bq kg ⁻¹)	a (Bq kg ⁻¹)	a (Bq kg ⁻¹)	a (Bq kg ⁻¹)
²³⁴ Th	63.29	-49(54)	-55(26)	166(21)	135(17)
²²⁶ Ra	185.96 (Non-sec. eq.)	8658(254)	2962(95)	562(26)	103(13)
	185.96 (Sec. eq.)	4906(336)	1695(118)	387(28)	115(9)
²¹⁴ Pb	295.22	8744(201)	2965(69)	537(13)	125(3)
	351.93	8607(197)	2911(67)	538(13)	120(3)
²¹⁴ Bi	609.31	8770(203)	2911(68)	528(13)	120(3)

	1120.29	8825(230)	3021(84)	550(18)	122(4)
^{228}Ac	338.42	3829(651)	1997(340)	2741(466)	367(62)
	911.16	3884(105)	2043(56)	2344(61)	485(13)
^{212}Pb	238.63	3082(69)	520(13)	364(8)	486(11)
^{208}Tl	583.19	3047(71)	513(15)	360(10)	472(10)

In Table 3.1.2, it is possible to see that the internal validation for the four samples was very good, since the ^{226}Ra , ^{228}Ra and ^{228}Th activity concentrations calculated using the gamma emissions corresponding to their daughters (^{214}Pb and ^{214}Bi , ^{228}Ac and ^{212}Pb and ^{208}Tl , respectively) were very similar to each other for each one of those three radionuclides. Furthermore, note that for the Scale-1, Scale-2 and Tionite samples, there was clearly no secular equilibrium between ^{226}Ra and ^{238}U , given that the calculations at 186 keV were much better in the case of non-secular equilibrium. Regarding the Ilmenite sample, the opposite occurs than for the three previous samples, that is, at 186 keV the obtained calculations considering secular equilibrium were much better than the ones resulted from not considering it. This is very consistent since Ilmenite is a mineral and, consequently, secular equilibrium must be reached. For further information about chemical compositions of all the samples analyzed in this work, see Table A.9 (in Supplementary Material-A).

3.1.3.5. Analysis of ^{222}Rn losses in phosphogypsum and aqueous samples

Depending on the origin of the NORM sample (mineral, scale, waste obtained by precipitation, etc.), ^{226}Ra can be either distributed uniformly along the grains of the material or adsorbed onto the grains surface. For the phosphogypsum case, large ^{222}Rn losses have been observed and, consequently, significant disequilibria between ^{226}Ra and ^{222}Rn can be obtained (for further information about studies related to ^{222}Rn losses, see Benke and Kearfott, 2000; Hightower and Watson, 1995; Kuzmanović et al., 2020; Lamonaca et al., 2014; Scholten et al., 2013; Tudyka et al., 2021. For this, the phosphogypsum samples previously studied (IAEA-434 and CSN-PG) have been selected. In order to study this issue, two ^{226}Ra measurements were made: one just after preparing them, and a second after waiting a month to assure ^{222}Rn and ^{226}Ra are in secular equilibrium (see Table 3.1.3).

Table 3.1.3

Analysis of ^{222}Rn losses in phosphogypsum samples (IAEA-434 and CSN-PG). Determination of ^{226}Ra by 186 keV gamma emission in the IAEA-434 and CSN-PG samples in the case of secular non-equilibrium between ^{238}U and ^{226}Ra (Non-sec. eq.).

E_γ (KeV), RN	IAEA-434 ($h = 7.6$ mm)			Z_{score}	
	a (Bq kg ⁻¹) (1st measure)	a (Bq kg ⁻¹) (2nd measure)	^{222}Rn losses (%)	(1st measure)	(2nd measure)
63 (^{234}Th)	156 ± 38				
186 (^{226}Ra , Non-sec. eq.)	766 ± 61			-0.2	
295 (^{214}Pb)	664 ± 24	692 ± 24	4 ± 5	-3.0	-2.3
352 (^{214}Pb)	648 ± 20	716 ± 21	10 ± 5	-3.6	-1.7
609 (^{214}Bi)	631 ± 21	732 ± 23	16 ± 5	-4.0	-1.3
1120 (^{214}Bi)	611 ± 46	751 ± 46	23 ± 12	-3.1	-0.5
	Average loss (%)		13 ± 4		

E_γ (KeV), RN	IAEA-434 ($h = 18.1$ mm)			Z_{score}	
	a (Bq kg ⁻¹) (1st measure)	a (Bq kg ⁻¹) (2nd measure)	²²² Rn losses (%)	(1st measure)	(2nd measure)
63 (²³⁴ Th)	-22 ± 24				
186 (²²⁶ Ra, Non-sec. eq.)	830 ± 77			0.6	
295 (²¹⁴ Pb)	640 ± 22	732 ± 20	14 ± 5	-3.7	-1.3
352 (²¹⁴ Pb)	641 ± 19	711 ± 18	11 ± 4	-3.8	-1.9
609 (²¹⁴ Bi)	632 ± 20	724 ± 19	15 ± 5	-4.0	-1.5
1120 (²¹⁴ Bi)	560 ± 37	734 ± 30	31 ± 10	-4.5	-1.1
	Average loss (%)		18 ± 3		
E_γ (KeV), RN	CSN-PG ($h = 15.4$ mm)			Z_{score}	
	a (Bq kg ⁻¹) (1st measure)	a (Bq kg ⁻¹) (2nd measure)	²²² Rn losses (%)	(1st measure)	(2nd measure)
63 (²³⁴ Th)	38 ± 14				
186 (²²⁶ Ra, Non-sec. eq.)	614 ± 35			-0.5	
295 (²¹⁴ Pb)	536 ± 17	583 ± 17	9 ± 5	-2.1	0.1
352 (²¹⁴ Pb)	555 ± 15	583 ± 15	5 ± 4	-1.3	0.1
609 (²¹⁴ Bi)	535 ± 16	581 ± 16	9 ± 4	-2.2	0.1
1120 (²¹⁴ Bi)	557 ± 29	571 ± 27	3 ± 7	-0.7	-0.3
	Average loss (%)		6 ± 3		

Two thicknesses were chosen to analyze the ²²²Rn losses in the IAEA-434 sample (where the volume of the cylindrical container is constant, the total interior height (H) is 60.5 ± 0.2 mm and the inner diameter ($\varnothing$) is 34.6 ± 0.2 mm). The obtained losses were $13 \pm 4\%$ and $18 \pm 3\%$ for $h = 7.6$ mm and 18.1 mm, respectively (average loss = $16 \pm 3\%$).

The CSN-PG sample was measured with a thickness of 15.4 mm, obtaining ²²²Rn losses of $6 \pm 3\%$ which are lower than the ones calculated in the case of the IAEA-434 sample. This fact could be related to the manufacturing procedure of the phosphogypsum samples. Probably, for the IAEA-434 sample, ²²⁶Ra was more deposited onto the surface of the PG grains favoring the ²²²Rn exhalation than in the CSN-PG, where the ²²⁶Ra is more uniformly distributed inside the grains. Consequently, this fact allows us to recommend determining the ²²⁶Ra activity concentration by using the 186 keV energy for samples whose ²²²Rn exhalation rates from the grains are high (see Table 3.1.3).

Table 3 also shows the calculations of ²²⁶Ra activity concentrations obtained using the 186 keV gamma emission for phosphogypsum materials. As it can be seen, these calculations are not only in very good agreement with respect to the reference values, but they are also better than the values calculated by the gamma emissions belonging to the ²²⁶Ra daughters after waiting a month (see 2nd measure in Table 3.1.3).

To finish the study related to the determination of the radon losses from a sample, a liquid standard was prepared by dissolving a mass of RGU-1 containing 165.6 ± 5 Bq kg⁻¹ of ²³⁸U and h value being 30.3 mm (see Table 4). In this case, there was a very large ²²²Rn loss due to its accumulation in the upper air chamber (where the thickness of the upper air chamber was 30.2 mm). For this sample, the average ²²²Rn loss was $68 \pm 5\%$ that was calculated comparing the ²²⁶Ra activity concentrations, which were obtained using the gamma emissions of ²¹⁴Pb and ²¹⁴Bi, with the reference value.

However, the ^{226}Ra activity concentration calculation using the 186 keV energy agreed very well with the reference value (see Table 3.1.4).

Furthermore, it is necessary to mention that the values of ^{222}Rn losses obtained in this Section are very consistent with the ones obtained in a previous study (Barba-Lobo et al., 2021b), where the percentages of the ^{222}Rn losses were 15(3)%, 11(2)% and 71(8)% for the IAEA-434, CSN-PG and dissolved RGU-1 samples, respectively.

Table 3.1.4

Determination of ^{226}Ra by its daughters and 186 keV gamma emissions in dissolved RGU-1 standard in the case of secular non-equilibrium between ^{226}Ra and ^{222}Rn ($h = 30.3$ mm).

RN	E_γ (keV)	a (Bq kg ⁻¹)	Reference (Bq kg ⁻¹)	z_{score}
^{234}Th	63.29	183(15)		1.1
^{226}Ra	185.96 (Secular equilibrium between ^{238}U and ^{226}Ra)	169(12)		0.3
^{214}Pb	295.22	53.5(1.7)	165.6 (5)	-62
	351.93	53.3(1.5)		-72
^{214}Bi	609.31	53.5(1.6)		-68
	1120.29	49(3)		-41

3.1.4. Conclusions

The main conclusions are the following:

1. In the present study, it has been developed a new method to calibrate in efficiency in order to determine natural γ -ray emitters in NORM samples using coaxial Ge detectors. For this, firstly the most intense gamma emissions (E_γ), which are characterized by not having interferences, of the radionuclides contained in the standards were chosen. Then, after compacting the standards until reaching the desired thickness values (h), the experimental values of the apparent full-energy peak efficiency ($FEPE$) were calculated for the different selected h and E_γ values. Finally, a function was chosen to fit the experimental $FEPE$ s varying h (from 0.5 cm to 5 cm) and fixing E_γ , ϵ_c (E_γ, h), which was an asymptotic exponential in this study, obtaining residues that were three times smaller than the ones obtained by other functions used in previous works. Regarding the comparison made between the experimental values calculated for $FEPE$ and the ones provided by Genie 2000, very low average z_{score} values (< 0.5) were obtained at all the selected energies, verifying both the good calculations carried out for experimental $FEPE$ and the great reliability of the Genie 2000 software.
2. Then, it has been proved that the calibration in efficiency varying E_γ is less accurate than the one obtained varying h , since in the first case, the true coincidence summing effects are more relevant as well as the uncertainties of the experimental $FEPE$ s increase due to the contribution of the gamma emission probability uncertainties. Besides, the residues resulted from the fittings done to calibrate varying E_γ were double than the ones obtained calibrating varying h . All this implies that the determination of artificial radionuclides would be more advisable to be carried out calibrating in efficiency by varying h and using standards which

contain those artificial radionuclides instead of calibrating varying E_γ , that is, using the relative measurement of the activity.

3. On the other hand, it has been checked that the minimum detectable activity concentration (*mda*) decreases as the sample thickness (mass) increases as well as the *mda* depends on the characteristics (density and activity concentrations of ^{226}Ra and ^{228}Th) of each sample analyzed. In addition, at 186 keV *mda* values were higher when the secular equilibrium between ^{238}U and ^{226}Ra was not considered in comparison with the ones corresponding to the opposite case.
4. The methodology followed in this work has been validated employing several certified and non-certified NORM samples. Thus, in the internal validation, very similar activity concentration values were obtained for a specific radionuclide regardless of the E_γ selected to accomplish its determination, proving the good consistency of the proposed methodology. Besides, an external validation was carried out for certified samples, where the $|Z_{score}|$ values resulted from this validation were less than 2, getting to fully check the very good validity of the methodology.
5. Finally, it has been demonstrated that the ^{226}Ra determination is much more recommendable to be carried out using its gamma emission (186 keV) than the ones corresponding to its daughters. This is especially true in samples characterized by having high ^{222}Rn losses such as phosphogypsum and aqueous samples, obtaining ^{222}Rn losses of $16 \pm 3\%$, $6 \pm 3\%$ and $68 \pm 5\%$ in the case of the IAEA-434, CSN-PG and dissolved RGU-1 samples, respectively, being these ^{222}Rn losses very consistent with the ones obtained in a previous work, where the same samples were analyzed.

Subchapter 3.2.: A general methodology to determine natural radionuclides by well-type HPGe detectors

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Subchapter 3.2.: A general methodology to determine natural radionuclides by well-type HPGe detectors

Abstract

This work aims to determine natural radionuclides (^{210}Pb , $^{228,226}\text{Ra}$, $^{234,228}\text{Th}$ and ^{40}K) in NORM samples by well-type HPGe detectors because they are of vital importance in studies on environmental samples. For this, a novel methodology has been developed, based on obtaining a general function for the full-energy peak efficiency (*FEPE*) versus the sample apparent density and composition, keeping the sample height constant. To obtain the general *FEPE* function, a calibration in efficiency has been accomplished using certified standards provided by IAEA (RGU-1 and RGTh-1), and KCl. Besides, different self-absorption correction functions were compared for cylindrical geometry, where chemical compositions need to be known. Then, a study on using an anti-Compton system was done, getting a lower detection limit and allowing to propose gamma spectrometry as an alternative technique to alpha-particle spectrometry. Finally, the followed methodology to calculate the *FEPE* was subjected to internal and external validations, checking its validity range.

Keywords: Gamma–Alpha-particle spectrometry; Well-type Ge detectors; Efficiency calibration; Self-absorption correction; Anti-Compton system; NORM.

3.2.1. Introduction

In the last decades, the natural radionuclides such as ^{210}Pb , $^{228,226}\text{Ra}$, $^{234,228}\text{Th}$ and ^{40}K are being of great interest due to their wide usage in many environmental fields. The knowledge and use of these radionuclides can be very useful in covering different problems present in the environment, such as the calculation of residence times of atmospheric aerosols (Baskaran, 2011). Another example is marine scavenging where ^{234}Th is widely used (Church and Sarin, 2008). ^{210}Pb determination is also interesting in order to date sediments or assess the erosion of a material (San Miguel et al., 2002; San Miguel et al., 2004).

When a material contains important concentrations of natural radionuclides, it has to be considered as a NORM sample (Naturally Occurring Radioactive Material) (for further information about NORM samples, see Barbero et al., 2014; Blasco et al., 2016; Gázquez et al., 2014; Hierro et al., 2014; Luque et al., 2015; Spasic-Jokic et al., 2013). There are many industries that produce, for example, metals or fertilizers which generate industrial wastes with high concentrations of natural radionuclides. Consequently, spectrometric techniques need to be employed in order to assess the radiotoxicity to which the workers are exposed. Furthermore, materials related to building construction must be subjected to a radiological control (European Commission, 1983).

On the other hand, in order to determine natural long-lived radionuclides by gamma spectrometry, an efficiency calibration of the detectors is necessary. Nowadays the calibration of detectors by Monte Carlo simulations has become generalized (for further information about Monte-Carlo simulations carried out in HPGe detectors, see Ahmed, 2019; Belgin and Aycik, 2015; Bochud et al., 2006; Laborie et al., 2002; Zare et al., 2016). Thus, there are many cases for which old detectors are not characterized, and the laboratories have to send them into the factory to carry out the characterization procedure, involving high costs for the characterization and the new Monte Carlo software, and needing to wait some time without gamma measurements.

In contrast to Monte Carlo simulations, well-type Ge detectors can be calibrated relatively quickly and using calibration standards that do not imply so high costs. Besides, they have a high absolute efficiency which is about 40% at low energies, that is, $E_\gamma \leq 150$ keV (where E_γ is the gamma emission energy). That efficiency value is approximately four times higher than the one obtained for any another coaxial detector for that same energy range, being this very important since self-absorption effects are more relevant for low energies. This agrees with many studies carried out on self-absorption corrections (San Miguel et al., 2002; Barba-Lobo et al., 2021c; Bonczyk, 2018; Carrazana et al., 2010; Długosz-Lisiecka and Ziomek, 2015; Jodłowski, 2006; Martínez-Ruiz et al., 2007; Montes et al., 2019; Suárez-Navarro et al., 2020). Regarding corrections related to self-absorption effects, in Appleby et al., 1992 a correction model was proposed, which is usually used in the case of coaxial well-type detectors. In the present study, the previous model has been employed and its validity has been checked, comparing it with other possible functions.

Furthermore, there are different techniques that are used to determine long-lived natural radionuclides, such as alpha-particle spectrometry with semiconductor detectors, Inductively Coupled Plasma Spectroscopy (ICP), Neutron Activation Analysis (NAA), Liquid Scintillation Counting (LSC) and Gamma-ray spectrometry. The former requires tedious procedures in the case of ^{228}Ra and ^{226}Ra determinations (Pérez-Moreno et al., 2019; Thomas et al., 2020). Then, regarding the ICP technique, it is necessary to use chemical isolation methods in order to determine radionuclides (Roos, 2008; Wallner et al., 2008). On the other hand, when employing the LSC technique, it is more recommendable to use it in the cases of the radionuclides whose half-lives are not very high because the frequency of the decay is proportional to the half-life (Hou et al., 2018; Hou and Roos, 2008). Regarding the NAA, a nuclear reactor would be required in order to apply this technique and, consequently, a very significant cost and power supply would be needed (Landsberger et al., 2013; Zaidi et al., 1999). For these reasons, gamma spectrometry has been proposed in this study as an alternative sensitive radiometric technique and with low cost per sample. In the case of alpha-particle spectrometry, since this technique is characterized by having low detection limits for most of the natural radionuclides, in this work it has been carried out an in-depth study related to the advantages and disadvantages of using an anti-Compton system.

Considering all the topics previously exposed, this work is focused on developing a novel methodology, which is explained in Materials and methods Section, to obtain a general *FEPE* function for determining natural long-lived radionuclides in the case of using coaxial well-type germanium detectors. Besides, an original study about benefits and drawbacks of using an anti-Compton system has been done considering several kinds of NORM samples, as well as a comparison between alpha-particle and gamma spectrometric techniques has been made.

3.2.2. Materials and methods

3.2.2.1. Materials

For this study, a coaxial well-type HPGe detector (model GCW3023) was employed, where HPGe means high purity germanium. This detector has a relative efficiency of 34.8% in relation to a NaI (Tl) detector with an active area of 3" x 3", as well as a full width at half-maximum (FWHM) of 1.33 keV at 122 keV (^{57}Co) and 2.04 keV at 1332 keV (^{60}Co), and a peak/Compton ratio of 56.2/1. Besides, it has a well depth of 40 mm and an active volume of 180 cm³. The detector was coupled to a multichannel analyzer and shielded with 10 cm thick Pb, using Genie 2000 as the software to generate the spectra. In order to avoid interferences from Pb X-ray, a 2 mm thick layer of Cu was placed between the Pb shield and the detector.

With regard to the anti-Compton system used in this study, it consists of seven NaI (TI) detectors which are connected between them and they are placed around the well-type HPGe detector to properly reduce the Compton continuum. It is necessary to clarify that this system is called “anti-Compton” system, however its function is to eliminate all the particles detected in coincidence. In the case of the photons, either photoelectric effect or Compton scattering occur, where the second phenomenon has higher probability to occur for the great majority of the photons. For this reason, this system is called anti-Compton system.

In order to obtain the experimental efficiency values of the detector in the calibration matrix, certified standards provided by the IAEA (International Atomic Energy Agency) were employed, being their codes RGU-1 and RGTh-1. These two calibration samples contain natural radionuclides belonging to ^{238}U - and ^{232}Th -series, where the reference values for activity concentration and densities are $4940 \pm 15 \text{ Bq kg}^{-1}$ and $3250 \pm 45 \text{ Bq kg}^{-1}$, and $1.63 \pm 2 \text{ g cm}^{-3}$, respectively, with uncertainties given at 1 sigma level. Both certified standards are mainly composed by SiO_2 , which was used to dilute U (7.09%) and Th (2.89% Th and 219 ppm of U) ores whose codes are BL-5 and OKA-2, respectively. On the other hand, high purity KCl was also used as a calibration standard for ^{40}K , where its reference activity concentration was obtained by the relation established by the IAEA, that is, 1% of natural K $\rightarrow 313 \text{ Bq kg}^{-1}$ of ^{40}K . (See IAEA, 1987; IAEA, 2020 for further information about the characteristics of RGU-1, RGTh-1 and RGK-1). For further information about chemical compositions of the calibration samples used in this study, see Table B.14 in Supplementary Material-B.

On the other hand, several real samples have been chosen in order to apply the methodology proposed in this study. Therefore, NORM samples were chosen due to their wide variety of chemical compositions and densities. Consequently, a proper validation procedure of the followed methodology can be carried out. So, the real samples selected were the following, which have been chosen because of having very different densities and compositions. They have been divided into two groups (non-certified and certified samples): 1. Non-certified samples: Ilmenite, Industrial waste (Scale-1), Phosphate Rock-1 (PR-1), Distilled water; 2. Certified samples: Soil (IAEA-326), K_2SO_4 (RGK-1), Phosphogypsum (IAEA-434), Phosphogypsum used in a CSN/CIEMAT Inter-Comparison exercise (CSN-PG), Phosphate Rock-2 (PR-2). See Table B.14 in Supplementary Material-B to know chemical compositions and apparent densities of all the real samples selected in this work. Regarding CSN and CIEMAT, they are the acronyms for the Spanish Nuclear Safety Council (“Consejo de Seguridad Nuclear”) and the Centre for Energy, Environment and Technology Research (“Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas”), respectively.

3.2.2.2. Methods

Regarding the calibration procedure in efficiency, cylindrical plastic vials were used as containers whose height (h), radius (a) and volume (V) were $3.50 \pm 0.02 \text{ cm}$, $0.670 \pm 0.010 \text{ cm}$ and $4.94 \pm 0.15 \text{ cm}^3$, respectively. Then, since the calibration samples were prepared at the same height, h , RGU-1 and RGTh-1 standards were mixed with other kinds of samples to get cover a density range as wide as possible. These other samples were PbS and activated carbon.

About the mixtures made to obtain standards whose densities were high, that is, between PbS and RGU-1/RGTh-1, a total of 13 mixtures were prepared in both cases, where the proportion of both standards varied from 10% to 97%. In this case, a code was employed in order to identify each mixture. Therefore, STi-U and STi-Th were the codes for mixtures made with RGU-1/RGTh-1 and PbS, respectively, being “i” the proportion of the standards in each one of the mixtures (see Tables B.1 and B.2, respectively, in Supplementary Material-B). On the other hand, with regard to the mixtures carried out in order to lower the density of the standards, that is, between activated carbon and RGU-1/RGTh-1, a total of 3 mixtures were made for each one of the standards. Analogously to

the previous case, a code was used to identify each mixture, being in this case Ci-U and Ci-Th, where “i” is the proportion of the standards in each mixture (see Tables B.6 and B.7, respectively, in Supplementary Material-B).

Apart from the mixtures of the standards (RGU-1 and RGTh-1) with PbS and activated carbon previously described, 9 calibration samples were prepared for both standards varying the grade of compaction of each one of them. In this case, the code used to identify each calibration sample was RGUi and RGThi, where “i” was ranged from 1 to 9, increasing the compaction grade as “i” increases (see Tables B.3 and B.4, respectively, in Supplementary Material-B). Therefore, a total of 25 calibration samples were prepared for RGU-1 and RGTh-1 in order to carry out the calibration in efficiency. On the other hand, in the case of KCl calibration standard, this was dissolved in water and, consequently, K concentration was varied getting 9 calibration samples. For these calibration samples, the identifier code was K-i, where “i” was ranged from 1 to 9, increasing the K concentration as “i” increases (see Tables B.5 in Supplementary Material-B).

Besides, it is necessary to clarify that the relative uncertainties related to the activities of ^{238}U , ^{232}Th and ^{40}K , that is, $A(^{238}\text{U})$ (Bq), $A(^{232}\text{Th})$ (Bq) and $A(^{40}\text{K})$ (Bq), respectively, which can be found in Tables B.1 – B.7, can be approximated by the relative uncertainties corresponding to the reference activity concentration values. This is possible because in order to proceed with the $A(^{238}\text{U})$, $A(^{232}\text{Th})$ and $A(^{40}\text{K})$ calculations, there are only two main contributions, that is, the reference activity concentrations and the masses of each standard contained in the vials, where the relative uncertainties related to the latter contribution can be completely neglected.

Once all the calibration samples were prepared, experimental full-energy peak efficiencies calculated in the calibration matrix (ε_{exp}) were obtained fixing the gamma emission energy (E_γ) and varying the calibration sample density (ρ) or varying the calibration sample mass (m) since the volume of sample container is fixed. After obtaining the experimental efficiencies, it was necessary to calculate another kind of full-energy peak efficiency, ε_0^{exp} , which represents the experimental detector efficiency calculated in the matrix of a sample whose mass tends to zero. These calculations were possible due to the relation between both kinds of efficiencies, that is

$$\varepsilon_{exp} = f \varepsilon_0^{exp} \quad (\text{Eq. 3.2.1})$$

where f is the self-absorption correction factor, having used in this case the one proposed in Appleby et al., 1992. The f factor is necessary to be employed in order to consider the attenuation effects when the sample mass (or density) is different from zero.

Consequently, for all the gamma energies belonging to the radionuclides that are contained in RGU-1 and RGTh-1 standards, 25 values of ε_{exp} were obtained, that is, a value for each calibration sample prepared. Analogously to ε_{exp} values obtained in the cases of RGU-1 and RGTh-1 standards, 9 values of ε_{exp} were calculated for KCl standard. See Tables B.8, B.9 and B.10 in Supplementary Material-B for further information about ε_{exp} values calculated in the cases of RGU-1, RGTh-1 and KCl standards, respectively, as well as the E_γ values selected to carry out the calibration in efficiency and their respective emission probabilities (P_γ). In those three tables, each ε_{exp} value is associated to a ηm value, where η and m are the mass attenuation coefficient and mass of each calibration sample that has been prepared. Once the ε_0^{exp} values were obtained for each energy, an average ε_0^{exp} value, ε_0 , was determined for each one of these energies (see Table B.11 in Supplementary Material-B).

3.2.3. Results and discussion

This Section has been divided into five subsections: Calibration in efficiency, self-absorption correction functions, an in-depth study on using anti-Compton system (including applications to both the detection limit calculations and gamma spectrometry versus alpha-particle spectrometry), internal and external validations of the methodology followed in this work and a proposed method to determine ^{226}Ra in phosphogypsum and aqueous samples.

3.2.3.1. Obtaining of the full-energy peak efficiencies (FEPEs) in the calibration matrices

The experimental *FEPEs* (ε_{exp}) in the calibration samples for a given energy E_γ , is obtained through the following equation:

$$\varepsilon_{exp}(E_\gamma, m) = \frac{G - B - F - I}{maP_\gamma t} = \frac{N}{maP_\gamma t} \quad (\text{Eq. 3.2.2})$$

where G , B , F , I and N are the gross counts, the continuum Compton, the background due to the environmental conditions of the laboratory, interference terms and the net counts, respectively. Then, P_γ is the gamma emission probability, which were taken from Toi Lund, 1999, a and m are the activity concentration and mass of the samples (in this case, calibration standards), respectively, t the counting time. Only gamma emissions without interferences have been selected so $I \sim 0$.

Once the ε_{exp} values have been calculated by Eq. 3.2.2, it is possible to obtain ε_0^{exp} by Eq. 3.2.1. Furthermore, it is necessary to know the function employed to quantify the self-absorption corrections. In this case, it has been used the correction function proposed in Appleby et al., 1992, which is given by the following expression:

$$f(x^2) = 2 \exp(-kx^2) [(kx^2)^{-1} \sinh(kx^2) - (kx^2)^{-2} (\cosh(kx^2) - 1)] \quad (\text{Eq. 3.2.3})$$

where $x^2 = \eta m$, being m and η the sample mass and mass attenuation coefficient, respectively, η being related to the sample linear attenuation coefficient (μ) and density (ρ) by $\eta = \mu/\rho$. Then, k is the geometric parameter characterizing the dimensions of the sample, which is given by $k = (\pi ah)^{-1}$, where a and h are the radius and height of the sample container used in the procedure of efficiency calibration, respectively, and whose values were previously mentioned in Materials and methods Section. In order to obtain the η value corresponding to a sample, it was necessary to use the Bragg's additivity law, which says that $\langle \eta \rangle = \sum_i x_i \eta_i$, where x_i and η_i are the proportion and mass attenuation coefficient of each major chemical element "i" contained in the sample, respectively, and $\langle \eta \rangle$ is the mass attenuation coefficient of the sample (see Barba-Lobo et al., 2021c; Suárez-Navarro et al., 2020; Mantero et al., 2015 for further information about Bragg's additivity law).

In Fig. 3.2.1, ε_{exp} for the calibration samples have been plotted as a function of x^2 (where η values for each chemical element were taken from NIST, 2004a) for each specific gamma energy selected in the calibration procedure. As can be seen from Fig. 3.2.1, the majority of the *FEPE* curves show a similar general behavior, that is, ε_{exp} values decrease as energy increase and form curves that are quite parallel similar to each other. However, there are some efficiency curves which do not follow that tendency, occurring this at the following energies: 46 keV, 583 keV, 609 keV, 768 keV and 1120 keV. For 46 keV, the reason of a different behavior is the self-absorption effects which are more relevant for lower energies. On the other hand, for the other three energies, the reason would be related to true coincidence summing effects (TCS), being summing-out effects for these three

energies (Gilmore and Hemingway, 1995; Tedjani et al., 2016; Venegas-Argumedo and Montero-Cabrera, 2015). Considering these motives, it is possible to understand why the behavior of those energies is so different compared with the other ones.

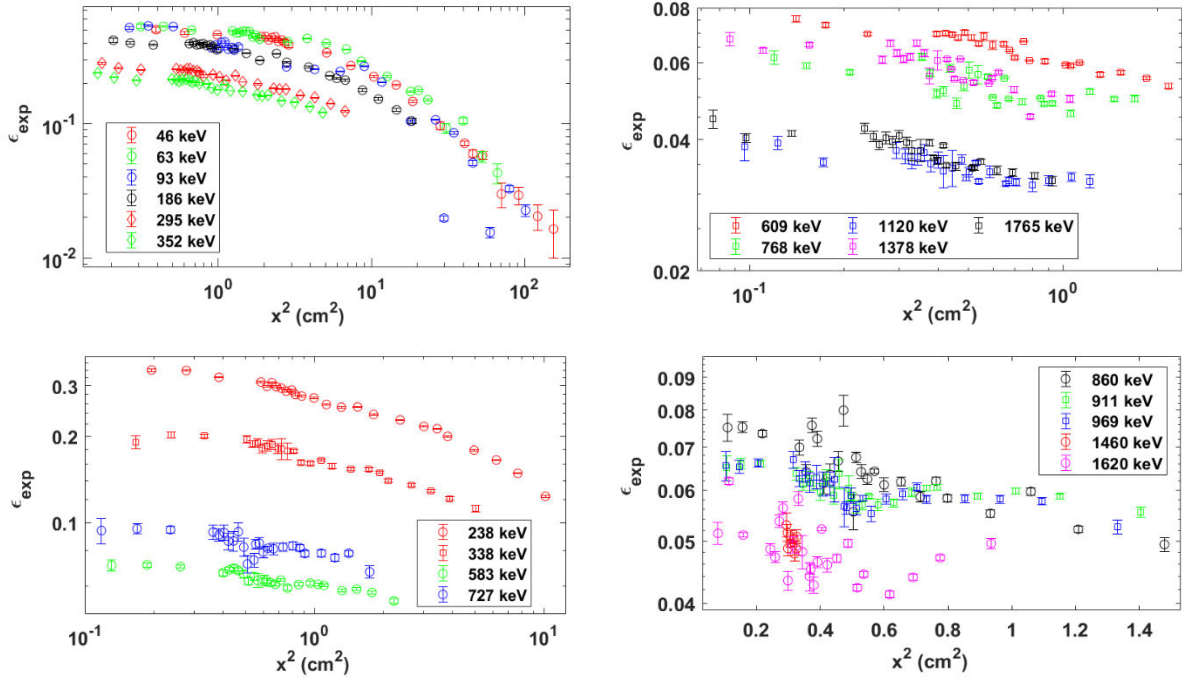


Figure 3.2.1. Experimental efficiency values (ϵ_{exp}) plotted versus x^2 , where $x^2 = \eta m$, for each gamma emission energy of the radionuclides belonging to the ^{238}U - and ^{232}Th -series and ^{40}K , and varying the density of the RGU-1 (mixed with PbS), RGTh-1 (mixed with PbS) and KCl (dissolved in water) standards.

Furthermore, from Fig. 3.2.1 it can be observed that ϵ_{exp} uncertainties (at 1 sigma level) are relatively small. Numerical values for ϵ_{exp} and uncertainties for each ηm value are shown in Tables B.8, B.9 and B.10. In these tables, ϵ_0^{exp} values are also shown. Therefore, from all the ϵ_0^{exp} values obtained for a same energy, an average ϵ_0^{exp} value (ϵ_0) has been determined for each gamma energy. These ϵ_0 values for each specific energy can be found in Table B.11 in Supplementary Material-B. In Table B.11, it can be seen that the uncertainties of ϵ_0 values are relatively small. This occurs in this way because they have been determined by propagation of uncertainties, so the uncertainties decrease as the number of experimental data increase. On the other hand, in order to look for a relationship between ϵ_0 and E_γ , $\ln(\epsilon_0)$ versus $\ln(E_\gamma/E_0)$, where $E_0 = 1$ keV, have been plotted in Fig. 3.2.2 for high energy values, that is, $E_\gamma > 150$ keV. From Fig. 3.2.2 it can be observed a clear linear tendency excepting for 583 keV, 609 keV, 768 keV and 1120 keV which suffer summing-out effects as it was previously mentioned. Discarding these energies, a linear fitting of $\ln(\epsilon_0)$ versus $\ln(E_\gamma/E_0)$ has been accomplished obtaining a relative average residue of 7.5%.

To calculate the relative average residue ($\langle \text{Res} \rangle$ (%)), the following equation was employed:

$$\langle \text{Res} \rangle = \sqrt{\frac{1}{s-1} \sum_{i=1}^s \left[100 \left(\frac{y_{fit}^{(i)}}{y_{exp}^{(i)}} - 1 \right) \right]^2} \quad (\text{Eq. 3.2.4})$$

where $y_{exp}^{(i)}$ and $y_{fit}^{(i)}$ are the values obtained experimentally and the ones obtained by a fitting function for a magnitude y , respectively, s being the number of experimental data.

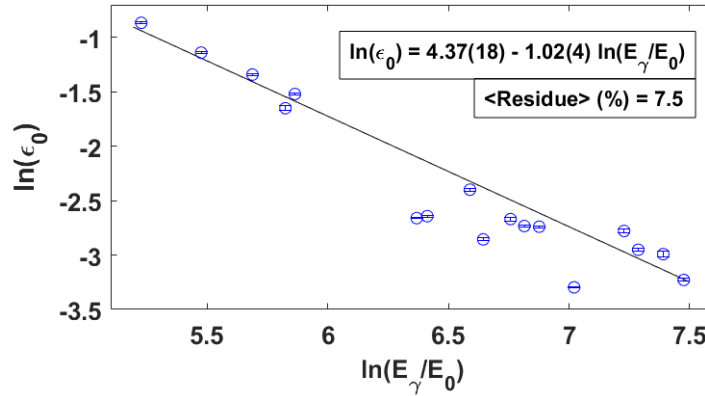


Figure 3.2.2. Fitting of ε_0 values versus $\ln(E_\gamma/E_0)$ at high energies, considering the gamma emissions of the radionuclides belonging to the ^{238}U - and ^{232}Th -series, as well as ^{40}K , and calculation of $\langle \text{Res} \rangle$ values resulted from this fitting.

3.2.3.2. Comparison between different possible self-absorption correction functions

In the calculations of ε_{exp} values, which have been shown in Tables B.8, B.9 and B.10, we have assumed that Eq. 3.2.3 is completely valid in order to correct self-absorption effects in the case of the samples measured by a well-type detector. Therefore, in this Section it has been done a test about the Eq. 3.2.3 validity, as well as a comparison between corrections given by Eq. 3.2.3 and other possible functions that provide a good fit of ε_{exp} values. For this, three kinds of functions (*Function-i*, where $i = 1, 2, 3$) have been selected in order to fit the ε_{exp} values that have been shown in Fig. 3.2.1. The parameters to be adjusted are designed by F_{ij} (parameter j from *Function-i*). These three functions are given by the following equations, which depend on the variable $x^2 = \eta m$, where η and m are the mass attenuation coefficient and the mass of the selected sample, respectively:

$$\text{Function-1: } \varepsilon^{(1)} = \varepsilon_0(E_\gamma) f(kx^2) = F_{11} f(F_{12} x^2) \quad (\text{Eq. 3.2.5})$$

where $F_{11} = \varepsilon_0(E_\gamma)$ are the efficiency values at each energy, which have been shown in Table B.11, and $f(kx^2)$ is the function given by Eq. 3.2.3, being $F_{12} = k$.

$$\begin{aligned} \text{Function-2: } \varepsilon^{(2)} = & 2 F_{21} \exp(-F_{22} x^2) [(F_{23} x^2)^{-1} \sinh(F_{24} x^2) \\ & - (F_{25} x^2)^{-2} (\cosh(F_{26} x^2) - 1)] \end{aligned} \quad (\text{Eq. 3.2.6})$$

where F_{2j} are the parameters resulted from fittings provided by *Function-2*, being j ranged from 1 to 6.

$$\text{Function-3: } \ln(\varepsilon^{(3)}) = \sum_{j=1}^3 F_{3j} \ln(x^2/x_0^2)^{j-1} \quad (\text{Eq. 3.2.7})$$

where F_{3j} are the parameters resulted from fittings provided by *Function-3* and $x_0^2 = \eta_0 m_0 = 1 \text{ cm}^2$ is introduced for the argument of the functions to be dimensionless.

In order to compare the fittings of ε_{exp} provided by those three functions, the most relevant gamma emission from ^{238}U - and ^{232}Th -series radionuclides were considered. Fig. 3.2.3 shows the fitting of ε_{exp} versus ηm values for the different functions. The ε_{exp} values are the same that the ones shown in Tables B.8, B.9, provided by each function for each one of the main gamma energies of the ^{238}U - and ^{232}Th -series. In Fig. 3 note that the fittings provided by *Function-1* agree very well with experimental data for all the emission energies except in the cases corresponding to low energies, that is, 46 keV and 63 keV, particularly for high ηm values when attenuation effects are more significant.

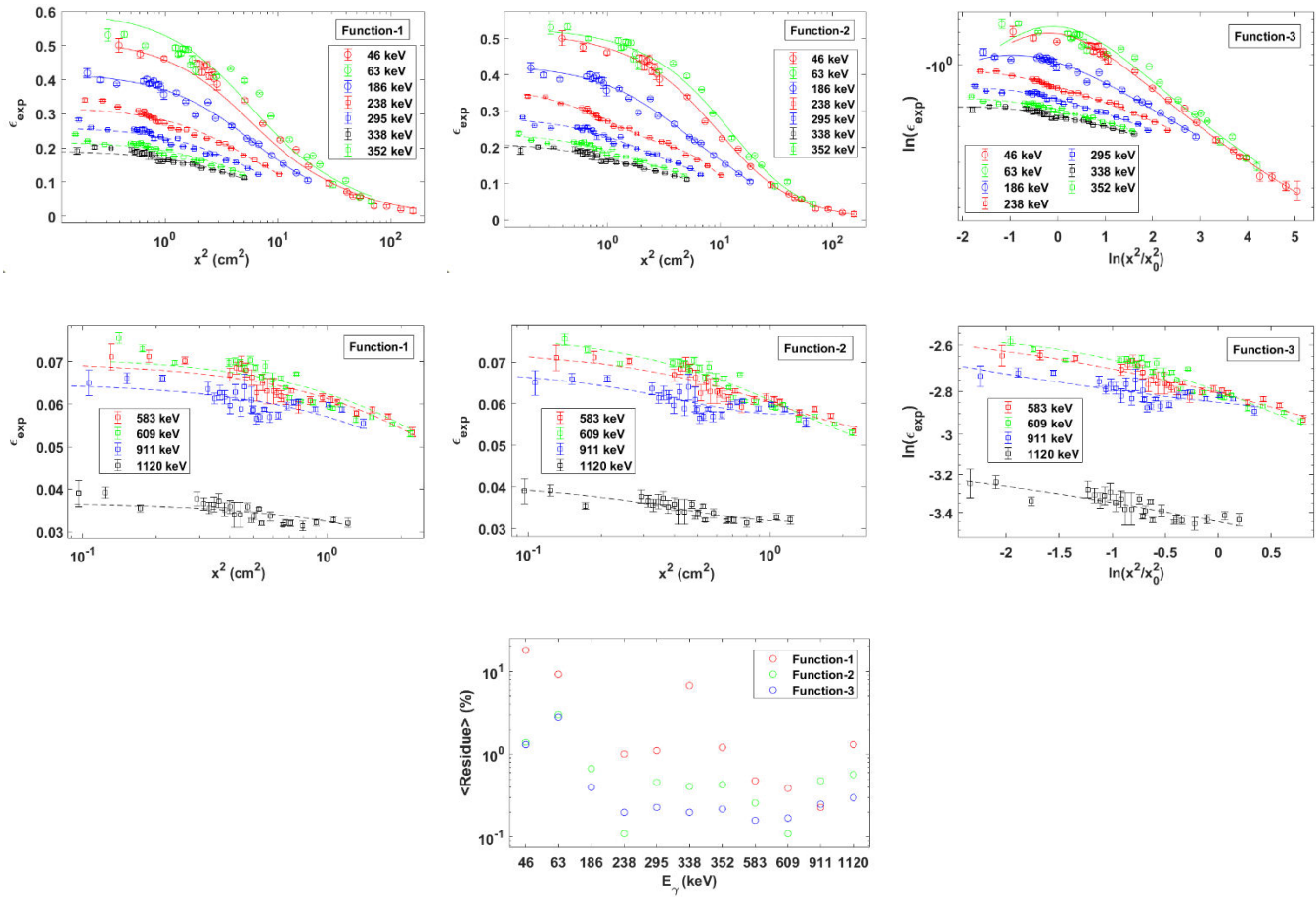


Figure 3.2.3. Comparison between the fittings done by different functions (*Function-i*, with “i” = 1, 2, 3) for ε_{exp} versus x^2 (in the cases of *Function-1* and *Function-2*), and for $\ln(\varepsilon_{exp})$ versus $\ln(x^2/x_0^2)$ (in the case of *Function-3*), being $x^2 = \eta m$ and $x_0^2 = \eta_0 m_0 = 1 \text{ cm}^2$.

Moreover, in Table B.12 (in Supplementary Material-B) it can be found the parameters resulted from the fittings provided by the three functions, as well as the relative average residues obtained for each fitting for a given energy. Regarding the fittings carried out in this Section as well as all the other sections, they were compared statistically by finding their confidence intervals using MATLAB (see MATLAB, 2021 for further information about the algorithms used to provide the fittings). In Table B.12 it can be observed that the residues provided by *Function-1* are much higher at low energies (18% and 9.2% at 46 keV and 63 keV, respectively) than at higher energies. This is due to the fact that one of requirements for validity of Eq. 3.2.3 is that photons must travel parallel to the radial axis of the sample container and the sample itself (cilindrycal geometry). Therefore, for samples whose densities and average atomic numbers, $\langle Z \rangle$, are very high (compared, for example, with the $\langle Z \rangle$ value of a soil, that is, $\langle Z \rangle \sim 10.6$), the previous requirement will not be fulfilled. As attenuation increases, the angle formed by the traveling direction of photons and the radial axis differs more and

more from zero, this being especially true for low energy photons. Consequently, the function given by Eq. 3.2.3 fails to correct self-absorption effects in well-type detectors for high density and high $\langle Z \rangle$ samples.

On the other hand, in Fig. 3.2.3 it can also be observed the fittings of ε_{exp} values versus ηm values provided by *Function-2* and *Function-3*, where in the case of *Function-3*, the fittings have been carried out for the logarithms of ε_{exp} and ηm . Thus, for both functions it can be seen a good agreement between the fittings and experimental data. The parameters and relative average residues resulted from these fittings are shown in Table B.12. As it can be seen from Table B.12 the residues related to the fittings provided by *Function-2* are lower than one excepting for 46 and 63 keV with 1.4% and 3% respectively. This also occurs for the results provided by *Function-3*. The relative average residues have been shown in Fig. 3.2.3. In this graphic, it can be note that the great majority of the fittings provided by *Function-1* are better as E_γ increases, being most of these residues less than 1.3%. In that same graphic, it is possible to see that the residues obtained in the cases of *Funtion-2* and *Function-3* ranged from 0.1% to 3.0%.

3.2.3.3. Study on advantages and disadvantages about using an anti-Compton system

One of the main objectives of using an anti-Compton system is to reduce the Compton continuum, and consequently, get higher efficiencies. Thus, given that the operation of this system consists in eliminating counts generated by photons that have been detected in coincidence by NaI (Tl) detectors, there might be some energies for which the anti-Compton system does not work properly. This means that the system could eliminate counts that should not be neglected. In this Section, a comparison between the counting rates obtained with the anti-Compton system switched on (n^a) and off (n) has been made. This comparison has been done with samples covering a wide range of densities and compositions.

In Fig. 3.2.4, it can be found the ratios of n^a and n plotted for the following nine samples: Scale-1, IAEA-326, Ilmenite, RGU-1, RGTh-1, RGK-1, RGU-1 + 70% PbS, RGTh-1 + 70% PbS and RGK-1 + 70% PbS. Those ratios have been plotted at 46 keV, 63 keV, 186 keV, 238 keV, 295 keV, 338 keV, 352 keV, 583 keV, 609 keV, 911 keV, 1120 keV and 1460 keV.

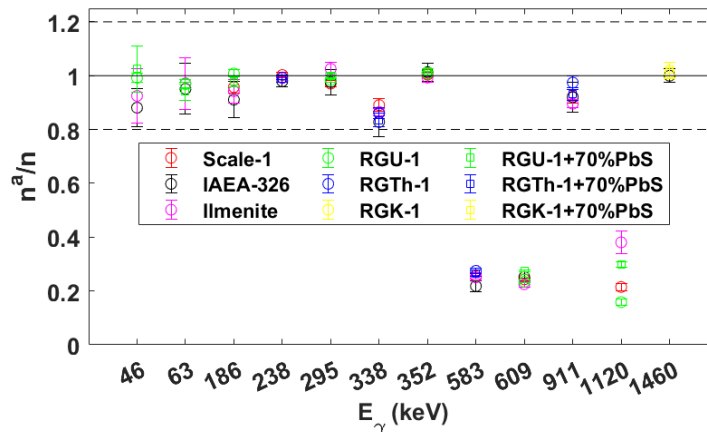


Figure 3.2.4. Comparison between the counting rates obtained for several types of samples, with the anti-Compton system switched on and off.

From Fig. 3.2.4, it can be seen that the anti-Compton system is working properly for many energies since most ratios are close to 1, obtaining a maximum deviation of approximately 15%. However,

there are three energies that clearly differ from the others: 583 keV, 609 keV and 1120 keV. As it was previously commented, these energies have summing-out effects, and consequently, for these energies, emissions of photons in cascade are being occasioned. If two photons are emitted in cascade it is possible that one of them could be scattered by Compton effect whereas the other interact by photoelectric effect. In this situation, the anti-Compton system is eliminating counts that should not be eliminated, since it is eliminating counts generated by photons suffering photoelectric effect, which contribute to the full-energy peak efficiency. Consequently, for 583 keV, 609 keV and 1120 keV, the counting rates obtained with the anti-Compton system on are lower than the ones obtained with this system off. Besides, there are many studies indicate that the true coincidence summing effects (TCS) are more significant in the well-type detectors (Laborie et al., 2000; Tedjani et al., 2016; Wang et al., 2018) so in these detectors, it is easier to check the mistakes made by the anti-Compton system for gamma emissions in cascade.

On the other hand, in Fig. 3.2.4 it is also possible to note that n^a/n ratios do not depend on the chemical compositions of the samples chosen for this study. For this reason, samples whose densities and compositions are so different from each other, have been selected. The fact that n^a/n values do not depend on the kind of sample is very understandable and it is explained below. If we take Eqs. 3.2.1 and 3.2.2 and consider that all the variables present in these equations are the same except ε_{exp} when using or not using the anti-Compton system, the self-absorption correction factor will be cancelled after dividing n^a between n . This is consistent because in both cases (with and without anti-Compton system), the measured sample is the same and, therefore, the correction given by the self-absorption factor is also the same. This is very useful because in the cases of 583 keV and 609 keV, n^a can be corrected perfectly by the n/n^a ratio, getting to solve the problem occasioned by the anti-Compton system for those two energies.

Nevertheless, in Fig. 3.2.4 it is easy to see that there is only one energy which does not follow the same tendency than the others, being this energy 1120 keV. In this case, the self-absorption effects affecting the counting rate with the anti-Compton system on (n^a) are different from those affecting the counting rate with the anti-Compton system off (n). This fact can be explained because 1120 keV is characterized by having summing-out effects, that is, $E_\gamma^{(3)} = E_\gamma^{(1)} + E_\gamma^{(2)}$, where $E_\gamma^{(3)}$ is 1120 keV and $E_\gamma^{(1)}$ and $E_\gamma^{(2)}$ are the energies corresponding to two other photons. Therefore, if $E_\gamma^{(1)}$ or $E_\gamma^{(2)}$ were energies corresponding to the low energy region, and considering that the anti-Compton system is not able to work properly when energies present summing-out effects, the self-absorption correction factor obtained for n^a would be different compared with the one obtained for n . This explanation is consistent and it is according to some studies that have proven the possibility that $E_\gamma^{(1)}$ or $E_\gamma^{(2)}$ can be a low energy (≤ 150 keV) in the case of 1120 keV (IND04-MetroMetal, 2013). Besides that, analogously to the explanation just given regarding the summing-out effects for 1120 keV, a similar situation could occur for 583 keV. In this latter case (583 keV), one of the possible values of $E_\gamma^{(1)}$ and $E_\gamma^{(2)}$ would be $E_\gamma^{(1)} = 57.766(5)$ keV (^{228}Ac) and $E_\gamma^{(2)} = 510.77(10)$. However, for 583 keV, the low energy (57.766(5) keV) is a gamma emission energy whose emission probability is very low ($< 0.50\%$). Consequently, that low energy is unusually detected and, therefore, for 583 keV it is possible to correct n^a . Gamma emission energies and probabilities were taken from Toi Lund, 1999.

Despite not being possible to correct n^a in the case of 1120 keV, it is not a significant problem because this energy is usually used in order to determine ^{226}Ra , but this radionuclide can also be determined by many other energies.

3.2.3.3.1. Applications of the anti-Compton system: Calculations of detection limits

The anti-Compton system is used to reduce the Compton continuum, so this system results useful to improve the “detector sensibility”, by doing the detection limit lower. This is possible because both the Compton continuum (B) and the lower limit of detection (L_D) are related by equations which have been taken from Bolívar, 1995; Currie, 1968; Debertin and Helmer, 1988. Therefore, making L_D lower, it could be helpful to be able to detect properly photons emitted by samples whose activities are very low, for example, water and vegetable samples.

Besides that, L_D is related to MDA (Minimum Detectable Activity) by another equation given below:

$$MDA = \frac{L_D}{\varepsilon t P_\gamma} \quad (\text{Eq. 3.2.8})$$

where ε , P_γ and t are the detector efficiency, the gamma emission probability and the measurement time, respectively. In our case, L_D values have been calculated at a significance level of 5% for all the selected samples.

To study the influence of the anti-Compton system on the detection limit, six samples covering a wide range of densities and chemical compositions have been chosen: Ilmenite, Scale-1, IAEA-326, (RGU-1, RGTh-1, RGK-1) + 70% PbS. Moreover, several E_γ values of interest have been selected throughout the energy region.

In Fig. 3.2.5, the MDA^a/MDA ratios have been plotted versus for the six samples mentioned above, where MDA^a and MDA are the minimum detectable activities when the anti-Compton system is on and off, respectively. In order to calculate the minimum detectable activities for both cases (MDA^a and MDA), the same measurement time was chosen for all the selected samples, being this of 172800 s (2 days). In that figure it is possible to note that the majority of the MDA^a/MDA ratios were ranged from 0.5 and 0.7 for all the samples and energies. It is necessary to clarify that at 186 keV, two cases were considered: With and without secular equilibrium between ^{238}U and ^{226}Ra . When secular equilibrium is not considered, the interference of ^{235}U ($I_{235\text{U}}$) on ^{226}Ra determination must be known. Thus, the interference can be estimated from the following equation:

$$I_{235\text{U}} = A_{235\text{U}} P_\gamma(235\text{U}) \varepsilon_{186\text{keV}} t = 0.02631 A_{238\text{U}} \varepsilon_{186\text{keV}} t \quad (\text{Eq. 3.2.9})$$

where $A_{235\text{U}}$, $A_{238\text{U}}$ are the ^{235}U and ^{238}U activities, respectively, $P_\gamma(235\text{U}) = 0.572(5)$ at 186 keV, $\varepsilon_{186\text{keV}}$ the efficiency value at 186 keV and t is the measurement time. Besides, it has been considered that $A_{235\text{U}}/A_{238\text{U}} = 0.046$ (Agha et al., 2011) as well as ^{238}U and ^{234}Th are in secular equilibrium. Therefore, since $A_{238\text{U}} = A_{234\text{Th}}$ and ^{234}Th can be determined, $I_{235\text{U}}$ can be calculated.

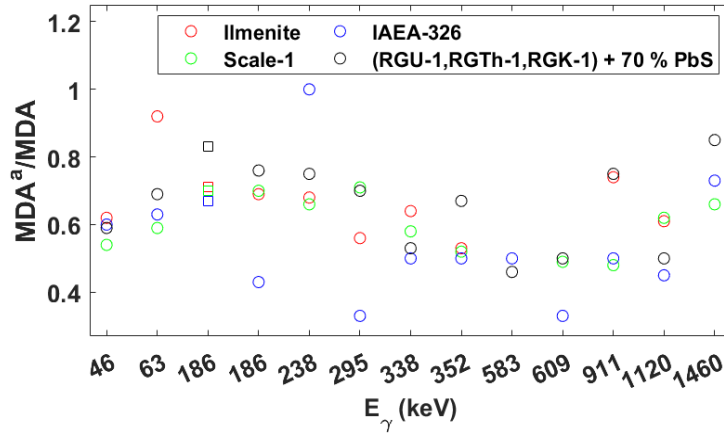


Figure 3.2.5. Comparison between the MDA values obtained with and without anti-Compton system (MDA^a and MDA , respectively) for several energies and types of samples. In the case of $E_\gamma = 186$ keV, the values of MDA^a/MDA corresponding to non-secular equilibrium between ^{238}U and ^{226}Ra have been shown by squares for each selected sample.

In the case of 186 keV without considering secular equilibrium between ^{238}U and ^{226}Ra , it is clearly seen in Fig. 3.2.5 that MDA^a/MDA values are higher compared with those values calculated when secular equilibrium between those two radionuclides is considered. This is very consistent since the minimum detectable activity is higher when the interference term (I) is introduced. In addition to Fig. 3.2.5, in Table B.13 (see Supplementary Material-B) it is possible to find the values of MDA , MDA^a and MDA^a/MDA for all the samples and energies chosen in this section, as well as for the cases in which secular equilibrium between ^{238}U and ^{226}Ra has been and not been considered.

3.2.3.3.2. Applications of the anti-Compton system: Comparison between gamma and alpha-particle spectrometric techniques

In this Section, it has been carried out a comparison between gamma and alpha-particle spectrometric techniques in order to propose gamma spectrometry as an alternative analysis technique to alpha-particle spectrometry to determine certain natural long-lived radionuclides (^{226}Ra and ^{228}Ra).

^{226}Ra and ^{228}Ra are two radionuclides that are usually measured by alpha-particle spectrometry due to their environmental interest. However, their determinations by this spectrometric technique are very tedious, making necessary to use physical-chemical procedures in order to separate the radionuclides of interest from the original matrix. In addition to the complicated methods employed to determine ^{226}Ra and ^{228}Ra by alpha-particle spectrometry, these methods take a long time to be carried out, being approximately three weeks and six months in the cases of ^{226}Ra and ^{228}Ra , respectively (Clulow et al., 1998; Pérez-Moreno et al., 2019; Thomas et al., 2020).

Therefore, given that using gamma spectrometry it is possible to determine ^{226}Ra and ^{228}Ra in a relatively simple and fast way, being the usual measurement times ranged from one to two days, this spectrometric technique is a very good alternative to alpha-particle spectrometry. However, this latter kind of spectrometry is characterized by having a very low detection limit for most samples, being its value approximately 5 mBq in the cases of ^{228}Ra , ^{226}Ra and 1 mBq for the other natural long-lived radionuclides of interest such as ^{238}U , ^{228}Th and ^{210}Po . Consequently, it is necessary to reduce the detection limit for gamma spectrometry to reach the usual detection limit values in the case of alpha-particle spectrometry. For this, a possible procedure, which would allow us to get the desired

detection limit values, would consist in concentrating the sample that is being tried to be measured by gamma spectrometry instead of alpha-particle spectrometry. In this case, a concentration factor (CF) would be necessary to calculate. In our case, given that the sample volume is always the same ($4.94(15) \text{ cm}^3$), the CF factor would be defined by $CF = MDA^\gamma / MDA^\alpha$, where MDA^γ and MDA^α are the minimum detectable activities for samples measured by gamma spectrometry and alpha-particle spectrometry, respectively. Thus, by concentrating that sample, it would be possible to minimize the sample mass and, therefore, getting a lower L_D value. Furthermore, since the anti-Compton system is very helpful to reduce L_D values, it would be recommendable to be used in order to make the L_D reduction easier.

In this Section, it has been carried out a study on the calculations of CF values from a theoretical point of view. For this, the same samples that were chosen in the Section 3.2.3.3.1 have been selected, excepting RGK-1 + 70% PbS. This sample was discarded because ^{40}K cannot be measured by alpha-particle spectrometry and, consequently, it is not possible to compare both techniques. Besides, in this Section, a sample of distilled water was chosen to study the CF values obtained in a liquid sample. On the other hand, apart from having chosen ^{226}Ra and ^{228}Ra in this Section to make that comparison, other radionuclides such as ^{210}Pb and ^{234}Th (being ^{210}Po and ^{238}U , respectively, the radionuclides used in the case of alpha-particle spectrometry), as well as ^{228}Th were also selected in order to achieve a more complete study. In Table 3.2.1 the CF^a and CF values, as well as the CF^a/CF ratios for all the samples previously mentioned can be found, where CF^a and CF are the concentration factors with the anti-Compton system on and off, respectively. In order to calculate the CF^a and CF factors for all the selected samples, a common measurement time (172800 s) was chosen.

In Table 3.2.1, it can be observed that the highest CF^a and CF values have been obtained in the cases of $E_\gamma = 46$, that is, for ^{210}Pb , occurring at $E_\alpha = 5304.38 \text{ keV}$ for ^{210}Po , where E_α is the alpha-particle emission energy. At 46 keV, CF^a values ranged from 25 to 1446, while CF values ranged from 42 to 2436 for distilled water and RGU-1 + 70% PbS, respectively. On the other hand, the lowest CF^a and CF values have been observed for $E_\gamma = 911 \text{ keV}$, corresponding to $E_\alpha = 5685.37 \text{ keV}$ in the case of alpha-particle spectrometry. For 911 keV, CF^a ranged from 3 to 20, whereas CF ranged from 4 to 41 for distilled water and Scale-1, respectively. As it could be expected the highest values of CF^a and CF are obtained for low E_γ because as E_γ decreases, the Compton continuum increases and, consequently, MDA and L_D also increase. It is worth noting that the lowest and highest values of CF^a and CF have been observed for samples whose activity concentrations are lower and higher, respectively, since MDA is higher as activity concentration of a sample increases.

Regarding 186 keV, both CF^a and CF values are higher when not considering secular equilibrium between ^{238}U and ^{226}Ra . This agrees with the results obtained in Section 3.2.3.3.1 because in absence of secular equilibrium, L_D and, therefore, MDA increase due to the interference term (I_{235U}). In this Section, the energy of 186 keV was selected to determine ^{226}Ra in order to make the calculations of possible ^{222}Rn losses unnecessary in the chosen samples. On the other hand, from Table 3.2.1 it is also possible to observe a significant reduction in CF when using the anti-Compton system leading to CF^a/CF ratios ranging between 0.5 and 0.7 for most samples and energies.

Table 3.2.1

Comparison between the detection limits obtained for several radionuclides (energies) by alpha and gamma spectrometry techniques ($RN^\gamma (E_\gamma)$ and $RN^\alpha (E_\alpha)$, respectively), where CF^a and CF are the

concentration factors when the anti-Compton system is switched on and off, respectively, and $CF' = CF^a / CF$.

RN ^γ (RN ^α)	E _γ (keV) (E _α (keV))	Ilmenite			Scale-1			IAEA-326			(RGU-1, RGTh-1) + 70% PbS			Distilled water		
		CF	CF ^a	CF'	CF	CF ^a	CF'	CF	CF ^a	CF'	CF	CF ^a	CF'	CF	CF ^a	CF'
²¹⁰ Pb (²¹⁰ Po)	46.5 (5304.38)	494	307	0.62	549	297	0.54	103	61	0.59	2436	1446	0.59	42	25	0.60
²³⁴ Th (²³⁸ U)	63.29 (4198)	305	281	0.92	101	59	0.58	84	52	0.62	1197	828	0.69	41	22	0.54
	186.2 (4784.34)	53	38	0.72	128	89	0.70	25	16	0.64	166	138	0.83	17	9	0.53
²²⁶ Ra (²²⁶ Ra)	(No sec. eq.) 186.2 (4784.34) (Sec. eq.)	29	20	0.69	73	51	0.70	14	7	0.50	93	70	0.75	9	5	0.56
²¹² Pb (²²⁸ Th)	238.64 (5423.15)	20	14	0.70	50	33	0.66	10	5	0.50	41	29	0.71	8	3	0.38
²²⁸ Ac (²²⁴ Ra)	911.07 (5685.37)	12	9	0.75	41	20	0.49	8	4	0.50	15	12	0.80	4	3	0.75

3.2.3.4. Validations of the methodology to calibrate in efficiency: Internal and external validation procedures

In order to test the validity of the methodology followed in this work to calibrate in efficiency, two kinds of validation procedures have been carried out: Internal and external validation procedures.

3.2.3.4.1. Internal validation procedure

In this validation, Phosphate Rock (PR-1) was mixed with six different proportions of PbS (0, 20%, 40%, 60%, 70% and 80%), increasing the PR-1 density and <Z>. PR-1 was selected for this validation because this sample contains all the radionuclides of interest that belong to the ²³⁸U-series as well as its chemical composition is very well known.

Five aliquots of PR-1 and PbS mixtures were measured by another detector (XtRa: Coaxial Extended Energy Range HPGe Detector), whose calibration in efficiency has already been tested, to give a reference value for activity concentrations (see Table B.14 in Supplementary Material-B). The radionuclide reference activity concentrations were determined for the main gamma emission energies belonging to the ²³⁸U-series, that is, 46 keV, 63 keV, 186 keV, 295 keV, 352 keV, 609 keV and 1120 keV. Once these reference activity concentrations were calculated for those two samples mentioned, the six mixtures of PR-1 and PbS, previously mentioned, were measured by the well-type detector. Then, by Eq. 3.2.2, it was possible to calculate the experimental efficiency values for all the energies and sample mixtures mentioned above. These experimental values, which have been obtained using the reference activities calculated by the XtRa calibration, let us call by ε_{Well}^{exp} . Therefore, ε_{Well}^{exp} allows us to differentiate that kind of efficiency from the efficiency values obtained by the well-type detector calibration, which let us call by ε_{Well} . Besides, the ε_{Well} values were calculated by the three functions proposed in Section 3.2.3.2 (*Function-i*, where $i = 1, 2, 3$), and,

therefore, obtaining $\varepsilon_{Well}^{(1)}$, $\varepsilon_{Well}^{(2)}$ and $\varepsilon_{Well}^{(3)}$, respectively, for the efficiency values in the case of the well-type detector. In this way, it was possible to compare the ε_{Well}^{exp} values with the three functions proposed in Section 3.2.3.2.

In Fig. 3.2.6, $\varepsilon_{Well}^{(i)}$ values have been plotted versus ε_{Well}^{exp} for the seven energies and six samples mixtures mentioned above, showing six efficiency values for each E_γ value. It is necessary to clarify that as the PbS proportion increases, the efficiency value decreases both for ε_{Well}^{exp} and $\varepsilon_{Well}^{(i)}$. Therefore, taking this into account, in Fig. 3.2.6 it is perfectly possible to distinguish between the efficiency values obtained for each PbS proportion.

On the other hand, in Fig. 3.2.6 it is possible to find plotted the fittings done of $\varepsilon_{Well}^{(i)}$ versus ε_{Well}^{exp} , which have been carried out by $\varepsilon_{fit}^{(i)}$ functions. This kind of fitting was done in order to make the comparison between $\varepsilon_{Well}^{(i)}$ versus ε_{Well}^{exp} easier. Besides, two cases have been considered: ideal and real cases. The equations employed for the ideal and real fittings were $\varepsilon_{fit}^{(i)} = \varepsilon_{Well}^{exp}$ and $\varepsilon_{fit}^{(i)} = a + b \varepsilon_{Well}^{exp}$, respectively, being a and b the parameters resulted from the non-ideal fitting. Thus, it has been observed that the efficiency values given by $\varepsilon_{Well}^{(1)}$ were more similar to the ones obtained by ε_{Well}^{exp} in comparison with the other cases ($\varepsilon_{Well}^{(2)}$ and $\varepsilon_{Well}^{(3)}$). This is consistent since the reference activity concentration values of PR-1 and PbS (see Table B.14 in Supplementary Material-B), which were used to obtain ε_{Well}^{exp} , were calculated using a self-absorption correction factor whose behavior is analogous to the one used in the case of the well-type detector (see Mantero et al., 2015; Pérez-Moreno et al., 2002 for further information about the self-absorption correction factor employed for XtRa detector).

Besides that, in Fig. 3.2.6 it can also be found the relative average residues for the three $\varepsilon_{fit}^{(i)}$ fitting functions corresponding to $\varepsilon_{Well}^{(i)}$ values. Thus, two types of relative average residues have been shown for the fittings done of $\varepsilon_{Well}^{(i)}$ values, $\langle Res \rangle_{ideal}$ and $\langle Res \rangle_{fit}$, which are related to the ideal and real fittings done by $\varepsilon_{fit}^{(i)}$, respectively. Therefore, it is easy to note that the residues resulted from $\varepsilon_{fit}^{(1)}$ fittings were lower for both cases ($\langle Res \rangle_{ideal} = 1.5\%$ and $\langle Res \rangle_{fit} = 0.52\%$) in comparison with the ones obtained by $\varepsilon_{fit}^{(2)}$ and $\varepsilon_{fit}^{(3)}$ functions, where those residues were 5.4% and 2.6% ($\varepsilon_{fit}^{(2)}$) and 5.5% and 1.4% ($\varepsilon_{fit}^{(3)}$) for $\langle Res \rangle_{ideal}$ and $\langle Res \rangle_{fit}$, respectively. This agrees with the explanation previously given regarding the similarity between the self-absorption correction factors used in the cases of XtRa and well-type detectors. Taking the results obtained by the three kinds of *Function-i*, it is easy to note that the internal validation has been really good for the three cases.

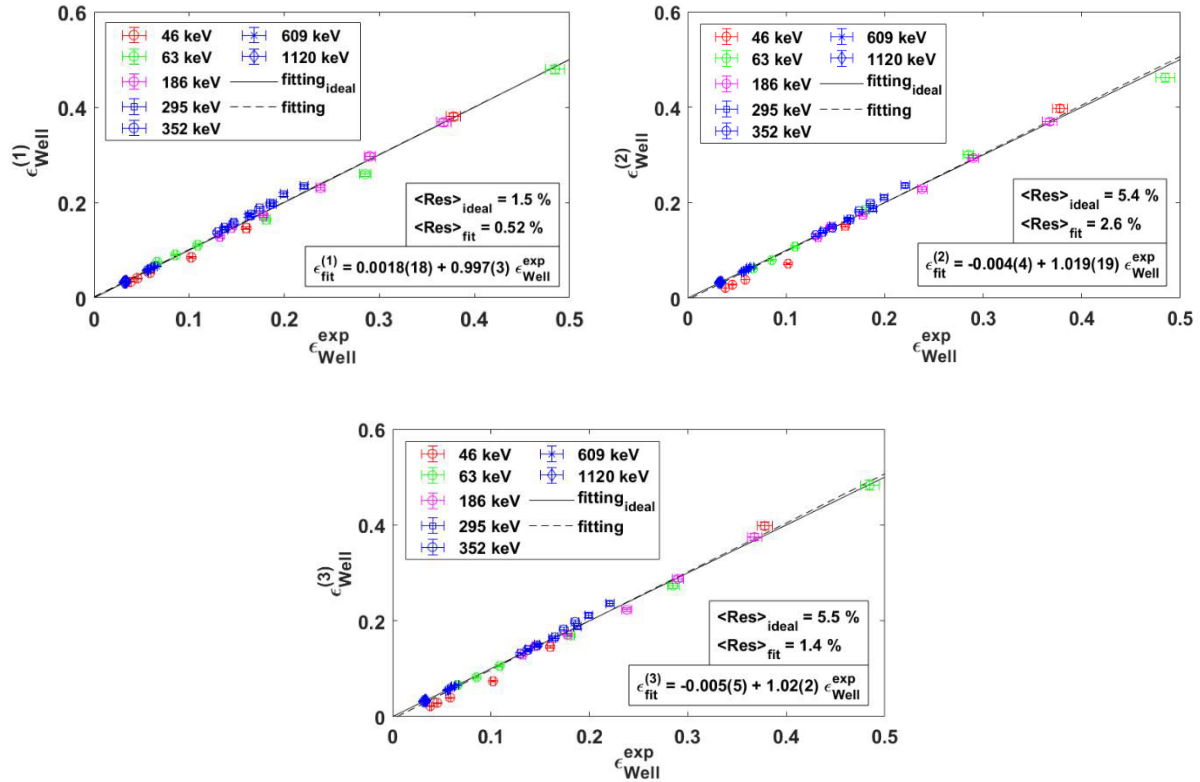


Figure 3.2.6. Internal validation procedure carried out using a phosphate rock sample (PR-1) mixed with different proportions of PbS. This validation was done for three types of fitting functions ($\epsilon_{fit}^{(i)}$, being “i” = 1, 2, 3), which were obtained after fitting $\epsilon_{Well}^{(i)}$ vs ϵ_{Well}^{exp} . Besides, the relative average residues were calculated considering both the fittings done by the ideal and real $\epsilon_{fit}^{(i)}$ functions ($\langle Res \rangle_{ideal}$ and $\langle Res \rangle_{fit}$, respectively).

3.2.3.4.2. External validation procedure

In this Section, the external validation for the methodology of calibration in efficiency has been carried out. The samples selected for the validation were IAEA-326, PR-2 and RGK-1.

In Table 3.2.2, it is possible to see the z_{score} values resulted from the comparison made between activity concentration values calculated through the well-type detector calibration, having employed for it the *Function-1*, which was analyzed in Section 3.2.3.2, as well as Eq. 3.2.2, and the values of reference activity concentrations given for certified real samples. Regarding the z_{score} equation, which was used in order to do this validation, it is given by the following mathematical expression:

$$z_{score} = \frac{a - a_r}{\sqrt{\sigma_a^2 + \sigma_{a_r}^2}} \quad (\text{Eq. 3.2.10})$$

where a_r (σ_{a_r}) and a (σ_a) are the reference and calculated activity concentration values (and uncertainties at 1 sigma level), respectively. Besides, $-2 \leq z_{score} \leq 2$ is the range for which a calculation is considered good.

Moreover, in Table 3.2.2 it is also possible to find two values of activity concentrations for ^{226}Ra calculated at 186 keV: With and without considering secular equilibrium between ^{238}U and ^{226}Ra .

Thus, in the former case, an equivalent probability has been obtained, P_γ^* , where $P_\gamma^* = P_\gamma(^{226}\text{Ra}) + ^{235}\text{U}/^{238}\text{U} P_\gamma(^{235}\text{U}) = 6.14(6)\%$, being $P_\gamma(^{226}\text{Ra}) = 3.51(6)\%$ and $P_\gamma(^{235}\text{U}) = 57.2(5)\%$ at 186 keV, and $^{235}\text{U}/^{238}\text{U} = 0.046$. On the other hand, in the latter case (non-secular equilibrium between ^{238}U and ^{226}Ra), it would be necessary to take Eq. 3.2.2 considering the interference term ($I_{235\text{U}}$), which was defined in Eq. 3.2.9.

In Table 3.2.2 the z_{score} values for IAEA-326, PR-2 and RGK-1 have been shown. Regarding the IAEA-326 sample, all the $|z_{score}|$ values were less than 2, being the majority of them less than 1. In the case of PR-2 sample, a very good agreement between reference and calculated activity concentrations was obtained, where all the $|z_{score}|$ values were less than 1.5. Finally, for RGK-1 sample, a z_{score} value of 0.6 was obtained. Therefore, according to the external validation for all the selected samples and energies it is possible to infer a good agreement between the activity concentrations obtained through the method proposed in this work and the certified values.

Table 3.2.2

External validation procedure done by the calculations of z_{score} values for several certified samples (IAEA-326, PR-2 and RGK-1). Besides, at 186 keV two cases have been considered: Without and with secular equilibrium between ^{238}U and ^{226}Ra (No sec. eq. and Sec. eq., respectively). Uncertainties given at 1 sigma level.

RN	E_γ (keV)	IAEA-326			RGK-1			Phosphate Rock-2 (PR-2)		
		a (Bq kg ⁻¹)	Reference	z_{score}	a (Bq kg ⁻¹)	Reference	z_{score}	a (Bq kg ⁻¹)	Reference	z_{score}
²¹⁰ Pb	46.5	46(4)	53(5)	-1.1				1583(72)		0.6
²³⁴ Th	63.29	30(3)	29.4(1.7)	0.3				1525(68)		-0.2
²²⁶ Ra	186.2 (No sec. eq.)	41(3)		1.8				1562(83)		0.3
	186.2 (Sec. eq.)	36(3)		0.9				1547(66)	1541(5)	0.1
²¹⁴ Pb	295.21	26.4(1.5)	33(3)	-1.8				1450(60)		-1.5
	351.92	26.9(1.3)		-1.7				1466(60)		-1.3
²¹⁴ Bi	609.31	27.9(1.7)		-1.3				1483(62)		-0.9
	1120.2	26(3)		-1.5				1446(74)		-1.3
²²⁸ Ac	338.42	44(3)	40(2)	1.2						
	911.07	39(2)		-0.4						
²¹² Pb	238.64	39.6(1.7)	39.1(1.7)	0.2						
²⁰⁸ Tl	583.19	41(3)		0.5						
⁴⁰ K	1460.83	568(25)	580(28)	-0.3	14359(606)	14000(200)	0.6			

On the other hand, since the self-absorption correction factor given by Eq. 3.2.3 does not work properly in the case of high-density samples with high values of $\langle Z \rangle$ (compared with the $\langle Z \rangle$ value of a soil, which is approximately 10.6), below it has been shown a study on the z_{score} values obtained for samples whose density and $\langle Z \rangle$ have been varied. For this, PR-2 sample has been chosen and it has been mixed with different PbS proportions (PbS proportions were ranged from 0% to 67.5%), getting PR-2 density and $\langle Z \rangle$ increase. Consequently, this study allows us to find out the interval of density and $\langle Z \rangle$ within which Eq. 3.2.3 works correctly. Given that the self-absorption effects are more relevant at low energies, the gamma emission energy of 63 keV (^{234}Th) has been chosen in order to do this study, having calculated the z_{score} value for each PbS proportion at this energy.

In Fig. 3.2.7 it is possible to find the z_{score} values resulted from the calculated activity concentrations at 63 keV for each mixture of PR-2 with PbS. In that figure, there is a clear z_{score} dependence on the proportion of PbS, where the z_{score} values were ranged from -0.24 to -4.9 for 0% and 67.5% of PbS, respectively. Besides, it is interesting to note that 37.5% was the PbS proportion from which the $|z_{score}|$ values began to be greater than 2, being approximately 15 cm² the ηm value obtained in this case, where $\eta = 1.52$ cm² g⁻¹. Therefore, from that ηm value, the self-absorption correction factor given by Eq. 3.2.3 begins to provide improper corrections for self-absorption effects. This agrees with the study on different self-absorption correction functions carried out in Section 3.2.3.2.

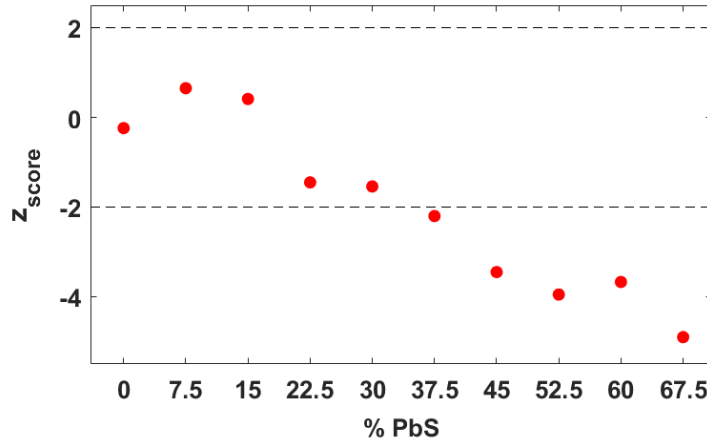


Figure 3.2.7. Values of z_{score} resulted from the calculated activity concentrations at 63 keV for each mixture of PR-2 with PbS.

3.2.3.5. A proposed method to determine ^{226}Ra under non-secular equilibrium with ^{222}Rn

In order to take advantage of the possibility of determining ^{226}Ra by its gamma emission energy (186 keV) as it was explained in Section 3.2.3.4.2, with or without considering that ^{238}U and ^{226}Ra are in secular equilibrium, some kinds of samples have selected in this Section, which are characterized by having ^{222}Rn losses. Therefore, for these types of samples, the ^{226}Ra determination proposed in this Section would be very helpful. The selected samples were IAEA-434, CSN-PG and RGU-1 standard dissolved in water (dissolved RGU-1), having been possible to dissolve this standard in water because of its previous digestion by using acids.

Regarding the samples that present a clear loss of ^{222}Rn , it is necessary to wait at least a month in order to ensure the secular equilibrium between ^{226}Ra and ^{222}Rn is reached. Consequently, the ^{226}Ra determination could not be carried out properly by its daughters (^{214}Pb and ^{214}Bi). Therefore, all the reasons previously exposed make necessary employ the proposed method in this Section to determine ^{226}Ra . (See Scholten et al., 2013; Lamonaca et al., 2014; Kuzmanović et al., 2020; Hightower and Watson, 1995; Benke and Kearfott, 2000; Tudyka et al., 2021 for further information about studies related to ^{222}Rn losses in different types of materials).

In Table 3.2.3 it has been shown the results of activity concentrations obtained for the three samples mentioned in this Section (IAEA-434, CSN-PG and dissolved RGU-1). Thus, it is easy to note that the ^{222}Rn losses were significant in the cases of IAEA-434 and CSN-PG (15(3)% and 11(2)%, respectively), which were measured without waiting for secular equilibrium between ^{226}Ra and ^{222}Rn being reached. On the other hand, in Table 3.2.3 it is also possible to check that the ^{222}Rn losses were even more relevant in the case of dissolved RGU-1, where the average ^{222}Rn losses obtained were

71(8)%. Consequently, taking these results into account, it has perfectly been proved the need for using the proposed method in this Section in order to carry out the ^{226}Ra determination.

Table 3.2.3

Study about ^{222}Rn losses carried out in phosphogypsum samples (IAEA-434 and CSN-PG), as well as in the dissolved RGU-1 sample. In the case of dissolved RGU-1, the reference value for activity concentration was $241.5(0.7) \text{ Bq kg}^{-1}$. Uncertainties given at 1 sigma level.

IAEA-434					CSN-PG				
RN	E_γ (keV)	a (Bq kg ⁻¹)	Reference	z_{score}	²²² Rn losses (%)	a (Bq kg ⁻¹)	Reference	z_{score}	²²² Rn losses (%)
²¹⁰ Pb	46.5	722(34)	680(29)	0.9		784(40)	781(15)	0.1	
²³⁴ Th	63.29	107(10)	120(6)	-1.1		52(13)	48.6(1.2)	0.3	
²²⁶ Ra	186.2 (No sec. eq.)	836(25)		1.4		661(24)		1.0	
	186.2 (Sec. eq.)	523(24)		-6.5		400(22)	634(13)	-9.2	
²¹⁴ Pb	295.21	666(28)	780(31)	-2.7	15(5)	581(26)	580(13)	0.0	11(4)
	351.92	655(27)		-3.0	16(5)	543(23)		-1.4	12(4)
²¹⁴ Bi	609.31	665(29)		-2.7	15(5)	566(27)	533(13)	1.1	11(4)
	1120.2	662(39)		-2.4	15(6)	566(42)		0.8	9(4)
					< ²²² Rn loss> (%) = 15(3)	< ²²² Rn loss> (%) = 11(2)			

Dissolved RGU-1					
RN	E_γ (keV)	a (Bq kg ⁻¹)	Reference	z_{score}	²²² Rn losses (%)
²¹⁰ Pb	46.5	227(10)		-1.5	
²³⁴ Th	63.29	242(10)		0.1	
²²⁶ Ra	186.2 (No sec. eq.)	210(12)		-2.6	
	186.2 (Sec. eq.)	224(9)	241.5(0.7)	-1.9	
²¹⁴ Pb	295.21	74(3)		-52	70(7)
	351.92	75(3)		-53	69(7)
²¹⁴ Bi	609.31	73(4)		-41	70(10)
	1120.2	64(10)		-18	74(27)
					< ²²² Rn loss> (%) = 71(8)

3.2.4. Conclusions

The main conclusion of this work are the following ones:

1. In the present work, a novel methodology to carry out the calibration in efficiency of a well-type Ge detector has been developed. This methodology to calibrate in efficiency consisted of varying the density (mass) of the chosen calibration samples fixing their thicknesses and for each gamma emission energy of interest (E_γ). By this methodology, it has been possible to find a general function for the efficiency, which depends on ε_0 and f , where they are the efficiency value when the sample mass tends to zero and the self-absorption correction factor, respectively. Thus, it has been checked that ε_0 can be written as a function of E_γ .

2. On the other hand, regarding the self-absorption corrections, a comparative study between different correction functions (*Function-i*) has been carried out. This comparison was made considering the main gamma emissions from radionuclides belonging to ^{238}U - and ^{232}Th -series, and, specifically emphasis has been placed on studying the results obtained in the case of *Function-1*. This function is the most used in order to correct self-absorption effects for samples measured by a well-type detector. Thus, it has been proved that this function does not work properly when the $\langle Z \rangle$ value of a sample is very high in comparison with the $\langle Z \rangle$ value of a soil (~ 10.6).
3. Besides that, an in-depth study on advantages and disadvantages about using an anti-Compton system has been done. Thus, a variation of the counting rate when using an anti-Compton system (n^a) has been observed in comparison with the value when it is not used (n). This variation was noted for some specific energies: 583 keV, 609 keV and 1120 keV, which are characterized by presenting summing-out effects. Besides, it was possible to correct the n^a values for 583 keV and 609 keV, since it has been checked that the n^a/n ratio does not depend on the kind of sample. Only for 1120 keV, it was not possible to carry out that n^a correction due to the self-absorption effects that were present in one of the energies related to its summing-out effects. Then, it has been proved that an anti-Compton system can be very helpful to reduce the lower limit of detection (L_D), as well as to achieve the gamma spectrometry is a clear alternative to alpha-particle spectrometry for some radionuclides, $^{228,226}\text{Ra}$, that are very complicated to be determined by the latter spectrometric technique.
4. Then, internal and external validation procedures of the methodology followed in this work have been carried out. Regarding the former kind of validation, a comparison between ε_{Well}^{exp} and $\varepsilon_{Well}^{(i)}$, being “i” ranged from 1 to 3, was made for several energies for PR-1 sample. Thus, $\varepsilon_{Well}^{(i)}$ values were calculated by each *Function-i*, observing that the best agreement between $\varepsilon_{Well}^{(i)}$ and ε_{Well}^{exp} was obtained in the case of *Function-1*. Consequently, the self-absorption correction factor given by *Function-1*, which is usually employed to correct self-absorption effects in the case of well-type detectors, has a very similar behavior compared with the one used for XtRa detectors. On the other hand, regarding the external validation, several certified real samples were selected and all the obtained $|z_{score}|$ values were less than 2, getting a great external validation. Furthermore, the PR-2 sample was mixed with different PbS proportions in order to demonstrate the validity range of *Function-1*, observing that the correction provided by this function is proper until approximately 37.5% of PbS (where $\eta m \sim 15 \text{ cm}^2$ for that PbS percentage, being $\eta = 1.52 \text{ cm}^2 \text{ g}^{-1}$).
5. Lastly, a study on ^{222}Rn losses in phosphogypsum and dissolved samples has been carried out in order to propose the ^{226}Ra determination be done by its gamma emission energy ($E_\gamma = 186 \text{ keV}$), making it unnecessary to wait for the secular equilibrium between ^{226}Ra and ^{222}Rn be reached.

Subchapter 3.3.: A general function for determining mass attenuation coefficients to correct self-absorption effects in samples measured by gamma spectrometry

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Subchapter 3.3.: A general function for determining mass attenuation coefficients to correct self-absorption effects in samples measured by gamma spectrometry

Abstract

This work is focused on obtaining a general function for calculating the mass attenuation coefficients of samples whose compositions are known such as waste, biota or NORM (Naturally Occurring Radioactive Materials) samples. After determining the general function, it is possible to assess the self-absorption effects by the self-absorption correction factor, which is really important to consider for samples measured by gamma spectrometry. In order to obtain a general function of the mass attenuation coefficients dependent on the gamma emission energy (E_γ) and the chemical elements (Z_i) with their respective concentrations (x_i), it was necessary to fit the tabulated values of the mass attenuation coefficients versus gamma energy in the range of 20 keV to 2000 keV for each chemical element. This is the energy range for the majority of gamma emissions of natural radionuclides. Once those fittings for each chemical element, Z , from 1 (H) to 92 (U) were done, the parameters, that resulted from those fittings, were fitted versus the atomic number, Z . This provides a general function that allows to calculate the mass attenuation coefficient by knowing the gamma emission energy and the sample composition. Finally, both the general function for calculating the mass attenuation coefficient and the self-absorption correction factor, which is used in gamma spectrometry with coaxial Ge detectors, were validated by comparisons made with the values provided by databases for several samples with widely different known densities, compositions and activity concentrations.

Keywords: Gamma spectrometry; Coaxial Ge detectors; Mass attenuation coefficient; Self-absorption; NORM; Bragg's law.

3.3.1. Introduction

The determination of the mass attenuation coefficient of a sample, η , is very significant for obtaining the self-absorption correction factor, f , to be used in gamma spectrometry measurements, since it lets transform the full energy peak efficiency (FEPE) calculated in the calibrating matrix (ε_c) into the real sample one (ε). There are numerous studies carried out on gamma spectrometry that take this type of correction into account (Abbas, 2001; Abbas et al., 2001; Ajemigbitse et al., 2020; Bolívar et al., 1997; Bonczyk, 2018; Carrazana et al., 2010; Długosz-Lisiecka and Ziomek, 2015; Eke and Boztosun, 2014; Guerra, 2018; Jodłowski, 2016; Mantero, 2013; Mantero et al., 2015; Martínez-Ruiz et al., 2007; Montes et al., 2019; San Miguel et al., 2002; Suárez-Navarro et al., 2020; Xhixha-Kaçeli, 2013). These self-absorption corrections are more relevant in the lower energy range (20 up to about 150 keV), an effect proved in many studies on gamma spectrometry measurements (Bonczyk, 2018; Carrazana et al., 2010; Długosz-Lisiecka and Ziomek, 2015; Jodłowski, 2016; Martínez-Ruiz et al., 2007; Montes et al., 2019; San Miguel et al., 2002; Suárez-Navarro et al., 2020).

On the other hand, the application of the self-absorption corrections to the calculation of the efficiency in the matrix of a real sample requires knowing the mass attenuation coefficient of both the reference and the real samples. Furthermore, if the composition of the real sample is very different from that of the reference sample and their densities are very different from each other, this may influence the validity of the method followed in this paper. This might happen because the correction introduced by the self-absorption factor would be very large, that is, it would have a very different value from 1 for energies that are within the range of low energies ($E_\gamma \leq 150$ keV). Consequently, if the corrections due to self-absorption effects are not considered, the values of calculated activity concentrations, for those radionuclides whose gamma emission energies are within the low energy range, can differ

greatly from the expected values (up to 20% of difference, or more). This can occur in this way because the activity concentration and the self-absorption factor are related by the next equation:

$$a = \frac{n}{P_\gamma \varepsilon_c f m} \quad (\text{Eq. 3.3.1})$$

where a is the activity concentration, n is the counting rate, P_γ is the gamma emission probability, ε_c is the efficiency of the detector calculated in the calibrating matrix, m is the mass of the real sample and f is the self-absorption factor.

For this reason, the main objective of this study was to find a general function for the mass attenuation coefficient versus the gamma energy (E_γ), sample elemental composition (x_i and Z_i , where x_i is the fraction of the “i” element whose atomic number is Z_i). We have focused the study on the determination of natural radionuclides in samples such as soils, industrial wastes, slags, waters, scales, etc., since these types of samples have great interest due to the new NORM regulations in many countries (Barbero et al., 2014; Blasco et al., 2016; Gázquez et al., 2014; Guerrero et al., 2016; Hierro et al., 2014; Luque et al., 2015; Pérez-Moreno et al., 2015).

It is interesting to note that this is the first study that provides a general analytical function for calculating the mass attenuation coefficient for gamma radiation in samples whose compositions are known, and this allows us to determine the self-absorption correction factor in gamma spectrometry measurements.

3.3.2. Methods and materials

The tabulated attenuation coefficients corresponding to the full range of Z ($Z = 1$ to $Z = 92$), in the energy range from 20 keV to 2000 keV were taken from the NIST Standard Reference Database 126 (NIST, 2004a). Firstly, for each atomic number (Z), the fitting of η versus energy was done by using an empirical function selected from those that gave the best fit quality by minimizing Chi-squared. Then, the obtained parameters were fitted versus Z . By substitution of these parameters versus Z in the original functions, the mass attenuation coefficient function depending on E_γ and Z , that is $\eta(E_\gamma, Z)$, was obtained. These $\eta(E_\gamma, Z)$ functions were obtained for two separate cases: a) low atomic numbers ($Z \leq 26$, Fe), and b) high atomic numbers ($Z > 26$).

Once the general $\eta(E_\gamma, Z)$ function is known, in order to properly check the validity of this function, samples with a wide range of densities and chemical compositions were selected. Considering these characteristics, NORM samples are very appropriate to do this study, where the sample densities are ranged from 0.3 g cm⁻³ for biota to 4 g cm⁻³ for some industrial samples. To determine the mass attenuation coefficient of the samples, Bragg's law was applied. It says that $\langle \eta \rangle = \sum_i x_i \eta_i$, where x_i is the proportion of each major chemical element “i” contained in the sample and $\langle \eta \rangle$ is the sample mass attenuation coefficient.

We point out that our main objective was to determine the self-absorption correction factor (f) to be applied to the calibrating sample FEPE (ε_c), obtaining it for the real sample (ε) in a specific geometry ($\varepsilon = f \varepsilon_c$). Besides that, the self-absorption correction factor is completely related to the mass attenuation coefficient and the sample density of both real and calibrating samples. In our case, the thickness of the real sample will be also taken into account (Pérez-Moreno et al., 2002).

The Certified Reference Material (CRM) and the real samples, which were selected to carry out the validation of the mass attenuation coefficients and the FEPE self-absorption correction factors, are described in Table C.6 that can be found in Supplementary Material-C. This table contains the thicknesses, densities and chemical compositions of the CRMs and real samples analyzed in this study.

Regarding the Certified Reference Materials, they were supplied by the IAEA (International Atomic Energy Agency). After a compaction and homogenization procedure to prepare the cylindrical gamma counting geometry ($\varnothing = 34.6 \pm 0.2$ mm) with variable thickness, they achieved the same apparent density (1.63 ± 0.02 g cm⁻³). The compositions and radionuclide activity concentrations can be consulted at (IAEA–A, 1987; IAEA–B, 1987; IAEA, 2020).

The chemical compositions of the samples (major elements) were determined in accredited external laboratories by both Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) and X-Ray Fluorescence (XRF). The standard uncertainties of the element concentrations are usually ranging the 5-10%. On the other hand, XRF is a very versatile and non-destructive technique, but it is applied only for solid samples very well crushed and homogenized, being the obtained uncertainties similar to ICP-OES.

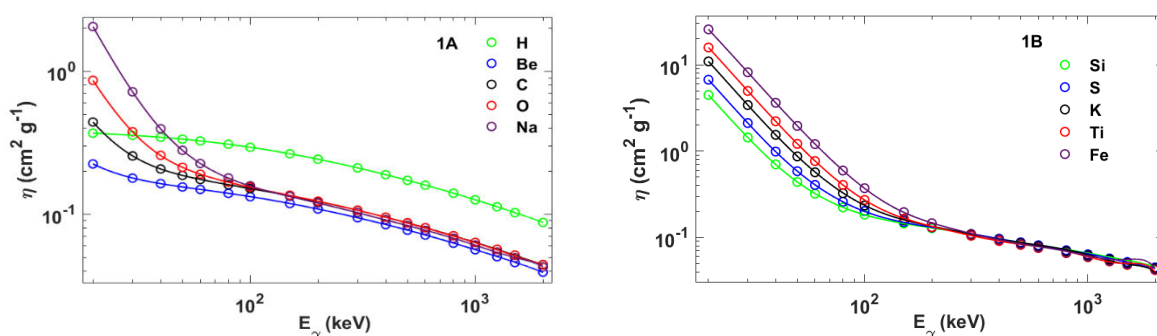
3.3.3. Results and discussion

The elements have been classified in two groups according to their Z : a) low Z ($Z \leq 26$), and b) high Z ($Z > 26$). This separation was done because it was not possible to fit $\eta(E_\gamma, Z)$ with the same fitting function for all the chemical elements.

3.3.3.1. Function of $\eta(E_\gamma, Z)$ for $Z \leq 26$

In our case, the following chemical elements were selected: H, Be, C, O, Na, Si, S, K, Ti, and Fe, distributed uniformly between $Z = 1$ and $Z = 26$ (Fe). In general, the major elements (concentrations around %) present in both environmental and NORM samples (raw materials, waste, final products, etc.) have atomic numbers lower than 26 (Fe), since Fe was selected as the border of both regions, and this will be justified in the following paragraphs (this criterion agrees with Pérez-Moreno et al., 2002).

In Fig. 3.3.1a, the tabulated attenuation coefficients (data provided by NIST) versus energy (fixing Z and varying the energy from 20 keV to 2000 keV) are plotted, observing a similar behaviour pattern for all elements, excepting $Z = 1$ (H). Two zones are clearly observed: 1) low energy (about 20-240 keV), where the photoelectric effect is dominant; 2) high energy (> 240 keV), where the Compton interaction is dominant.



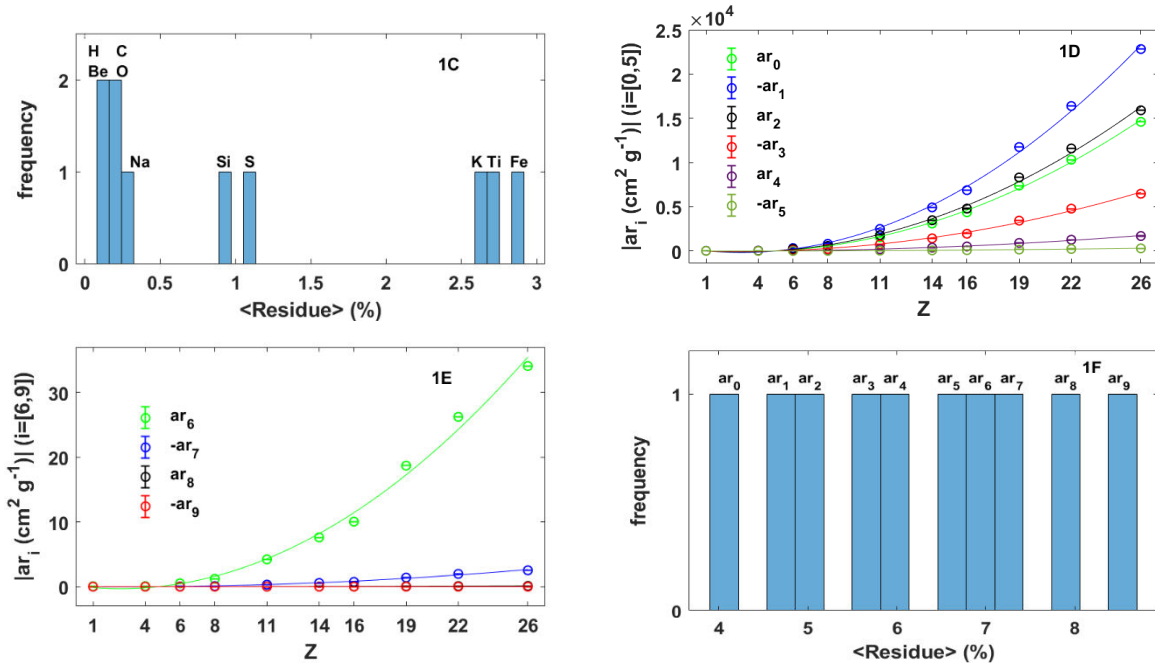


Fig. 3.3.1. a) From graphics 1A to 1C: Fitting of the $\eta(E_\gamma, Z)$ function by fixing Z and varying E_γ , showing by a histogram the relative residues (%) obtained; b) From graphics 1D to 1F: Regressions of the parameters resulted in the previous fittings, ar_i , showing their respective relative residues obtained after each regression for low Z values.

Several polynomial functions (η vs $\ln(E_\gamma/E_0)$, see Eq. 3.3.1) from $m = 1$ to $m = 10$ (m is the polynomial order) were fitted by least squares, where the highest-quality fittings (evaluated using the Chi-square test) were obtained for $m = 9$. Note that the total number of tabulated points was around 20.

$$\eta(Z, E_\gamma) = \sum_{i=0}^{i=m} ar_i \ln(E_\gamma/E_0)^i \quad (\text{Eq. 3.3.2})$$

where ar_i are the parameters and $E_0 = 1$ keV to remove the units from the logarithm argument.

The reason why polynomial functions were chosen to fit η vs $\ln(E_\gamma/E_0)$ was because this kind of function is much easier to program than others, allowing that the fittings are more optimized. The functions used to fit η vs $\ln(E_\gamma/E_0)$ are mathematical functions because the aim of this study is to provide a very good correction of self-absorption effects and, consequently, calculate activity concentration values more exact. This is consistent with the explanation seen previously (in the Introduction section), which proved the need to correct properly the self-absorption effects.

Apart from the fitting functions used in this work, there are other functions to determine the mass attenuation coefficients which are physical equations (see Section 3.3.3.4). However, as it will be seen in the comparisons made between different methods (Section 3.3.3.4), these types of functions do not provide any good results in the fittings carried out for the mass attenuation coefficients. Consequently, these kinds of functions are not useful for calculating self-absorption corrections in gamma spectrometry measurements. This agrees with Pérez-Moreno et al., 2002, where mathematical functions to fit mass attenuation coefficients were also used.

The uncertainties obtained for the parameters of Eq. 3.3.2 are very low (see Table C.1 in Supplementary Material-C). To evaluate the goodness of the Eq. 2 fittings for each value of Z , a frequency histogram is shown in Fig. 3.3.1a (graphic 1C) for their average relative residues (%). These average relative residues increase with Z from 0.09% ($Z = 1$) to 2.9% ($Z = 26$, Fe). The limit $Z = 26$ was selected due to the fitting function begins to give significant differences for energies about 1500 keV, as can be seen in Fig. 3.3.1a.

On the other hand, we also observe in Fig. 3.3.1a that the mass attenuation coefficient in the case of hydrogen has a very peculiar behaviour compared to the other cases. This is because, in the case of hydrogen, the Compton scattering is much more important than the photoelectric effect; since for very low Z values, Compton scattering dominates over the photoelectric effect. Likewise, as we increase the Z value, we see that the photoelectric effect becomes increasingly important at low energies. This begins to be visible in the case of beryllium, and it becomes very important in the case of iron.

Regarding the ar_i parameters shown in Table C.1 and plotted in Fig. 3.3.1b (graphics 1D and 1E), they were fitted versus Z to obtain the general function $\eta(E_\gamma, Z)$. In this case, the best fittings of ar_i vs Z were obtained by using polynomial functions of order 2 (Eq. 3.3.3):

$$ar_i(Z) = \sum_{j=1}^3 ar_{ij} Z^{j-1} \quad (\text{Eq. 3.3.3})$$

where ar_{ij} are the parameters that resulted after fitting ar_i varying Z . The obtained fittings are plotted in Fig. 3.3.1b.

Thus, the values obtained for ar_{ij} , whose values can be seen in Table C.2 (in Supplementary Material-C), present very low uncertainties. The average value of relative residues resulted from the fittings for each parameter ar_i (represented in graphic 1F) clearly increases as the subscript “i” increases.

3.3.3.2. Function of $\eta(E_\gamma, Z)$ for $Z > 26$

To obtain the general function $\eta(E_\gamma, Z)$ in this case, a procedure similar to the previous case was applied. So the first step was to select the chemical elements: Co, Cu, Zn, Ge, Zr, Ru, Sn, Cs, Nd, Yb, Hg, Rn, Ra, Th, and U.

In this case ($Z > 26$ after the shell change), it was necessary to divide the fitting function into two parts (see graphics from 2A to 2C in Fig. 3.3.2a). The first one corresponds to the photoelectric effect zone (low energy), where $\ln(\eta(E_\gamma, Z))$ shows a clear linear relation with the logarithm of gamma energy (η is an exponential function of the energy), while the Compton region ($E_\gamma > 100\text{-}240$ keV) can be reproduced by a polynomial function of η versus the logarithm of gamma energy. Note that a fifth-degree polynomial is the function that provides the best fit within the high energy region. In Fig. 3.3.2a the dashed line of the fitted line corresponds to the photoelectric effect region (linear regression), while the solid line corresponds to the Compton effect region.

Besides that, it is necessary to clarify that “shell change” refers to the discontinuity of the mass attenuation coefficient for a specific energy. This happens because for energies below that specific energy, the photons are not able to produce photoelectric effect. Consequently, for each discontinuity of the mass attenuation coefficient, there is a shell change.

The regression functions are given in this case by the following equations:

$$\eta(Z, E_\gamma) = \exp(br_1 + br_2 \ln(E_\gamma/E_0)) \quad (\text{Eq. 3.3.4})$$

$$\eta(Z, E_\gamma) = \sum_{i=0}^5 cr_i \ln(E_\gamma/E_0)^i \quad (\text{Eq. 3.3.5})$$

where br_i and cr_i are the parameters corresponding to η data fittings in the region where the photoelectric and Compton effects are more important, respectively.

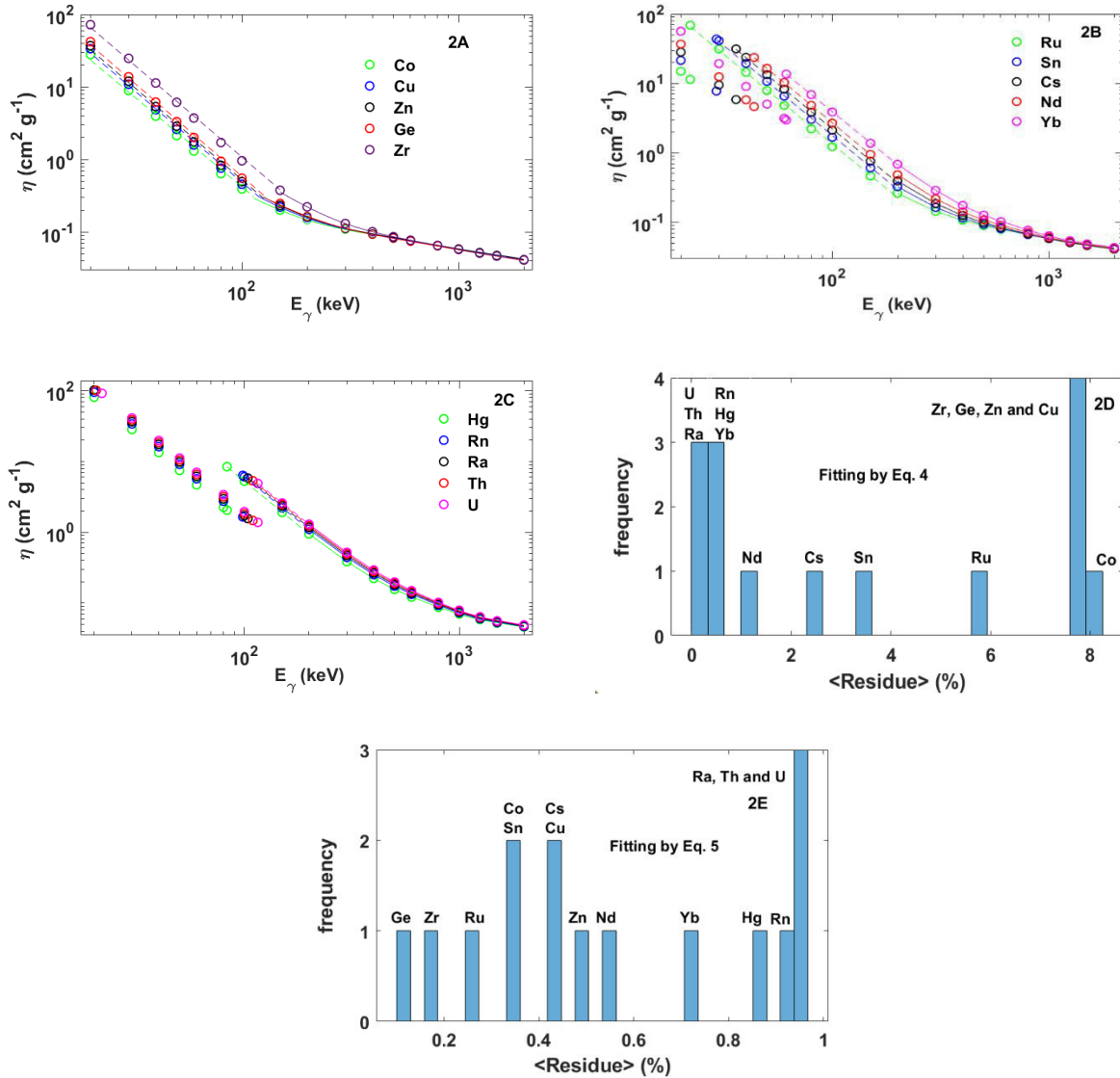


Figure 3.3.2. a) From graphics 2A to 2C: Mass attenuation coefficients $\eta(E_\gamma, Z)$ versus E_γ for several selected elements (high Z values) and the obtained fittings for each energy region after the shell change; b) Graphics 2D and 2E: Histograms representing the average relative residue (in %) for each fitting done for high Z values. Dashed and solid lines represent the fitted curves for the Eqs. 4 (low energy) and 5 (high energy), respectively.

The quality of these fittings can be tested by the histograms of Fig. 3.3.2b (see graphics 2D and 2E). Thus, we see that Eq. 3.3.4 (linear relation for low energies) works very well for higher Z , Sn (3.5%)

up to U (0.2%), while for lower Z, Ru to Co (very close to Fe and low Z region), higher deviations are found (6-8%).

On another hand, for Eq. 3.3.5 (high energy region, $E_\gamma >$ around 240 keV), very good fittings were obtained, since the residues ranged from 0.1% to 1.0% for all element up to $Z = 92$. Furthermore, it is interesting to note that in the zone of transition metals located in the fourth period of the periodic table, the atomic number that corresponds exactly to the middle of that interval of Z is 25.5, which rounded is 26, that is, the atomic number of Fe. This may be another reason in addition to those discussed above in Section 3.3.3.1, why iron is the upper limit of the low Z range.

Regarding the values obtained for the br_i and cr_i parameters, which are shown in Table C.3 (in Supplementary Material-C), these parameters need, in turn, to be fitted by varying Z analogously to how we proceeded previously with the ar_i parameters. Note that the values of both br_i and cr_i also have a quite clear behaviour as shown in Fig. 3.3.3. The regression functions of the br_i and cr_i parameters are given by the following equations:

$$br_i(Z) = \sum_{j=1}^3 br_{ij} \ln(Z)^{j-1} \quad , \quad cr_i(Z) = \sum_{j=1}^3 cr_{ij} \ln(Z)^{j-1} \quad (\text{Eq. 3.3.6})$$

where br_{ij} and cr_{ij} are the parameter values that resulted after the $br_i(Z)$ and $cr_i(Z)$ regressions, respectively, varying Z .

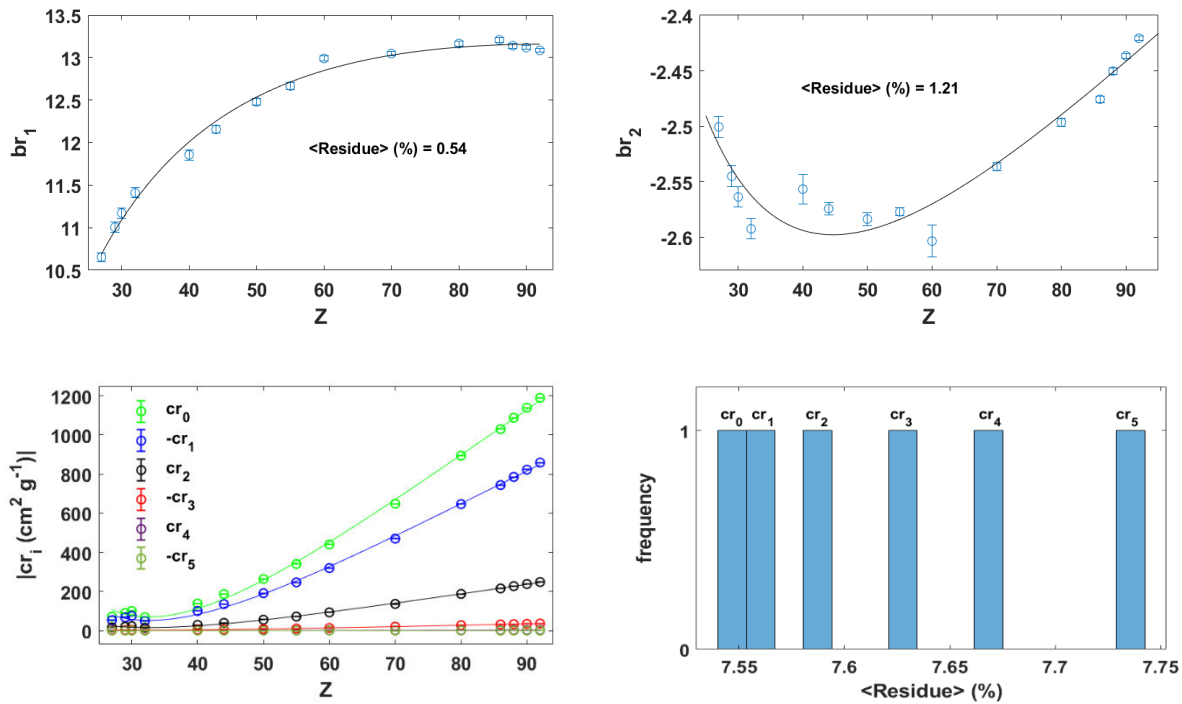


Figure 3.3.3. Fittings done for br_i and cr_i versus Z and average relative residues (in %) resulted from each regression.

In Fig. 3.3.3, it can be seen the regressions carried out using the functions given by Eq. 3.3.6. The values of br_{ij} and cr_{ij} are shown in Table C.4 (in Supplementary Material-C), and these regressions agree very well with the values obtained for br_i and cr_i (see Fig. 3.3.3). Furthermore, the residues for the cr_i regressions are also shown, being represented by a histogram. Thus, we can see in the

histogram that the residues increase as the value of subscript “i” increases (these residues go from 7.55% to 7.74%), analogous to the case previously analysed in Section 3.3.3.1.

On the other hand, it is necessary to clarify that for some chemical elements whose Z values are within the high Z range, it is required to take a third fitting region. In this case, we are talking about the range of energies (energies about 20–65 keV) prior to the abrupt jump (shell change), that occurs in the zone where the photoelectric effect dominates. This abrupt jump of η only occurs within the energy range of interest for a few chemical elements selected in this study whose Z values are really large (Cs, Nd, Yb, Hg, Rn, Ra, Th and U, that is, from $Z = 55$ to $Z = 92$) (see Fig. 3.3.4).

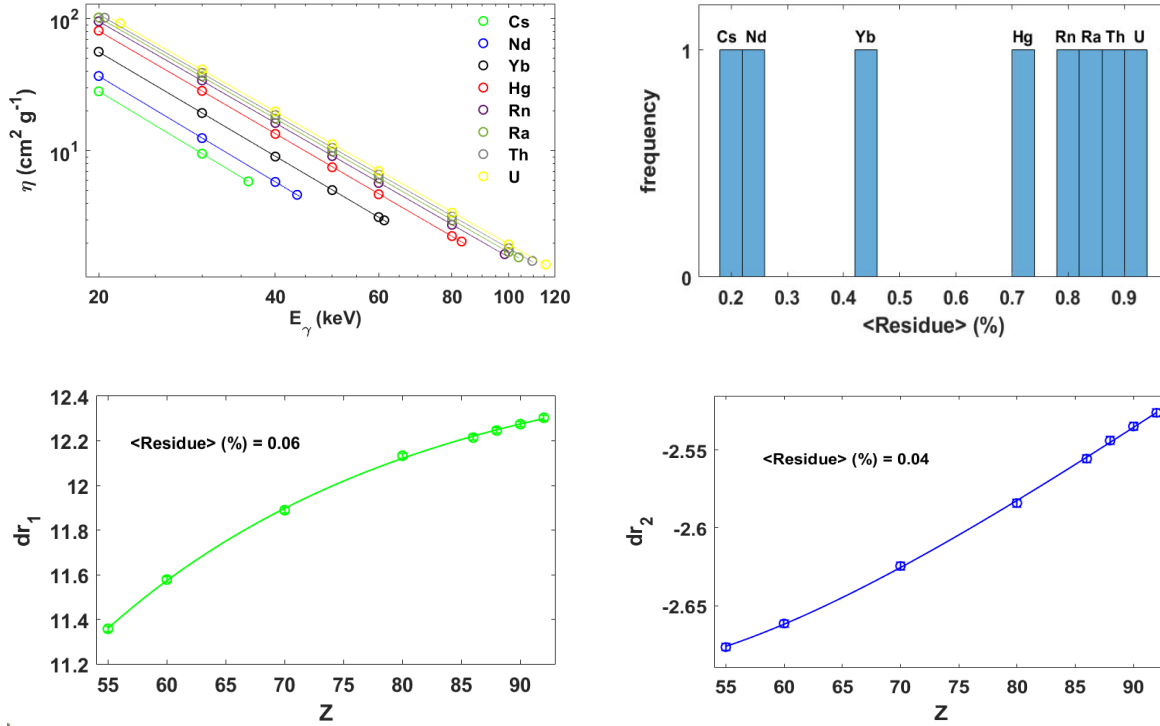


Figure 3.3.4. Regression of $\eta(E_\gamma, Z)$ data by fixing Z and varying E_γ and fitting of the parameters resulted, dr_i , representing graphically their respective relative residues (%) obtained after each fit carried out for the high Z values for the region before the shell change.

In Fig. 3.3.4, a clear linear behaviour of η versus the energy logarithm is observed, so the following function was chosen:

$$\eta(Z, E_\gamma) = \exp(dr_1 + dr_2 \ln(E_\gamma/E_0)) \quad (\text{Eq. 3.3.7})$$

where dr_i represents the parameters that resulted after η value fittings for the region before the shell change.

In Fig. 3.3.4, we can see that the regressions provided by Eq. 3.3.7, whose dr_i parameter values are shown in Table C.5 (in Supplementary Material-C), are in very good agreement with the tabulated η data. Likewise, the relative residues are shown in the histogram that appear in this same figure; their values being between 0.2% (case of Cs) and 0.9% (case of U) and increasing as Z increases. In turn, in Fig. 3.3.4, dr_i parameters are fitted with Z , and the following function gave good results:

$$dr_i(Z) = \sum_{j=1}^3 dr_{ij} \ln(Z)^{j-1} \quad (\text{Eq. 3.3.8})$$

where dr_{ij} are the parameters that resulted after dr_i regressions with the Z values.

Regarding the dr_i fittings done by Eq. 3.3.8, the relative residues obtained were less than 0.1%. So, the quality of the regressions provided by this equation was very good. Besides, the parameter values resulted from these fittings, dr_{ij} , have been shown in Table C.5.

By substituting the previous parameters depending on energy (E_γ) and the atomic number (Z), the general functions of $\eta(E_\gamma, Z)$ have been obtained for the considered regions of E_γ and Z (see next equations shown in Table 3.3.1).

Table 3.3.1

General functions of $\eta(E_\gamma, Z)$ for the considered regions of E_γ and Z .

For low Z values ($Z \leq 26$)		
$\eta(Z, E_\gamma) = \sum_{i=0}^9 \left(\sum_{j=1}^3 ar_{ij} Z^{j-1} \right) \ln(E_\gamma/E_0)^i$	E_γ from 20 to 2000 keV	
For high Z values ($Z > 26$)	Taking the region before the change shell into account	Without taking the region before the change shell into account
$\eta(Z, E_\gamma) = \exp \left(\sum_{j=1}^3 \left(dr_{1j} + dr_{2j} \ln(E_\gamma/E_0) \right) \ln(Z)^{j-1} \right)$	$Z \geq 55$ and E_γ about 20 – 65 keV	
$\eta(Z, E_\gamma) = \exp \left(\sum_{j=1}^3 \left(br_{1j} + br_{2j} \ln(E_\gamma/E_0) \right) \ln(Z)^{j-1} \right)$	$Z > 26$ and E_γ about 65 – 240 keV	$Z > 26$ and E_γ about 20 – 240 keV
$\eta(Z, E_\gamma) = \sum_{i=0}^5 \left(\sum_{j=1}^3 cr_{ij} \ln(Z)^{j-1} \right) \ln(E_\gamma/E_0)^i$	$Z > 26$ and E_γ about 240 – 2000 keV	$Z > 26$ and E_γ about 240 – 2000 keV

3.3.3.3. Validation procedures for the general $\eta(E_\gamma, Z)$ and the self-absorption correction factor functions

In this section we carried out a validation procedure to test the quality of the fittings done using the general $\eta(E_\gamma, Z)$ and self-absorption factor functions when it is applied to CRM and the real samples mentioned In Section 3.3.2. Firstly, it was necessary to calculate the values given by the general $\eta(E_\gamma, Z)$ function. Given that this function depends on Z and E_γ , it is possible to obtain the mass attenuation coefficient for each chemical element contained in the samples that have been selected for these validations, as well as for all the energies of interest. So, there are several cases that can be considered to calculate the values of $\eta(E_\gamma, Z)$ for these samples.

1. In the case of the samples only contain chemical elements whose Z values are $Z \leq 26$, only first equation shown in Table 3.3.1 will be necessary to use.
2. On the other hand, if the samples only contain elements with $Z > 26$ and the shell changes have been taken into account (some elements have $Z \geq 55$), it will be necessary to use the second (only for $Z \geq 55$), third and fourth equations shown in Table 1, where each equation has to be applied within the energy range established for each one of them in this table.
3. Another possible case similar to the previous one (case 2) would be necessary to be applied when shell changes have not been considered, that is, elements with $Z > 26$ but without any element that has $Z \geq 55$. Therefore, in this case only the third and fourth equations shown in Table 3.3.1 will be use within their respective energy ranges.
4. Another case would be a mixture involving cases 1 and 2.
5. And the last case would be a mixture involving cases 1 and 3.

In addition, for determining η of a sample, the Bragg's law was applied, and the standard uncertainty for η calculated. In this case, the only relevant uncertainty source was the concentration of each chemical element in the sample (x_i , being the uncertainty of x_i about 5-10%), which was determined by both ICP-OES or XRF techniques. For example, if the Bragg's law is applied to a sand sample or an Ilmenite sample, and considering the uncertainty of x_i is about 7%, it has been checked that the uncertainties obtained for η were 5% and 4%, respectively, while in the case of the self-absorption correction factor (f), the uncertainties were 0.4% and 1.1%, respectively.

On the other hand, it is necessary to clarify that in the case of the mass attenuation coefficient of hydrogen, we chose to do the calculation using the $\eta(E_\gamma, Z)$ function obtained in the individual fit for $Z = 1$, since its behaviour is very different from the rest of the elements.

After calculating the mass attenuation coefficients of the samples by the general $\eta(E_\gamma, Z)$ function, it is possible to know the self-absorption factor. The self-absorption correction factor is needed for calculating the full energy peak efficiency (FEPE) in gamma spectrometric measurements with Ge detectors and its correction is especially significant at low energies ($E_\gamma \leq 150$ keV).

The self-absorption factor in a cylindrical geometry can be calculated by the following equation (Debertin and Helmer, 1988):

$$f = f(E_\gamma, h, x_i) = \frac{\eta_c \rho_c (1 - \exp(-\eta \rho h))}{\eta \rho (1 - \exp(-\eta_c \rho_c h))} \quad (\text{Eq. 3.3.9})$$

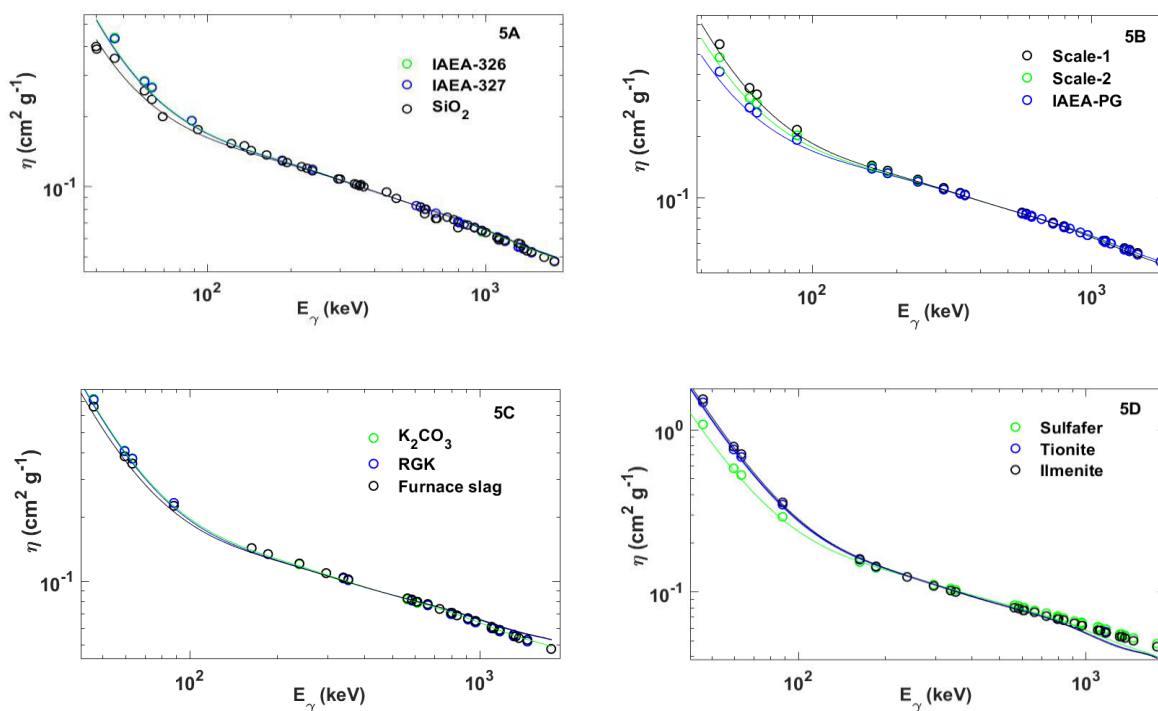
where η_c (η) and ρ_c (ρ) are the mass attenuation coefficients and the density of the calibrating sample (real sample), respectively, h is the real sample height, and x_i is the proportion of each chemical element contained in the calibrating sample (real sample).

Once the application procedures of the general $\eta(E_\gamma, Z)$ and $f(E_\gamma, h, x_i)$ functions to real and calibrating samples have been described step by step, validation procedures have been carried out for both functions in the following sections (Sections 3.3.3.3.1 and 3.3.3.3.2, respectively).

3.3.3.3.1. Validation of the general $\eta(E_\gamma, Z)$ function for different samples compositions

In this validation, the values of the mass attenuation coefficients were compared with the values obtained by interpolating the data provided by NIST for each energy of interest. These interpolations were carried out using a Microsoft Excel sheet (let us call it ExS).

In Fig. 3.3.5 we made a separation between samples that only contain chemical elements with Z values less than 26 (see graphics from 5A to 5E in Fig. 3.3.5a) and those samples that, in addition to containing this class of chemical elements, contain others whose Z values belong to the high Z range (see graphics from 5F to 5I in Fig. 3.3.5b). The RGU-1 and RGTh-1 standards are in the latter type of samples.



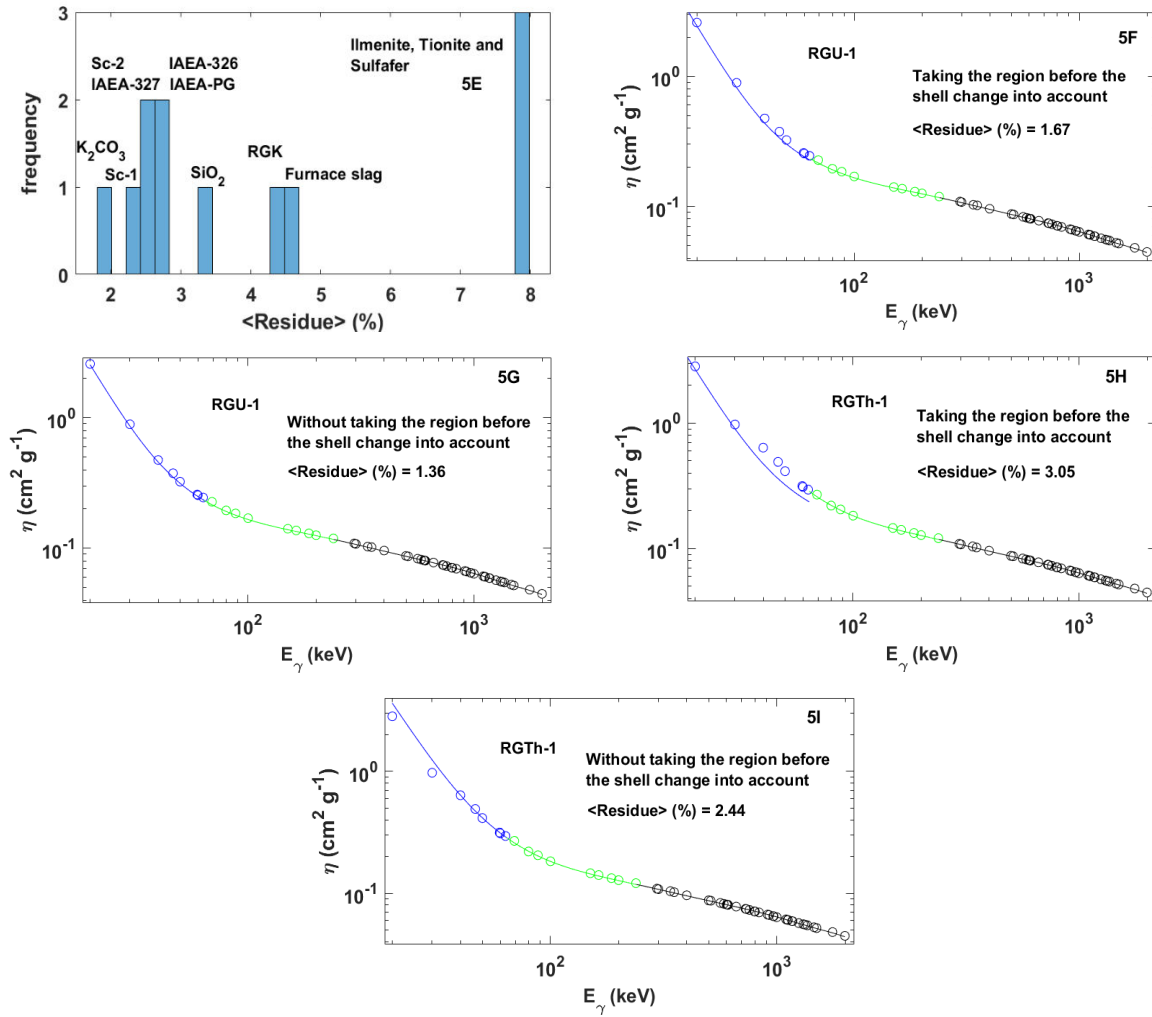


Figure 3.3.5. a) From graphics 5A to 5E: Validation of $\eta(E_\gamma, Z)$ function for numerous NORM samples containing low Z chemical elements; b) From graphics 5F to 5I: Analogously for the RGU-1 and RGTh-1 standards distinguishing three zones: before the shell change (in blue) and after the shell change (exponential and polynomial regressions in green and black, respectively).

In graphic 5A, it can be found the soil samples such as IAEA-326, IAEA-327 and sand (SiO_2), showing a great agreement between both ExS and mass attenuation coefficients given by the general function. This agreement can be seen in graphic 5E (Fig. 3.3.5a), where the residues obtained are relatively small (2.50-3.36%). For industrial samples as Scale-1, Scale-2 and IAEA-PG (see graphic 5B), again very good fittings are obtained with residues ranging from 2.2% to 2.7%.

On the other hand, it can be seen the graphic 5C where the comparisons corresponding to K_2CO_3 , Furnace slag and RGK-1 standard can be found. In these cases, the residues are between 1.81% and 4.54%. In the graphic 5D, the cases related to Ilmenite, Tionite, and Sulfafer samples have been shown. For these three cases, the general function gives values slightly below the ones given by ExS for energies higher than 1100 keV. This is happening because these three samples have extreme chemical compositions, where the percentage of iron is about 35%. Furthermore, Tionite and Ilmenite samples, a very significant amount of titanium is present (about 30%). Despite these quite extreme chemical compositions, the relative residues are below 8% for the three samples, so the general function works very well. It is necessary to clarify that “extreme chemical compositions” refer to

when the average Z of a sample, $\langle Z \rangle$, is very different than typical samples such as soils ($\langle Z \rangle \approx 10.6$), water ($\langle Z \rangle = 7.9$), etc.

On the other hand, in the graphics 5F and 5G of Fig. 3.3.5b, the comparison for the RGU-1 standard has been shown. Moreover, two cases have been distinguished. In the first case (graphic 5F), the general function corresponding to the zone before the shell change has been considered. The second case (graphic 5G) is one in which this general function has not been considered. The region before the shell change has been represented in blue. Then the zone corresponding to the regression given by Eq. 3.3.4 has been plotted in green. Finally, the zone corresponding to the fitting given by Eq. 3.3.5 has been shown in black.

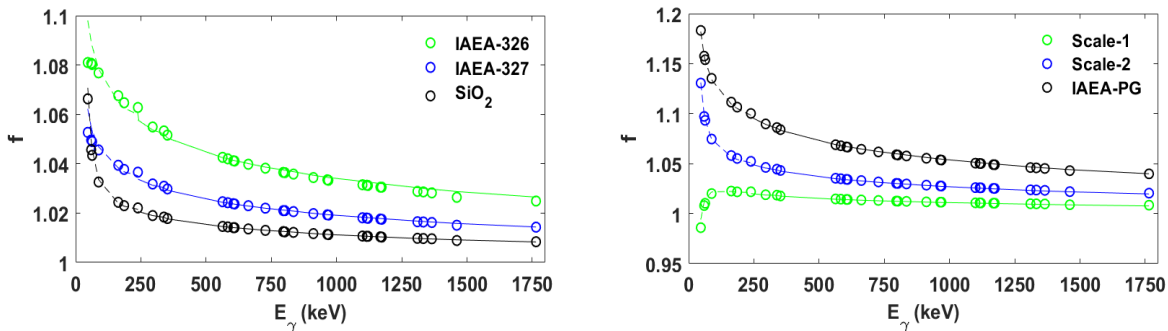
In the case corresponding to the region before the shell change (graphic 5F), a slight discontinuity can be visualized which is causing the obtained residue to be higher than the second case (graphic 5G). In the latter case, it can be seen clearly that the $\eta(E_\gamma, Z)$ function is continuous throughout the energy range. Consequently, the fitting has better quality in the second case (graphic 5G).

Analogous to the case of the RGU-1 standard, it has been proceeded with the RGTh-1 standard (the graphics 5H and 5I of Fig. 3.3.5b). For this last standard, the improvement of the fittings done when the shell changes have been neglected is even more significant than in the case of the RGU-1 standard. Thus, in addition to correcting a very clear discontinuity in the $\eta(E_\gamma, Z)$ function, the residue has been significantly reduced (from 3.05% to 2.44%). The reason why the fittings are better without considering the general function related to the shell change is because, as we saw earlier in Section 3.3.3.2, this type of function only begins to be important for $Z \geq 55$ within our energy range of interest. This implies that since the average atomic number of the RGU-1 and RGTh-1 standards is about 14, the general function related to the shell change can be completely neglected, and a better validation is obtained without it.

3.3.3.3.2. Validation by using the self-absorption factors for gamma spectrometry in cylindrical geometry

This validation has been carried out by comparisons made between the values of the self-absorption factor obtained from ExS and the general $f(E_\gamma, h, x_i)$ function.

These comparisons have been shown in Fig. 3.3.6. In this figure the energy range goes from 46.5 keV to 238 keV for the general function given by Eq. 3.3.4 and from 238 keV to 1764.5 keV for the general function given by the Eq. 3.3.5.



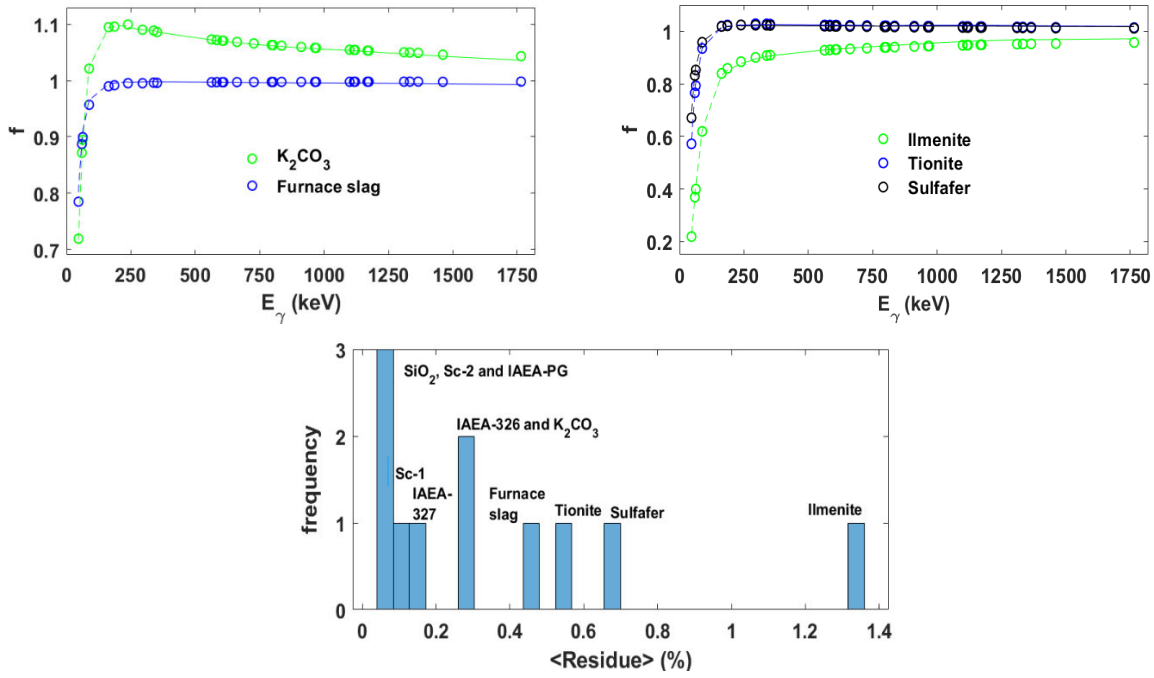


Figure 3.3.6. Validation of the $f(E_\gamma, h, x_i)$ function carried out for numerous NORM samples, distinguishing the zone of the fit done by Eq. 3.3.4 (dashed line) from that of the fit done by Eq. 3.3.5 (solid line).

In the first row (left side) of Fig. 3.3.6, the cases corresponding to samples IAEA-326, IAEA-327, and SiO_2 can be found. There is clearly a great similarity between the values given by ExS and the ones given by the general functions, where the average residues (represented in the histogram of Fig. 3.3.6) ranged 0.06-0.27%. In that same row (right side), the cases related to the Scale-1, Scale-2, and IAEA-PG samples were shown. In this case, like the previous one, the validation was very good since the residues obtained were between 0.06% and 0.11%. Then, in the second row (left side), the comparisons made for K_2CO_3 and Furnace slag samples can be seen, for which the residues obtained were 0.27% and 0.44%, respectively. So, the similarity between the values given by ExS and the ones given by the general function continues to be very good.

Finally, in the last row of Fig. 3.3.6 (right side), the cases for Ilmenite, Tionite, and Sulfafer samples have been shown. In these cases, the values given by the general function are very similar to the ones given by ExS for the three samples. It is only noticed that for the Ilmenite sample, the f values obtained by the general function are slightly above the tabulated values for energies higher than 1100 keV. This is understandable because the Ilmenite sample not only has a quite extreme chemical composition, as we saw earlier, but also has a density much higher than that of the standard (almost double). However, the average residue obtained for the Ilmenite is only 1.36%. Therefore, the validation of the general $f(E_\gamma, h, x_i)$ function has been very good for this sample, and even better in the cases of the Sulfafer and Tionite samples for which the average residues have been 0.69% and 0.56%, respectively.

On the other hand, after analyzing the residues resulted from the fittings done for the self-absorption factor, it is interesting to know the contribution of this factor to the activity concentration uncertainty (σ_a). Therefore, a comparative analysis of the uncertainties belonging to the magnitudes presented in Eq. 3.3.1 has been carried out. After doing this analysis, it has been checked that the uncertainty due to the counting rate (σ_n) is about 89% of σ_a , while the contribution due to the gamma emission

probability is about 8%. Lastly, the contributions due to the efficiency of the detector calculated in the calibrating matrix (σ_{ec}), the self-absorption factor (σ_f) and the sample mass (σ_m) are about 2%, 1% and 0%, respectively. Consequently, the contribution of the self-absorption factor uncertainty to σ_a can be completely neglected in a first-order approximation.

3.3.3.4. Comparisons between the method proposed in this work and other methods already known

In this section, comparisons between the method proposed in this study and other alternative methods already known have been made to highlight the advantages of the method considered in this article. In order to do this, it has been selected other methods based on software such as WinXCOM and NXCOM or simulations as Monte Carlo methods, which are able to calculate mass attenuation coefficients. Furthermore, comparisons made with experimental methods as empirical calibrations have also been considered. Finally, three comparisons have been made between the results obtained for the mass attenuation coefficients by ExS and WinXCOM, the method proposed in this work (by $\eta(E_\gamma, Z)$) and WinXCOM as well as physical equations and WinXCOM. These last three comparisons have been made to evaluate the uncertainties (relative residues) resulted from the calculations of η using different methods.

The advantages of the proposed method versus WinXCOM program is that this program needs to renormalize all the fractions by weight so that they add up to unity, while the proposed method does not need to renormalize them. Regarding to NXCOM program, the advantages of the proposed method versus NXCOM is that this program lists the calculations of mass attenuation coefficients on a standard energy grid, without energies for edges of absorption, of the well-known XCOM program (see El-Khayatt, 2011). However, the method proposed in this work can consider any energy desired, including the energies for edges of photoelectric absorption. In addition, another advantage of the proposed method versus, in this case, Monte Carlo methods is focused on the computational cost, this being not so high in our case. This implies that the proposed method lets calculate the mass attenuation coefficients for many energies without the need for a large computational cost.

Furthermore, the proposed analytical functions can be implemented as equations in the Microsoft Excel sheets or any mathematical software used to calculate activity concentrations, and therefore in the evaluation of the corrections due to self-absorption effects.

Regarding experimental methods related to a simple empirical calibration of the detector, it would be possible to carry out the calculations of mass attenuation coefficients if all the samples analyzed had the same chemical compositions and density. However, this is not our case, since that we have considered samples whose chemical compositions take many possibilities of compositions and densities into account. Moreover, by a simple empirical calibration of the detector, it would be necessary to use many point sources in order to cover all the energies of interest. Consequently, calculating mass attenuation coefficients by a simple empirical calibration of the detector would be a very expensive and tedious work.

To make the comparisons related to the uncertainties, that is, the relative residues obtained by different methods, the real samples provided by IAEA have been selected (IAEA-326, IAEA-327 and IAEA-PG). This selection has been made because these real samples are certified, and therefore their chemical compositions and other characteristics can be easily consulted.

In Table C.7 (in Supplementary Material-C) it can be seen the relative residues obtained after comparing ExS, $\eta(E_\gamma, Z)$ and physical equations with WinXCOM. In the case of the physical equations only contributions due to photoelectric effect and Compton scattering have been considered

in order to simplify the total cross-section. Therefore, for the physical equations, the total mass attenuation coefficient was calculated by

$$\eta_T = N_A A_r^{-1} (a Z^m E_\gamma^{-n} + b Z E_\gamma^{-1}) \quad (\text{Eq. 3.3.10})$$

where N_A is the Avogadro's number ($6.022045 \times 10^{23} \text{ mol}^{-1}$), A_r and Z are the relative atomic mass and the average atomic number of each certified sample, respectively, E_γ is the gamma emission energy, a ($\text{cm}^2 \text{ keV}^{1.0001}$) and b ($\text{cm}^2 \text{ keV}$) are the parameters obtained after fitting the data provided by WinXCOM, $m = 4$ and $n = 1.0001$ (see NIST 2004b for further information about these equations).

In this table it is very easy to see the great agreement between the values of mass attenuation coefficients calculated by ExS and WinXCOM, where the average residues have been about 1%. This great similarity between ExS and WinXCOM was expectable because both methods use the same procedure to calculate the values of the mass attenuation coefficients, that is, using interpolations. However, the methods based on interpolations have a clear drawback which is the continuous usage of them required to calculate η for each energy of interest. Regarding the comparisons made between $\eta(E_\gamma, Z)$ and WinXCOM, it can also be seen clearly the good agreement between both methods, where the average residues obtained have been less than 2%.

On the other hand, the relative residues resulted from the comparisons made between physical equations and WinXCOM have been very high (25-29%). Consequently, these physical equations are not proper to fit accurately the mass attenuation coefficients.

3.3.4. Conclusions

The main conclusions of this study are:

1. In the present work, a novel methodology has been carried out in order to determine the mass attenuation coefficient, for any sample and energy, by a general analytical function. To do this, it was previously necessary to use the tabulated data, provided by NIST, of the mass attenuation coefficients for certain chemical elements. Furthermore, it was necessary to distinguish between two types of Z ranges (low and high Z ranges), having been proven that iron is the chemical element that makes the difference between low and high Z values.
2. Regarding the regressions done within the low Z range ($Z \leq 26$), it was possible to fit correctly the data provided by NIST (from 20 keV to 2000 keV) by an only one fitting function. Regarding the high Z range ($Z > 26$), it has been considered necessary to do the regression separately, distinguishing between the low and high energy zones. Then, it has been checked that the region before the shell change begins to be important in our case for Z values higher than 55. For this region, it was necessary to carry out the fittings using a different regression function than ones used for the region after the shell change. Furthermore, it has been proven that the fitting function corresponding to the region prior to the shell change has not been necessary in our case.
3. Then, a validation procedure has been done for both functions: the general functions of the mass attenuation coefficient and the self-absorption factor. For this, numerous types of samples were selected. Thus, it has been observed that both general functions ($\eta(E_\gamma, Z)$ and $f(E_\gamma, h, x_i)$) agree very well with the results obtained by ExS. Moreover, the uncertainties

introduced by these two general functions have been assessed, proving that the contribution of σ_f to σ_a is not relevant for any sample.

4. On the other hand, comparisons between the method proposed in this study and other alternative methods have been made, observing that the proposed method has many and clear advantages versus the other ones mentioned. Lastly, it has been made an assessment of the relative residues obtained after comparing the η values calculated by ExS, $\eta(E_\gamma, Z)$ and physical equations with the ones obtained by WinXCOM. Regarding the two first comparisons, it has been checked the good agreement between those methods. On the other hand, in the case of the calculations done by physical equations, it has been clearly proved that they do not provide a proper fitting of the mass attenuation coefficient (25-29% of residues), and therefore they are not useful to correct self-absorption effects.

Subchapter 3.4.: A practical and general methodology for efficiency calibration of coaxial Ge detectors

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Subchapter 3.4.: A practical and general methodology for efficiency calibration of coaxial Ge detectors

Abstract

The correct determination of artificial and natural radionuclides like ^{152}Eu , $^{137, 134}\text{Cs}$, $^{60, 57}\text{Co}$, etc., and $^{234, 228}\text{Th}$, $^{228, 226}\text{Ra}$, ^{210}Pb and ^{40}K , respectively, is essential for many environmental science fields. For this, a general function was obtained for the full-energy peak efficiency (*FEPE*) by gamma-ray spectrometry using coaxial Ge detectors. Then, the experimental *FEPE* values, obtained fixing the energy, E_γ , were fitted varying the thickness, h , of cylindrical standards. The parameters resulted from these fittings were fitted, in turn, versus E_γ , obtaining a general efficiency function, $\varepsilon_c(E_\gamma, h)$. $\varepsilon_c(E_\gamma, h)$ was validated, obtaining very good z_{score} , except for E_γ affected by TCS effects. Consequently, a practical and general method was developed, recalibrating the detector by varying the sample-detector distance, d . $\varepsilon_c(E_\gamma, h, d)$ was obtained, achieving very good z_{score} . Furthermore, this practical method was also employed to correct high self-absorptions and high dead times.

Keywords: Gamma-ray spectrometry; Efficiency calibration; Artificial and natural radionuclides; True coincidence summing; Self-absorption; Dead time

3.4.1. Introduction

There are several natural and artificial radionuclides of interest within the field of the environmental radioactivity, such as $^{234, 228}\text{Th}$, $^{228, 226}\text{Ra}$, ^{210}Pb and ^{40}K , as well as ^{241}Am , ^{152}Eu , $^{137, 134}\text{Cs}$, ^{133}Ba , $^{60, 57}\text{Co}$. In order to determine these radionuclides by gamma-ray spectrometry, it is of vital importance to use different types of detector efficiency corrections. Among the most important efficiency corrections, there are the following: true coincidence summing (TCS), self-absorption and dead time corrections.

Regarding the former correction type, they are often applied to determine artificial radionuclides, given that the majority of artificial radionuclides have TCS effects (^{152}Eu , $^{137, 134}\text{Cs}$, $^{60, 57}\text{Co}$, etc.). However, some natural radionuclides like ^{214}Bi and ^{208}Tl , which are daughters of ^{226}Ra and ^{228}Th corresponding to the ^{238}U - and ^{232}Th -series, respectively, also suffer TCS effects (Gilmore and Hemingway, 1995; Tedjani et al., 2016; Venegas-Argumedo and Montero-Cabrera, 2015). Therefore, this type of correction is indispensable to be considered in order to know the radionuclide activity concentrations in a proper way. Furthermore, it is necessary to clarify that there are two kinds of TCS effects: “summing in” and “summing out” effects. The former takes place when two photons are detected simultaneously and they are added to a specific full-energy peak, where those two photons have energies that do not belong to that specific peak. The second type consists in the opposite phenomenon, that is, one of those two simultaneous photons is taken away from that specific peak and included in another peak.

In the case of the TCS corrections, nowadays the corrections provided by MCNP, GEANT4, PENELOPE or FLUKA simulation codes have become generalized (Ahmed, 2019; Belgin and Aycik, 2015; Bochud et al., 2006; Laborie et al., 2002; Maidana et al., 2016; Sahiner and Meriç, 2014; Suárez-Navarro, 2020; Zhu et al., 2009). However, in order to carry out these corrections by using simulation software, it is necessary to characterize the detector parameters and, consequently, expensive costs and several months are required, being the detector inoperative during the time taken to carry out the detector characterization procedure.

With respect to the self-absorption corrections, they are very useful to be employed due to the possible chemical composition and density differences between the samples used to calibrate the detectors and the other samples, which are called as problem samples. The reason is because when the composition and density of the calibration and problem samples are very different from each other, the photons are attenuated differently and, consequently, a self-absorption correction is required to introduce these differences in the detector efficiency calculation when this is obtained in the problem sample matrices (Carrazana et al., 2010; San Miguel et al., 2002; Xhixha-Kaçeli et al., 2013). Besides that, self-absorption corrections are essential in the cases of the radionuclides whose gamma emissions belong to the low energy range, that is, energies less than 150 keV, since the self-absorption effects are much more relevant for that energy range (Barba-Lobo et al., 2021c; Bonczyk, 2018; Długosz-Lisiecka and Ziomek, 2015).

On the other hand, regarding the dead time corrections, they are usually employed in the cases for which samples, whose radionuclides have very high activity concentrations, are measured. In these cases, given that there is a large number of disintegrations per second, the detector is not able to detect all photons that reach the detector. Consequently, a great number of events are not considered and, therefore, not included in the activity concentration calculations, determining the radionuclides in an improper way.

For all reasons previously mentioned, this study aims to develop a new and simple methodology to correct TCS and self-absorption effects, as well as high dead times. For this, a recalibration of the detector was accomplished, obtaining a general efficiency function in the calibration matrix, $\varepsilon_c(E_\gamma, h, d)$, based on the full-energy peak efficiency (FEPE), and which depends on the gamma emission energy (E_γ), the sample thickness (h) and the distance (d) existing between the bottom of the selected geometry (cylindrical in our case) and the detector window.

3.4.2. Materials and methods

3.4.2.1. Materials

In order to carry out this study, an extended range high purity germanium detector (XtRa) was employed. The XtRa detector has a relative efficiency of 38.4% in relation to a 3" $\times$ 3" NaI (TI) detector, a full width at half maximum (FWHM) of 1.74 keV and 0.88 keV at 1332 keV and 122 keV, respectively, and a peak-Compton relation of 67.5:1. The XtRa detector is connected to a FET preamplifier whose model is 2002 CSL, where the bias voltage value used for this detector was 3500 V. In order to proceed with the cooling of this detector, LN₂ was employed for it.

On the other hand, to accomplish the corrections related to TCS effects and high dead times, a simple and general mechanism was designed, which consists in a cylindrical polyvinyl chloride (PVC) tube that was pierced from two opposite sides. Therefore, through the holes made on the surface of the hollow tube, it is possible to introduce screws that are thick and long enough to properly hold the sample support, allowing us to place the samples at a distance from the detector window (see Fig. 3.4.1). As can be seen in Fig. 3.4.1, the PVC tube was attached to a base, which is also composed of PVC, making the tube more stable. Regarding the holes made on the tube surface, it is necessary to clarify that the first hole is placed at 25 mm of height from the detector window and the second one is 10 mm above the first one, being this height the same one between two consecutive holes.

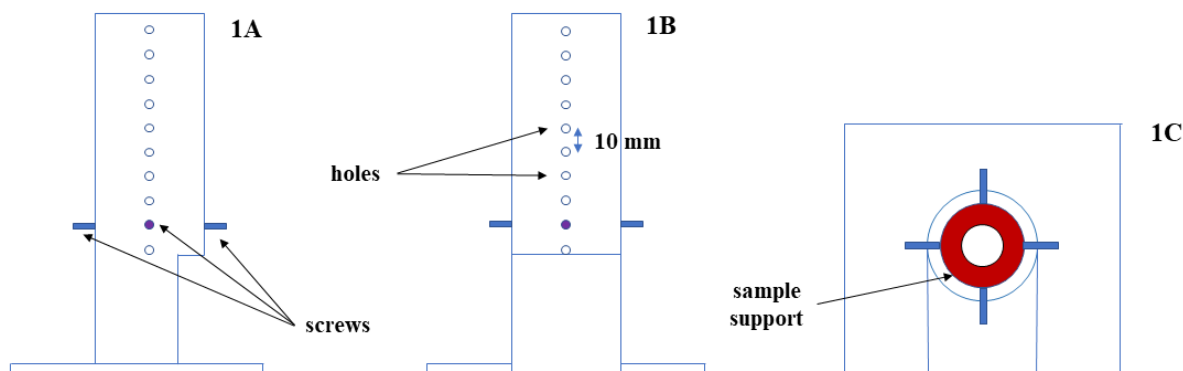


Figure 3.4.1. Several perspectives of the system employed, a PVC tube, in order to proceed with the efficiency corrections: 1A) Profile; 1B) Side used to fit the PVC tube with the detector; 1C) Top.

Regarding the samples selected to accomplish this work, certified standards provided by the IAEA (International Atomic Energy Agency) were employed to proceed with the detector calibration, whose codes and reference activity concentrations are RGU-1, RGTh-1 and RGK-1, and $4940(15) \text{ Bq kg}^{-1}$, $3250(45) \text{ Bq kg}^{-1}$ and $14000(200) \text{ Bq kg}^{-1}$, respectively. These calibration standards contain radionuclides belonging to the ^{238}U - and ^{232}Th -series, as well as ^{40}K , respectively, being all radionuclides in secular equilibrium in the two series. For further information about RGU-1, RGTh-1 and RGK-1 standards, see IAEA, 1987; IAEA, 2020. Then, several problem NORM (Naturally Occurring Radioactive Materials) samples were also chosen which are characterized by having a very wide variety of chemical compositions and densities, allowing us to do a much more complete study. These problem samples can be classified into two groups: samples whose activity concentrations are known and not known. See Barbero et al., 2014; Gázquez et al., 2014; Hierro et al., 2014; Spasic-Jokic et al., 2013 for further information about NORM samples.

With respect to the former type, they are the following: a soil sample (Soil-1), a milk powder sample (Milk powder), two water and furnace slag samples (Furnace slag, Water-1 and Water-5), as well as another soil sample (Soil-2), that were employed in the Inter-comparison – CSN/CIEMAT exercises carried out in 2016, 2018, 2019 and 2020, respectively. In addition, samples used in the Inter-comparison – IARMA exercise carried out in 2020 were selected, which were a seaweed sample (IARMA-097) and three water samples (IARMA-098, IARMA-099 and IARMA-100). Besides that, three soil samples provided by the IAEA were chosen (IAEA-326, IAEA-327 and IAEA-375), as well as a potassium carbonate sample (K_2CO_3) and a tin concentrate sample (Sn-Sample). Regarding CSN, CIEMAT and IARMA, they are the acronyms for the Spanish Nuclear Safety Council (“Consejo de Seguridad Nuclear”), the Centre for Energy, Environment and Technology Research (“Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas”) and the International Atomic Reference Material Agency, respectively.

Then, regarding the latter sample kind (samples whose activity concentrations are not known), the following samples were selected: three industrial wastes known as scales (Scale-A, Scale-B and Scale-C). See Table D.11 in Supplementary Material-D for further information about all samples chosen in this study. Furthermore, it is necessary to clarify that in this study, there is not any sample whose radioactive index is higher than the thresholds defined for radioactive facilities.

3.4.2.2. Methods

In order to obtain the $\varepsilon_c(E_\gamma, h)$ function, that is, the efficiency function without incorporating TCS corrections, the results obtained in a previous work (Barba-Lobo et al., 2021a) was used. In Barba-Lobo et al., 2021a, a methodology to calibrate in efficiency varying the sample thickness was developed without studying any correction type in depth. However, in the present study, TCS and self-absorption effects, as well as high dead-times were studied in depth, developing an exhaustive methodology in order to correct them. To proceed with the obtaining of $\varepsilon_c(E_\gamma, h)$, the calibration standards were compacted until reaching the desired thickness values (h), where h values were ranged from 5 mm to 45 mm in the case of RGU-1 standard, from 5 mm to 50 mm in the cases of the RGTh-1 and RGK-1 standards. For the three standards, an apparent density about $1.63(2) \text{ g cm}^{-3}$ was measured. Then, the experimental values of the full-energy peak efficiency (*FEPE*) were calculated for the different selected h and E_γ values. Finally, a function was chosen to fit the experimental *FEPEs* varying h and fixing E_γ , $\varepsilon_c(h)$.

Once the experimental *FEPE* values were fitted by $\varepsilon_c(h)$, varying h and fixing E_γ , the parameters resulted from these fits, $pr_i(E_\gamma)$, were also fitted versus E_γ . It is necessary to clarify that in order to carry out the fits for $pr_i(E_\gamma)$, only high energies were selected, that is, $E_\gamma > 150 \text{ keV}$ (see Table D.3 in Supplementary Material-D for further information about the E_γ chosen in this study). Let us call this efficiency function as $\varepsilon_c(E_\gamma > 150 \text{ keV}, h)$. The reason why only E_γ values belonging to the high energy range were selected was because there were only a few E_γ values of interest less than 150 keV. Therefore, a general efficiency function was obtained for any h and E_γ values found between 5 mm and 50 mm, and 186 keV and 1765 keV, respectively. After determining the general $\varepsilon_c(E_\gamma > 150 \text{ keV}, h)$ function, it was necessary to introduce the self-absorption corrections, in order to calculate the detector efficiency in any problem sample matrix. Note that this general function, which has been obtained by using calibration standards that contain only natural radionuclides, can also be employed to determine artificial radionuclides.

On the other hand, to introduce the TCS corrections in the obtained efficiency function, a PVC tube was employed which was previously described. Several values of the distance between the geometry bottom and the detector window, d , were chosen: 0, 25, 35, 45, 55 and 65 mm. In this case, to carry out the detector calibration in efficiency, only the RGU-1 standard was used. This standard was prepared for a fixed h value of 25 mm, and it was measured for each one of the d values mentioned.

Then, there are several methods to determine and correct the dead time, among which is the method called as the two sources method. This method consists of comparing the counting rates obtained from two individual point sources and the ones obtained in a combination of the two sources (Grozdanov et al., 2015; Karabidak, 2017; Knoll, 2000). An alternative method, which does not need for any source combinations or tedious procedures, as well as it has not been studied in previous works, will be employed in this study in order to correct the dead time. The method proposed in this study for the high dead time corrections (see Section 3.4.3.5) is analogous to the one previously described for TCS corrections. The dead time depends on the resolution time of the Ge detector and on the electronics (preamplifier, amplifier, Analog-to-Digital Converter (ADC), etc.). Therefore, the dead time has a strong dependence on the total efficiency and the sample activity for a specific detection system. In applications involving a high rate of incoming radiation, detection systems can lose a significant amount of data. Consequently, increasing the source-detector distance, the particle rate that reach the detector is reduced and, therefore, the dead time of the system will be reduced,

being our methodology to correct the dead time based on this idea. In this case, the same d values were also selected to carry out the dead time corrections (0, 25, 35, 45, 55 and 65 mm).

3.4.3. Results and discussion

3.4.3.1. Obtaining of the $\varepsilon_c(E_\gamma > 150 \text{ keV}, h)$ function

Firstly, it is necessary to define the equation used to calculate the experimental *FEPE* values, given that they are required in order to obtain the $\varepsilon_c(E_\gamma, h)$ function:

$$\varepsilon_c^{exp} = \frac{G - B - F - I}{P_\gamma a m_c t} \quad (\text{Eq. 3.4.1})$$

where G, B, F , and I are the total number (gross) of counts for the photopeak of interest whose gamma emission energy is E_γ , the Compton continuum, the background and the interference term, respectively. Then, each E_γ is characterized by having a probability of gamma emission, P_γ , which were taken from DDEP, 2017. On the other hand, a and m_c are the activity concentration and mass of the standard, respectively, used in the calibration procedure, being t the measurement time.

Regarding the P_γ value obtained for 186 keV (^{226}Ra), secular equilibrium between ^{238}U and ^{226}Ra was considered. Let us call the emission probability resulted from this case as P_γ^* , where $P_\gamma^* = P_\gamma(^{226}\text{Ra}) + ^{235}\text{U}/^{238}\text{U} P_\gamma(^{235}\text{U}) = 6.14(6)\%$, being $P_\gamma(^{226}\text{Ra}) = 3.51(6)\%$ and $P_\gamma(^{235}\text{U}) = 57.2(5)\%$ at 186 keV, and $^{235}\text{U}/^{238}\text{U} = 0.046$ (Agha et al., 2011). Besides, the emission probability value related to this case, as well as the ones corresponding to the other energies selected for natural radionuclides have been shown in Table D.3.

Once the experimental *FEPEs* have been calculated, they can be fitted by a semi-empirical function. In our case, it has been checked that the function which provides the best fits for the experimental *FEPEs* is the one given by the following equation:

$$\varepsilon_c(h) = pr_1 \exp(pr_2 h) + pr_3 \quad (\text{Eq. 3.4.2})$$

where pr_i (with $i = 1, 2, 3$) are parameters resulted from the fits of the experimental *FEPEs* versus h (standard thickness) for each E_γ (gamma emission energy) value, being possible to find the pr_i values resulted from the fits at each E_γ value in Tables D.1 and D.2 (see Supplementary Material-D). See Barba-Lobo et al., 2021a for further information about the obtained experimental *FEPEs* and the fits carried out for them.

After obtaining the pr_i values, they have been plotted versus E_γ (see Fig. 3.4.2). Furthermore, in Fig. 3.4.2 it is also possible to see the fits carried out for pr_i versus E_γ . It is easy to realize that pr_i values can be fitted by using a lineal function, which can be written by the following equation:

$$\ln(|pr_i(E_\gamma)|) = pr_{i1} + pr_{i2} \ln(E_\gamma/E_0) \quad (\text{Eq. 3.4.3})$$

where pr_{ij} (with $j = 1, 2$) are the parameters resulted from the fits and $E_0 = 1 \text{ keV}$.

Besides, the pr_{ij} parameter values have been shown in Fig. 3.4.2, as well as the relative average residuals, $\langle \text{Residual} \rangle$ (%), and R^2 values resulted from these fits, where the obtained $\langle \text{Residual} \rangle$ and R^2 values were 3.7%, 4.6% and 4.1%, and 0.994, 0.91 and 0.990 for pr_1 , pr_2 and pr_3 , respectively. Therefore, the fitting functions agreed very well with the pr_i values.

If $pr_i(E_\gamma)$ function given by Eq. 3.4.3 is inserted in Eq. 3.4.2 for each i value, it is possible to rewrite Eq. 3.4.2 in the following way:

$$\varepsilon_c(E_\gamma, h) = \exp[pr_{11} + pr_{12} \ln(E_\gamma/E_0)] \exp(\exp[pr_{21} + pr_{22} \ln(E_\gamma/E_0)] h) + \exp[pr_{31} + pr_{32} \ln(E_\gamma/E_0)] \quad (\text{Eq. 3.4.4})$$

where $\varepsilon_c(E_\gamma, h)$ is the general efficiency function obtained varying the gamma emission energy, which can be called as $\varepsilon_c(E_\gamma > 150 \text{ keV}, h)$ if only high E_γ values are taken.

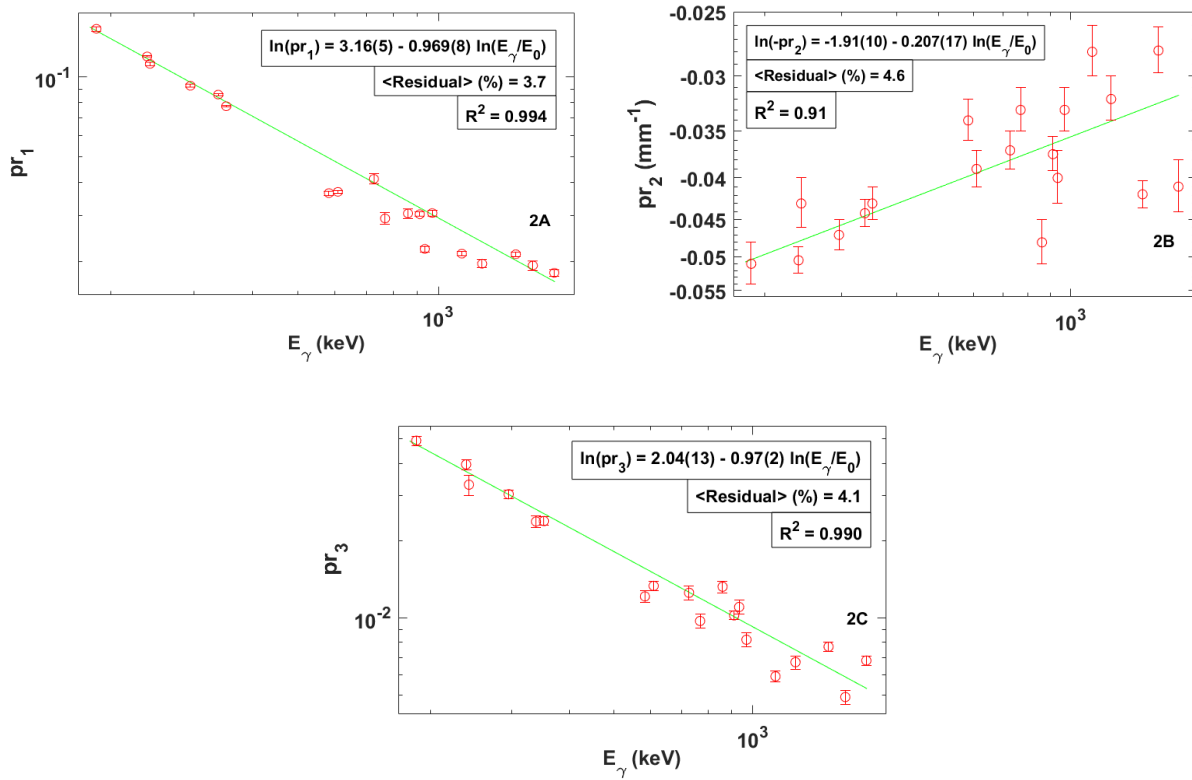


Figure 3.4.2. Fits carried out for the pr_i parameters in order to obtain the general efficiency function at high energies, $\varepsilon_c(E_\gamma > 150 \text{ keV}, h)$: 2A) pr_1 ; 2B) pr_2 ; 2C) pr_3 . Furthermore, relative average residuals and R^2 values have been calculated for each fit of $\ln(pr_i)$ versus $\ln(E_\gamma/E_0)$.

On the other hand, it is necessary to clarify that not all gamma energies selected in the detector calibration were employed to carry out the pr_i fits. In Table D.3, a specification was made on which E_γ values were chosen in order to fit pr_i . Furthermore, in Table D.3, it is interesting to observe that the majority of the E_γ values that have been discarded to fit pr_i , having checked that they were outliers, are gamma energies belonging to ^{214}Bi (such as 609 keV, 768 keV, 1120 keV and 1238 keV) and ^{208}Tl (583 keV). The data considered as outliers were those for which $(y_{\text{exp}} - y_{\text{fit}})/\sigma_{\text{exp}} > 3$, where y_{exp} , σ_{exp} and y_{fit} are the experimental value and its uncertainty at 2 sigma level, and the

value provided by the fitting function, respectively. Note that they are energies clearly affected by TCS effects, and this will be demonstrated in this Section and in Section 3.4.3.2. Consequently, the pr_i values corresponding to those energies do not usually follow the same behaviour than the ones obtained for the other energies, this occurring more clearly for pr_1 since this parameter is characterized by having more dependence on E_γ , while this dependence is much less significant in the pr_2 case.

Once the $\varepsilon_c(E_\gamma > 150 \text{ keV}, h)$ function has been obtained, applications of $\varepsilon_c(E_\gamma > 150 \text{ keV}, h)$ to problem samples, as well as validations of this function have been carried out. For this, it is necessary to transform it to the detector efficiency obtained in any problem sample matrix. For this, it is required to apply the self-absorption correction factor given by the Cutshall's model (Cutshall et al., 1983; Debertain and Helmer, 1988):

$$f_a^c(E_\gamma, h, \eta, \eta_c, \rho, \rho_c) = \frac{\eta_c \rho_c (1 - \exp(-\eta \rho h))}{\eta \rho (1 - \exp(-\eta_c \rho_c h))} \quad (\text{Eq. 3.4.5})$$

where h and E_γ are the problem sample thickness and the energy for which the self-absorption correction is being applied, respectively, ρ and ρ_c are the apparent densities corresponding to the problem and calibration samples, respectively. Then, η and η_c are the mass attenuation coefficients for the problem and calibration samples, respectively, which depends on their respective chemical compositions. Besides, in Eq. 3.4.5, it has been considered that the thicknesses of the calibration and problem samples are the same, that is, h .

Furthermore, in Eq. 3.4.5 only the photons parallel to the symmetry axis are detected. However, the non-coaxial photons are also considered, being the angle between the photon trajectory and the coaxial axis of the detector very small. See Barba-Lobo et al., 2021c; Cutshall et al., 1983; Debertain and Helmer, 1988 for further information about the conditions required in order to properly apply Eq. 3.4.5.

Therefore, the efficiency function calculated in the problem sample matrix, $\varepsilon(E_\gamma > 150 \text{ keV}, h, \eta)$, would be given in the following way:

$$\varepsilon(E_\gamma > 150 \text{ keV}, h, \eta) = f_a^c(E_\gamma > 150 \text{ keV}, h, \eta) \varepsilon_c(E_\gamma > 150 \text{ keV}, h) \quad (\text{Eq. 3.4.6})$$

where $\varepsilon_c(E_\gamma > 150 \text{ keV}, h)$ and $f_a^c(E_\gamma > 150 \text{ keV}, h, \eta)$ are the efficiency in the calibration matrix and the self-absorption correction factor, respectively, which are calculated for gamma energies higher than 150 keV.

Taking Eqs. 3.4.1 and 3.4.6, it is possible to determine both artificial and natural radionuclides contained in problem samples. Therefore, in Tables 3.4.1 – 3.4.3, the validations related to $\varepsilon_c(E_\gamma > 150 \text{ keV}, h, \eta)$ have been carried out. For this, samples that contain artificial and natural radionuclides have been selected, where the results for the former radionuclide type have been shown in Table 3.4.1, while the ones corresponding to the latter type can be found in Tables 3.4.2 and 3.4.3. Therefore, as can be seen in Table 3.4.1, for all samples chosen, that is, Water-1, Water-5, Milk powder, Soil-1 and Soil-2, the obtained $|z_{score}|$ values were less than 2 in general, achieving a very good validation in the case of artificial radionuclides. Regarding the artificial radionuclides, decay corrections have been considered to calculate their activity concentrations, and information about

their half-lives, $T_{1/2}$, as well as their gamma emission probabilities can be found in Table D.4 (see Supplementary Material-D).

Table 3.4.1

External validation procedure of the general $\varepsilon_c(E_\gamma > 150 \text{ keV}, h)$ function in the case of artificial radionuclides contained in a soil sample (Soil-1), a milk powder sample (Milk powder), two water samples (Water-1 and Water-5), as well as another soil sample (Soil-2), that were employed in Inter-comparison – CSN/CIEMAT exercises carried out in 2016, 2018, 2019 and 2020, respectively.

RN	E_γ (keV)	Water-1			Water-5			Milk powder		
		a (Bq kg ⁻¹)	Reference values (Bq kg ⁻¹)	z_{score}	a (Bq kg ⁻¹)	Reference values (Bq kg ⁻¹)	z_{score}	a (Bq kg ⁻¹)	Reference values (Bq kg ⁻¹)	z_{score}
54 Mn	834.8	4.6(4)	4.3(2)	0.5	3.0(4)	2.50(12)	1.1			
59 Fe	1099.25	12.0(9)	9.9(1.0)	1.6	5.4(9)	5.9(5)	-0.5			
60 Co	1173.20	5.0(4)	4.79(18)	0.5	2.0(4)	2.10(7)	-0.2	29.0(8)	26.8(1.0)	1.7
65 Zn	1115.60	8.1(7)	6.8(3)	1.7	5.6(8)	5.9(4)	-0.3			
134 Cs	795.8	1.9(4)	1.92(19)	-0.2	1.7(4)	1.8(2)	-0.1	49.5(1.1)	48(2)	0.7
137 Cs	661.8	3.4(3)	3.3(2)	0.5	1.2(4)	1.55(7)	-0.9	14.9(5)	14.0(6)	1.2
RN	E_γ (keV)	Soil-1			Soil-2					
		a (Bq kg ⁻¹)	Reference values (Bq kg ⁻¹)	z_{score}	a (Bq kg ⁻¹)	Reference values (Bq kg ⁻¹)	z_{score}			
54 Mn	834.8	10.9(4)	10.3(6)	0.8						
59 Fe	1099.25				2.1(8)	2.1(5)	0.0			
60 Co	1173.20	8.8(3)	9.6(6)	-1.1	7.2(4)	7.5(8)	-0.3			
133 Ba	356.0									
134 Cs	795.8	6.2(3)	5.4(3)	2.0	9.3(5)	6.7(9)	2.5			
137 Cs	661.8	5.3(2)	4.8(3)	1.4	5.3(4)	4.9(7)	0.5			
152 Eu	344.3									

In order to proceed with the previous validations, it was necessary to use the following equation to calculate the z_{score} values:

$$z_{score} = \frac{a - a_r}{\sqrt{\sigma_a^2 + \sigma_{a_r}^2}} \quad (\text{Eq. 3.4.7})$$

where a and a_r are the calculated and reference activity concentrations, respectively, whose uncertainties given at 1 sigma level are σ_a and σ_{a_r} , respectively. z_{score} values in the range from -2 to 2 are considered good.

On the other hand, regarding the results obtained for natural radionuclides, in Tables 3.4.2 and 3.4.3, two cases have been distinguished. The case corresponding only to ^{40}K for which the K_2CO_3 sample was chosen. Given that ^{40}K has an only gamma emission (1460.83 keV), the K_2CO_3 sample thickness was varied, getting three K_2CO_3 samples whose h values are well distributed throughout the h range ($h = 9.1 \text{ mm}$, 23.2 mm and 46.4 mm), achieving to accomplish both external and internal validations

at the same time. Furthermore, the calculations resulted from $\varepsilon_c(E_\gamma > 150 \text{ keV}, h)$ have been compared with the ones obtained by the efficiency function, $\varepsilon_c^{RGK-1}(h)$. $\varepsilon_c^{RGK-1}(h)$ is the function obtained in Barba-Lobo et al., 2021a which resulted from the calibration in efficiency fixing E_γ and varying h by using the RGK-1 standard, while $\varepsilon_c(E_\gamma > 150 \text{ keV}, h)$ was obtained varying E_γ as was previously explained. As can be seen in Table 3.4.2, similar z_{score} values were obtained for both efficiency functions. There is only one case ($h = 46.4 \text{ mm}$) where $|z_{score}|$ was more than 2. However, this is consistent since that h value was very close to the upper limit of the selected h range, that is, 50 mm. Therefore, a very good validation was achieved in the case of ^{40}K by $\varepsilon_c(E_\gamma > 150 \text{ keV}, h)$.

Table 3.4.2

External validation procedure of the general $\varepsilon_c(E_\gamma > 150 \text{ keV}, h)$ function in the case of natural radionuclides (^{40}K) contained in K_2CO_3 sample, where the reference value for the ^{40}K activity concentration is $(17800 \pm 255) \text{ Bq kg}^{-1}$. Besides, an internal validation was carried out varying the K_2CO_3 thickness (h). Besides, these results were compared with the ones obtained by the efficiency function, $\varepsilon_c^{RGK-1}(h)$, which resulted from the calibration in efficiency fixing E_γ and varying h using the RGK-1 standard.

$h \text{ (mm)}$	$\varepsilon_c(E_\gamma > 150 \text{ keV}, h)$		$\varepsilon_c^{RGK-1}(h)$	
	$a \text{ (Bq kg}^{-1}\text{)}$	z_{score}	$a \text{ (Bq kg}^{-1}\text{)}$	z_{score}
9.1	18228 ± 499	0.8	17462 ± 478	-0.6
23.2	17486 ± 415	-0.6	17472 ± 415	-0.7
46.4	16815 ± 400	-2.1	16767 ± 399	-2.2

Table 3.4.3

External validation procedure of the general $\varepsilon_c(E_\gamma > 150 \text{ keV}, h)$ function in the case of natural radionuclides contained in the soil samples IAEA-326 and IAEA-327, and a furnace slag sample which was used in an Inter-comparison – CSN/CIEMAT exercise carried out in 2019.

RN	$E_\gamma \text{ (keV)}$	IAEA-326			IAEA-327			Furnace slag		
		$a \text{ (Bq kg}^{-1}\text{)}$	Reference values $\text{(Bq kg}^{-1}\text{)}$	z_{score}	$a \text{ (Bq kg}^{-1}\text{)}$	Reference values $\text{(Bq kg}^{-1}\text{)}$	z_{score}	$a \text{ (Bq kg}^{-1}\text{)}$	Reference values $\text{(Bq kg}^{-1}\text{)}$	z_{score}
226 Ra	185.96	35(3)		0.6	38(5)		0.7	107(8)		0.1
214 Pb	295.22	29.8(9)		-0.9	35(2)		0.3	103(3)	106.3(1.7)	-0.9
	351.93	30.1(8)	33(3)	-0.8	36(2)	34(3)	0.5	104(3)		-0.7
214 Bi	609.31	25.5(7)		-2.2	26.3(1.1)		-1.9	86(2)		-7.1
	1120.29	26.3(1.4)		-1.8	31(3)		-0.3	79(4)		-6.5
228 Ac	338.42	40(7)		0.0	43(8)		0.5	131(22)		0.0
	911.16	38.8(1.2)	40(2)	-0.5	42(2)	39(3)	1.0	134(4)	130(5)	0.8
212 Pb	238.63	38.2(9)		-0.5	37.7(1.1)		-0.2	140(3)		1.7
208 Tl	583.19	30.5(9)	39.1(1.7)	-4.5	30.1(1.5)	38.2(1.8)	-4.0	109(3)		-3.6
40 K	1460.83	591(13)	580(28)	0.4	660(17)	621(27)	1.2	148(5)	161(6)	-1.6

Then, in Table 3.4.3, the validation cases corresponding to the two soil samples (IAEA-326 and IAEA-327), as well as the one related to the furnace slag sample (Furnace slag), can be found. It is

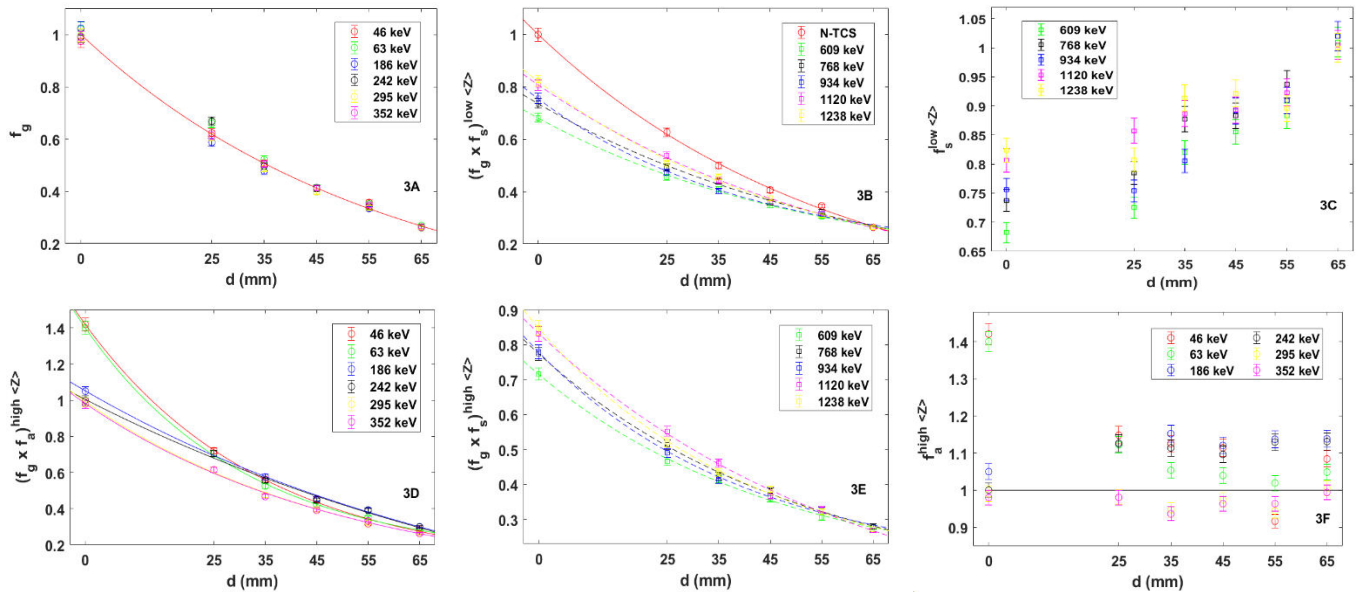
easy to realize that for all gamma energies, very good z_{score} values were obtained excepting three E_γ cases: 583 keV, 609 keV and 1120 keV. These three energies, where the first two energies belong to ^{214}Bi and the third one corresponds to ^{208}Tl , are clearly affected by the TCS effects and, consequently, TCS corrections are required. This is very consistent with the dissimilarities existing between the behavior of the pr_i parameters obtained at these energies compared with the one related to the pr_i values resulted from the fits done at other energies, this having been previously proven in Section 3.4.3.1. Therefore, in Section 3.4.3.2, a novel and simple methodology has been carried out in order to correct the TCS effects.

3.4.3.2. Corrections of the $\varepsilon_c(E_\gamma, h)$ function varying the distance: $\varepsilon_c(E_\gamma, h, d)$

Since TCS corrections are needed when the efficiency is calculated as a function on the energy, in this Section a practical and general method, which was previously described in Section 3.4.2.2, has been proposed for this correction type. Therefore, firstly, it is necessary to define the equations that have been employed to accomplish the proposed methodology. The efficiency function given by Eq. 4, $\varepsilon_c(E_\gamma, h)$, needs to be corrected by several correction factors when the distance, d , between the geometry bottom and the detector window is varied. Therefore, the resulted efficiency function, $\varepsilon_c(E_\gamma, h, d)$, can be calculated in the problem sample matrix, that is, $\varepsilon(E_\gamma, h, d, \eta)$, which is given by the following equation:

$$\varepsilon(E_\gamma, h, d, \eta) = f_a \varepsilon_c(E_\gamma, h, d) = f_T \varepsilon'_c(E_\gamma, h, d) = f_g f_s f_a \varepsilon'_c(E_\gamma, h, d) \quad (\text{Eq. 3.4.8})$$

where f_g is the correction factor related to the geometry which only depends on the distance d , f_s is the correction factor due to TCS effects, which depends on the energy, E_γ , problem sample thickness, h , the distance, d , and the density and mass attenuation coefficient of the calibration standard, ρ_c and η_c , respectively, f_a is the correction corresponding to the self-absorption effects, whose dependence was studied in Eq. 3.4.5, and f_T is the total correction which involves the other three previous corrections. On the other hand, $\varepsilon'_c(E_\gamma, h, d)$ is obtained from $\varepsilon_c(E_\gamma, h)$ for each d value, since the h range covered by $\varepsilon_c(E_\gamma, h)$ goes from 5 mm to 45 mm in the case of the RGU-1 standard.



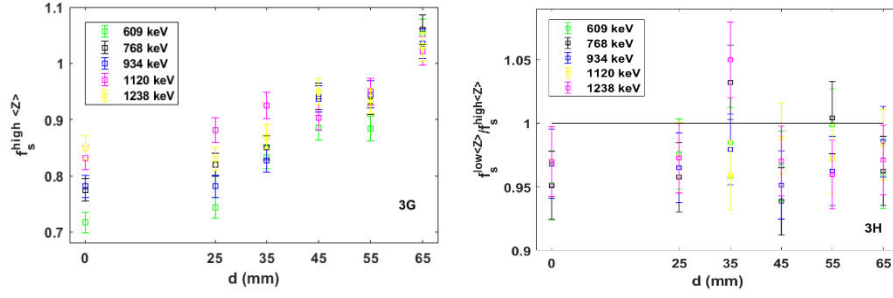


Figure 3.4.3. From 3A to 3C: f_g and f_s factors corresponding to the N-TCS and TCS energies when the sample $\langle Z \rangle$ is low; From 3D to 3G: f_g , f_s and f_a factors corresponding to the N-TCS and TCS energies when the sample $\langle Z \rangle$ is high, and 3H is a comparison between $f_s^{low\langle Z \rangle}$ and $f_s^{high\langle Z \rangle}$. This study has been done varying the distance between the geometry bottom and the detector window, d , and fixing the sample thicknesses at $h = 25$ mm.

Then, two types of samples were chosen to carry out a much more complete study on the TCS corrections varying the distance (d). The RGU-1 standard and a tin concentrate sample (Sn-Sample) were selected for this study since their chemical compositions and densities are very different from each other, and their average atomic numbers, $\langle Z \rangle$, belong to the low and high $\langle Z \rangle$ range, that is, $\langle Z \rangle \leq 26$ and $\langle Z \rangle > 26$, respectively. The apparent density and $\langle Z \rangle$ values were approximately 1.63 g cm^{-3} and 3.54 g cm^{-3} , and 13 and 50 in the cases of RGU-1 and Sn-Sample, respectively. See Barba-Lobo et al., 2021c for further information about the criteria followed in order to establish the limits of each $\langle Z \rangle$ range.

On the other hand, since RGU-1 and Sn-Sample are samples whose activity concentrations are known, the corrected efficiencies given by Eq. 3.4.8 can be calculated for each selected d value (0, 25, 35, 45, 55 and 65 mm) using Eq. 3.4.1, where the sample thickness has been fixed at $h = 25$ mm. Consequently, the corrected efficiencies, provided by Eq. 3.4.8, can be given by the following functions: $\varepsilon_c(E_\gamma, d)$ and $\varepsilon(E_\gamma, d, \eta)$ for the calibration and problem sample matrices, respectively, since h is fixed. Besides, the non-corrected efficiency, which was also shown in Eq. 3.4.8, that is, $\varepsilon'_c(E_\gamma, h, d)$, can be given by the $\varepsilon'_c(E_\gamma, d)$ function because of the same previous reason. Then, it is necessary to clarify that Sn-Sample has been considered as a sample whose activity concentrations are known because it was measured by the XtRa taking five aliquots of this sample. Therefore, since the XtRa calibration has been fully validated Barba-Lobo et al., 2021a, it is possible to classify Sn-Sample as a sample whose activity concentrations are known. The reference activity concentration values are $4989(58) \text{ Bq kg}^{-1}$ and $1270(17) \text{ Bq kg}^{-1}$ for all radionuclides belonging to the ^{238}U - and ^{232}Th -series, respectively, because it has been checked that they are in secular equilibrium.

As can be seen in Fig. 3.4.3, two cases have been considered to carry out the $\varepsilon'_c(E_\gamma, d)$ corrections: graphics from 3A to 3C show the corrections done using the RGU-1 standard, and from graphics 3D to 3G, the ones corresponding to the case employing the Sn-Sample can be found. For the first case, it is possible to observe that all E_γ values that were not affected by TCS effects (let us call N-TCS energies), that is, 46 keV, 63 keV, 186 keV, 242 keV, 295 keV and 352 keV, can be corrected by a very similar factor value, that is, the geometrical correction factor, f_g (see graphic 3A). Therefore, the correction provided by f_g function is completely known since it only depends on d .

On the other hand, in Fig. 3.4.3 (graphic 3B), it is possible to observe that the total corrections, that is, $f_g \times f_s$, done for all energies different from N-TCS energies, which let us call TCS energies, were

dissimilar. This is very consistent because the TCS energies (609 keV, 768 keV, 934 keV, 1120 keV and 1238 keV which all belong to ^{214}Bi) are affected by TCS effects and, consequently, each one of those energies is corrected by a different f_s value. Besides, it is interesting to realize that some energies such as 1120 keV and 1238 keV can be corrected more easily than other energies like 609 keV and 934 keV. This makes that this TCS correction method is very useful to identify which E_γ are affected more significantly by TCS effects. Moreover, in graphic 3B, note that as d increases, the TCS effects are less significant and, consequently, the TCS energies become N-TCS energies, making the correction given by f_s tend to be 1 at $d = 65$ mm. This is very consistent since as d increases, the absolute efficiency (ε_{ab}) decreases and, consequently, a diminution of the TCS effects is occasioned because ε_{ab} and TCS are related to each other Debertin and Helmer, 1988. On the other hand, as can be seen in graphics 3A and 3B, fits of the corrections were provided to prove the physical meaning of them:

$$(f_g \times f_s)^k = a_{T1}^k \exp(a_{T2}^k d) + a_{T3}^k \quad (\text{Eq. 3.4.9})$$

where a_{Tj}^k (with $j = 1, 2, 3$) are the parameters resulted from the $(f_g \times f_s)^k$ fits versus d , and $k = \text{low } \langle Z \rangle$ or $\text{high } \langle Z \rangle$ to distinguish between the parameters obtained after the correction fits provided for the low $\langle Z \rangle$ and high $\langle Z \rangle$ sample cases, that is, RGU-1 and Sn-Sample, respectively. In Table D.5 (see Supplementary Material-D), the $a_{Tj}^{\text{low } \langle Z \rangle}$ parameters have been shown, where the relative average residual values, $\langle \text{Residual} \rangle$ (%), obtained after each fit were less than 2.4% in general. Therefore, very good fits carried out for $(f_g \times f_s)^{\text{low } \langle Z \rangle}$ were done.

Then, regarding the graphic 3C, the correction given by the f_s factor has been plotted versus d for TCS energies. It was possible to determine f_s function for RGU-1 standard since the $(f_g \times f_s)^{\text{low } \langle Z \rangle}$ and f_g functions were previously obtained. The differences explained above with respect to the dissimilar TCS corrections depending on E_γ can be seen more clearly in graphic 3C.

Once the cases corresponding to the low $\langle Z \rangle$ sample (RGU-1 standard) have been analyzed, the resulted corrections for the high $\langle Z \rangle$ sample (Sn-Sample) were considered below, which have been shown in Fig. 3.4.3 (graphics from 3D to 3G). In graphics 3D and 3E, it is possible to observe the total corrections provided for N-TCS and TCS energies, respectively. In graphic 3D, the corrections given by $(f_g \times f_a)^{\text{high } \langle Z \rangle}$ for N-TCS energies were clearly very similar at all these energies excepting for 46 keV and 63 keV, being this difference greater as d decreases. Therefore, given that in order to calculate the activity concentrations for each d value, the self-absorption corrections provided by the Cutshall's model have been considered, $(f_g \times f_a)^{\text{high } \langle Z \rangle}$ values should be very similar regardless of the selected N-TCS energy and they should tend to be 1. In other words, the f_a function, shown in Eq. 3.4.8, can be written in the following way:

$$f_a = \frac{f_a^{\text{real}}}{f_a^C} \quad (\text{Eq. 3.4.10})$$

where f_a^C is the self-absorption correction provided by the Cutshall's model, which was given by Eq. 3.4.5, and f_a^{real} is the self-absorption correction that should be obtained, that is, the real correction which needs to be considered in order to properly correct the self-absorption effects.

To observe more clearly the f_a function behavior, f_a values have been plotted versus d in Fig. 3.4.3 (graphic 3F). As can be seen in this graphic, the self-absorption corrections provided by the Cutshall's model are not good for 46 keV and 63 keV at $d = 0$ and, consequently, for this d value, f_a^C function is not working at low energies for high $\langle Z \rangle$ samples. This fact is very consistent, since one of the requirements for f_a^C is the need for parallelism between the travel direction of the emitted photons and the coaxial detector axis (Cutshall et al., 1983; Debertin and Helmer, 1988; Jodłowski, 2006). Therefore, for high $\langle Z \rangle$ samples and low energies at $d = 0$, this requirement is not being fulfilled. However, note that in graphic 3F, as d increases, the f_a values obtained for low energies were closer to 1. This is very reasonable because as d increases, the solid angle decreases and, therefore, the previous parallelism condition is easier to be fulfilled. Consequently, the methodology proposed in this work to correct TCS effects is very useful to be employed in order to make the f_a^C function work properly. In Section 3.4.3.4, this methodology proposed to use f_a^C in a proper way has been studied in depth.

On the other hand, regarding the corrections carried out by the $(f_g \times f_a)^{high \langle Z \rangle}$ function, previously mentioned in Fig. 3.4.3 (graphic 3D), fits were accomplished for these corrections, having employed the function described in Eq. 3.4.9. Besides, the parameters, $a_{Tj}^{high \langle Z \rangle}$ (with $j = 1, 2, 3$), and the $\langle \text{Residual} \rangle$ values resulted from these fits for N-TCS energies can be found in Table D.6 (see Supplementary Material-D), where the obtained $\langle \text{Residual} \rangle$ values were less than 4.5%.

With respect to the cases corresponding to the TCS energies for Sn-Sample, the corrections were shown in Fig. 3.4.3 (graphics 3E and 3G). In graphic 3E, the total corrections can be found, which were given by $(f_g \times f_s)^{high \langle Z \rangle}$. Note that in this case, f_a was considered to be 1 in order to make easier the obtaining of the $f_s^{high \langle Z \rangle}$ function. This approximation for f_a is very reasonable because in graphic 3F, it is possible to observe that f_a was very close to 1 at $E_\gamma = 352$ keV. Consequently, since the lowest E_γ value belonging to the TCS energies is 609 keV, considering $f_a \sim 1$ is a very good approximation in this case (relative differences of f_a from 1 less than 5%). By using the $(f_g \times f_s)^{high \langle Z \rangle}$ function, which was shown in graphic 3E, it was possible to calculate the corrections provided by $f_s^{high \langle Z \rangle}$, which were plotted versus d in graphic 3G. As can be seen in graphic 3G, the corrections carried out by $f_s^{high \langle Z \rangle}$ were not the same than the ones resulted from the case studied in graphic 3C, being these differences more significant for 768 keV, 934 keV and 1120 keV. The reason is because for these E_γ , energies lower than 150 keV are involved in the TCS effects and, consequently, the chemical composition of the selected sample is influencing the correction provided by f_s , which can be easily checked in graphic 3H where $f_s^{low \langle Z \rangle} / f_s^{high \langle Z \rangle}$ was plotted versus d . This agrees with previous studies (Barba-Lobo et al., 2021b; IND04-MetroMetal, 2013). However, note that as can be seen in graphics 3C and 3G, these differences between the TCS corrections accomplished for the two samples (RGU-1 and Sn-Sample) became less significant as d increases (see graphic 3H). This occurs in this way because since as d value increases, TCS effects are less relevant and, consequently, the f_s dependence on chemical sample composition can be neglected.

On the other hand, it is very interesting to realize that in graphics 3C and 3G, the TCS corrections obtained for 609 keV were higher than the ones resulted for the cases corresponding to 1120 keV. This agrees very well with the z_{score} values shown in Table 3.4.3 (see Section 3.4.3.1), where the $|z_{score}|$ values obtained for 609 keV were worse than the ones resulted for 1120 keV, which is due to the TCS effects being more relevant for the first gamma emission energy than for the second one.

Regarding the fits done for the obtained $(f_g \times f_s)^{high <Z>}$ values, the function previously defined by Eq. 3.4.9 was chosen. In Table D.7 (see Supplementary Material-D), the $a_{Ti}^{high <Z>}$ parameter values resulted from the $(f_g \times f_s)^{high <Z>}$ fits can be found, as well as their obtained $\langle \text{Residual} \rangle$ values, which were less than 3.6% (see Barba-Lobo et al., 2021b for further information about the equation employed to obtain $\langle \text{Residual} \rangle$).

After this comprehensive study carried out in Section 3.4.3.2, the methodology is used to determine a general efficiency function, $\varepsilon_c(E_\gamma, d)$, which will be employed to correct TCS effects. Then, the methodology proposed in Section 3.4.3.2 is also employed to properly correct self-absorption effects by f_a^C (Section 3.4.3.4).

3.4.3.3. TCS corrections varying the d distance: obtaining and validation of the $\varepsilon_c(E_\gamma, d)$ function

In this Section, a study on the TCS corrections varying the d distance has been accomplished. For this, the methodology previously described in Section 3.4.2.2 (methods) has been employed, which consists of calibrating the XtRa detector varying the d distance in this case. The RGU-1 standard was selected and compacted until reaching a thickness value, h , of 25 mm, and it was measured at each selected d value: 0, 25, 35, 45, 55 and 65 mm, the h value being 25 mm for all cases. In this efficiency calibration, the following gamma emission energies were chosen: 46 keV, 63 keV, 186 keV, 242 keV, 295 keV, 352 keV, 609 keV, 768 keV, 934 keV, 1120 keV and 1238 keV.

Therefore, once the $\varepsilon_c'(E_\gamma, h, d)$ corrections were accomplished by the corrections previously provided in Eq. 3.4.8, the corrected experimental $FEPE$ values were plotted versus E_γ for each d value in order to obtain a general efficiency function in the calibration matrix, $\varepsilon_c(E_\gamma, d)$ (see Fig. 3.4.4). As can be seen in Fig. 3.4.4, the corrected experimental $FEPE$ values as well as their fits were shown versus E_γ for each d distance, where the fitting function proposed in this case is given by the following equation:

$$\ln(\varepsilon_c(E_\gamma, h, d)) = \sum_{i=1}^4 b_i \ln(E_\gamma/E_0)^{i-1} \quad (\text{Eq. 3.4.11})$$

where b_i are the parameters resulted from the corrected $FEPE$ fits, $E_0 = 1$ keV, E_γ is the gamma energy, h is the standard thickness which was fixed at 25 mm for all cases and d is the distance between the geometry bottom and the detector window. Note that in Fig. 3.4.4, the energies belonging to low energy range (46 keV and 63 keV) were considered in order to fit the corrected experimental $FEPE$ values. The reason was because of having an adequate number of $FEPE$ values and, consequently, proper fits were provided by $\varepsilon_c(E_\gamma, d)$. On the other hand, it is necessary to clarify that since the obtention of $\varepsilon_c(E_\gamma > 150 \text{ keV}, h)$ (see Section 3.1) was carried out at $d = 0$, it is possible to calculate the efficiency values at 46 keV (^{210}Pb) and 63 keV (^{234}Th) by using the other efficiency function $\varepsilon_c(h)$, which was obtained by varying h and fixing E_γ for natural radionuclides. Consequently, in the case of the $\varepsilon_c(E_\gamma > 150 \text{ keV}, h)$, it was not necessary to consider the 46 keV and 63 keV points to proceed with the fits, since at these energies, the efficiency values can perfectly be provided by $\varepsilon_c(h)$.

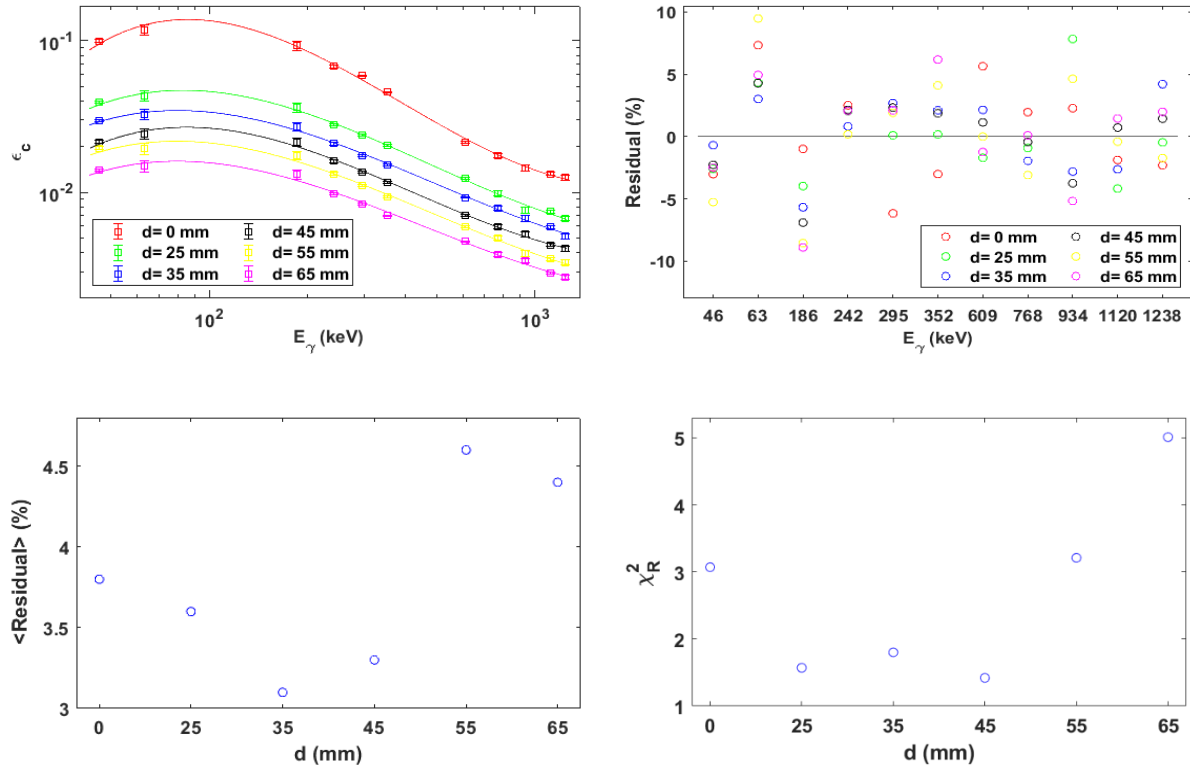


Figure 3.4.4. Fits of the corrected efficiency, ϵ_c , versus E_γ , using logarithmic scale, for each d value and fixing the thickness of the calibrating sample (RGU-1) at 25 mm. Then, the relative residuals and relative average residuals, as well as χ_R^2 values obtained for each d value have been shown.

Therefore, after obtaining the $\epsilon_c(E_\gamma, d)$ function at each d value, where the resulted b_i parameter values for each d value can be consulted in Table D.9 shown in Supplementary Material-D, it was necessary to decide on what d distance was the optimum value for $\epsilon_c(E_\gamma, d)$. For this, an analysis on the relative residual and reduced chi-square (χ_R^2) values obtained after each fit was carried out. In Fig. 3.4.4, it is possible to observe the relative residuals calculated for each E_γ and d values. Furthermore, when averaging the relative residuals obtained for each d over all E_γ values, the relative average residuals, $\langle \text{Residual} \rangle$, can be known for each d . In Fig. 3.4.4, $\langle \text{Residual} \rangle$ and χ_R^2 values calculated for each d can also be found. In our case, the critical χ_R^2 value was 2.01 at 0.05 significance level, since 7 degrees were obtained (see Bevington and Keith, 1969 for further information about tabulated χ_R^2 values). Therefore, after analyzing the resulted χ_R^2 values plotted in Fig. 3.4.4, it was possible to reduce the number of the possible d values to three, that is, 25, 35 and 45 mm, which were the only cases whose χ_R^2 values were less than the one considered as critical. Consequently, in order to be able to decide on what d value is the most appropriate, $\langle \text{Residual} \rangle$ values were employed, $d = 35$ mm being the d value whose $\langle \text{Residual} \rangle$ was lower than the ones obtained for the other two d value. Therefore, $d = 35$ mm was considered as the optimum d value for the $\epsilon_c(E_\gamma, d)$ function. In Tables D.8 and D.9, it is also possible to find the corrected experimental efficiency values obtained, and the $\langle \text{Residual} \rangle$ and χ_R^2 values resulted from each fit provided by $\epsilon_c(E_\gamma, d)$ at each d value, respectively.

On the other hand, validations of the $\epsilon_c(E_\gamma, d)$ function for $d = 35$ mm were carried out. For this, several problem samples were chosen: a seaweed sample (IARMA-097), three water samples (IARMA-098, IARMA-099 and IARMA-100), as well as mixtures of IAEA-375 with 52.5% of Sn-

Sample (IAEA-375 + 52.5% Sn-Sample). As can be seen in Table 3.4.4, very good z_{score} values were obtained for all artificial radionuclides contained in those five samples. Besides, in the case of the natural radionuclides, all z_{score} values were also less than 2, even for 583 keV, 609 keV and 1120 keV, for which the z_{score} values were -1.7, -0.9 and -0.3, respectively, in the case of IAEA-375 + 52.5% Sn-Sample. For these two same energies, the z_{score} values obtained in Section 3.1.1 were bad because the TCS effects are much more significant when the $\varepsilon_c(E_\gamma, h)$ function is employed. Consequently, the $\varepsilon_c(E_\gamma, d)$ function obtained for $d = 35$ mm can be used for artificial and natural radionuclides to correct the TCS effects and obtain very good results for both radionuclide types.

Table 3.4.4

External validation procedure of the general $\varepsilon_c(E_\gamma, d = 35 \text{ mm})$ function in the case of artificial radionuclides contained in a seaweed sample (IARMA-097) and three water samples (IARMA-098, IARMA-099 and IARMA-100), that were employed in Inter-comparison – IARMA exercise carried out in 2020. Besides, external validations were applied in the case of the natural radionuclides, selecting for this, the mixture of IAEA-375 with 52.5% of the Sn-Sample (IAEA-375 + 52.5% Sn-Sample).

IARMA-097					IARMA-098			IARMA-099		
RN	E_γ (keV)	a (Bq kg ⁻¹)	Reference values (Bq kg ⁻¹)	z_{score}	a (Bq kg ⁻¹)	Reference values (Bq kg ⁻¹)	z_{score}	a (Bq kg ⁻¹)	Reference values (Bq kg ⁻¹)	z_{score}
57 Co	122.06	4.9(3)	4.8(3)	0.2	0.82(15)	< 1	-	2.23(11)	2.70(14)	-1.7
60 Co	1173.20	8.4(4)	7.1(5)	1.9	2.53(18)	2.40(10)	0.5	3.9(2)	3.8(2)	0.1
133 Ba	356.0	7.8(3)	8.3(4)	-0.6	2.70(19)	3.20(13)	-1.6	4.5(2)	5.1(3)	-1.3
134 Cs	795.8	15.7(4)	14.8(7)	0.6	4.4(2)	4.3(2)	0.1	6.7(3)	6.6(3)	0.1
137 Cs	661.8	6.6(3)	6.3(3)	0.5	3.29(19)	2.90(12)	1.3	4.7(2)	4.2(2)	1.2
152 Eu	344.3	9.6(6)	9.0(4)	0.7	1.9(4)	1.90(10)	0.2	4.0(4)	3.7(2)	0.7
241 Am	59.54	9.1(3)	8.0(3)	1.3	4.1(2)	3.70(15)	1.2	8.6(3)	7.5(3)	1.5
IARMA-100					IAEA-375 + 52.5 % Sn-Sample					
RN	E_γ (keV)	a (Bq kg ⁻¹)	Reference values (Bq kg ⁻¹)	z_{score}	RN	E_γ (keV)	a (Bq kg ⁻¹)	Reference values (Bq kg ⁻¹)	z_{score}	
54 Mn	834.8				234 Th	63.29	2772(139)	2630(31)	1.0	
57 Co	122.06	0.36(2)	< 1	-	226 Ra	185.96	3055(244)		1.7	
59 Fe	1099.25					295.22	2491(125)		-1.1	
60 Co	1173.20	4.9(3)	4.8(2)	0.2	214 Pb	351.93	2461(123)	2629(31)	-1.3	
133 Ba	356.0	8.1(3)	9.0(4)	-1.0		609.31	2512(126)		-0.9	
134 Cs	795.8	5.5(3)	5.1(2)	0.7	214 Bi	1120.29	2589(129)		-0.3	
137 Cs	661.8	10.6(3)	9.5(4)	1.2		338.42	620(31)	677(9)	-1.7	
152 Eu	344.3	10.1(6)	9.2(5)	0.9	228 Ac	911.16	730(37)		1.4	
241 Am	59.54	10.5(5)	10.0(4)	0.5	212 Pb	238.63	745(37)	677(9)	1.8	
					208 Tl	583.19	622(31)		-1.7	

3.4.3.4. Methods to properly correct self-absorption effects by f_a^C function when high $\langle Z \rangle$ samples are considered

As explained in Section 3.4.3.2, the self-absorption corrections provided by f_a^C (defined in Eq. 3.4.5) do not work in an adequate way when these corrections are applied to determine radionuclides contained in high $\langle Z \rangle$ samples. Therefore, in this Section, several methods were proposed to make the corrections given by f_a^C work in a proper way. For this, a Sn-Sample, whose apparent density and

$\langle Z \rangle$ are high, was selected. Furthermore, to test the corrections provided by f_a^C , a gamma energy belonging to the low energy range (< 150 keV) was selected, that is, $E_\gamma = 63$ keV (^{234}Th).

Firstly, several Sn-Sample thicknesses, h , were taken: 3, 6, 12, 24 and 48 mm, which are well distributed throughout the thickness range used in the XtRa calibration. Besides, in this first case, the d value was fixed at 0 mm, that is, right above the detector window. Therefore, it was possible to check for which Sn-Sample h range, the corrections given by f_a^C were valid. To proceed with this test, z_{score} were calculated for each h value at $E_\gamma = 63$ keV, which can be found in Fig. 3.4.5 (graphic 5A). As can be seen in graphic 5A, the z_{score} values were very good for small h values, that is, h values less than 12 mm. From $h = 12$ mm, the self-absorption effects became very important and, consequently, the corrections provided by f_a^C are not valid. Therefore, it is recommendable to select small h values when samples, whose density and $\langle Z \rangle$ are very high, are measured by using gamma spectrometry, making the self-absorption effects much less significant.

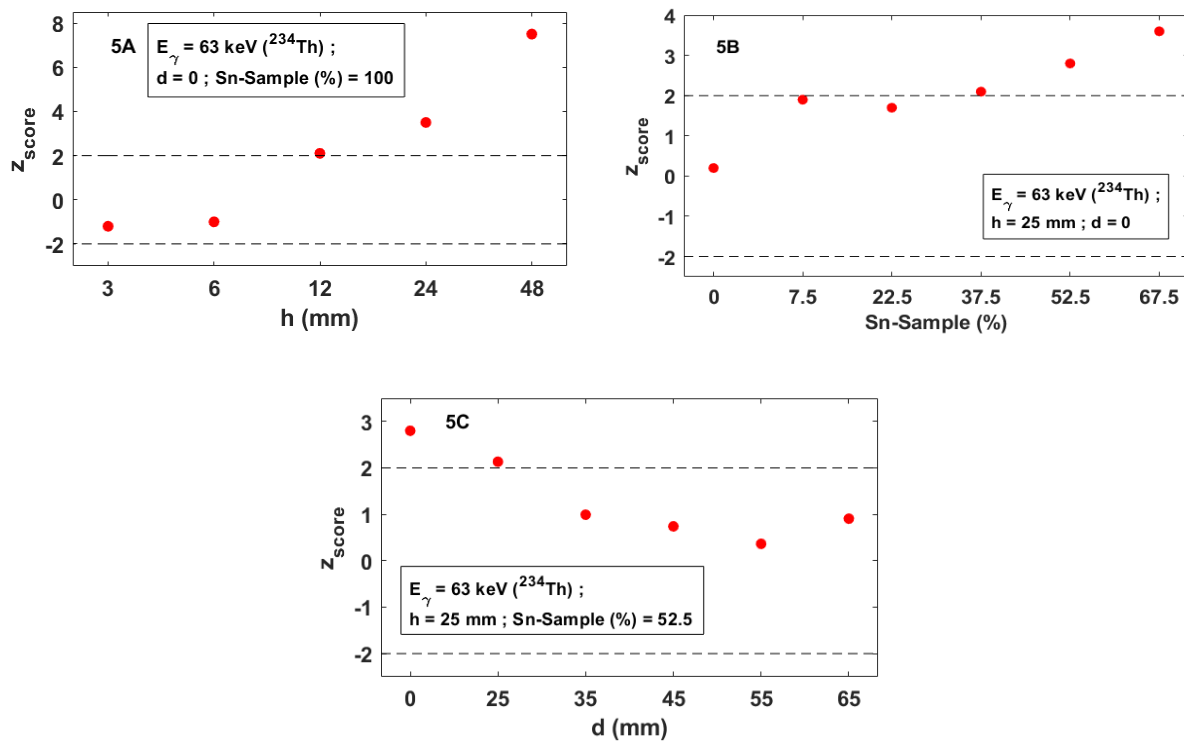


Figure 3.4.5. 5A and 5B: Study on the validity of the self-absorption corrections. For this, the z_{score} value was obtained when the Sn-Sample thickness and the Sn-Sample proportion in the mixture with IAEA-375 are increased, respectively, where h was fixed at 25 mm in graphic 5B, d value being zero in both graphics; 5C: Study on the improvement of the self-absorption corrections when the distance d is increased. This study was done taking the mixture IAEA-375 with Sn-Sample fixing h at 25 mm, where the proportion of the latter is constant and equal to 52.5%.

On the other hand, the Sn-Sample was mixed with a soil sample (IAEA-375) to test the validity of f_a^C when the proportion of the Sn-Sample is varied. Several proportions (given in %) of Sn-Sample were chosen: 0, 7.5, 22.5, 37.5, 52.5 and 67.5. In these cases, the thickness value used to prepare the mixtures between Sn-Sample and IAEA-375 was $h = 25$ mm, where d is zero for all of them. In Fig. 3.4.5 (graphic 5B), the z_{score} values were obtained for each Sn-Sample proportion. Therefore, as can be seen in graphic 5B, the validity of f_a^C was not good when the Sn-Sample proportion began to be

relevant, that is, from 37.5%. Besides, since the f_a^C function depends on the sample mass attenuation coefficient, η , it was calculated to find the η value for which the corrections provided by f_a^C start to be improper. The obtained η value was $1.59 \text{ cm}^2 \text{ g}^{-1}$, this η value being very similar with the one calculated in previous works on well-type Ge detectors, where the validity of the self-absorption corrections was also tested (Barba-Lobo et al., 2021b). In the case of the well-type Ge detectors, the self-absorption corrections provided by the Appleby's model were taken Appleby et al., 1992, obtaining a critical η value of $1.52 \text{ cm}^2 \text{ g}^{-1}$ at $E_\gamma = 63 \text{ keV}$ (^{234}Th), which proves that both self-absorption correction models, Cutshall's and Appleby's models, have behaviors very similar.

Then, one of the mixtures previously employed in graphic 5B was selected for the study of the validity of the corrections given by f_a^C varying d . For this, the mixture characterized by having 52.5% of Sn-Sample was used, where h was fixed at 25 mm (h value used in Section 3.4.3.3). This Sn-Sample percentage was selected instead of, e.g., 37.5%, in order to check in a more appropriate way how the d distance variation influence the validity of the self-absorption corrections provided by the Cutshall model. In Fig. 3.4.5 (graphic 5C), it is possible observe what happens when d is varied. Therefore, as can be seen in graphic 5C, as d value was increased, the z_{score} values were better, achieving z_{score} values less than 2 from $d = 35 \text{ mm}$. Consequently, the conditions, that are required to properly use f_a^C , are fulfilled from $d = 35 \text{ mm}$. This agrees with the results previously obtained in graphic 3F (see Fig. 3.4.3), which was shown in Section 3.4.3.2.

3.4.3.5. Dead time corrections by varying the d distance

After having proved that $\varepsilon_c(E_\gamma, d = 35 \text{ mm})$ is the function that best corrects TCS effects, a study on the dead time corrections was accomplished in this Section by using the same methodology which was employed in Section 3.4.3.3 in order to correct TCS effects. Three scale samples (Scale-A, Scale-B and Scale-C) were selected for this study, which were characterized by being very active and whose thicknesses were 25 mm for the three cases. The reason why very active samples were chosen was because as the activity concentration of a sample increases, the dead time increases, since a larger number of events are not detected. Considering this reasoning, it is possible to define the equation for the dead time, t_d , which can be experimentally calculated in the following way:

$$t_d^{exp}(\%) = 100 (t_r - t_l)/t_r \quad (\text{Eq. 3.4.12})$$

where t_d^{exp} is the dead time obtained experimentally by Eq. 3.4.12, and t_r and t_l are the real and live times, respectively, the former being the total time interval during which the events should be recorded, and the latter is the time interval for which the events have been truly recorded.

In order to carry out this study, the dead time values resulted from each scale sample, were plotted versus d in Fig. 3.4.6. In this figure, it is possible to observe how the experimental dead time, t_d^{exp} , was reduced as the d distance was increased. As can be seen in this figure, Scale-B was clearly the most active sample since the t_d^{exp} values for this scale were the highest ones obtained for all selected d values, where the t_d^{exp} values were reduced from approximately 60% ($d = 0$) to 10% ($d = 65 \text{ mm}$). Making use of this same reasoning in order to deduce which scale sample contains radionuclides whose activity concentrations are higher, it is possible to realize that Scale-C and Scale-A were the second and third most active scales, respectively, for which the t_d^{exp} values were reduced approximately from 47% ($d = 0$) to 6% ($d = 65 \text{ mm}$) and from 32% ($d = 0$) to 4% ($d = 65 \text{ mm}$), respectively. Besides, it is necessary to clarify that the uncertainties associated to t_d^{exp} were not taken

into account because of being completely negligible. In order to correct the dead time, the method proposed in this Section has been successful, obtaining t_d^{exp} reductions of up to 50% for the three selected scale samples.

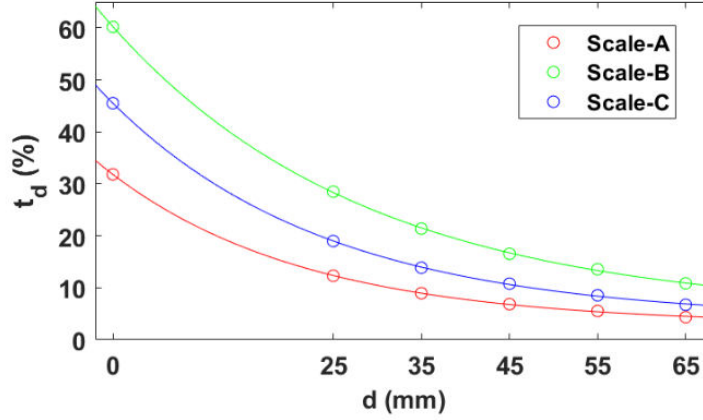


Figure 3.4.6. Dead-time corrections carried out varying the distance d from 0 to 65 mm for three scale samples (Scale-A, Scale-B and Scale-C), whose thicknesses have been fixed at 25 mm, including fits done for these dead-time corrections.

Taking the t_d^{exp} values plotted versus d in Fig. 3.4.6, it is possible to observe that they have a clear tendency, proving their physical meaning. Therefore, fits of t_d^{exp} versus d was carried out for each scale type in order to verify their physical meaning. For this, the following equation was selected:

$$t_d(\%) = c_1 \exp(c_2 d) + c_3 \quad (\text{Eq. 3.4.13})$$

where c_i (with $i = 1, 2, 3$) are the parameters resulted from the fits provided by the theoretical dead time function, t_d , versus the d distance, which were shown in Table D.10 (see Supplementary Material-D), where the <Residual> values obtained for each fit were less than 2%.

3.4.4. Conclusions

The main conclusions resulting from this research are:

1. In the present work, a general efficiency function, $\varepsilon_c(E_\gamma, h)$, has been obtained in order to determine artificial and natural radionuclides. For this, a novel method has been proposed in this study which consists of calibrating the detector (in our case, XtRa), fixing and varying the selected gamma energies (E_γ) and standard thicknesses (h), respectively. Taking the parameters resulted from fitting the experimental $FEPE$ versus h , $pr_i(E_\gamma)$, they are fitted, in turn, versus E_γ . To proceed with the method proposed to obtain $\varepsilon_c(E_\gamma, h)$, standards which contain only natural radionuclides were used for the calibration. This makes this method be very useful given that it allows us to determine artificial radionuclides without needing to calibrate by using point sources that contain the desired artificial radionuclides.

2. The $\varepsilon_c(E_\gamma, h)$, considering only high energies, that is, $\varepsilon_c(E_\gamma > 150 \text{ keV}, h)$, was validated for several sample types which contain artificial and natural radionuclides. Regarding the validations carried out for samples that contain only artificial radionuclides, very good $|z_{score}|$ values were obtained which were less than 2 for all cases. For the other samples that contain natural radionuclides, very good z_{score} values were obtained for all radionuclides, except for ^{214}Bi (609 keV and 1120 keV) and ^{208}Tl (583 keV). Since those three gamma energies are affected by TCS effects, a method was proposed in order to carry out TCS corrections. This method consisted of recalibrating the XtRa detector varying the sample-detector distance, d , and fixing the thickness standard, h , obtaining a general efficiency function, $\varepsilon_c(E_\gamma, d)$. For this, it was necessary to check the behavior of the efficiency corrections depending on the sample type in order to assure how different these corrections are depending on the selected sample. Therefore, two samples were chosen (RGU-1 and Sn-Sample), whose densities and chemical compositions are very different from each other. It was possible to observe that for those two samples, the TCS effects were corrected as d increased. Moreover, it was found that the TCS corrections were different in the cases of RGU-1 and Sn-Sample, since sometimes E_γ values less than 150 keV are involved in the TCS effects. However, these differences were decreased as d increased, since as d increased, the TCS effects were less significant.
3. Regarding the method proposed to correct the TCS effects, several d values were chosen (from 0 to 65 mm), and the RGU-1 standard was employed whose thickness was fixed at 25 mm. The corrected experimental *FEPEs* were fitted versus E_γ for each d , demonstrating that for $d = 35 \text{ mm}$, the fitting function, $\varepsilon_c(E_\gamma, d = 35 \text{ mm})$ provided the best fit. Then, $\varepsilon_c(E_\gamma, d = 35 \text{ mm})$ was validated for several samples, achieving very good z_{score} for artificial and natural radionuclides, even in the cases of $E_\gamma = 583 \text{ keV}$, 609 keV and 1120 keV. Regarding the possible systematic errors associated to the results provided by $\varepsilon_c(E_\gamma, d = 35 \text{ mm})$, we can conclude that there is no relevant systematic error since all $|z_{score}|$ values resulted from using this function were less than 2.
4. It was also possible to prove that the self-absorption corrections provided by the Cutshall's model (f_a^C) does not work properly at low energies when selecting samples whose densities and $\langle Z \rangle$ are very high. Consequently, several methods were proposed in order to make the corrections provided by f_a^C be valid. One of these proposed methods consisted of varying h , proving that as h decreased, the f_a^C validity increased. Regarding the other method, it consisted of placing the sample at different d values (from 0 to 65 mm) and fixing h at 25 mm. The f_a^C validity increased as d increased, which is very consistent since as d increases, the parallelism requirements established by the Cutshall's model are fulfilled better. Finally, the same method employed to correct the TCS effects and make the f_a^C validity be good, was used in order to correct the dead time, t_d . For this, three very active scales were chosen, achieving t_d reductions up to 50%, which demonstrated the good validity of the proposed method.

Subchapter 3.5.: A new efficiency calibration methodology for different atmospheric filter geometries by using coaxial Ge detectors

This subchapter was submitted to Air Quality, Atmosphere and Health, which status is currently Under Review.

Subchapter 3.5.: A new efficiency calibration methodology for different atmospheric filter geometries by using coaxial Ge detectors

Abstract

The study of the different pollutants present in the atmospheric aerosols such as trace elements and radionuclides is essential to assess the air quality. To analyze the particulate matter (PM) deposited onto atmospheric filters, that have different dimensions and geometries (rectangular, circular, slotted and square filters), are usually employed. Regarding the pollutants existing in the atmospheric aerosols, radionuclides are usually analyzed due to their multiple applications such as either in the environmental radiological control or as tracers of atmospheric processes. Therefore, this study aims to develop a new and general methodology to calibrate in efficiency coaxial Ge detectors to properly determine radionuclides present in the PM by gamma-ray spectrometry for several filter types. For this, granular certified reference materials (CRM) containing only natural radionuclides (^{238}U -series, ^{232}Th -series and ^{40}K) were selected. Several granular solid CRMs were chosen allowing us to reproduce the same PM deposition geometry and to assure the homogeneity of the added CRMs. These are the main advantages in relation to the typical methods that use liquid CRMs. Furthermore, for filters whose surfaces are relatively large, they were cut in several pieces and placed one on top of the other, achieving the same geometry than the PM deposited onto the filter. Then, the experimental full-energy peak efficiencies (*FEPEs*) were obtained for each energy of interest (E_γ) and they were fitted versus E_γ , finding a general *FEPE* function for each filter type. Finally, this methodology was validated for both natural and artificial radionuclides (from 46 keV to 1332 keV) by using different filter types employed in proficiency test exercises, obtaining $|z_{\text{score}}| < 2$ for all cases.

Keywords: Atmospheric filters; Particulate matter; Atmospheric aerosols; Efficiency calibration; Gamma-ray spectrometry; Ge detectors

3.5.1. Introduction

In the last decades, the research of the air quality and its health impacts are essential topics within the environmental and atmospheric sciences. For this, the particulate matter (PM) needs to be studied in depth since it can provide a very valuable information about the pollution levels present in the atmospheric aerosols. In addition, the assessment of the pollution associated to the atmospheric aerosols can be employed in order to get a better comprehension about the different factors involved in the global climate (Davidson et al., 2005; Fuzzi et al., 2015; Lu et al., 2016; Ouyang, 2013), as well as about the evolution of certain diseases such as the ones caused by the SARS-CoV-2 virus (Mehmood et al., 2021-a; Mehmood et al., 2021-b; Paez-Osuna et al., 2022).

The atmospheric PM is collected onto filters with different geometry and dimensions depending on the objective of the study, where the PM_{10} , $\text{PM}_{2.5}$, and $\text{PM}_{1.0}$ are the most used samplers (Barba-Lobo et al., 2022c; Dueñas et al., 2009; Ordúz et al., 2012). Furthermore, there is another type of sampler, the cascade impactor (CI), that is very useful since it allows us to classify the particulate matter present in the atmospheric aerosols as a function of the aerodynamic diameter (*ad*) of the particles (Aba et al., 2020; Kwon et al., 2003). This sampler can provide us information about the affinity existing between the different pollutants present in the atmospheric aerosols and the size of the aerosol particles. In the cases of the PM_{10} , the air flow needs to be fixed at $68 \text{ m}^3 \text{ h}^{-1}$ following the USEPA Compendium Method IO-2.1 (EPA, 1999), while for $\text{PM}_{2.5}$ and $\text{PM}_{1.0}$ samplers, the air flow is fixed

at $30 \text{ m}^3 \text{ h}^{-1}$ according to the European Standard UNE-EN 14907 (European Standard EN 14907, 2005). In order to be able to carry out samplings spending a sampling duration as short as possible, it is recommendable to make use of a very high-volume air aerosol sampler, model ASS-500 (Valkovic, 2000). This sampler allows us to reach air flows ranged about $500 \text{ m}^3 \text{ h}^{-1}$ and $600 \text{ m}^3 \text{ h}^{-1}$. Furthermore, this last type of sampler is very recommendable to reduce the minimum detectable activity concentration (*mda*), since it is inversely proportional to the air flow, which makes possible to get *mda* values about $1 \text{ } \mu\text{Bq m}^{-3}$.

Among the different types of pollutants present in the atmospheric aerosols, radionuclides can be found. They can be employed for multiple purposes such as the environmental radiological control, the obtention of information about the origin of a certain contaminant source, the calculation of the residence times of atmospheric aerosols and the trace of air masses and atmospheric processes (Abdo et al., 2021; Baskaran and Shaw, 2001; Papastefanou and Bondietti, 1991; Renoux, 1987; Srinivas et al., 2014). For this, there are several radionuclides such as ^7Be , ^{210}Po , $^{214, 212, 210}\text{Pb}$ and $^{214, 212, 210}\text{Bi}$ that are usually employed in the atmospheric studies (Dalaka et al., 2019; Papastefanou and Ioannidou, 1996; Poet et al., 1972; Tokieda et al., 1996).

To determine the activity concentrations of radionuclides in the atmospheric aerosols, a calibration in efficiency of the selected detector is needed. For this, this study aims to develop a new and general methodology based on the use of granular solid CRMs for the efficiency calibration of coaxial Ge detectors, which are widely employed for the determination of gamma-ray emitters by using numerous atmospheric filter types.

3.5.2. Materials and methods

3.5.2.1. Materials

In this study, several types of atmospheric filters were selected to develop the new methodology for the efficiency calibration, considering the great majority of the filter types employed by laboratories when analyzing the particulate matter. The filters selected in our case were quartz fiber filters characterized by having different geometries and dimensions: rectangular filters ($20 \times 25 \text{ cm}^2$), circular filters (diameters = 47 mm, 150 mm), slotted filters (which are employed for the CI samplers, $13.6 \times 14.3 \text{ cm}^2$), and square polypropylene filters ($44 \times 44 \text{ cm}^2$), which are used in the case of the very high-volume samplers, as the ASS-500 sampling station. Let us call these filters as R, C-47, C-150, SL and SQ, respectively, to easily be identified.

For the determination of the gamma-ray emitters, an extended energy range (XtRa) high purity germanium (HPGe) detector (model GX3519 provided by Canberra) was chosen. The XtRa detector has a relative efficiency of 38.4% at 1332 keV (^{60}Co) in relation to a $3'' \times 3''$ NaI(Tl) detector, a full width at half maximum (FWHM) of 1.74 keV and 0.88 keV at 1332 keV and 122 keV, respectively, and a peak-to-Compton ratio of 67.5:1. The XtRa detector is connected to a conventional electronic chain, which is composed on a preamplifier, an amplifier, an analog-to-digital converter and a multichannel analyzer, where the software employed for the acquisition and analysis of the gamma spectra was Genie 2000 (Canberra Industries, 2004).

In order to carry out the efficiency calibration of the XtRa detector, standards provided by the International Atomic Energy Agency (IAEA), RGU-1, RGTh-1 and RGK-1, were used, which are Certified Reference Materials (CRM) and contain natural radionuclides belonging to the ^{238}U -series,

^{232}Th -series, and ^{40}K , whose certified activity concentrations were $4940(15) \text{ Bq kg}^{-1}$, $3250(45) \text{ Bq kg}^{-1}$, and $14000(200) \text{ Bq kg}^{-1}$, respectively, where the uncertainties are given at one sigma confidence level (IAEA, 1987).

For the validation of the methodology developed in this study, atmospheric filters selected to carry out the inter-comparison exercises in 2017 and 2021, which were organized by the CSN and CIEMAT, were employed, where the acronyms CSN and CIEMAT are referred to the Spanish Nuclear Safety Council (“Consejo de Seguridad Nuclear”) and the Centre for Energy, Environment and Technology Research (“Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas”), respectively.

3.5.2.2. Method

To carry out the efficiency calibration of the detector by using the quartz fiber filters (R, C-47, C-150 and SL), some amount of RGU-1 was added and very well extended onto each filter type, achieving the homogeneity of this certified material throughout all the filter surfaces. In the case of the SL filters, the calibration was carried out using two filters, where $0.5115(2) \text{ g}$ and $0.5014(2) \text{ g}$ are the RGU-1 amounts added to each filter. In the case of the C-47 filters, three filters were used, where the added masses were $0.4953(2) \text{ g}$, $0.4941(2) \text{ g}$ and $0.5009(2) \text{ g}$, respectively, while for C-150 filters, three filters were also chosen, where the added masses were $0.5029(2) \text{ g}$, $0.4898(2) \text{ g}$ and $0.5006(2) \text{ g}$, respectively. Then, for the R filters, three filters were used for the calibration, where the added masses were $0.6018(2) \text{ g}$, $0.5913(2) \text{ g}$ and $0.5914(2) \text{ g}$, respectively. In the case of the R filters, these filters were cut in several rectangular pieces which were placed one piece on top of the other, getting the same geometry than the one achieved when measuring this filter type ($6.3 \times 10 \text{ cm}^2$). Then, the RGU-1 standard is spread for each one of these pieces, covering the same regions than the ones where the particulate matter is deposited onto the R filters during the samplings. When proceeding in this way for the R filters, it is possible to make it easier to get the homogeneity of the RGU-1 standard when adding onto this filter type, as well as to get reproducing the distribution of the particulate matter when depositing onto the problem filters.

In the case of the SQ filters, RGU-1, RGTh-1 and RGK-1 standards were selected for the efficiency calibration. The three standards were well mixed among them, and three filters were employed, where the amount of the added mixtures were $2.5011(2) \text{ g}$, $2.5017(2) \text{ g}$ and $2.4906(2) \text{ g}$, respectively, where the amount of each standard was one third of the mass of each mixture added. Analogously to the case corresponding to the R filters, the SQ filters were also cut in pieces where each one had the same dimensions than the any problem filter ones after being folded to be measured ($11 \times 11 \text{ cm}^2$). Furthermore, the mixture of the three standards was spiked to each piece, covering the same regions than the ones covered when depositing the particulate matter onto the problem filters.

By using this methodology developed in this study, a more proper efficiency calibration is achieved in comparison with the typically used methods, where certified liquid samples are added to the filters by using a pipette. The usage of certified liquid samples makes it easier the existence of inhomogeneities and it is more likely that the concentrations of the radionuclides present in these standards can be altered since they are dissolutions. Moreover, since the particulate matter is a solid sample, it is more recommendable to calibrate in efficiency by using solid samples than liquid ones. This allows us to reproduce the same distribution of the particulate matter when depositing onto the filters, as well as to obtain similar self-absorption effects for the emitted photons in the cases of the

calibration and problem filters. In the case of the bigger filters (R and SQ filters), these filters were cut in several pieces following the same geometry and dimensions than the ones obtained when measuring the problem filters. This is another reason why this methodology is more proper than the typical methods which employ the calibration filters without cutting them. This makes it more difficult to achieve the homogeneity of the spiked standard, not reproducing the distribution of the particulate matter deposited onto the problem filters in a proper way.

To determine natural and artificial radionuclides by gamma-ray spectrometry, nowadays the detector calibrations by Monte Carlo simulations have become generalized, even in the case of using atmospheric filters (Aba et al., 2020). There are many cases for which detectors are not characterized because of being relatively old. To proceed with it, high costs for the characterization and the new Monte Carlo software are involved. During the characterization procedure, the detectors must be outside the laboratory, and consequently, inoperative for several months. In contrast to Monte Carlo simulations, in this study an experimental methodology has been developed by which it is possible to calibrate coaxial detectors relatively quickly for atmospheric filters using calibration standards, which do not imply so high costs.

Therefore, this is the first study to address in depth the experimental calibration of coaxial Ge detectors for atmospheric filters by using granular solid CRMs, developing an exhaustive calibration filter preparation method to reproduce the particulate matter deposition geometry with a high accuracy.

To carry out these calibrations, the experimental *FEPEs*, ε_{exp} , were calculated by using the following equation:

$$\varepsilon_{exp}(E_\gamma) = \frac{G - B - F - I}{P_\gamma a_c m_c t} = \frac{N}{P_\gamma a_c m_c t} \quad (\text{Eq. 3.5.1})$$

where G , B , F , I and N are the total number (gross) of counts, the Compton continuum, the background due to environmental conditions existing in the laboratory, the interference term and the net counts, respectively, where all of them are referred to the full-energy peak of interest. Then, P_γ is the probability of gamma emission (taken from DDEP, 2017), a_c and m_c are the activity concentration and the mass added to each filter of the calibration standard, respectively, which have been used in the calibration procedure. Then, E_γ are the selected gamma emission energies and t is the measurement time. Furthermore, it has been considered that $I \sim 0$ for all selected E_γ .

After the counting of the filters by using the XtRa detector, the experimental efficiencies were calculated for each filter type. For this, the full-energy peak efficiency (*FEPE*) was calculated for each selected gamma emission energy (E_γ). Afterwards, an average *FEPE* value was calculated for each energy in the case of each sampler type. Finally, the logarithms of the experimental *FEPEs* were fitted versus $\ln(E_\gamma/E_0)$, where $E_0 = 1$ keV, achieving to obtain a general efficiency function for each filter type.

3.5.3. Results and discussion

3.5.3.1. Calibration in efficiency for each filter type

In Tables E.1, E.3, E.5, E.7 and E.9 (see Supplementary Material-E), the $\varepsilon_{exp}^{i(j)}$ values obtained in the cases of the SL, C-150, C-47, R and SQ filters were shown, respectively, for each filter chosen to accomplish the calibrations in efficiency, where $i = \text{SL, C-150, C-47, R, SQ}$, and $j = 1, 2, 3$ is the number of the filter used for each type of geometry. Furthermore, in Tables E.1, E.3, E.5, E.7 and E.9, the average experimental efficiencies, ε_{exp}^i , have been provided for each filter type.

The average of the full energy peak efficiency, ε_{exp}^i , was plotted versus E_γ for each filter type by using logarithmic scales for both axes of the graph (Fig. 3.5.1). As can be seen in this figure, the behavior of ε_{exp}^i versus E_γ , by using logarithmic scales for both variables, is clearly polynomial type. Consequently, the following function was chosen in order to fit $\ln(\varepsilon_{exp}^i)$ versus $\ln(E_\gamma/E_0)$ (Bolívar et al., 1996; El-Daoushy and García-Tenorio, 1995; Gilmore and Hemingway, 1995; Martínez-Ruiz et al., 2007):

$$\ln(\varepsilon_{exp}^i)(E_\gamma) = \sum_{k=0}^3 a_k^i \ln\left(\frac{E_\gamma}{E_0}\right)^k \quad (\text{Eq. 3.5.2})$$

where a_k^i are the parameters resulting from the fits, $k = 0, 1, 2, 3$, and $i = \text{SL, C-150, C-47, R, SQ}$. Then, E_γ is the gamma emission energy of interest and $E_0 = 1$ keV. It is necessary to clarify that the E_γ , which were selected to carry out the calibrations (see Tables E.1, E.3, E.5, E.7 and E.9), were chosen because of having the highest P_γ values corresponding to the radionuclides belonging to the ^{238}U -series, ^{232}Th -series, and ^{40}K , achieving to obtain high counting rates and, therefore, to accomplish these calibrations relatively quickly.

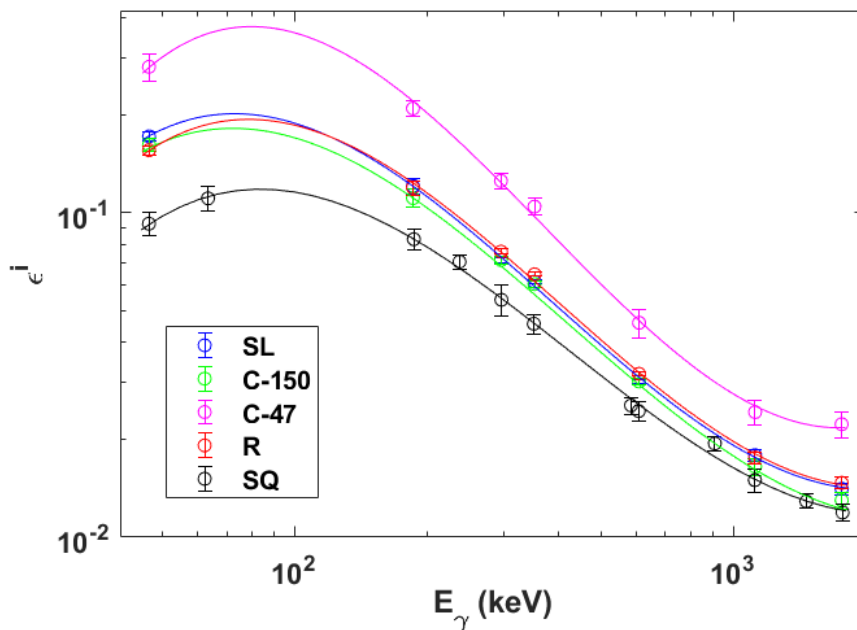


Figure 3.5.1. Experimental efficiencies resulting from the efficiency calibration carried out for five types of filters: Slotted filters (SL), Circular filters whose diameters are 47 mm and 150 mm (C-47 and C-150, respectively), Rectangular filters (R) and Squared filters (SQ). Besides, the fittings accomplished for the experimental efficiencies, ε_{exp}^i , versus the gamma emission energy, E_γ , where i = SL, C-150, C-47, R, SQ, have also been shown.

In Tables E.2, E.4, E.6, E.8 and E.10 (see Supplementary Material-E), the a_k^i parameters can be found for the SL, C-150, C-47, R and SQ filters, respectively. Furthermore, in Tables E.1, E.3, E.5, E.7 and E.9, the relative residuals, Res (%), resulting from the fits provided by Eq. 3.5.2 can be found for each selected energy in the cases of SL, C-150, C-47, R and SQ filters, respectively, where the Res values were calculated by using the following equation:

$$Res = 100 \left(\frac{y_{fit}^{(E_\gamma)}}{y_{exp}^{(E_\gamma)}} - 1 \right) \quad (\text{Eq. 3.5.3})$$

where $y_{exp}^{(i)}$ and $y_{fit}^{(i)}$ are the values obtained experimentally and the ones obtained by a fitting function for a magnitude y , respectively, for each energy E_γ .

As can be seen in Fig. 3.5.2, all $|Res|$ values were less than 9.2, but it is easy to realize that the great majority of the $|Res|$ values were less than 3 and, consequently, the fits provided by Eq. 3.5.2 agreed very well with the ε_{exp}^i values for the five filter types (see Tables E.1, E.3, E.5, E.7 and E.9 in order to check numerically the values obtained for Res). Furthermore, in Tables E.2, E.4, E.6, E.8 and E.10, it is possible to find the R^2 values resulting from each fitting, where R^2 were 0.9995, 0.9993, 0.998, 0.9991 and 0.998 in the cases of the SL, C-150, C-47, R and SQ filters, respectively, which further corroborate the great fits provided by Eq. 3.5.2.

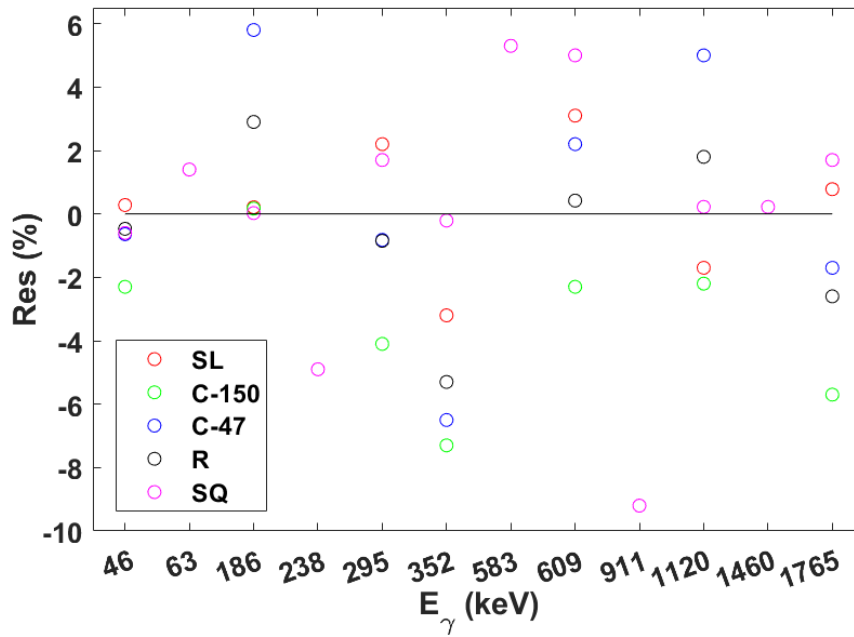


Figure 3.5.2. Relative residuals, Res (%), resulting from fitting the experimental $FEPES$ versus the gamma emission energy, E_γ , by using the general efficiency function found for each filter type (SL, C-150, C-47, R and SQ).

3.5.3.2. Validation of the efficiency calibration methodology

In this Section, the validations of the methodology developed in this study are shown. For this, filters of the C-47, R and SQ types were employed, which were selected for the Inter-comparison exercises organized by the CSN and CIEMAT in 2017 and 2021. It is necessary to clarify that the filters of the C-150 and SL types are unusually employed in the Inter-comparison exercises and for this reason, they were not included in this Section. However, they have also been included in this study due to the great importance that these filter types have for a proper and complete analysis of the particulate matter present in atmospheric aerosols. Furthermore, considering the very low values obtained for Res in the case of the C-150 and SL filters when comparing the resulting experimental $FEPES$ for each filter type replica, it is possible to test the very good interval validation achieved at each selected E_γ .

In order to proceed with these validations, it was necessary to make use of the z_{score} , which can be obtained by the following equation:

$$z_{score} = \frac{a_i - med(a_i)}{\sigma(med(a_i))} \quad (\text{Eq. 3.5.4})$$

where a_i is the activity concentration value obtained for each radionuclide by using this methodology, $med(a_i)$ is the median value of the activity concentration for each radionuclide resulting from considering the values provided by all the laboratories that participate in the Inter-comparison exercise, and $\sigma(med(a_i))$ is the absolute deviation of the $med(a_i)$.

In Tables 3.5.1, 3.5.2 and 3.5.3, the validations carried out by using the filters C-47, R and SQ, respectively, were shown, where both natural and artificial radionuclides ($^{214}, ^{210}\text{Pb}$, ^{214}Bi and ^{226}Ra , and ^{54}Mn , $^{60}, ^{57}\text{Co}$, ^{65}Zn , $^{137}, ^{134}\text{Cs}$ and ^{241}Am , respectively) were selected in order to achieve more complete validations.

Table 3.5.1

Validation of the efficiency calibration carried out for the circular filters whose diameter is 47 mm (C-47). For this, a filter employed in an Inter-Comparison exercise organized by the CSN and the CIEMAT in 2017 was selected.

RN	E_γ (keV)	a (Bq filter ⁻¹)	$med(a)$ (Bq filter ⁻¹)	z_{score}
^{226}Ra	185.96	0.88(8)	0.50(10)	2.0
^{214}Pb	351.93	0.47(2)	0.50(4)	-0.3
^{214}Bi	609.31	0.49(4)	0.48(5)	0.1
^{210}Pb	46.54	1.70(4)	1.77(15)	-0.2
^{54}Mn	834.84	1.06(2)	1.10(12)	-0.3
^{57}Co	122.10	0.388(8)	0.39(4)	0.0
^{60}Co	1332.50	0.720(15)	0.72(3)	0.0
^{134}Cs	604.70	0.60(8)	0.62(4)	-0.2
^{137}Cs	661.80	0.469(9)	0.43(3)	0.6
^{241}Am	59.54	0.207(6)	0.210(15)	-0.1

Table 3.5.2

Validation of the efficiency calibration carried out for the rectangular filters (R). For this, a filter employed in an Inter-Comparison exercise organized by the CSN and the CIEMAT in 2017 was selected.

RN	E_γ (keV)	a (Bq filter ⁻¹)	$med(a)$ (Bq filter ⁻¹)	z_{score}
^{226}Ra	185.96	1.2(2)	1.00(2)	0.5
^{54}Mn	834.84	1.15(12)	0.801(13)	1.5
^{60}Co	1332.50	0.85(9)	0.704(12)	0.9
^{134}Cs	604.70	0.75(8)	0.620(13)	0.9
^{137}Cs	661.80	0.60(7)	0.484(9)	0.9

Table 3.5.3

Validation of the efficiency calibration carried out for the squared filters (SQ). For this, a filter employed in an Inter-Comparison exercise organized by the CSN and the CIEMAT in 2021 was selected.

RN	E_γ (keV)	a (Bq filter ⁻¹)	$med(a)$ (Bq filter ⁻¹)	z_{score}
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²²⁶ Ra	185.96	1.7(2)	2.00(8)	-1.1
⁵⁴ Mn	834.84	1.06(2)	1.00(4)	0.4
⁵⁷ Co	122.10	0.173(15)	0.203(8)	-1.0
⁶⁰ Co	1332.50	1.94(3)	2.06(8)	-0.4
⁶⁵ Zn	1115.55	1.95(13)	1.84(8)	0.4
¹³⁴ Cs	801.93	0.33(3)	0.350(14)	0.4
¹³⁷ Cs	661.80	0.433(15)	0.412(17)	0.3
²⁴¹ Am	59.54	0.264(11)	0.352(15)	-1.3

As can be seen in Tables 3.5.1, 3.5.2 and 3.5.3, the $|z_{\text{score}}|$ values obtained for each chosen artificial and natural radionuclide agreed well with the median obtained in the proficiency tests, accomplishing that all of them were less than 2. This clearly demonstrates the very good validation of the methodology proposed in this study, for both artificial and natural radionuclides as well as for both low and high energies (≤ 150 keV and > 150 keV, respectively). Furthermore, making use of this satisfactory validation, it is also possible to conclude that the homogeneity accomplished during the preparation of the calibration filters was very proper. This allows us to consider it as a very recommendable methodology for the efficiency calibration of coaxial Ge detectors by using a very wide variety of filter types. Furthermore, this methodology can be applied in a very proper way for the determination of natural and artificial radionuclides whose gamma emission energies are distributed throughout all the energy range of interest (from 46 keV to 1332 keV).

3.5.4. Conclusions

The main conclusions of this study are the following:

1. In this study, an original methodology has been developed for the full-energy peak efficiency (*FEPE*) calibration of coaxial Ge detectors by using a great variety of atmospheric filters. These filters are characterized by having different geometries and dimensions (rectangular, circular, square and slotted filters), which are usually used when carrying out research related to the particulate matter (PM) present in atmospheric aerosols.
2. To prepare the calibration samples (filters), granular certified reference materials were selected, and they were well spread throughout the same regions than the ones covered by the PM when depositing onto the problem filters. This allows us to achieve a very high homogeneity of the calibration standard material added, reproducing the same distribution than the one followed by the PM onto the filters. Furthermore, because of the significant dimensions in the cases of the rectangular and square filters, it was necessary to cut them in several pieces which were placed one piece on top of the other. This was carried out following the same geometry and dimensions than the ones obtained when measuring the problem filters, where the calibration standards were spiked onto each one of these pieces. This makes it easier to achieve the homogeneity of the certified material spread and to reproduce the PM distribution onto the filter surface for filters whose surfaces are relatively large.
3. After preparing the calibration filter, the different filter types were counted by gamma-ray spectrometry, obtaining the experimental *FEPEs* for each filter and each selected energy. Afterwards, the experimental *FEPEs* were fitted by using a polynomial function, allowing us

to find a general *FEPE* function for each filter type covering a very wide gamma emission energy range (from 46 keV to 1765 keV). The relative average residual and R^2 values resulting from these fits were very good, which were 1.6%, 3.4%, 3.2%, 2.1% and 2.5%, and 0.9995, 0.9993, 0.998, 0.9991 and 0.998, respectively, for the SL, C-150, C-47, R and SQ filters, respectively. This proves the good agreement between the experimental *FEPEs* and the values provided by the semiempirical general function found for the *FEPE*.

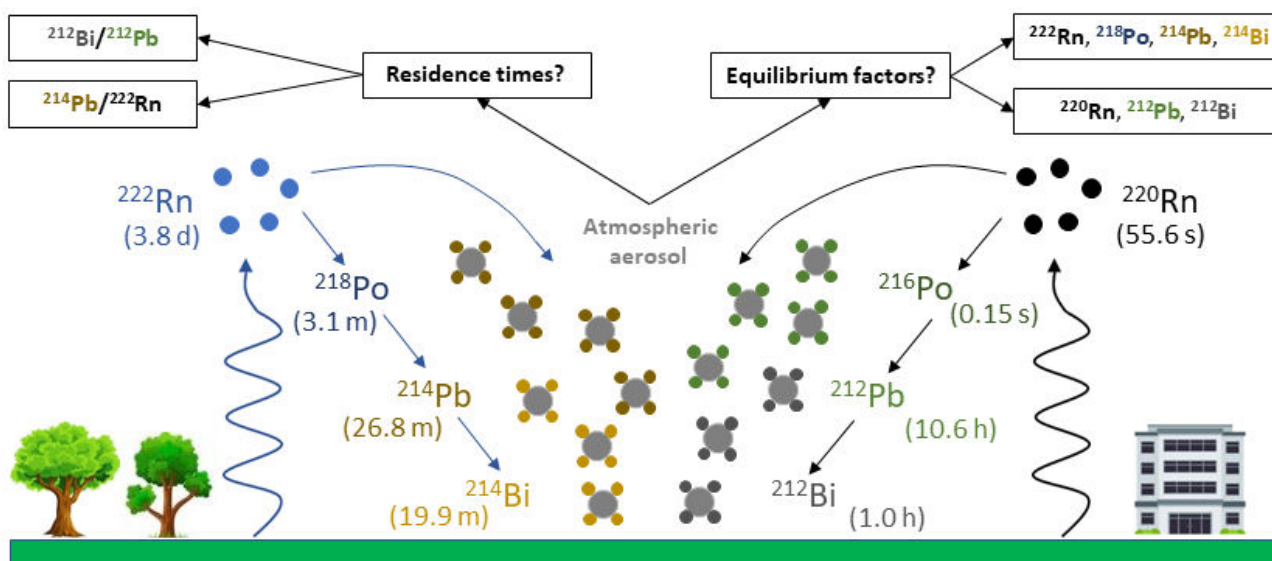
4. Finally, the methodology developed in this study was subjected to several validation tests by using filters employed in Inter-Comparison exercises. A very good validation was achieved for both natural and artificial radionuclides whose gamma emission energies are well distributed throughout the energy range of interest, obtaining $|z_{score}|$ values less than 2 for all cases. This allows us to conclude that this methodology is very recommendable in order to determine natural and artificial radionuclides, that are present in atmospheric aerosols, for a very wide energy range and variety of filter types.

Subchapter 3.6.: A new efficiency calibration methodology for different atmospheric filter geometries by using coaxial Ge detectors

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Subchapter 3.6: A new efficiency calibration methodology for different atmospheric filter geometries by using coaxial Ge detectors

Graphical Abstract



Abstract

Progeny of ^{222}Rn and ^{220}Rn , (^{212}Pb , ^{212}Bi , ^{214}Pb and ^{214}Bi) are essential to assess radiological hazard, external and internal doses, residence times and equilibrium factors. Precise measurements of these nuclides are quite complex due to their very short half-lives. This study outlines a new and precise methodology to measure these nuclides. Radon-222 and ^{220}Rn were measured using a radon monitoring system, while their respective progenies were collected in an atmospheric filter using an ASS-500 sampler and measured by gamma-ray spectrometry. The ^{212}Pb concentrations were very similar to the thoron ones, where all $^{212}\text{Bi}/^{212}\text{Pb}$ ratios were consistently less than 1. The relative uncertainties, σ_r , of the ^{212}Pb and ^{212}Bi activity concentrations, and $^{212}\text{Bi}/^{212}\text{Pb}$ activity ratio are generally less than 10%. Moreover, $^{214}\text{Pb}/^{222}\text{Rn}$ ratios were about 0.7, agreeing well with previous works. The σ_r for ^{214}Pb , ^{214}Bi and $^{214}\text{Bi}/^{214}\text{Pb}$ were generally less than 6%. This methodology was applied to estimate aerosol residence times using the $^{214}\text{Pb}/^{222}\text{Rn}$ and $^{212}\text{Bi}/^{212}\text{Pb}$ activity ratios, and to obtain equilibrium factors, achieving consistent results. Furthermore, the methodology consistency and validity range were studied with time elapsed between sampling end and counting start, and the sampling durations, finding the optimum times to precisely determine ^{212}Pb , ^{212}Bi , ^{214}Pb and ^{214}Bi .

Keywords: ^{220}Rn – ^{212}Pb – ^{212}Bi , ^{222}Rn – ^{214}Pb – ^{214}Bi ; Aerosol residence times; Equilibrium factors; Gamma-ray spectrometry

3.6.1. Introduction

A fraction of ^{220}Rn (thoron, half-life, $T_{1/2} = 56$ s), produced from radioactive decay of ^{224}Ra in the Earth's upper crust escapes the surface of the soils to the atmosphere. An assessment of inhalation dose from thoron requires a reliable method to measure ^{220}Rn concentration and its decay products in indoor and thus novel methods are being developed (Kanse et al., 2021). Among the radioactive progeny of thoron, ^{212}Pb has the longest half-life ($T_{1/2} = 10.6$ h, Auranen and McCutchan, 2020), and

thus allows to obtain detectable levels of this radionuclide in surface air. ^{212}Pb decays to ^{212}Bi ($T_{1/2} = 1.01$ h). Due to its relatively long half-life, ^{212}Pb can be used as a tracer in environmental studies. In areas where ^{232}Th concentrations are higher in the upper crust, including soil at land-air interface, with higher background thoron concentration, special care needs to be taken to get reliable data of the decay products of ^{220}Rn for dose assessment (Balakrishnan et al., 2021; Haanes and Rudjord, 2018; Tokonami et al., 2004). Furthermore, recent findings have revealed that reassessment of risks due to radon exposure may need to take the presence of thoron and its progeny into account (Haanes and Rudjord, 2018; Tokonami, 2020).

It is well-known that radon (^{222}Rn , $T_{1/2} = 3.82$ d) and its progeny are the main source of ionization in the lower troposphere, due to its long half-life compared to ^{220}Rn and ^{219}Rn as well as the main natural source of equivalent dose to the public (Considine et al., 2005; Crawford et al., 2013; Crawford et al., 2015; Zhang et al., 2011; Zhang et al., 2021). Radon is the second leading cause of lung cancer after smoking. Because the progeny of ^{222}Rn , ^{220}Rn and ^{219}Rn are highly particle-active and are charged at the time of their production, they are absorbed onto particulate matter present in air and hence ionizing radiation from particulate matter is a critical element in air quality. Inhaled particles could act as transport vehicles for radionuclides in their way inside the lungs, which may emit radiation after inhalation and deposition in the respiratory tract being able to damage the vascular structure (Macias-Verde et al., 2021; Pontedeiro et al., 2007; Yu et al., 2006) and also to affect different body organs (Gao et al., 2019). ^{214}Pb ($T_{1/2} = 26.8$ min) and ^{214}Bi ($T_{1/2} = 19.9$ min) are radon daughters that emit beta particles and many gamma rays with high branching ratios (e.g. 352 keV, 37.6%, and 609 keV, 46%) (DDEP, 2017; Ivanovich and Harmon, 1992). Lead-214 and ^{214}Bi have been used as tracers in several environmental applications. Examples include: i) as tracers to investigate the mixing of rain and seawater (Patiris et al., 2021); ii) to determine U concentrations in building materials and minerals (Kuzmanovic et al., 2021; Nuchdang et al., 2018; Pontedeiro et al., 2007) and iii) residence time estimation of cloud droplets and raindrops (Moriizumi et al., 2015).

The residence time calculated using the short-lived progeny of ^{222}Rn provides insights on how long an air mass stays in a specific zone. Assuming steady-state between the production and removal rates, using a box model (Lozano et al., 2011), T_r can be estimated from the disequilibria between the parent and daughter nuclide. In the case of ^{238}U - and ^{232}Th -series radionuclides, the daughter nuclide is useful to determine the age when the half-life of the parent radionuclide is much larger than the daughter radionuclide. Consequently, for the case corresponding to $^{212}\text{Bi}/^{212}\text{Pb}$, it is possible to use their ratio to obtain T_r . However, for the other case ($^{214}\text{Bi}/^{214}\text{Pb}$), it is not suitable given that their half-lives are very similar to each other. Therefore, for this latter case, it is necessary to select another ratio and $^{214}\text{Pb}/^{222}\text{Rn}$ is a possibility although the geochemical properties of Pb and Rn are not similar.

In dosimetry, it is more convenient to characterize the short-lived progeny of radon through the potential alpha energy concentration (PAEC), which is the sum of the alpha particle decay energy of all the short-lived progeny of radon in a volume of air (J m^{-3}). Although originally defined for radon progeny, it is possible to extend it to include thoron progeny as well (Chalupnik et al., 2021). Other parameters often used to determine exposure and radiation dose by inhalation are the equilibrium-equivalent decay product concentration of airborne radon/thoron progeny and the equilibrium factor. The equilibrium-equivalent decay product concentration is the activity concentration of any radon/thoron daughter in equilibrium which leads to a determined value of the PAEC (Vargas et al., 2016). The equilibrium factor is defined as the ratio of the measured PAEC and the PAEC when all radon decay products are in secular equilibrium with ^{222}Rn (UNSCEAR, 2000).

For all the reasons previously mentioned, this study aims to develop a new methodology to determine ^{212}Pb , ^{212}Bi , ^{214}Pb and ^{214}Bi , as well as their ratios ($^{212}\text{Bi}/^{212}\text{Pb}$ and $^{214}\text{Bi}/^{214}\text{Pb}$) in atmospheric

aerosols. Due to their low concentrations and short half-lives, precise measurements of these nuclides are complex. In comparison with other works related to the ^{212}Pb , ^{212}Bi , ^{214}Pb and ^{214}Bi determinations (e.g., Bem et al., 2002), our work is the first one to address these determinations by using an ASS-500 which is able to reach air flows ranged from $500\text{ m}^3\text{ h}^{-1}$ to $600\text{ m}^3\text{ h}^{-1}$, and a square filter whose dimensions are $44\text{ cm} \times 44\text{ cm}$. Furthermore, in our study, the obtained equations take into account the decay corrections in every moment, that is, during the sampling, between the sampling end and counting start, and during the counting, without needing to wait for the transient radioactive equilibrium. This makes our methodology more suitable to determine those radionuclides.

In addition, this study is the first one to address in-depth the determination of $^{212}\text{Pb} - ^{212}\text{Bi}$ and $^{214}\text{Pb} - ^{214}\text{Bi}$ outdoors. This methodology is applied to estimate the residence times of air aerosols, as well as to obtain the equilibrium factors for radon and thoron and their respective daughters which are essential for the internal dose calculation. For the estimation of aerosol residence times, the $^{214}\text{Bi}/^{222}\text{Rn}$ and $^{212}\text{Bi}/^{212}\text{Pb}$ activity ratios were employed, whereas this is the first study to use the $^{212}\text{Bi}/^{212}\text{Pb}$ ratio for the purpose previously mentioned. Furthermore, a comprehensive analysis is carried out on the optimum sampling and counting times, and the times elapsed between the sampling start and counting end to minimize the uncertainties of the ^{212}Pb , ^{212}Bi , ^{214}Pb and ^{214}Bi activity concentrations, which has not been addressed in other studies.

3.6.2. Materials and methods

3.6.2.1. Materials and calibrations

All atmospheric sample collections took place at the El Carmen campus of Huelva University in Huelva (a province of Andalusia, Spain), whose geographical coordinates are $37^{\circ}16'12''\text{N}$ $6^{\circ}55'28''\text{W}$. The sampling altitude was 6 m above the ground. Several polypropylene filters ($44\text{ cm} \times 44\text{ cm}$) were selected for aerosol sample collection. Different air samples were collected using a high-volume aerosol sampler, model ASS-500 (details on ASS-500 sampler in Valkovic, 2000). In Section 3.6.3.3, a comparison of the precisions determining the radionuclides of interest will be made between the ASS-500 and a PM_{10} samplers, where the air flow of any PM_{10} sampler needs to be fixed at $68\text{ m}^3\text{ h}^{-1}$ according to the US EPA Compendium Method IO-2.1 (EPA, 1999).

Assay of ^{212}Pb , ^{212}Bi , ^{214}Pb and ^{214}Bi was conducted by gamma-ray spectrometry, using an extended energy range coaxial Ge detector (XtRa). The XtRa detector has a relative efficiency of 38.4% at 1332 keV (^{60}Co) (with respect to a $3'' \times 3''$ NaI (Tl) detector), a full width at half maximum of 1.74 keV and 0.88 keV at 1332 keV and 122 keV, respectively, and a peak-to-Compton ratio of 67.5:1. The XtRa detector is connected to a device for the data acquisition and the gamma spectra visualization using the Genie 2000 software (Canberra Industries, 2004; Zhu et al., 2009). This detector was shielded with a Fe layer of 15 cm thickness, internally with a thin Pb layer. To avoid interferences from Pb X-ray in the obtained gamma spectra, a layer of 2 mm thick Cu plate was placed on the top of the Pb layer.

For the XtRa efficiency calibration, polypropylene $44 \times 44\text{ cm}^2$ filters were used for problem and calibration filters. A known amount of RGU-1 ($4940(15)\text{ Bq kg}^{-1}$) and RGTh-1 ($3250(45)\text{ Bq kg}^{-1}$) standards were well mixed between them and uniformly spread on three calibration filters, covering the same as that in sample collection. Then, they were subsequently folded achieving the same dimensions than the ones used for the measurements of any problem filter, that is, $11 \times 11\text{ cm}^2$. Three filters were chosen to check the reproducibility of the efficiency obtained for each selected energy.

The detector was calibrated with the same radionuclides that are of interest in this study (^{214}Pb (352 keV), ^{214}Bi (609 keV), ^{212}Pb (238 keV) and ^{212}Bi (via ^{208}Tl (583 keV)). The true coincidence summing (TCS) correction was not considered since the radionuclides determined in the sample and calibration filters are identical, where both types of filters have the same geometry and dimensions and are measured at the same distance from the detector window, that is, just above the detector window to maximize the detector efficiency. For these reasons, the self-absorption effects were negligible (Barba-Lobo et al., 2021b; Barba-Lobo and Bolívar, 2022a). The quality control of the XtRa calibration for this type of filters was tested participating in several inter-comparison exercises organized by the Spanish Nuclear Safety Council (CSN), obtaining satisfactory results in all of them. The minimum detectable activities (*MDAs*) obtained for a counting time of 1 hour were 3 Bq, 8 Bq, 5 Bq and 7 Bq for the ^{212}Pb (238 keV), ^{212}Bi (583 keV), ^{214}Pb (352 keV) and ^{214}Bi (609 keV), respectively. For a sampling time of 1 hour and an air flow of $600 \text{ m}^3 \text{ h}^{-1}$, *MDA* concentrations (*mda*) about 5 mBq m^{-3} , 13 mBq m^{-3} , 8 mBq m^{-3} and 12 mBq m^{-3} , respectively, were obtained.

The measured activity concentrations of ^{212}Pb , ^{214}Pb and ^{214}Bi were compared to their respective parents (thoron and radon), and the initial activities of ^{222}Rn and ^{220}Rn at the beginning of collection were measured. A measurement system, which was settled at the same place chosen to carry out the samplings, was utilized in order to determine the concentration levels of radon and thoron existing at the beginning of each sampling. This system is based on Atmospheric Radon Monitoring (ARMON), which is comprised of a semiconductor detector inside a 20 L spherical detection volume, with a potential difference of 8000 V between sphere's the inner layer of the sphere and a Passivated Implanted Planar Silicon (PIPS) detector. In this system, the Si detector detects α -particles resulting from ^{216}Po and ^{218}Po decays, from the thoron and radon, respectively. The detector has a $1 \mu\text{m}$ filter which is placed at sphere entrance to trap all thoron and radon daughters, which are generated before entering this sphere. The *mda* were about 50 mBq m^{-3} and 200 mBq m^{-3} for thoron and radon, respectively. For further information about the ARMON system employed in this study and its calibration, see Vargas et al., 2015; Grossi et al., 2012. Regarding the quality control of the ARMON calibration, a chamber containing an active certified reference material is often measured by the ARMON and another system used for radon and thoron measurements (RAD7 version 5541, provided by DURRIDGE), which was already validated. For all these measurements carried out by the ARMON and RAD7, very similar curves of radon were obtained, validating the ARMON calibration.

Considering the previous materials mentioned, our experimental setup consisted of an ASS-500 aerosol sampler, using polypropylene filters of $44 \times 44 \text{ cm}^2$, a XtRa Ge detector for the measurement of gamma-emitter radionuclides, and an ARMON for the measurement of radon and thoron.

3.6.2.2. Obtaining the equations related to the $^{212}\text{Pb} - ^{212}\text{Bi}$ and $^{214}\text{Pb} - ^{214}\text{Bi}$ determinations

In order to determine the activity concentrations of ^{212}Pb , ^{212}Bi , ^{214}Pb and ^{214}Bi in air at the beginning of the samplings, it is necessary to know precisely the activity of these radionuclides for the particulate matter deposited on the filters during the samplings, that is, A_{ps} (where p refers to the parent radionuclides, that is, ^{212}Pb or ^{214}Pb) and A_{ds} (where d refers to the daughter radionuclide, that is, ^{212}Bi or ^{214}Bi), can be obtained by the following equations (Supplementary Material-F for further information about the detailed demonstrations to obtain these equations and all the others shown in this Section):

$$A_{ps} = a_p \phi C_{ps} \quad (\text{Eq. 3.6.1})$$

where ϕ is the flow resulting from each sampling, $\Delta t_s = t_s^{(2)} - t_s^{(1)}$, where $t_s^{(1)}$ and $t_s^{(2)}$ are the times when each sampling starts and ends, respectively, $C_{ps} = \lambda_p^{-1}(1 - e^{-\lambda_p \Delta t_s})$, λ_p is the decay constant of the parent radionuclide (that is, ^{212}Pb or ^{214}Pb) and a_p is the activity concentration of the parent radionuclide in air aerosol at $t_s^{(1)}$.

Then, using Bateman equation, the activity of A_{ds} is given as:

$$A_{ds} = \frac{a_p \phi \lambda_d}{\lambda_d - \lambda_p} [C_{ps} - C_{ds}] + a_d \phi C_{ds} \quad (\text{Eq. 3.6.2})$$

where λ_d and a_d are the decay constant and the activity concentration in air at $t_s^{(1)}$ of ^{212}Bi or ^{214}Bi , respectively, and $C_{ds} = \lambda_d^{-1}(1 - e^{-\lambda_d \Delta t_s})$.

From Eqs. 3.6.1 and 3.6.2, the daughter/parent activity ratio can be determined which is useful to get information about the disequilibrium between the daughter and parent radionuclides referred to the particulate matter deposited during the sampling:

$$\frac{A_{ds}}{A_{ps}} = \frac{\lambda_d}{\lambda_d - \lambda_p} + \frac{C_{ds}}{C_{ps}} \left(\frac{a_d}{a_p} - \frac{\lambda_d}{\lambda_d - \lambda_p} \right) \quad (\text{Eq. 3.6.3})$$

The evolution of the activities of the parent and daughter radionuclides on the filters, and their ratios ($A_{ds}(t)/A_{ps}(t)$), at any time ' t ' can be known as follows:

$$A_{ps}(t) = A_{ps} C_{ps^{(2)}-t} \quad (\text{Eq. 3.6.4})$$

$$A_{ds}(t) = \frac{A_{ps} \lambda_d}{\lambda_d - \lambda_p} [C_{ps^{(2)}-t} - C_{ds^{(2)}-t}] + A_{ds} C_{ds^{(2)}-t} \quad (\text{Eq. 3.6.5})$$

$$\frac{A_{ds}(t)}{A_{ps}(t)} = \frac{\lambda_d}{\lambda_d - \lambda_p} + \frac{C_{ds^{(2)}-t}}{C_{ps^{(2)}-t}} \left(\frac{A_{ds}}{A_{ps}} - \frac{\lambda_d}{\lambda_d - \lambda_p} \right) \quad (\text{Eq. 3.6.6})$$

where A_{ps} and A_{ds} are given in Eqs. 3.6.1 and 3.6.2, respectively, $C_{ps^{(2)}-t} = e^{-\lambda_p(t-t_s^{(2)})}$ and $C_{ds^{(2)}-t} = e^{-\lambda_d(t-t_s^{(2)})}$.

After the sample collection, the filters were measured by a XtRa detector. Genie 2000 software was used to get the net counts (N) corresponding to each selected gamma energy of the radionuclides. N_p and N_d can be given by:

$$N_p = P_{\gamma p} \varepsilon_p A_{ps} C_{ps^{(2)}-c^{(1)}} C_{pc} \quad (\text{Eq. 3.6.7})$$

$$N_d = P_{\gamma d} \varepsilon_d \left\{ \frac{A_{ps} \lambda_d}{\lambda_d - \lambda_p} [C_{ps(2)-c(1)} C_{pc} - C_{ds(2)-c(1)} C_{dc}] + A_{ds} C_{ds(2)-c(1)} C_{dc} \right\} \quad (\text{Eq. 3.6.8})$$

where P_γ and ε are the gamma emission probability and the efficiency for a given energy (p and d denote parent and daughter nuclides, respectively). $C_{ps(2)-c(1)} = e^{-\lambda_p \Delta t_{s(2)-c(1)}}$, $C_{ds(2)-c(1)} = e^{-\lambda_d \Delta t_{s(2)-c(1)}}$, $C_{pc} = \lambda_p^{-1} (1 - e^{-\lambda_p \Delta t_c})$, $C_{dc} = \lambda_d^{-1} (1 - e^{-\lambda_d \Delta t_c})$, $\Delta t_c = t_c^{(2)} - t_c^{(1)}$, being $t_c^{(1)}$ and $t_c^{(2)}$ the times corresponding to the start and end of the counting, respectively, and $\Delta t_{s(2)-c(1)} = t_c^{(1)} - t_s^{(2)}$.

Taking Eqs. 3.6.7 and 3.6.8, as well as Eqs. 3.6.1 and 3.6.2, the activity concentrations of the parent and daughter radionuclides in air, that is, at $t_s^{(1)}$, a_p and a_d , respectively, can be calculated as follows:

$$a_p = N_p [P_{\gamma p} \varepsilon_p \phi C_{ps} C_{ps(2)-c(1)} C_{pc}]^{-1} \quad (\text{Eq. 3.6.9})$$

$$a_d = \frac{1}{\phi C_{ds}} \left\{ \frac{N_d (P_{\gamma d} \varepsilon_d)^{-1}}{C_{ds(2)-c(1)} C_{dc}} - \frac{N_p (P_{\gamma p} \varepsilon_p)^{-1} \lambda_d}{\lambda_d - \lambda_p} \left[\frac{1}{C_{ds(2)-c(1)} C_{dc}} - \frac{1}{C_{ps(2)-c(1)} C_{pc}} \right] - \frac{N_p (P_{\gamma p} \varepsilon_p C_{ps} C_{ps(2)-c(1)} C_{pc})^{-1} \lambda_d}{\lambda_d - \lambda_p} [C_{ps} - C_{ds}] \right\} \quad (\text{Eq. 3.6.10})$$

Furthermore, using Eqs. 3.6.9 and 3.6.10, a_d/a_p is completely determined and, therefore, this ratio provides useful information about the disequilibria between the parent and daughter radionuclides at $t_s^{(1)}$:

$$\frac{a_d}{a_p} = \frac{"a_d"}{a_p} - \frac{\frac{C_{ps} \lambda_d}{\lambda_d - \lambda_p} [C_{ps(2)-c(1)} C_{pc} - C_{ds(2)-c(1)} C_{dc}]}{C_{ds} C_{ds(2)-c(1)} C_{dc}} - \frac{\lambda_d}{\lambda_d - \lambda_p} \left[\frac{C_{ps}}{C_{ds}} - 1 \right] \quad (\text{Eq. 3.6.11})$$

where $"a_d" = N_d [P_{\gamma d} \varepsilon_d \phi C_{ds} C_{ds(2)-c(1)} C_{dc}]^{-1}$, that is, the activity concentration of the daughter radionuclide in the case that it did not have any dependence on the evolution of its parent activity concentration.

Considering Eqs. 3.6.9, 3.6.10 and 3.6.11, it is possible to know the uncertainties related to a_p , a_d and a_d/a_p :

$$\sigma(a_p) = a_p \frac{\sigma_{N_p}}{N_p} \quad (\text{Eq. 3.6.12})$$

$$\sigma(a_d) = \sqrt{(\beta + \gamma)^2 \sigma_{N_p}^2 + (a_d + (\beta + \gamma)N_p)^2 \left(\frac{\sigma_{N_d}}{N_d}\right)^2} \quad (\text{Eq. 3.6.13})$$

$$\sigma\left(\frac{a_d}{a_p}\right) = \frac{a_d}{a_p} \sqrt{\left(\frac{\sigma(a_p)}{a_p}\right)^2 + \left(\frac{\sigma(a_d)}{a_d}\right)^2} \quad (\text{Eq. 3.6.14})$$

where σ_{N_p} and σ_{N_d} are the uncertainties of N_p and N_d , respectively, $\frac{a_d + (\beta + \gamma)N_p}{N_d} = \frac{\partial a_d}{\partial N_d}$ and $\beta + \gamma = -\frac{\partial a_d}{\partial N_p}$.

For the samplings that will be carried out (see Sections from 3.6.3.1 to 3.6.3.5), the sampling time, Δt_s , was fixed at 0.5 h and 1.0 h, the time elapsed between the sampling end and the counting start, $\Delta t_{s(2)-c(1)}$, varied from about 0.3 h to 3 h, the counting time, Δt_c , was fixed at 0.5 h and 1.0 h, and the air flow varied from about 500 m³ h⁻¹ and 600 m³ h⁻¹. The counting and sampling strategy was established according to the half-life of the ²¹²Bi (1 hour), which is the radionuclide more difficult to measure considering its very short half-life and its relatively low concentration in air. So, the sampling and counting times were selected to be as short as possible to avoid significant decay of the analyzed radionuclides, and to minimize the uncertainties resulting when propagating uncertainties in the case of the activity concentrations in air.

3.6.2.2.1. Applications of the developed methodology: residence time and equilibrium factor estimations

From the disequilibrium between the daughter and parent radionuclides, the residence times of the atmospheric aerosols can be determined. Therefore, the methodology developed in this study in order to determine ²¹²Pb, ²¹⁴Pb, ²¹²Bi and ²¹⁴Bi was applied to the obtention of the residence times for air aerosols.

If between the two radionuclides selected to calculate those ratios, there is no intermediate decay products, T_r can be estimated by the following equation (Długosz-Lisiecka and Bem, 2012):

$$T_r = \frac{1}{\lambda_d(a_p/a_d - 1)} \quad (\text{Eq. 3.6.15})$$

where λ_d is the decay constant of the daughter radionuclide.

The uncertainty related to T_r can be calculated using:

$$\sigma(T_r) = \frac{1}{\lambda_d(1 - a_d/a_p)^2} \sigma(a_d/a_p) \quad (\text{Eq. 3.6.16})$$

where $\sigma(a_d/a_p)$ is the uncertainty related to a_d/a_p .

If there is an intermediate decay product, another equation is employed to estimate T_r (Robbins, 1978):

$$T_r = \left(\frac{-A + B}{2} \right)^{-1} \quad (\text{Eq. 3.6.17})$$

where $A = (\lambda_d + \lambda_{d'})$, $B = \sqrt{(\lambda_d + \lambda_{d'})^2 - 4 \lambda_d \lambda_{d'} (1 - a_p/a_d)}$, λ_d and $\lambda_{d'}$ are the decay constants of the daughter radionuclide and the intermediate decay product, respectively. The uncertainty associated to Eq. 3.6.17 can be known as follows:

$$\sigma(T_r) = \frac{4 \lambda_d \lambda_{d'} a_p/a_d^2}{B (-A + B)^2} \sigma(a_d/a_p) \quad (\text{Eq. 3.6.18})$$

Then, the methodology developed in this study was also employed to estimate the equilibrium factors of the radon and thoron daughters, F_{eq} , which are useful in order to get information about how significative the exposure to radiation is. In a general way, F_{eq} is defined as follows:

$$F_{eq} = C_{eq}/C_{Rn} \quad (\text{Eq. 3.6.19})$$

where C_{Rn} is the activity concentration of radon or thoron and C_{eq} is the equivalent activity concentration of the short-lived daughters of the radon or thoron, respectively, considering radioactive equilibrium between them. Therefore, depending on C_{eq} is referred to the radon or thoron daughters, this can be obtained by using one equation or another (Nader, 2019):

$$C_{eq}^{222} = 0.105 a_{218Po} + 0.515 a_{214Pb} + 0.380 a_{214Bi} \quad (\text{Eq. 3.6.20})$$

$$C_{eq}^{220} = 0.913 a_{212Pb} + 0.087 a_{212Bi} \quad (\text{Eq. 3.6.21})$$

where C_{eq}^{222} and C_{eq}^{220} are the equivalent activity concentrations when employing the daughters of the radon and thoron, respectively, and the activity concentrations of ^{218}Po , ^{214}Pb , ^{214}Bi , ^{212}Pb and ^{212}Bi in air. Besides, given that ^{218}Po is a very short-lived radionuclide (^{218}Po half-life ~ 3 minutes), it is very acceptable to assume secular equilibrium between ^{222}Rn and ^{218}Po .

3.6.3. Results and discussion

3.6.3.1. Determination of the ^{212}Pb , ^{214}Pb , ^{212}Bi and ^{214}Bi concentrations

Aerosol samplings of 1 hour of duration were carried out by using an ASS-500 sampler at “El Carmen” University Campus on July 22, 2021, starting at 5:00 UTC and finishing at 11:00 UTC.

The concentrations of ^{220}Rn and ^{212}Pb decrease since sunrise, that is, from about 6:00 UTC (Table 1). The ^{220}Rn concentration decreases from 509(163) mBq m⁻³ at 6:00 UTC to 105(75) mBq m⁻³ at 10:00 UTC. The corresponding values for ^{212}Pb decreased from 583(14) mBq m⁻³ at 6:00 UTC to 102(3) mBq m⁻³ at 10:00 UTC. Radon-222 and thoron usually reach their maximum concentrations at dawn,

which took place between 5:00 UTC and 6:00 UTC on July 22, 2021. Furthermore, the ^{212}Pb values obtained at the beginning of sampling are statistically comparable with ^{220}Rn concentrations considering a significance level of 5%. Then, the $^{212}\text{Bi}/^{212}\text{Pb}$ activity ratio in all samples are less than 1 (Table 3.6.1), which is very consistent to the expected activity ratio values. The ^{212}Pb is the parent of the ^{212}Bi . Therefore, in the case that there is no excess accumulation, the $^{212}\text{Bi}/^{212}\text{Pb}$ activity ratio must be ≤ 1 . Excess accumulation of the $^{212}\text{Pb} - ^{212}\text{Bi}$ happens rarely due to the high difference between their half-lives (10.6 hours (^{212}Pb) and 1 hour (^{212}Bi)). In addition, this reasoning can be corroborated by other works such as Bigu, 1993; He et al., 2017.

It is necessary to highlight the precision obtained for $a_{212\text{Pb}}$, $a_{212\text{Bi}}$ and $a_{212\text{Bi}}/a_{212\text{Pb}}$ using the methodology described in Section 3.6.2.2, with relative uncertainties ranged from 2.3% to 2.9%, from 7.8% to 11%, and from 8.3% to 12%, respectively. The $\Delta t_{s(2)-c(1)}$ values obtained for all samplings were relatively short, < 0.43 hours. This is essential to determine ^{212}Bi and ^{212}Pb and their activity ratios. Regarding the uncertainty in thoron activity, it is relatively high, due to its very short half-life.

Table 3.6.1

Flow (ϕ), activity concentrations of ^{212}Pb , ^{212}Bi and ^{220}Rn , $^{212}\text{Bi}/^{212}\text{Pb}$ activity ratio, duration of sampling (Δt_s) and counting (Δt_c) and time elapsed between collection end and counting start ($\Delta t_{s(2)-c(1)}$) for the samplings done on July 22, 2021 using an ASS-500 sampler.*

Filter code	ϕ ($\text{m}^3 \text{ h}^{-1}$)	Δt_s (h)	$\Delta t_{s(2)-c(1)}$ (h)	Δt_c (h)	^{212}Pb (mBq m^{-3})	^{212}Bi (mBq m^{-3})	$\frac{^{212}\text{Bi}}{^{212}\text{Pb}}$	^{220}Rn (mBq m^{-3})
A101	596	0.97(5:00 UTC)	0.35	0.94	510(12)	179(17)	0.35(0.03)	457(154)
A102	490	0.92(6:00 UTC)	0.42	0.94	583(14)	281(22)	0.48(0.04)	509(163)
A103	550	0.92(7:00 UTC)	0.43	0.94	384(9)	164(17)	0.43(0.04)	409(146)
A104	589	0.93(8:00 UTC)	0.40	0.94	331(8)	149(15)	0.45(0.05)	155(90)
A105	519	0.92(9:00 UTC)	0.43	0.94	215(6)	134(14)	0.62(0.07)	<50
A106	582	1.05(10:00 UTC)	0.25	1.00	102(3)	71(8)	0.69(0.08)	105(75)

(*) Numbers in parenthesis denotes uncertainty (1σ) associated with the data. Besides, for each Δt_s , the start times of each sampling are also specified in parenthesis.

For the $^{214}\text{Pb} - ^{214}\text{Bi}$ pair and ^{222}Rn (Table 3.6.2), all values obtained for $a_{214\text{Pb}}$ were less than those for radon. The average activity ratio of $a_{214\text{Pb}}/a_{222\text{Rn}}$, was found to be 0.73(0.03), which agrees well with the values reported earlier in literature for meteorological conditions characterized by not very windy and non-rainy days, and a relative humidity about 50% (Chen and Harley, 2018; Pontedeiro et

al., 2007). It is interesting to note that ^{214}Pb and radon followed the similar behavior, since their concentrations decreased from dawn. The activity concentrations of ^{214}Bi were in a good agreement with the expected ones. The $a_{214\text{Bi}}/a_{214\text{Pb}}$ ratios ranged from 0.41(0.02) to 0.59(0.03), which are significantly less than 1 and provide information on the factors and processes causing the disequilibria between ^{214}Pb and ^{214}Bi . The $a_{214\text{Bi}}/a_{214\text{Pb}}$ ratio did not show a significant variation as occurred for the $a_{214\text{Pb}}/a_{222\text{Rn}}$ ratio, which is consistent since they are associated to the same air aerosols.

The uncertainties of $a_{214\text{Pb}}$, $a_{214\text{Bi}}$ and $a_{214\text{Bi}}/a_{214\text{Pb}}$ ranged from 1.0% to 2.9%, from 3.9% to 6.3%, and from 4.9% to 6.5%, respectively. The relative uncertainties of $a_{214\text{Pb}}$ were very similar to the ones obtained for $a_{212\text{Pb}}$ (see Table 3.6.1), while relative uncertainties for $a_{214\text{Bi}}$ were significantly smaller than the $a_{212\text{Bi}}$ ones (see Table 3.6.1). This is coherent because the uncertainties related to a_d (activity concentration uncertainty of the daughter radionuclide, see Eq. 3.6.13) are inversely proportional to N_d . Since the net counts obtained for the full-energy peak used for ^{214}Bi (at 609 keV) were an order of magnitude higher than the N_d values associated to the full-energy peak used for ^{212}Bi (583 keV), it is reasonable that $\sigma(a_d)$ for ^{214}Bi is less than the ^{212}Bi one.

Table 3.6.2

Flow (ϕ), activity concentrations of ^{214}Pb , ^{214}Bi and ^{222}Rn , $^{214}\text{Bi}/^{214}\text{Pb}$ and $^{214}\text{Pb}/^{222}\text{Rn}$ activity ratios, duration of sampling (Δt_s) and counting (Δt_c) and time elapsed between collection end and counting start ($\Delta t_{s(2)-c(1)}$) for the samplings done on July 22, 2021 using an ASS-500 sampler.*

Filter code	ϕ ($\text{m}^3 \text{ h}^{-1}$)	Δt_s (h)	$\Delta t_{s(2)-c(1)}$ (h)	Δt_c (h)	^{214}Pb (Bq m^{-3})	^{214}Bi (Bq m^{-3})	$\frac{^{214}\text{Bi}}{^{214}\text{Pb}}$	^{222}Rn (Bq m^{-3})	$\frac{^{214}\text{Pb}}{^{222}\text{Rn}}$
A101	596	0.97(5:00 UTC)	0.35	0.94	19.2(0.4)	7.8(0.3)	0.41(0.02)	26.3(1.8)	0.73(0.05)
A102	490	0.92(6:00 UTC)	0.42	0.94	17.1(0.4)	9.6(0.4)	0.56(0.03)	22.8(1.6)	0.75(0.06)
A103	550	0.92(7:00 UTC)	0.43	0.94	14.7(0.3)	7.0(0.3)	0.48(0.03)	19.9(1.4)	0.74(0.06)
A104	589	0.93(8:00 UTC)	0.40	0.94	11.5(0.3)	5.5(0.3)	0.48(0.03)	15.9(1.2)	0.72(0.06)
A105	519	0.92(9:00 UTC)	0.43	0.94	10.5(0.3)	4.8(0.3)	0.46(0.03)	12.9(1.1)	0.81(0.07)
A106	582	1.05(10:00 UTC)	0.25	1.00	5.96(0.14)	3.54(0.16)	0.59(0.03)	10.0(0.9)	0.60(0.06)

(*) Numbers in parenthesis denotes uncertainty (1σ) associated with the data. Besides, for each Δt_s , the start times of each sampling are also specified in parenthesis.

Besides studying how significative the disequilibrium between ^{212}Pb and ^{212}Bi , and between ^{214}Pb and ^{214}Bi are in air aerosols using a_d/a_p , it is also interesting to know the evolution of both couples of radionuclides before and after ending the samplings. This is possible to be assessed making use of the Eqs. 3.6.3 (during sampling) and 3.6.6 (after sampling) and employing the same values for a_p , a_d and Δt_s than the ones obtained for each sampling. Therefore, it is possible to reproduce the theoretical behavior that A_{ds}/A_{ps} (activity ratios during sampling) and $A_{ds}(t)/A_{ps}(t)$ (activity ratios after sampling) would follow in the case of the $^{212}\text{Pb} - ^{212}\text{Bi}$ and $^{214}\text{Pb} - ^{214}\text{Bi}$ couples for the particulate matter deposited on the filters.

In Fig. F1 (see Supplementary Material-F), A_{ds}/A_{ps} and $A_{ds}(t)/A_{ps}(t)$ were plotted for each couple of radionuclides and for each of the six samplings, where the time intervals that start from the end of the samplings were fixed at 3 hours, covering a very wide time range to get a proper analysis of A_{ds}/A_{ps} and $A_{ds}(t)/A_{ps}(t)$ (1 hour during sampling + 3 hours after sampling). The A_{ds}/A_{ps} ratios obtained for $^{212}\text{Pb} - ^{212}\text{Bi}$ were less than 1 during sampling (Fig. F1). The $A_{ds}(t)/A_{ps}(t)$ ratios, they reached values higher than 1 when the total time was 4 hours. However, this is consistent because of the excess accumulation of the daughter radionuclides. This agrees well with other previous works (Katona et al., 2004; Moriizumi et al., 2015). For the $^{214}\text{Pb} - ^{214}\text{Bi}$ couple, the A_{ds}/A_{ps} ratios reached values > 1 hour, where the $A_{ds}(t)/A_{ps}(t)$ ratios were more than three times higher than 1 for a total time of 4 hours. For the $^{214}\text{Pb} - ^{214}\text{Bi}$ couple, the excess accumulation of the daughter radionuclides was more significant than the one obtained for $^{212}\text{Pb} - ^{212}\text{Bi}$ pair. This is reasonable because in $^{214}\text{Pb} - ^{214}\text{Bi}$ pair their half-lives are similar to each other and, consequently, the effect of excess accumulation can be produced more easily than the $^{212}\text{Pb} - ^{212}\text{Bi}$ pair.

3.6.3.2. Comparison of residence times using $^{212}\text{Bi}/^{212}\text{Pb}$ and $^{214}\text{Pb}/^{222}\text{Rn}$ activity ratios and estimation of equilibrium factors

The atmospheric aerosol residence times calculated for the samplings carried out on July 22, 2021 are shown in Table 3.6.3. Let us call T_r as T_r^{212} and T_r^{214} when making use of $^{212}\text{Bi}/^{212}\text{Pb}$ and $^{214}\text{Pb}/^{222}\text{Rn}$, respectively, to estimate T_r . Furthermore, in Table 3.6.3, the equilibrium factors are also shown for the samplings that took place on July 22, 2021 in the case of the radon and thoron and their respective daughters using Eqs. 3.6.20 and 3.6.21, respectively.

Table 3.6.3

Residence times estimated using $^{212}\text{Bi}/^{212}\text{Pb}$ (T_r^{212}) and $^{214}\text{Pb}/^{222}\text{Rn}$ (T_r^{214}), and equilibrium factors for thoron daughters (F_{eq}^{220}), and for radon daughters (F_{eq}^{222}) for the samplings carried out on July 22, 2021*. Furthermore, z_{score} was calculated for each T_r couple obtained for each sampling, $z_{score}^{T_r}$ **.

Filter code	T_r^{212} (h)	T_r^{214} (h)	$z_{score}^{T_r}$	F_{eq}^{220}	F_{eq}^{222}
A101	0.78(0.10)	2.0(0.6)	-2.0	1.1(0.3)	0.59(0.04)
A102	1.3(0.2)	2.2(0.6)	-1.4	1.1(0.4)	0.65(0.05)
A103	1.10(0.18)	2.1(0.6)	-1.6	0.9(0.3)	0.62(0.05)
A104	1.2(0.2)	1.9(0.5)	-1.3	2.0(1.2)	0.61(0.05)
A105	2.4(0.7)	3.2(1.5)	-0.5	-	0.67(0.06)
A106	3.2(1.2)	1.1(0.3)	1.7	1.0(0.7)	0.55(0.05)

(*) Numbers in parenthesis denotes uncertainty (1σ) associated with the data. (**) The $z_{score}^{T_r}$ obtained for each T_r couple was calculated comparing T_r^{212} with T_r^{214} , since T_r^{214} was determined by using a larger number of validated measurement systems (XtRa and ARMON).

The T_r^{212} and T_r^{214} ranged from ~ 0.8 hour to 3 hours (Table 3.6.3), which were statistically compatible to each other considering uncertainties at 2 sigma level, that is, for a confidence interval of 95% (significance level of 5%). This statistical compatibility can be checked by using the z_{score} calculated for each T_r^{212} - T_r^{214} couple, $z_{score}^{T_r}$, where all $|z_{score}^{T_r}|$ were found to be ≤ 2 . This is consistent since both pairs are expected to yield similar values for T_r .

The equilibrium factors calculated using F_{eq}^{220} or F_{eq}^{222} were statistically compatible with ≤ 1 for all samples considering a confidence interval of 68% (uncertainties given at 1 sigma level), which agree well with those found in previous studies (Chen and Harley, 2018; Pontedeiro et al., 2007). This is consistent since the equivalent activity concentration related to ^{218}Po , ^{214}Pb and ^{214}Bi or to ^{212}Pb and ^{212}Bi must be less than or equal to the one related to the ^{222}Rn or ^{220}Rn , respectively.

3.6.3.3. Comparison of the ^{212}Pb , ^{214}Pb , ^{212}Bi and ^{214}Bi activity concentration precisions using an ASS-500 and PM_{10} samplers

A comparison between the $\sigma(a_p)$, $\sigma(a_d)$ and $\sigma(a_d/a_p)$ values (Eqs. 3.6.12, 3.6.13 and 3.6.14, respectively) resulted from using an ASS-500 and a PM_{10} samplers. This comparison allows us to know which sampler is more appropriate to achieve more precise calculations for a_p , a_d and a_d/a_p by employing the methodology developed in Section 3.6.2.2 For this, a_p and a_d and, therefore, a_d/a_p were assumed to be the same than the ones using a PM_{10} sampler. This is an acceptable assumption because in the zone where the samplings were carried out, there is a PM_{10} sampler settled very near of the ASS-500 sampler (< 2 meters of distance). It is necessary to clarify that only the ASS-500 sampler could be used for the samplings because there was only one gamma detector available to measure filters. Consequently, since ^{212}Pb , ^{212}Bi , ^{214}Pb and ^{214}Bi are radionuclides characterized by their short half-lives, only the ASS-500 sampler was employed. Taking the same a_p and a_d values, as well as the same values for Δt_s , $\Delta t_{s(2)-c(1)}$ and Δt_c for each of the six samplings, it is possible to calculate N_p and N_d using Eqs. 3.6.7 and 3.6.8, respectively, and, therefore, $\sigma(a_p)$, $\sigma(a_d)$ and $\sigma(a_d/a_p)$ can be determined making use of Eqs. 3.6.12, 3.6.13 and 3.6.14, respectively. In Figs. 3.6.1 and 3.6.2, this comparison is shown for $^{212}\text{Pb} - ^{212}\text{Bi}$ and $^{214}\text{Pb} - ^{214}\text{Bi}$, respectively. Furthermore, this comparison is shown numerically as well in Tables F1 and F2 (in Supplementary Material-F), respectively.

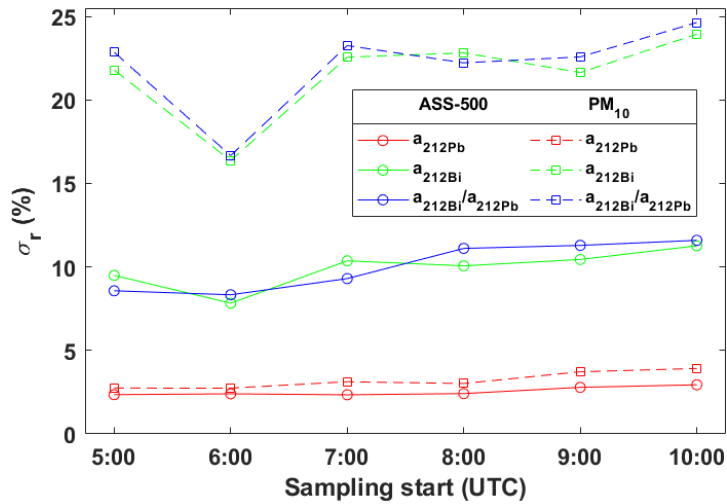


Figure 3.6.1. Comparison of the precisions calculated the activity concentrations of the ^{212}Pb and ^{212}Bi , as well as for their ratios, in air using an ASS-500 and a PM_{10} samplers for the samplings carried out on July 22, 2021, where the relative uncertainties, σ_r (%), are plotted for each sampling start time.

As can be seen in Fig. 3.6.1, the relative uncertainties obtained for $a_{212\text{Pb}}$ when using a PM_{10} sampler were somewhat higher than the ones achieved in the case of the ASS-500 sampler. However, for $a_{212\text{Bi}}$ and $a_{212\text{Bi}}/a_{212\text{Pb}}$, the relative uncertainties were significantly higher than the ones obtained for the ASS-500 sampler (approximately two times higher). This is consistent since $\sigma(a_d)$ (see Eq. 3.6.13) is proportional to $\phi^{-1/2}$, where ϕ is the air flow reached by each sampler. Consequently, while ϕ for PM_{10} samplers needs to be fixed at $68 \text{ m}^3 \text{ h}^{-1}$ according to the US EPA Compendium Method IO-2.1 (EPA, 1999), the flow for ASS-500 samplers does not need to be fixed by the regulations, which can reach values ranging from $500 \text{ m}^3 \text{ h}^{-1}$ to $600 \text{ m}^3 \text{ h}^{-1}$. This allows to sample a significantly higher volume of air, which is essential to determine ^{212}Bi in a much more precise way.

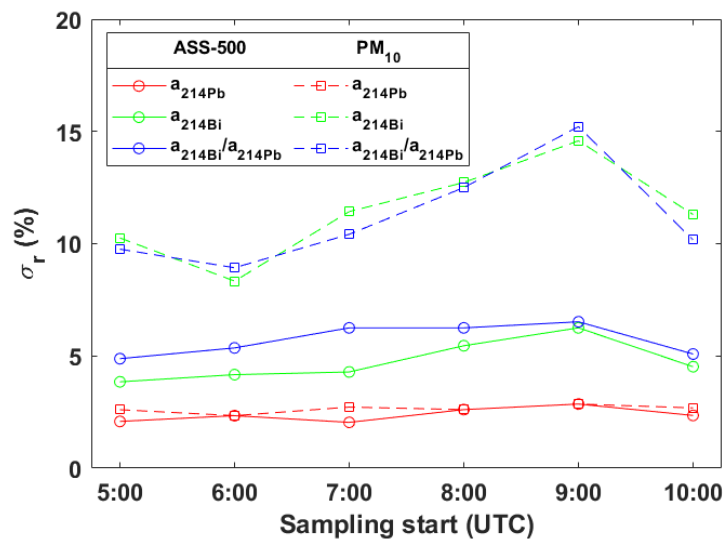


Figure 3.6.2. Comparison of the precisions calculated the activity concentrations of the ^{214}Pb and ^{214}Bi , as well as for their ratios, in air using an ASS-500 and a PM_{10} samplers for the samplings carried out on July 22, 2021, where the relative uncertainties, σ_r (%), are plotted for each sampling start time.

For ^{214}Pb and ^{214}Bi (see Fig. 3.6.2), the relative uncertainties related to $a_{214\text{Pb}}$ when using a PM_{10} sampler were similar to the ones previously obtained for the ASS-500 sampler. However, the precisions determining ^{214}Bi and $^{214}\text{Bi}/^{214}\text{Pb}$ were clearly worse for the PM_{10} sampler, getting relative uncertainties approximately two times higher than the ones resulting when using the ASS-500 sampler. This is consistent due to the same reason that was previously explained, that is, because of ϕ . Consequently, this proves that an ASS-500 sampler is much more suitable to be utilized to determine ^{212}Pb , ^{214}Pb , ^{212}Bi and ^{214}Bi .

3.6.3.4. Consistency and reproducibility of ^{212}Pb , ^{214}Pb , ^{212}Bi and ^{214}Bi activity concentrations and their ratios

The consistency and reproducibility of the methodology described in Section 3.6.2.2 was checked and its validity range was studied by estimating the total critical times ($\Delta t_s + \Delta t_{s(2)-c(1)} + \Delta t_c$), within which the ^{212}Pb , ^{214}Pb , ^{212}Bi and ^{214}Bi can be precisely determined. For this, two samplings were carried out using the ASS-500 sampler: first one on September 13, 2021, and the second one on September 15, 2021. For the first sampling, a Δt_s value of 1 hour was selected, and for the second one it was only 30 minutes, where for each sampling only one filter was used, which was measured six times in a row by the XtRa detector (30 minutes for each counting time).

The a_p , a_d and a_d/a_p of both couples of radionuclides were calculated for each measurement. Tables 3.6.4 and 3.6.5 show these concentrations for each $\Delta t_{s(2)-c(1)}$ value in the cases of the $^{212}\text{Pb} - ^{212}\text{Bi}$ and $^{214}\text{Pb} - ^{214}\text{Bi}$, respectively, for the sampling carried out on September 13, 2021.

Table 3.6.4

Flow (ϕ), counting duration (Δt_c), activity concentrations of ^{212}Pb and ^{212}Bi and $^{212}\text{Bi}/^{212}\text{Pb}$ activity ratio for different $\Delta t_{s(2)-c(1)}$ values (1 hour-sampling, September 13, 2021). The activity concentration obtained for ^{220}Rn at 8:00 UTC was 473(159) mBq m^{-3} .*

Filter code	ϕ ($\text{m}^3 \text{h}^{-1}$)	$\Delta t_{s(2)-c(1)}$ (h)	Δt_c (h)	^{212}Pb (mBq m^{-3})	^{212}Pb Z_{score}	^{212}Bi (mBq m^{-3})	^{212}Bi Z_{score}	$\frac{^{212}\text{Bi}}{^{212}\text{Pb}}$	$\frac{^{212}\text{Bi}}{^{212}\text{Pb}}$ Z_{score}
A107	612	0.45	0.50	313(8)	-0.7	72(7)	0.2	0.23(0.02)	0.2
		0.98	0.50	320(8)	0.1	69(25)	0.0	0.22(0.08)	0.0
		1.50	0.50	324(8)	0.6	67(37)	-0.1	0.21(0.11)	-0.1
		2.00	0.50	317(8)	-0.2	-72(51)**	-	-	-
		2.52	0.50	325(8)	0.7	-180(74)**	-	-	-

3.02	0.50	313(8)	-0.7	-322(102)**	-	-	-
Average values		319(3)	0.5	69(15)	0.1	0.22(0.05)	0.1

(*) Numbers in parenthesis denotes uncertainty (1σ) associated with the data. (**) Activity concentrations not used in calculating average values, where z_{score} values are calculated with respect to the average values.

All a_{212Pb} were precisely calculated, getting relative uncertainties less than 2.6%, and all a_{212Pb} were statistically compatible with the one obtained for thoron (473(159) mBq m⁻³) for a confidence interval of 68%, where the average a_{212Pb} was 319(3) mBq m⁻³. Besides, all $|z_{score}^{212Pb}|$ were less than 0.7, achieving an average z_{score}^{212Pb} of 0.5. Therefore, the consistence and reproducibility of the methodology developed in this study was good in the case of the ²¹²Pb. For the ²¹²Bi, it is possible to observe that the three first a_{212Bi} values agreed well with the average one (69(15) mBq m⁻³), obtaining an average z_{score}^{212Bi} of 0.1, this same tendency being the one followed by the a_{212Bi}/a_{212Pb} ratios, which further proves the good reproducibility of the methodology. Note that from the fourth counting, that is, the case corresponding to $\Delta t_{s(2)-c(1)} = 2$ hours, a_{212Bi} started to be negative. This is consistent since 3.5 half-lives of the ²¹²Bi have been consumed and, consequently, the equation that provides a_{212Bi} (see Eq. 3.6.10) is not necessary because the ²¹²Bi is already following the same behavior that its parent, that is, they are in secular equilibrium. According to the results shown in Table 3.6.4 for a_{212Bi} , it is possible to establish that the total time ($\Delta t_s + \Delta t_{s(2)-c(1)} + \Delta t_c$) within which the ²¹²Bi determination can be precisely accomplished was approximately 2.5 hours.

Table 3.6.5

Flow (ϕ), counting duration (Δt_c), activity concentrations of ²¹⁴Pb and ²¹⁴Bi and ²¹⁴Bi/²¹⁴Pb activity ratio for different $\Delta t_{s(2)-c(1)}$ values (1 hour-sampling, September 13, 2021). The activity concentration obtained for ²²²Rn at 8:00 UTC was 9.6(0.9) Bq m⁻³.*

Filter code	ϕ (m ³ h ⁻¹)	$\Delta t_{s(2)-c(1)}$ (h)	Δt_c (h)	²¹⁴ Pb (Bq m ⁻³)	z_{score}^{214Pb}	²¹⁴ Bi (Bq m ⁻³)	z_{score}^{214Bi}	$\frac{^{214}Bi}{^{214}Pb}$	$z_{score}^{214Bi/^{214}Pb}$
A107	612	0.45	0.50	7.71(0.18)	-1.4	3.2(0.3)	1.9	0.41(0.04)	1.7
		0.98	0.50	7.62(0.19)	-1.8	1.5(0.6)	-1.3	0.19(0.08)	-1.2
		1.50	0.50	7.9(0.2)	-0.6	-1.2(1.4)**	-	-	-
		2.00	0.50	7.8(0.3)	-0.7	-4(3)**	-	-	-
		2.52	0.50	8.1(0.4)	0.2	-15(6)**	-	-	-
		3.02	0.50	9.1(0.5)	2.0	-47(13)**	-	-	-
		Average values		8.03(0.13)	1.1	2.4(0.3)	1.6	0.30(0.05)	1.5

(*) Numbers in parenthesis denotes uncertainty (1σ) associated with the data. (**) Activity concentrations not used in calculating the average values, where z_{score} values are calculated with respect to the average values.

For the $^{214}\text{Pb} - ^{214}\text{Bi}$ (see Table 3.6.5), all $a_{214\text{Pb}}$ were approximately 0.8 times the one obtained for radon ($9.6(0.9) \text{ Bq m}^{-3}$). This is consistent with $^{214}\text{Pb}/^{222}\text{Rn}$ measurements previously shown in Section 3.6.3.1 (see Table 3.6.2). In addition, all $a_{214\text{Pb}}$ were statistically comparable with the average one ($8.03(0.13)$) for a significance level of 5%, achieving an average $z_{score}^{214\text{Pb}}$ of 1.1, demonstrating the good consistency and reproducibility of the methodology in the case of the ^{214}Pb . Then, for the ^{214}Bi , the two first values of $a_{214\text{Bi}}$ shown in Table 3.6.5 agreed well with the average one ($2.4(0.3) \text{ Bq m}^{-3}$), obtaining $|z_{score}^{214\text{Bi}}|$ values less than 1.9, occurring the same for $z_{score}^{214\text{Bi}/^{214}\text{Pb}}$. Note that $a_{214\text{Bi}}$ started to be negative from a certain $\Delta t_{s(2)-c(1)}$ (1.50 hours), as previously occurred for the ^{212}Bi , which is reasonable because the total time consumed for $\Delta t_{s(2)-c(1)} = 1.50$ hours was 3 hours. Consequently, the estimated total time within which ^{214}Bi can be determined in a proper way was approximately 2.5 hours.

With respect to the sampling carried out on September 15, 2021 whose duration was 0.5 hours, a study analogous to the previous one (sampling carried out on September 13, 2021) was done. In Tables F3 and F4 (see Supplementary Material-F), the results of a_p , a_d and a_d/a_p were shown for $^{212}\text{Pb} - ^{212}\text{Bi}$ and $^{214}\text{Pb} - ^{214}\text{Bi}$, respectively, varying $\Delta t_{s(2)-c(1)}$ and fixing Δt_c at 0.5 hours. All $a_{212\text{Pb}}$ were similar to each other, achieving an average $z_{score}^{212\text{Pb}}$ of 0.7, and the $|z_{score}^{212\text{Bi}}|$ values were less than 0.8 for positive $a_{212\text{Bi}}$ (see Table F3). The $a_{212\text{Bi}}$ values became negative when $\Delta t_{s(2)-c(1)} \approx 2$ hours, that is, for a total time of about 3 hours that is similar to the total critical time found for the previous sampling (September 13, 2021) which is consistent. For the ^{214}Pb and ^{214}Bi (see Table F4), all $a_{214\text{Pb}}$ were statistically compatible with the average one ($2.36(0.07) \text{ Bq m}^{-3}$) for a significance level of 5%. For the ^{214}Bi , the $z_{score}^{214\text{Bi}}$ resulting from the first four measurements were less than 0.7. Therefore, the total time estimated to properly determine the ^{214}Bi was about 2 hours which agrees with the total time found for ^{214}Bi in the previous sampling (September 13, 2021), which further proves the consistency and reproducibility of the developed methodology.

The fact that $a_{212\text{Bi}}$ and $a_{214\text{Bi}}$ started to be negative from a certain total time can also be explained from a mathematical point of view. Rewriting Eq. 3.6.10 as $a_d = (\phi C_{ds})^{-1} (F_1 - F_2 - F_3)$, where $F_1 = \frac{\partial a_d}{\partial N_d} N_d \phi C_{ds} > 0$ and $-(F_2 + F_3) = \frac{\partial a_d}{\partial N_p} N_p \phi C_{ds} < 0$, it is possible to analyze the behavior of the F_i factors ($i = 1, 2, 3$), which are plotted in Figs. F2 and F3 (see Supplementary Material-F), having fixed Δt_c at 0.5 hours, and Δt_s at 1 hour and 0.5 hours (for samplings carried out on September 13, 2021 and September 15, 2021, respectively). As can be seen in Figs. F2 and F3 ($\Delta t_s = 1 \text{ h}$ and 0.5 h , respectively), the F_1 factor is much higher than F_2 and F_3 when $\Delta t_{s(2)-c(1)}$ tends to be zero for both cases (^{212}Bi and ^{214}Bi). However, as $\Delta t_{s(2)-c(1)}$ increases, F_2 and F_3 are gaining importance, especially for F_2 . Consequently, at a certain $\Delta t_{s(2)-c(1)}$ value, $F_2 + F_3$ are higher than F_1 and, therefore, $a_{212\text{Bi}}$ and $a_{214\text{Bi}}$ become negative. This occurs when $\Delta t_{s(2)-c(1)}$ is about 2 and 1.5 hours for ^{212}Bi and ^{214}Bi , respectively (case for $\Delta t_s = 1 \text{ h}$), which is consistent with the $\Delta t_{s(2)-c(1)}$ values found when $\Delta t_s = 0.5 \text{ h}$, that are about 2 hours for ^{212}Bi and ^{214}Bi .

To complete the analysis about how the precision of the calculations for ^{212}Pb , ^{212}Bi , ^{214}Pb and ^{214}Bi , and their ratios depended on $\Delta t_{s(2)-c(1)}$, Δt_s as well as the concentrations in air, that is, a_i ($i = p$ (parent) or d (daughter)), a theoretical study is shown below in the case of the relative uncertainties obtained for a_d/a_p considering different values of $\Delta t_{s(2)-c(1)}$, Δt_s and a_p when samplings are carried out using an ASS-500 sampler. Therefore, this analysis allows us to know the precision level by which is possible to calculate the disequilibrium existing between the parent and daughter for each couple of radionuclides.

3.6.3.5. Dependence of the a_d/a_p precision on varying $\Delta t_{s(2)-c(1)}$, Δt_s and a_p

An estimative analysis was performed on the precision (relative uncertainty, σ_r) by which is possible to determine the disequilibria between $^{212}\text{Pb} - ^{212}\text{Bi}$ and $^{214}\text{Pb} - ^{214}\text{Bi}$. The σ_r values were plotted in Fig. 3.6.3 considering different C values, $C = a_d/a_p$, achieving to simulate several levels of disequilibrium, where $C = 0.25$ (high disequilibrium), $C = 0.50$ (medium disequilibrium) and $C = 0.75$ (low disequilibrium). Furthermore, the sampling duration, Δt_s , was fixed at 0.5 hours and 1 hour, the counting time, Δt_c , was fixed at 0.5 hours for all cases analyzed, and the time elapsed between the sampling end and the counting start, $\Delta t_{s(2)-c(1)}$, was ranged from 0.5 hours to 3 hours. Then, the activity concentration of the parent radionuclides, a_p , was fixed at 0.1, 0.2 and 0.3 Bq m $^{-3}$ (for ^{212}Pb), and at 5, 12.5 and 20 Bq m $^{-3}$ (for ^{214}Pb), covering the typical a_p values obtained for each radionuclide in the cases of low, medium and high concentration levels, respectively.

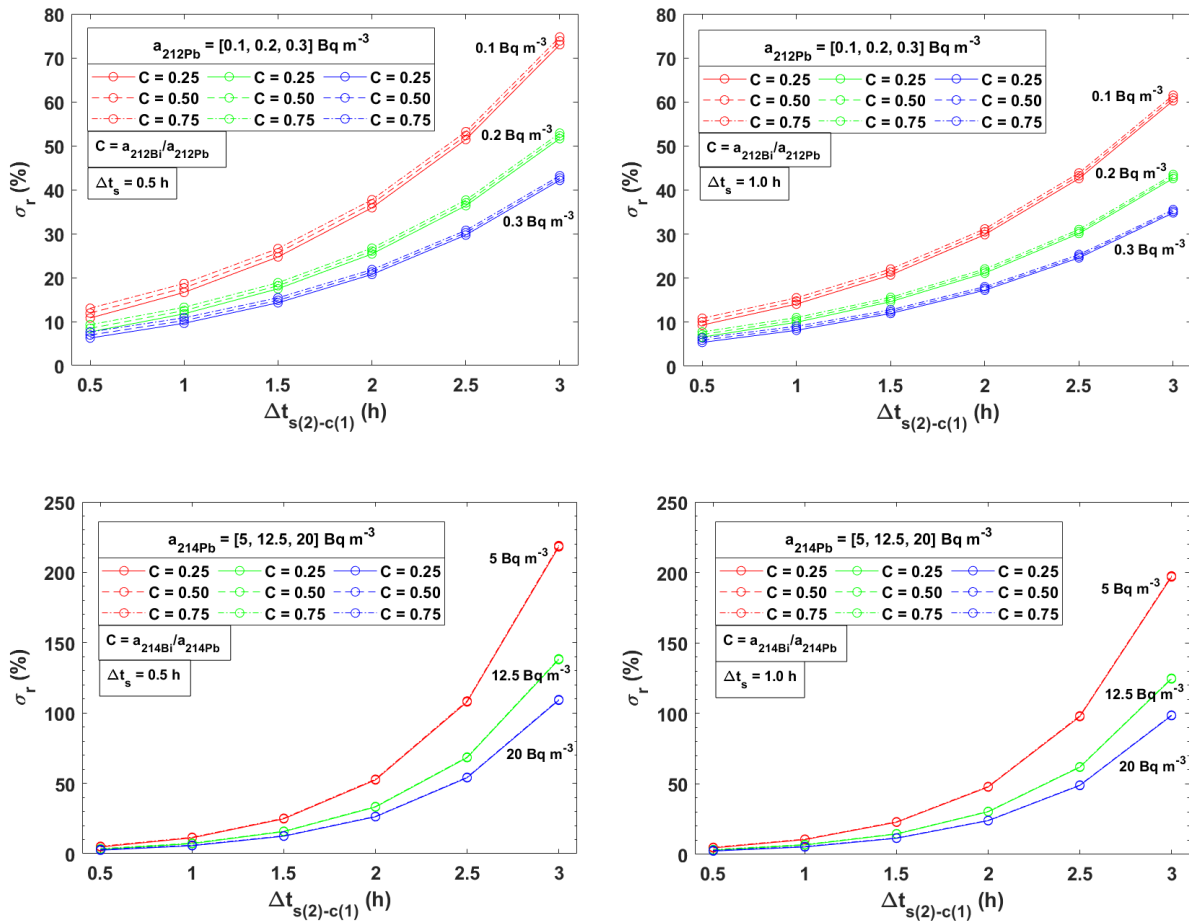


Figure 3.6.3. Calculated relative uncertainties, σ_r (%), for several activity concentration ratios, C , of ^{212}Bi - ^{212}Pb and ^{214}Bi - ^{214}Pb . Counting times were fixed at 0.5 h and the time elapsed between the sampling end and the counting beginning, $\Delta t_{s(2)-c(1)}$, was varied from 0.5 h to 3 h (sampling time: 0.5 h and 1 h). The activity concentrations of the parent radionuclides in air, $a_{212\text{Pb}}$ and $a_{214\text{Pb}}$, were fixed at 0.1, 0.2, 0.3 Bq m^{-3} and 5, 12.5, 20 Bq m^{-3} , respectively.

It is possible to observe that the σ_r dependence on a_p becomes stronger as $\Delta t_{s(2)-c(1)}$ increases. This is consistent with the σ_r behavior previously shown in Figs. 3.6.1 and 3.6.2 for a_d/a_p when using an ASS-500 sampler (see Section 3.6.3.3), where σ_r did not change significantly when varying a_p , since for the samplings analyzed in Section 3.6.3.3, $\Delta t_{s(2)-c(1)}$ was not a high value (~ 0.4 hours). The σ_r increases more quickly as $\Delta t_{s(2)-c(1)}$ increases in the case of the $^{214}\text{Pb} - ^{214}\text{Bi}$ compared to $^{212}\text{Pb} - ^{212}\text{Bi}$. For $\Delta t_s = 0.5$ hours and $\Delta t_{s(2)-c(1)} = 2.5$ hours, σ_r values ranged from 50% to 110% in the case of $^{214}\text{Bi}/^{214}\text{Pb}$, while for $^{212}\text{Bi}/^{212}\text{Pb}$, the σ_r values ranged from 30% to 53%. Then, for $\Delta t_s = 1$ hour and $\Delta t_{s(2)-c(1)} = 2.5$ hours, σ_r reached values ranged from 50% to 100% for $^{214}\text{Bi}/^{214}\text{Pb}$, while for $^{212}\text{Bi}/^{212}\text{Pb}$, the σ_r values ranged from 25% to 44%. Consequently, a good precision is more difficult to be achieved for the $^{214}\text{Bi}/^{214}\text{Pb}$ ratio, which is logical because the half-lives of ^{214}Pb and ^{214}Bi are much smaller than the ^{212}Pb and ^{212}Bi ones.

Note that for the same a_p value, σ_r has a weak dependence on C regardless of the selected $\Delta t_{s(2)-c(1)}$ value, which is especially true for the $^{214}\text{Pb} - ^{214}\text{Bi}$ couple. This means that the disequilibrium for each couple of radionuclides can be determined with the similar precision regardless of how significative that disequilibrium is. This agrees well with the behavior shown in Figs. 3.6.1 and 3.6.2, where σ_r was almost constant for all samplings studied.

Regarding the σ_r dependence on $\Delta t_{s(2)-c(1)}$, it is possible to observe that σ_r increases as $\Delta t_{s(2)-c(1)}$ increases for all cases considered, which is logical since as $\Delta t_{s(2)-c(1)}$ increases, more disintegrations of the radionuclides take place and, consequently, it is more complicated to get information of the disequilibria in a precise way. Furthermore, note that σ_r values are smaller when $\Delta t_s = 1$ hour than the ones obtained when $\Delta t_s = 0.5$ hours for the same value of $\Delta t_s + \Delta t_{s(2)-c(1)}$, but as shown in Section 3.6.3.4, as Δt_s increases, a_d becomes negative for shorter $\Delta t_{s(2)-c(1)}$ values. However, in Section 3.6.3.4, it has been demonstrated that the total times ($\Delta t_s + \Delta t_{s(2)-c(1)} + \Delta t_c$), within which the ^{212}Pb , ^{212}Bi , ^{214}Pb and ^{214}Bi , and their ratios can be determined, are very similar regardless of the selected Δt_s value, proving the consistency of the methodology developed in this study.

3.6.4. Conclusions

The main conclusions of this work are:

1. In the present study, a novel and precise methodology was developed to determine ^{212}Pb , ^{212}Bi , ^{214}Pb and ^{214}Bi contained in atmospheric aerosols using an ASS-500 sampler. The results obtained for the ^{212}Pb agreed well with the ones measured for ^{220}Rn . The activity concentrations for the ^{212}Bi were less than the ^{212}Pb ones. Regarding the $^{214}\text{Pb} - ^{214}\text{Bi}$ couple, the ^{214}Pb activity concentrations obtained in air were in good agreement with the measured ^{222}Rn , where the disequilibria found between ^{214}Bi and ^{214}Pb (between 0.5 and 0.7) agree with previous studies for similar meteorological conditions. All activity concentrations obtained for ^{214}Bi in air were less than ^{214}Pb ones, which is consistent with the expected behavior of

them. The precisions obtained for ^{214}Pb and ^{214}Bi concentrations and their activity ratios in air were good.

2. The residence times were estimated using $^{212}\text{Bi}/^{212}\text{Pb}$ and $^{214}\text{Pb}/^{222}\text{Rn}$ ratios, obtaining statistically compatible residence times for each sampling, achieving all $|z_{\text{score}}| \leq 2$. All F_{eq} values achieved for both series (radon and thoron daughters) were consistent with the data reported in the literature, which all of them were statistically compatible with ≤ 1 .
3. The precisions of the ^{212}Pb , ^{212}Bi , ^{214}Pb and ^{214}Bi determinations obtained when using an ASS-500 sampler were two times better than those obtained when using a PM_{10} sampler, which is due to the difference between their air flows.
4. For the tests of the consistency, reproducibility and validity range of the methodology, two samplings were carried out, whose durations (Δt_s) were 1 h and 0.5 h, respectively, and the counting durations (Δt_c) were fixed at 0.5 h. The time elapsed between sampling end and counting start, $\Delta t_{s(2)-c(1)}$, was varied verifying that all activity concentrations for each radionuclide were very similar to each other. The total times ($\Delta t_s + \Delta t_{s(2)-c(1)} + \Delta t_c$) within which ^{212}Bi and ^{214}Bi can be precisely determined were found to be 2 – 2.5 hours for $\Delta t_s = 0.5$ h and 1 h.
5. An analysis of the dependence of relative uncertainty, σ_r , on the ^{212}Pb and ^{214}Pb activity concentrations in air, Δt_s and $\Delta t_{s(2)-c(1)}$ was carried out for the $^{212}\text{Bi}/^{212}\text{Pb}$ and $^{214}\text{Bi}/^{214}\text{Pb}$ activity ratios. For specific ^{212}Pb and ^{214}Pb concentrations, almost the same values for σ_r were found regardless of the disequilibrium level between ^{212}Bi and ^{212}Pb , and between ^{214}Bi and ^{214}Pb . Furthermore, the σ_r values were smaller when $\Delta t_s = 1$ h than the ones obtained when $\Delta t_s = 0.5$ h for the same $\Delta t_s + \Delta t_{s(2)-c(1)}$ value. However, regardless of the selected Δt_s value, the estimated total times, within which the developed methodology provides relatively precise results, were very similar, which also verifies the good consistency and reproducibility of this methodology.

Chapter 4: General Conclusions

4.1. CONCLUSIONS

From the analysis of the results obtained in the research articles shown in this Thesis, it is possible to obtain the following main conclusions:

1. When calibrating in efficiency varying the energy, E_γ , low precision and accuracy are obtained compared with those resulting when calibrating varying the sample thickness, h . This is caused by the much more significant influence of the true coincidence summing (TCS) effects for the first case, as well as the uncertainties of the experimental *FEPEs* increase due to the contribution of the gamma emission probability uncertainties. Consequently, in the case of determining artificial radionuclides, it would be more advisable to be carried out analogously to the procedure followed when measuring natural radionuclides, that is, calibrating in efficiency by varying h instead of E_γ , and using standards which contain those artificial radionuclides. For a proper efficiency calibration, well homogenized standards are essential in order to assure the concentration of each radionuclide is the same regardless of the standard aliquot selected for its measurement.
2. To correct the self-absorption effects to obtain the *FEPE* for the problem samples and thus considering the differences between the calibration and problem samples regarding their compositions and densities, a general function for the mass attenuation coefficient was obtained. For this, two regions were distinguished: $Z \leq 26$ and $Z > 26$, where $Z = 26$ is the atomic number for Fe.
3. The validity ranges of the self-absorption corrections provided by different models (Cutshall and Appleby models for coaxial and well-type detectors, respectively) were analyzed in depth. For both models, improper self-absorption effect corrections were obtained for samples whose apparent density and average atomic number, $\langle Z \rangle$, are relatively high, finding a critical value of the linear attenuation coefficient about 3 cm^{-1} at 63 keV (^{234}Th) when applying both models.
4. When carrying out an efficiency calibration varying E_γ , a novel method was developed to correct the TCS effects, where several distances between the sample bottom and detector, d , were chosen (from 0 to 65 mm) for the efficiency calibration. The corrected experimental *FEPEs* were fitted versus E_γ for each d , demonstrating that for $d = 35 \text{ mm}$, the fitting function $\varepsilon_c(E_\gamma, d = 35 \text{ mm})$ provided the best fit. The $\varepsilon_c(E_\gamma, d = 35 \text{ mm})$ function was validated for a wide variety of sample types, achieving good z_{score} values in general for artificial and natural radionuclides.
5. The methodology employed for the TCS effect corrections was also used to properly correct the self-absorption effects in the case of coaxial detectors, demonstrating that as d increased, the correction provided by the Cutshall model was more proper.
6. In the case of the ^{226}Ra determination for samples characterized by having high ^{222}Rn losses such as phosphogypsum and aqueous samples, it was proven that it is much more recommendable to be carried out using its gamma emission (186 keV) than using its daughters (^{214}Pb and ^{214}Bi). When selecting $E_\gamma = 186 \text{ keV}$ for the ^{226}Ra determination, the precision of the obtained activity concentration is less than that resulting when using ^{214}Pb and ^{214}Bi . This is due to the need for considering the contribution of the ^{235}U interference uncertainty at 186 keV, and because of the Compton continuum is relatively high at that energy. Moreover, the minimum detectable activity concentration at 186 keV is higher compared with that obtained for its daughters at energies such

as 352 keV and 609 keV, respectively, which also occurs because of the relatively high Compton continuum at 186 keV.

7. For the determination of radionuclides in atmospheric filters, the granular certified reference materials (CRMs), selected for the efficiency calibration, were added onto the filters reproducing the same geometry than the particulate matter (PM) one when depositing onto the filter. This makes this efficiency calibration method be more accurate than the typical methods that use liquid CRMs. When using rectangular and square filters, they were cut in several pieces which were placed one piece on top of the other, making easier to get the same geometry than the one achieved when measuring these filter types, and properly reproducing the distribution of the PM deposited onto the problem filters.
8. For the methodology developed to determine the short-lived progenies of the radon and thoron (^{214}Pb and ^{214}Bi , and ^{212}Pb and ^{212}Bi , respectively), its consistency, reproducibility and validity range were tested, carrying samplings whose durations (Δt_s) were 1 h and 0.5 h, and the counting durations (Δt_c) were fixed at 0.5 h. The time elapsed between sampling end and counting start, $\Delta t_{s(2)-c(1)}$, was varied verifying that all activity concentrations for each radionuclide were very similar to each other. The total times ($\Delta t_s + \Delta t_{s(2)-c(1)} + \Delta t_c$) within which ^{212}Bi and ^{214}Bi can be precisely determined were found to be 2 – 2.5 hours for $\Delta t_s = 0.5$ h and 1 h, and $\Delta t_c = 0.5$ h.
9. The residence times obtained for each sampling by using the couples $^{214}\text{Pb}/^{222}\text{Rn}$ and $^{212}\text{Bi}/^{212}\text{Pb}$, that were ranged between about 1 h and 3 h, shew slight differences but they were statistically compatible in general. Regarding the equilibrium factors obtained for each sampling in the case of the radon and thoron daughters, all of them were statistically compatible with ≤ 1 , proving the good validity of the developed methodology.

4.2 FUTURE LINES OF RESEARCH

Considering the findings achieved in this Thesis, it is possible to establish several future lines of research such as:

- To calibrate in efficiency also considering the radius of the sample as another variable. This would allow us to obtain a *FEPE* function which could be applied for a wider range of geometry types.
- To develop an experimental model for the proper self-absorption correction in the case of well-type detectors when measuring samples whose apparent density and $\langle Z \rangle$ are relatively high. This would allow us to properly determine radionuclides contained in those sample types without needing to use simulation codes and to characterize the detectors chosen for the measurement of those samples.
- Regarding the ^{226}Ra measurement, to study in depth the ^{222}Rn losses for a wide variety of sample matrices and geometries, and varying the time elapsed between the sample preparation and its measurement. This research would be very interesting, allowing us to know for which cases the ^{226}Ra determination can be carried out by means of its daughters, and those cases for which it is necessary to employ its gamma emission energy (186 keV) for its proper measurement.
- The analysis of the air aerosol residence time dependence on the aerodynamic diameter (ad) of the particles that the aerosols are composed of. This could be interested in order to check the

affinity of the radionuclides with the ad , proving how different the air aerosol residence time is if considering couples of radionuclides belonging to air aerosols with different ad .

4.3 CONCLUSIONES

Del análisis de los resultados obtenidos en los artículos de investigación mostrados en esta Tesis, es posible llegar a las siguientes conclusiones:

1. Cuando se calibra en eficiencia variando la energía, E_γ , se obtienen una precisión y exactitud peores en comparación con las resultantes de calibrar variando el espesor de la muestra, h . Esto es causado por la influencia mucho más significativa de los efectos verdaderos de suma por coincidencia para el primer caso, así como que las incertidumbres de las *FEPEs* experimentales aumentan debido a la contribución de la incertidumbre de la probabilidad de emisión gamma. Consecuentemente, en el caso de determinar radionucleidos artificiales, sería más aconsejable llevarla a cabo de forma análoga al procedimiento seguido cuando se miden radionucleidos naturales, es decir, calibrando en eficiencia variando h en lugar de E_γ , y usando patrones que contengan esos radionucleidos artificiales. Para una calibración en eficiencia apropiada, es esencial que los patrones estén bien homogeneizados para asegurar que las concentraciones de cada radionucleido son las mismas independientemente de la alícuota de patrón seleccionada para su medida.
2. Para corregir los efectos de autoabsorción para obtener la *FEPE* para la muestra problema y, por lo tanto, considerándose las diferencias entre las muestras de calibración y problema en lo referente a sus composiciones y densidades, se obtuvo una función general para el coeficiente de atenuación másico. Para ello, se distinguieron entre dos regiones: $Z \leq 26$ y $Z > 26$, donde $Z = 26$ es el número atómico para el Fe.
3. Los rangos de validez de las correcciones de autoabsorción proporcionadas por diferentes modelos (modelos de Cutshall y Appleby para detectores coaxiales y de tipo pozo, respectivamente) fue analizada en profundidad. Para ambos modelos, se obtuvieron correcciones de autoabsorción inapropiadas para muestras cuya densidad aparente y número atómico promedio, $\langle Z \rangle$, son relativamente altos, encontrándose un valor crítico del coeficiente de atenuación lineal en torno a 3 cm^{-1} a 63 keV (^{234}Th) cuando se aplican ambos modelos.
4. Cuando se calibra en eficiencia variando E_γ , un nuevo método se ha desarrollado para corregir los efectos TCS, donde diversas distancias entre la base de la muestra y el detector, d , fueron escogidas (desde 0 a 65 mm) para la calibración en eficiencia. Las *FEPEs* experimentales corregidas fueron ajustadas versus E_γ para cada d , demostrándose que para $d = 35 \text{ mm}$, la función de ajuste $\varepsilon_c(E_\gamma, d = 35 \text{ mm})$ proporcionó el mejor ajuste. La función $\varepsilon_c(E_\gamma, d = 35 \text{ mm})$ fue validada para una amplia variedad de tipos de muestras, lográndose valores satisfactorios de Z_{score} en general para radionucleidos naturales y artificiales.
5. La metodología empleada para las correcciones de efectos TCS fue también usada para corregir de una forma apropiada los efectos de autoabsorción en el caso de detectores coaxiales, demostrándose que conforme d aumentaba, la corrección proporcionada por el modelo de Cutshall era más adecuada.
6. En el caso de la determinación de ^{226}Ra para muestras caracterizada por tener elevadas pérdidas de ^{222}Rn tales como fosfoyesos y muestras de aguas, se ha demostrado que es mucho más

recomendable llevarlo a cabo mediante su emisión gamma (186 keV) en lugar de usar sus descendientes (^{214}Pb y ^{214}Bi). Al seleccionar $E_\gamma = 186$ keV para la determinación de ^{226}Ra , la precisión de la concentración de actividad obtenida es menor que la resultante de usar ^{214}Pb y ^{214}Bi . Esto es debido a la necesidad de considerar la contribución de la incertidumbre de la interferencia de ^{235}U a 186 keV, y porque el Continuo de Compton es relativamente grande a esa energía. Además, la mínima concentración de actividad detectable a 186 keV es mayor en comparación con la obtenida para sus descendientes para energías como 352 keV y 609 keV, respectivamente, lo cual también ocurre por el Continuo de Compton relativamente grande a 186 keV.

7. Para la determinación de radionucleidos en aerosoles atmosféricos, materiales granulares de referencia certificados (MRC), seleccionados para la calibración en eficiencia, se añadieron a los filtros reproduciendo la misma geometría que la de la materia particulada (MP) al depositarse en el filtro. Esto hace que este método de calibración en eficiencia tenga mayor exactitud que los métodos típicos, los cuales usan MRCs líquidos. Al usarse filtros rectangulares y cuadrados, éstos fueron cortados en diversos trozos y colocados uno encima del otro, haciendo que se consiga con mayor facilidad la misma geometría que la lograda al medir este tipo de filtro, y reproduciéndose adecuadamente la distribución de MP depositada en los filtros problema.
8. Para la metodología desarrollada para determinar los descendientes de corta semivida del radón y torón (^{214}Pb y ^{214}Bi , y ^{212}Pb y ^{212}Bi , respectivamente), su consistencia, reproducibilidad y rango validez fueron comprobados, llevando a cabo muestreos cuyas duraciones (Δt_s) fueron de 1 h y 0.5 h, y las duraciones de recuento (Δt_c) fueron fijadas a 0.5 h. El tiempo transcurrido entre fin de muestreo e inicio de recuento, $\Delta t_{s(2)-c(1)}$, se varió verificándose que todas las concentraciones de actividad para cada radionucleido eran muy similares entre sí. El tiempo total ($\Delta t_s + \Delta t_{s(2)-c(1)} + \Delta t_c$) dentro del cual el ^{212}Bi and ^{214}Bi se pueden determinar con precisión, fueron de 2 – 2.5 horas para $\Delta t_s = 0.5$ h y 1 h, y $\Delta t_c = 0.5$ h.
9. Los tiempos de residencia obtenidos para cada muestreo usando las parejas $^{214}\text{Pb}/^{222}\text{Rn}$ y $^{212}\text{Bi}/^{212}\text{Pb}$, que estuvieron comprendidos entre en torno a 1 h y 3h, mostraron leves diferencias, pero fueron compatibles estadísticamente en general. Respecto a los factores de equilibrio obtenidos para cada muestreo en el caso de los descendientes del radón y torón, todos ellos fueron estadísticamente compatible con ≤ 1 , demostrándose la buena validez de la metodología desarrollada.

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ANNEX I – SUPPLEMENTARY MATERIAL

SUPPLEMENTARY MATERIAL-A

Table A.1

Experimental efficiency values (ϵ_c^{exp}) calculated in the calibration matrix of the RGU-1 standard.

$E(\text{keV})$ $h \text{ (mm)}$	46	63	93	186	242	295	352
5	0.224(2)	0.233(3)	0.231(3)	0.1675(16)	0.1227(12)	0.1037(6)	0.0869(4)
10	0.173(3)	0.195(3)	0.197(4)	0.141(2)	0.1074(15)	0.0883(8)	0.0741(5)
15	0.1425(19)	0.166(2)	0.177(3)	0.1207(14)	0.0904(10)	0.0755(5)	0.0638(4)
20	0.117(2)	0.134(3)	0.140(4)	0.1022(18)	0.0819(14)	0.0659(7)	0.0577(5)
25	0.0998(19)	0.118(2)	0.124(3)	0.0926(14)	0.0679(10)	0.0587(6)	0.0508(4)
30	0.0889(16)	0.1066(19)	0.112(2)	0.0857(12)	0.0642(9)	0.0541(5)	0.0454(3)
35	0.0778(16)	0.0942(19)	0.097(2)	0.0731(12)	0.0590(9)	0.0485(5)	0.0417(3)
40	0.0708(13)	0.0843(16)	0.099(2)	0.0690(10)	0.0540(7)	0.0447(4)	0.0380(3)
45	0.0634(13)	0.0756(16)	0.088(2)	0.0646(10)	0.0477(7)	0.0405(4)	0.0348(3)
RN	210Pb	234Th	234Th	226Ra+235U	214Pb	214Pb	214Pb
P_γ	0.0425(4)	0.0375(8)	0.0215(19)	0.0614(6)	0.0727(2)	0.1841(4)	0.3560(7)
$E(\text{keV})$ $h \text{ (mm)}$	609	768	934	1120	1238	1765	
5	0.0433(3)	0.0344(8)	0.0280(10)	0.0246(4)	0.0239(6)	0.0218(3)	
10	0.0385(3)	0.031(10)	0.0265(13)	0.0221(5)	0.0202(7)	0.0188(4)	
15	0.0332(2)	0.0275(7)	0.0218(9)	0.0196(3)	0.0186(5)	0.0164(3)	
20	0.0301(3)	0.0245(9)	0.0192(11)	0.0181(4)	0.0176(7)	0.0145(4)	
25	0.0269(2)	0.0217(7)	0.0181(9)	0.0165(3)	0.0157(6)	0.0134(3)	
30	0.0247(2)	0.0212(6)	0.0170(8)	0.0151(3)	0.0140(5)	0.0123(3)	
35	0.0228(2)	0.0191(6)	0.0149(8)	0.0138(3)	0.0135(5)	0.0112(3)	
40	0.02101(17)	0.0179(5)	0.0141(6)	0.0131(2)	0.0121(4)	0.0106(2)	
45	0.01933(17)	0.0158(5)	0.0142(7)	0.0116(2)	0.0111(4)	0.0092(2)	
RN	214Bi	214Bi	214Bi	214Bi	214Bi	214Bi	
P_γ	0.4549(19)	0.04892(16)	0.0310(10)	0.1491(3)	0.05831(14)	0.1531(5)	

Table A.2

Experimental efficiency values (ϵ_c^{exp}) calculated in the calibration matrix of the RGTh-1 and RGK-1 standards.

$E(\text{keV})$ $h \text{ (mm)}$	129	238	338	583	727	860	911
5	0.139(4)	0.1343(12)	0.0920(10)	0.0431(4)	0.0474(11)	0.0377(12)	0.0356(4)
10	0.119(3)	0.1107(11)	0.0767(12)	0.0380(3)	0.0408(7)	0.0318(7)	0.0311(2)
15	0.094(2)	0.091(4)	0.064(2)	0.0329(2)	0.0348(5)	0.0274(6)	0.02695(19)
20	0.093(3)	0.085(2)	0.0591(7)	0.0305(2)	0.0327(6)	0.0250(7)	0.0249(2)
25	0.077(4)	0.0755(16)	0.0506(8)	0.0279(3)	0.0284(8)	0.0226(8)	0.0222(3)
30	0.074(3)	0.0673(12)	0.0470(6)	0.0253(3)	0.0271(7)	0.0210(7)	0.0206(2)
35	0.068(3)	0.0617(11)	0.0429(7)	0.0238(3)	0.0251(7)	0.0188(7)	0.0183(2)
40	0.058(3)	0.0555(8)	0.0377(6)	0.0215(2)	0.0216(6)	0.0190(6)	0.0169(2)
45	0.055(2)	0.0506(8)	0.0348(5)	0.0199(2)	0.0200(5)	0.0165(5)	0.01584(18)
50	0.0516(17)	0.0478(9)	0.0336(4)	0.01831(16)	0.0187(4)	0.0152(4)	0.01491(14)
RN	228Ac	212Pb	228Ac	208Tl	212Bi	208Tl	228Ac
P_γ	0.0250(7)	0.436(5)	0.114(4)	0.3058(11)	0.0665(4)	0.0446(4)	0.262(8)

$E(\text{keV})$ $h(\text{mm})$	968	1460	1588
5	0.0343(5)	0.0252(2)	0.0231(8)
10	0.0297(3)	0.0218(4)	0.0186(5)
15	0.0277(2)	0.0188(3)	0.0169(4)
20	0.0239(3)	0.0170(3)	0.0160(3)
25	0.0215(4)	0.0156(3)	0.0142(4)
30	0.0203(3)	0.0140(2)	0.0130(4)
35	0.0175(3)	0.01255(18)	0.0118(5)
40	0.0164(3)	0.01151(17)	0.0107(3)
45	0.0152(2)	0.01094(17)	0.0096(4)
50	0.01442(18)	0.01048(18)	0.0091(4)
RN	228Ac	40K	228Ac
P_γ	0.159(5)	0.1055(11)	0.0306(12)

Table A.3

ar_1 , ar_2 and ar_3 , χ_R^2 and relative residue values obtained for each energy after fitting efficiencies in the RGU-1 calibration matrix.

$E_\gamma(\text{keV})$	ar_1	$-ar_2(\text{mm}^{-1})$	ar_3	χ_R^2	$\langle Res \rangle (\%)$
46.539	0.235(6)	0.064(4)	0.052(3)	0.78	1.62
63.288	0.234(5)	0.049(3)	0.052(3)	0.90	1.57
92.56	0.217(6)	0.049(3)	0.063(4)	3.01	3.49
185.96	0.152(3)	0.051(3)	0.049(2)	1.55	1.83
241.979	0.112(2)	0.043(3)	0.033(3)	2.74	2.44
295.224	0.0926(12)	0.047(2)	0.0303(11)	1.88	1.25
351.932	0.0775(6)	0.043(2)	0.0238(9)	2.15	0.83
609.312	0.0368(4)	0.039(2)	0.0133(6)	1.25	0.90
768.356	0.0292(15)	0.033(2)	0.0097(6)	0.53	2.31
934.06	0.0224(6)	0.040(3)	0.0110(7)	0.49	1.91
1120.285	0.0215(4)	0.028(2)	0.0059(3)	0.70	1.41
1238.11	0.0197(7)	0.032(2)	0.0067(4)	0.50	2.44
1764.494	0.0182(5)	0.041(3)	0.0068(3)	1.15	2.30

Table A.4

ar_1 , ar_2 and ar_3 , χ_R^2 and relative residue values obtained for each energy after fitting efficiencies in the RGTh-1 and RGK-1 calibration matrices.

$E_\gamma(\text{keV})$	ar_1	$-ar_2(\text{mm}^{-1})$	ar_3	χ_R^2	$\langle Res \rangle (\%)$
129.03	0.122(5)	0.047(3)	0.041(3)	1.73	3.89
238.63	0.1195(7)	0.0505(19)	0.0396(18)	1.68	2.82
338.42	0.0857(7)	0.0442(17)	0.0237(12)	1.88	2.62
583.19	0.0364(7)	0.034(2)	0.0121(6)	2.05	1.58

727.30	0.0412(18)	0.037(2)	0.0125(8)	0.25	1.16
860.00	0.0305(12)	0.048(3)	0.0132(7)	1.23	3.23
911.16	0.0303(6)	0.0374(18)	0.0102(4)	2.02	1.11
968.97	0.0306(8)	0.033(2)	0.0082(5)	2.08	1.97
1460.83	0.0214(4)	0.0419(16)	0.0077(3)	0.93	1.18
1588.23	0.0194(8)	0.0279(18)	0.0049(3)	2.05	2.84

Table A.5

Efficiency values obtained with Genie 2000 and comparison of these values with the efficiencies obtained experimentally in the case of RGU-1 standard.

$E(\text{keV})$ $h \text{ (mm)}$	63	352	609	1120	Z (63)	Z (352)	Z (609)	Z (1120)
5	0.237(3)	0.0870(4)	0.0434(3)	0.0247(4)	1.06	0.23	0.21	0.34
10	0.185(6)	0.0745(6)	0.0385(3)	0.0216(5)	1.57	0.58	0.00	0.70
15	0.167(2)	0.0638(4)	0.0332(2)	0.0196(3)	0.39	0.00	0.00	0.00
20	0.134(3)	0.0576(5)	0.0302(3)	0.0181(4)	0.00	0.22	0.21	0.00
25	0.121(2)	0.0512(4)	0.0269(3)	0.0168(4)	0.68	0.69	0.00	0.48
30	0.1073(19)	0.0455(3)	0.0248(2)	0.0152(3)	0.25	0.19	0.33	0.12
35	0.0947(19)	0.0417(3)	0.0228(2)	0.0138(3)	0.20	0.00	0.00	0.00
40	0.0848(16)	0.0381(3)	0.02100(17)	0.0131(2)	0.23	0.09	0.03	0.00
45	0.0760(16)	0.0349(3)	0.01932(17)	0.0116(2)	0.18	0.25	0.04	0.00
				$\langle Z \rangle$	0.51	0.25	0.09	0.18

Table A.6

Efficiency values obtained with Genie 2000 and comparison of these values with the efficiencies obtained experimentally in the case of RGTh-1 and RGK-1 standards.

$E(\text{keV})$ $h \text{ (mm)}$	238	583	911	1460	Z (238)	Z (583)	Z (911)	Z (1460)
5	0.1326(5)	0.0436(4)	0.0357(4)	0.0257(2)	1.31	0.89	0.21	1.62
10	0.1122(4)	0.0381(3)	0.0312(2)	0.0221(4)	1.28	0.30	0.47	0.54
15	0.0923(3)	0.03306(19)	0.02706(18)	0.0190(3)	0.33	0.44	0.42	0.49
20	0.0847(3)	0.0307(2)	0.0250(2)	0.0172(3)	0.15	0.68	0.21	0.37
25	0.0756(4)	0.0280(3)	0.0222(3)	0.0157(3)	0.06	0.27	0.00	0.34
30	0.0674(3)	0.0255(2)	0.0207(2)	0.0142(2)	0.08	0.46	0.16	0.37
35	0.0616(3)	0.0238(3)	0.0183(2)	0.01264(18)	0.09	0.00	0.00	0.35
40	0.0555(3)	0.0216(2)	0.0170(2)	0.01159(17)	0.00	0.32	0.10	0.34
45	0.0506(2)	0.01992(19)	0.01586(18)	0.01101(17)	0.00	0.26	0.10	0.28
50	0.04740(19)	0.01843(15)	0.01489(14)	0.01053(18)	0.44	0.58	0.12	0.19
				$\langle Z \rangle$	0.37	0.42	0.18	0.49

Table A.7

Parameters resulted from fittings given by function B and comparison of relative average residues and χ_R^2 values obtained from both fittings functions (functions A and B).

E (keV)	br_1	$-br_2(mm^{-1})$	Function B		Function A	
			$\langle Res \rangle$ (%)	χ_R^2	$\langle Res \rangle$ (%)	χ_R^2
63	0.252(5)	0.0279(15)	4.14	7.11	1.57	0.90
352	0.0921(14)	0.0225(6)	2.79	27.13	0.83	2.15
911	0.0371(5)	0.0192(6)	2.92	9.97	1.11	2.02
1460	0.0260(5)	0.0196(7)	3.72	8.71	1.18	0.93
			$\langle Res \rangle_T = 3.39$		$\langle Res \rangle_T = 1.17$	

Table A.8

Parameters resulting from fittings given by function C and comparison of the relative average residues obtained from both fitting functions (functions A and C).

h (mm)	$-cr_1$	cr_2	$-cr_3$	cr_4	$\langle Res \rangle$ (%) (function C)	$\langle Res \rangle$ (%) (function A)
5	27(2)	14.8(1.2)	2.7(2)	0.149(12)	4.74	1.03
10	24(2)	12.7(1.0)	2.29(18)	0.126(10)	3.44	2.13
15	30(2)	16.0(1.3)	2.9(2)	0.160(13)	2.93	1.97
20	32(3)	16.9(1.4)	3.0(2)	0.167(13)	6.34	2.30
25	24.2(1.9)	12.5(1.0)	2.23(17)	0.123(10)	3.63	1.89
30	30(2)	15.5(1.2)	2.8(2)	0.152(12)	3.38	2.15
35	21.7(1.7)	10.9(9)	1.94(16)	0.106(9)	5.04	2.25
40	27.3(2)	13.9(1.1)	2.5(2)	0.136(11)	2.78	2.14
45	24.0(1.9)	12.0(1.0)	2.12(17)	0.116(9)	4.24	2.69
					$\langle Res \rangle_T = 4.45$	$\langle Res \rangle_T = 2.23$

Table A.9

Chemical composition (in %) of all the samples analyzed in this work.

	RGU-1	RGTh-1	RGK-1	IAEA-326	K ₂ CO ₃	Scale-1	Scale-2	IAEA-434 and CSN-PG
H								2.21
C					8.7			
O	53.354	53.5398	36.727	54.303	34.8	48.0	48.0	55.0

F							1.2
Na	0.03			0.59		3.0	4.0
Mg		0.02		0.615		5.0	9.0
Al	0.01	0.04		5.5		10.0	12.0
Si	46.4	45.0		32.68		10.0	9.0
P		0.129		0.075		0.7	0.9
S			18.398			10.0	12.0
K			44.875	1.9	56.5	5.0	2.0
Ca	0.03	0.42		1.16		7.3	3.1
Ti	0.008			0.45			
Mn		0.014		0.06		1.0	
Fe	0.03	0.13		2.667			
Ba		0.6235					
Pb	0.008	0.003					
Th		0.081					
U	0.04						
		Tionite	Ilmenite				
O	33.0		30.0				
Ti	30.0		30.0				
Fe	37.0		40.0				

SUPPLEMENTARY MATERIAL-B

Table B.1

U-ORE standard mixed with different proportions of PbS (ST10 – U indicates 10 % of uranium-ore standard and 90 % of PbS), where M_{TOTAL} is the total mass taken initially to prepare the mixtures and M_{U} and % of U are the mass of U-ORE standard and its corresponding percentage, respectively, in M_{TOTAL} . Then, M_{vial} is the total mass contained in the prepared vials, where $M_{\text{U-vial}}$ and $A(^{238}\text{U})$ are the mass of the U-ORE standard and the ^{238}U activity, respectively, in those mentioned vials.

Standard	$(M_{\text{TOTAL}} \pm 0.002) \text{ g}$	$(M_{\text{U}} \pm 0.002) \text{ g}$	% of U	$(M_{\text{vial}} \pm 0.002) \text{ g}$	$(M_{\text{U-vial}} \pm 0.002) \text{ g}$	$A(^{238}\text{U}) \text{ (Bq)}$
ST10-U	30.012	3.005	10.01	19.178	1.920	9.49(3)
ST20-U	30.059	6.021	20.03	16.851	3.375	16.67(5)
ST30-U	30.015	9.028	30.08	14.357	4.318	21.33(6)
ST40-U	30.065	12.033	40.02	12.800	5.123	25.31(8)
ST50-U	30.006	15.094	50.30	11.424	5.747	28.39(9)
ST55-U	30.009	16.497	54.97	10.879	5.980	29.54(9)
ST60-U	30.011	18.004	59.99	10.680	6.407	31.65(10)
ST70-U	30.001	21.013	70.04	9.533	6.677	32.98(10)
ST80-U	30.018	24.013	80.00	8.854	7.076	34.96(11)
ST85-U	30.000	25.502	85.01	8.670	7.370	36.41(11)
ST90-U	30.001	27.004	90.01	8.306	7.476	36.93(11)
ST94-U	30.000	28.202	94.01	8.116	7.630	37.69(11)
ST97-U	30.008	29.100	96.97	7.864	7.626	37.67(11)

Table B.2

Th-ORE standard mixed with different proportions of PbS (ST10 – Th indicates 10 % of thorium-ore standard and 90 % of PbS), where M_{TOTAL} is the total mass taken initially to prepare the mixtures and M_{Th} and % of Th are the mass of Th-ORE standard and its corresponding percentage, respectively, in M_{TOTAL} . Then, M_{vial} is the total mass contained in the prepared vials, where $M_{\text{Th-vial}}$ and $A(^{232}\text{Th})$ are the mass of the Th-ORE standard and the ^{232}Th activity, respectively, in those mentioned vials.

Standard	$(M_{\text{TOTAL}} \pm 0.002) \text{ g}$	$(M_{\text{Th}} \pm 0.002) \text{ g}$	% of Th	$(M_{\text{vial}} \pm 0.002) \text{ g}$	$(M_{\text{Th-vial}} \pm 0.002) \text{ g}$	$A(^{232}\text{Th}) \text{ (Bq)}$
ST10-Th	30.001	3.008	10.03	18.691	1.874	6.09(9)
ST20-Th	30.008	6.003	20.00	15.508	3.102	10.08(14)
ST30-Th	30.003	9.001	30.00	13.812	4.144	13.47(19)
ST40-Th	30.082	12.007	39.91	12.351	4.930	16.0(2)
ST50-Th	30.026	15.000	49.96	10.729	5.360	17.4(2)
ST55-Th	30.057	16.533	55.01	10.339	5.687	18.5(3)
ST60-Th	30.189	18.005	59.64	9.748	5.814	18.9(3)
ST70-Th	30.004	21.004	70.00	9.066	6.347	20.6(3)
ST80-Th	30.011	24.002	79.98	8.864	6.772	22.0(3)
ST85-Th	30.025	25.516	84.98	8.113	6.895	22.4(3)
ST90-Th	30.058	27.033	89.94	7.862	7.071	23.0(3)
ST94-Th	30.027	28.202	93.92	7.629	7.165	23.3(3)
ST97-Th	30.024	29.105	96.94	7.442	7.214	23.5(3)

Table B.3

U-ORE standard varying the grade of compaction having been calculated the ^{238}U activity value ($A(^{238}\text{U})$) for each case, where M_{vial} is the total mass contained in the prepared vials.

Standard	$(M_{\text{vial}} \pm 0.002) \text{ g}$	$A(^{238}\text{U}) \text{ (Bq)}$
RGU1	4.881	24.11(7)
RGU2	5.194	25.66(8)
RGU3	5.452	26.93(8)
RGU4	5.707	28.19(9)
RGU5	5.993	29.61(9)
RGU6	6.303	31.14(9)
RGU7	6.652	32.86(10)
RGU8	6.905	34.11(10)
RGU9	7.354	36.33(11)

Table B.4

Th-ORE standard varying the grade of compaction having been calculated the ^{232}Th activity value ($A(^{232}\text{Th})$) for each case, where M_{vial} is the total mass contained in the prepared vials.

Standard	$(M_{\text{vial}} \pm 0.002) \text{ g}$	$A(^{232}\text{Th}) \text{ (Bq)}$
RGTh1	4.888	15.9(2)
RGTh2	5.190	16.9(2)
RGTh3	5.455	17.7(3)
RGTh4	5.700	18.5(3)
RGTh5	6.002	19.5(3)
RGTh6	6.301	20.5(3)
RGTh7	6.652	21.6(3)
RGTh8	6.903	22.4(3)
RGTh9	7.356	23.9(3)

Table B.5

KCl standard dissolved in water varying the K concentration and having been calculated the ^{40}K activity value ($A(^{40}\text{K})$) for each case, where M_{vial} is the total mass contained in the prepared vials and $M_{\text{K-vial}}$ is the mass of the KCl standard in those mentioned vials.

Standard	$(M_{\text{vial}} \pm 0.002) \text{ g}$	$(M_{\text{K-vial}} \pm 0.002) \text{ g}$	$A(^{40}\text{K}) \text{ (Bq)}$
K-1	5.014	0.204	3.42(5)
K-2	5.083	0.325	5.44(8)
K-3	5.103	0.453	7.58(11)
K-4	5.244	0.575	9.63(14)
K-5	5.243	0.700	11.71(17)
K-6	5.412	0.825	13.8(2)
K-7	5.456	0.954	16.0(2)

K-8	5.571	1.073	18.0(3)
K-9	5.562	1.199	20.1(3)

Table B.6

U-ORE standard mixed with different proportions of activated carbon (C25 – U indicates 25 % of uranium-ore standard and 75 % of activated carbon), where the meaning of all the magnitude abbreviations shown in this table can be found in Table B.1.

Standard	(M _{TOTAL} ± 0.002) g	(M _U ± 0.002) g	% of U	(M _{vial} ± 0.002) g	(M _{U-vial} ± 0.002) g	A(²³⁸ U) (Bq)
C25-U	30.057	7.503	24.96	1.614	0.403	1.991(6)
C50-U	30.016	15.003	49.98	2.057	1.028	5.078(15)
C75-U	30.005	22.501	74.99	2.864	2.151	10.63(3)

Table B.7

Th-ORE standard mixed with different proportions of activated carbon (C25 – Th indicates 25 % of thorium-ore standard and 75 % of activated carbon), where the meaning of all the magnitude abbreviations shown in this table can be found in Table B.2.

Standard	(M _{TOTAL} ± 0.002) g	(M _{Th} ± 0.002) g	% of Th	(M _{vial} ± 0.001) g	(M _{Th-vial} ± 0.002) g	A(²³² Th) (Bq)
C25-Th	30.011	7.511	25.03	1.643	0.441	1.34(2)
C50-Th	30.005	15.007	50.01	2.323	1.162	3.78(5)
C75-Th	30.028	22.524	75.01	3.216	2.412	7.84(11)

Table B.8

Experimental efficiencies when the sample mass is not and is zero (ε_{exp} and ε_0^{exp} , whose uncertainties at 1 sigma level are $\sigma(\varepsilon_{exp})$ and $\sigma(\varepsilon_0^{exp})$, respectively) obtained for the different prepared U-ORE standards. Then, E_γ and P_γ are the selected gamma emission energies and their emission probabilities, respectively, of the radionuclides belonging to the ²³⁸U-series. On the other hand, k , η , m and $f(k\eta m)$ are the geometric parameter, the sample mass attenuation coefficient, the sample mass and the self-absorption correction factor, respectively.

46.5 KeV ----- 210Pb ; $P_\gamma = 0.0425(4)$						
ηm	ε_{exp}	$\sigma(\varepsilon_{exp})$	$k\eta m$	$f(k\eta m)$	ε_0^{exp}	$\sigma(\varepsilon_0^{exp})$
0.39189	0.50	0.02	0.05318	0.94888	0.53	0.02
0.60191	0.475	0.011	0.08168	0.92311	0.515	0.012
0.98206	0.461	0.005	0.13327	0.87912	0.524	0.006
1.91335	0.446	0.010	0.25964	0.78438	0.569	0.013
2.03605	0.445	0.009	0.27629	0.77313	0.576	0.012
2.13718	0.421	0.009	0.29002	0.76406	0.552	0.012
2.23714	0.439	0.010	0.30358	0.75527	0.581	0.013
2.34926	0.444	0.010	0.31879	0.74560	0.595	0.013
2.47078	0.410	0.010	0.33528	0.73536	0.558	0.014

2.60758	0.421	0.009	0.35385	0.72411	0.581	0.012
2.70676	0.404	0.018	0.36731	0.71613	0.57	0.03
2.88277	0.387	0.017	0.39119	0.70234	0.55	0.02
5.10106	0.339	0.005	0.69221	0.56203	0.603	0.009
7.34574	0.271	0.003	0.99682	0.46592	0.582	0.006
10.35762	0.224	0.004	1.40553	0.38032	0.590	0.011
14.51699	0.1948	0.0019	1.96996	0.30693	0.635	0.006
18.60917	0.147	0.003	2.52526	0.26074	0.562	0.012
28.18487	0.097	0.007	3.82469	0.19593	0.49	0.04
40.70507	0.072	0.003	5.52368	0.14852	0.48	0.02
46.11309	0.060	0.004	6.25755	0.13437	0.45	0.03
53.30568	0.058	0.004	7.23358	0.11916	0.49	0.03
70.6674	0.030	0.006	9.58957	0.09341	0.32	0.06
91.53547	0.029	0.005	12.42136	0.07403	0.40	0.07
121.84023	0.020	0.004	16.53372	0.05682	0.36	0.07
155.0584	0.016	0.007	21.04143	0.04527	0.36	0.16
63.29 KeV ----- ^{234}Th ; $P_\gamma = 0.038(3)$						
ηm	ε_{exp}	$\sigma(\varepsilon_{exp})$	$k\eta m$	$f(k\eta m)$	ε_0^{exp}	$\sigma(\varepsilon_0^{exp})$
0.31031	0.530	0.018	0.04211	0.95919	0.553	0.019
0.43715	0.532	0.009	0.05932	0.94323	0.564	0.010
0.6676	0.499	0.005	0.09059	0.91526	0.545	0.005
1.23489	0.493	0.008	0.16757	0.85166	0.579	0.009
1.31408	0.474	0.007	0.17832	0.84334	0.562	0.008
1.37936	0.477	0.007	0.18718	0.83657	0.570	0.008
1.44387	0.490	0.008	0.19593	0.82997	0.591	0.010
1.51623	0.488	0.008	0.20575	0.82267	0.594	0.010
1.59466	0.488	0.008	0.21640	0.81487	0.599	0.010
1.68296	0.443	0.008	0.22838	0.80623	0.549	0.010
1.74697	0.457	0.012	0.23706	0.80006	0.572	0.015
1.86056	0.427	0.013	0.25248	0.78930	0.541	0.016
2.83611	0.409	0.005	0.38486	0.70595	0.579	0.007
3.80035	0.432	0.003	0.51571	0.63737	0.678	0.005
5.08105	0.397	0.005	0.68950	0.56307	0.706	0.009
6.85867	0.3593	0.0019	0.93072	0.48385	0.743	0.004
8.59218	0.2929	0.0017	1.16596	0.42581	0.688	0.004
12.67055	0.225	0.005	1.71939	0.33503	0.672	0.015
18.02593	0.1737	0.0015	2.44612	0.26632	0.652	0.006
20.31294	0.177	0.003	2.75647	0.24590	0.720	0.012
23.37942	0.151	0.003	3.17259	0.22345	0.675	0.013
30.78674	0.093	0.008	4.17776	0.18376	0.51	0.04
39.68147	0.105	0.005	5.38478	0.15153	0.70	0.03

52.61905	0.057	0.005	7.14041	0.12047	0.47	0.04
66.76444	0.043	0.007	9.05994	0.09820	0.44	0.07
92.6 KeV ----- 234Th ; $P_\gamma = 0.056(3)$						
ηm	ε_{exp}	$\sigma(\varepsilon_{exp})$	$k\eta m$	$f(k\eta m)$	ε_0^{exp}	$\sigma(\varepsilon_0^{exp})$
0.26191	0.520	0.014	0.03554	0.96539	0.539	0.015
0.34875	0.536	0.007	0.04733	0.95431	0.562	0.007
0.50711	0.530	0.004	0.06881	0.93460	0.567	0.004
0.8981	0.368	0.007	0.12187	0.88855	0.414	0.008
0.9557	0.384	0.006	0.12969	0.88207	0.436	0.007
1.00317	0.361	0.006	0.13613	0.87678	0.412	0.007
1.05009	0.403	0.008	0.14250	0.87160	0.463	0.009
1.10271	0.407	0.007	0.14964	0.86585	0.470	0.008
1.15975	0.360	0.007	0.15738	0.85968	0.419	0.008
1.22397	0.370	0.007	0.16609	0.85282	0.434	0.008
1.27052	0.353	0.013	0.17241	0.84790	0.417	0.015
1.35314	0.373	0.015	0.18362	0.83928	0.445	0.018
2.78909	0.266	0.003	0.37848	0.70963	0.375	0.004
4.26288	0.2540	0.0009	0.57847	0.60854	0.417	0.0015
6.25176	0.2457	0.0015	0.84836	0.50828	0.483	0.003
8.99058	0.2681	0.0013	1.22002	0.41451	0.647	0.003
11.69853	0.2044	0.0011	1.58749	0.35245	0.580	0.003
18.01606	0.1046	0.0019	2.44478	0.26642	0.393	0.007
26.25628	0.1070	0.0008	3.56298	0.20607	0.519	0.004
29.83836	0.0198	0.0009	4.04907	0.18801	0.105	0.005
34.58095	0.0855	0.0012	4.69264	0.16850	0.507	0.007
46.02413	0.051	0.002	6.24547	0.13458	0.380	0.015
59.7858	0.0155	0.0013	8.11293	0.10808	0.143	0.012
79.75271	0.0328	0.0015	10.82244	0.08386	0.391	0.018
101.67042	0.023	0.002	13.79668	0.06723	0.337	0.03
186.2 KeV ----- 226Ra ; $P_\gamma^*(226\text{Ra} + 235\text{U}) = 0.062(4)$; $P_\gamma(226\text{Ra}) = 0.0351(6)$; $P_\gamma(235\text{U}) = 0.572(5)$						
ηm	ε_{exp}	$\sigma(\varepsilon_{exp})$	$k\eta m$	$f(k\eta m)$	ε_0^{exp}	$\sigma(\varepsilon_0^{exp})$
0.20599	0.419	0.014	0.02795	0.97262	0.431	0.014
0.26589	0.399	0.007	0.03608	0.96488	0.414	0.007
0.37539	0.387	0.004	0.05094	0.95095	0.407	0.004
0.64682	0.395	0.006	0.08777	0.91773	0.430	0.007
0.6883	0.401	0.007	0.09340	0.91281	0.440	0.008
0.72249	0.388	0.007	0.09804	0.90879	0.427	0.008
0.75628	0.391	0.008	0.10263	0.90484	0.432	0.009
0.79418	0.396	0.008	0.10777	0.90044	0.439	0.009
0.83526	0.384	0.008	0.11334	0.89571	0.429	0.009
0.88151	0.386	0.007	0.11962	0.89043	0.434	0.008

0.91503	0.377	0.014	0.12417	0.88664	0.425	0.016
0.97453	0.356	0.014	0.13224	0.87996	0.404	0.016
1.25857	0.361	0.005	0.17079	0.84916	0.425	0.006
1.52229	0.335	0.003	0.20657	0.82206	0.407	0.004
1.86275	0.296	0.004	0.25278	0.78909	0.375	0.005
2.39956	0.334	0.002	0.32562	0.74133	0.450	0.003
2.79799	0.287	0.002	0.37969	0.70893	0.405	0.003
3.8872	0.264	0.005	0.52749	0.63177	0.418	0.008
5.33477	0.228	0.002	0.72393	0.55024	0.415	0.004
5.93324	0.218	0.003	0.80514	0.52212	0.418	0.006
6.75454	0.211	0.003	0.91659	0.48787	0.433	0.006
8.74249	0.178	0.005	1.18636	0.42147	0.422	0.012
11.12316	0.153	0.004	1.50941	0.36381	0.419	0.011
14.60145	0.127	0.003	1.98142	0.30578	0.415	0.010
18.37735	0.105	0.005	2.49381	0.26293	0.40	0.02
295.2 K eV ----- 226Ra ----- 214Pb ; $P_\gamma = 0.193(2)$						
ηm	ε_{exp}	$\sigma(\varepsilon_{exp})$	$k\eta m$	$f(k\eta m)$	ε_0^{exp}	$\sigma(\varepsilon_0^{exp})$
0.17353	0.282	0.004	0.02355	0.97686	0.289	0.004
0.22221	0.260	0.002	0.03015	0.97052	0.268	0.002
0.31129	0.2530	0.0013	0.04224	0.95907	0.2638	0.0014
0.53228	0.255	0.003	0.07223	0.93153	0.274	0.003
0.56641	0.252	0.002	0.07686	0.92739	0.271	0.002
0.59454	0.246	0.002	0.08068	0.92399	0.267	0.002
0.62235	0.256	0.003	0.08445	0.92065	0.278	0.003
0.65354	0.255	0.003	0.08869	0.91693	0.278	0.003
0.68735	0.247	0.003	0.09327	0.91293	0.270	0.003
0.7254	0.248	0.002	0.09844	0.90845	0.273	0.002
0.75299	0.241	0.004	0.10218	0.90522	0.267	0.004
0.80196	0.227	0.005	0.10883	0.89954	0.252	0.006
0.92055	0.2332	0.0015	0.12492	0.88601	0.263	0.002
1.01505	0.2222	0.0009	0.13774	0.87546	0.2538	0.0010
1.1275	0.2103	0.0014	0.15300	0.86316	0.244	0.002
1.29264	0.2284	0.0007	0.17541	0.84558	0.2701	0.0008
1.43825	0.2049	0.0007	0.19517	0.83055	0.2467	0.0008
1.80303	0.1971	0.0017	0.24467	0.79472	0.248	0.002
2.30507	0.1834	0.0007	0.31280	0.74939	0.2447	0.0009
2.49323	0.1814	0.0011	0.33833	0.73349	0.2473	0.0015
2.77061	0.1812	0.0011	0.37597	0.71108	0.255	0.002
3.44602	0.1624	0.0017	0.46762	0.66116	0.246	0.003
4.24845	0.1566	0.0013	0.57651	0.60941	0.257	0.002
5.4363	0.1413	0.0012	0.73771	0.54527	0.259	0.002

6.69897	0.1237	0.0016	0.90905	0.49005	0.252	0.003
351.92 KeV -----	226Ra --- 214Pb ; $P_\gamma = 0.376(4)$					
ηm	ε_{exp}	$\sigma(\varepsilon_{exp})$	$k\eta m$	$f(k\eta m)$	ε_0^{exp}	$\sigma(\varepsilon_0^{exp})$
0.16211	0.2392	0.003	0.02200	0.97836	0.244	0.003
0.20751	0.2207	0.0014	0.02816	0.97243	0.2270	0.0014
0.29058	0.21089	0.0009	0.03943	0.96171	0.2193	0.0009
0.49667	0.21401	0.0017	0.06740	0.93588	0.229	0.002
0.52852	0.2119	0.0015	0.07172	0.93199	0.227	0.002
0.55477	0.20707	0.0015	0.07528	0.92880	0.223	0.002
0.58072	0.21263	0.0018	0.07880	0.92566	0.230	0.002
0.60982	0.21542	0.0016	0.08275	0.92216	0.234	0.002
0.64136	0.20894	0.0017	0.08703	0.91838	0.228	0.002
0.67688	0.20377	0.0016	0.09185	0.91416	0.223	0.002
0.70262	0.20794	0.003	0.09535	0.91113	0.228	0.003
0.74831	0.19844	0.003	0.10155	0.90577	0.219	0.003
0.83942	0.19757	0.0010	0.11391	0.89524	0.2207	0.0011
0.9068	0.18561	0.0006	0.12305	0.88757	0.2091	0.0007
0.98326	0.17924	0.0010	0.13343	0.87899	0.2039	0.0011
1.09842	0.19539	0.0005	0.14906	0.86631	0.2255	0.0006
1.19533	0.17575	0.0004	0.16221	0.85587	0.2054	0.0005
1.44548	0.17388	0.0011	0.19615	0.82981	0.2095	0.0013
1.79694	0.16426	0.0005	0.24384	0.79530	0.2065	0.0006
1.92085	0.16051	0.0007	0.26066	0.78368	0.2048	0.0009
2.11204	0.16256	0.0007	0.28660	0.76630	0.2121	0.0009
2.57923	0.14811	0.0011	0.35000	0.72642	0.204	0.002
3.13164	0.1441	0.0009	0.42496	0.68361	0.2108	0.0013
3.95579	0.13409	0.0008	0.53680	0.62741	0.2137	0.0013
4.82088	0.12122	0.0011	0.65419	0.57682	0.210	0.002
609.31 KeV -----	226Ra --- 214Bi ; $P_\gamma = 0.461(5)$					
ηm	ε_{exp}	$\sigma(\varepsilon_{exp})$	$k\eta m$	$f(k\eta m)$	ε_0^{exp}	$\sigma(\varepsilon_0^{exp})$
0.14106	0.0755	0.0014	0.01914	0.98113	0.0770	0.0014
0.17504	0.0730	0.0008	0.02375	0.97666	0.0747	0.0008
0.23744	0.0697	0.0005	0.03222	0.96854	0.0720	0.0005
0.39545	0.0698	0.0009	0.05366	0.94843	0.0735	0.0009
0.42081	0.0700	0.0008	0.05710	0.94527	0.0741	0.0008
0.44171	0.0696	0.0008	0.05994	0.94267	0.0738	0.0008
0.46237	0.0684	0.0009	0.06274	0.94011	0.0727	0.0010
0.48554	0.0703	0.0009	0.06589	0.93725	0.0750	0.0010
0.51066	0.0685	0.0008	0.06930	0.93417	0.0733	0.0009
0.53893	0.0663	0.0008	0.07313	0.93072	0.0712	0.0009
0.55943	0.0688	0.0014	0.07591	0.92823	0.074	0.002

0.59581	0.0657	0.0016	0.08085	0.92384	0.071	0.002
0.64561	0.0661	0.0006	0.08761	0.91788	0.0720	0.0007
0.67506	0.0639	0.0003	0.09161	0.91438	0.0699	0.0003
0.70282	0.0615	0.0005	0.09537	0.91110	0.0675	0.0005
0.74922	0.0671	0.0003	0.10167	0.90566	0.0741	0.0003
0.78105	0.0606	0.0003	0.10599	0.90196	0.0671	0.0003
0.87525	0.0604	0.0006	0.11877	0.89114	0.0677	0.0007
1.01899	0.0593	0.0003	0.13828	0.87502	0.0678	0.0003
1.05755	0.0590	0.0004	0.14351	0.87077	0.0677	0.0005
1.13108	0.0598	0.0004	0.15349	0.86276	0.0693	0.0005
1.31337	0.0563	0.0007	0.17822	0.84340	0.0667	0.0008
1.52479	0.0569	0.0005	0.20691	0.82179	0.0692	0.0006
1.8503	0.0552	0.0005	0.25109	0.79022	0.0699	0.0006
2.17482	0.0530	0.0007	0.29512	0.76065	0.0697	0.0009
768.36 KeV ----- 226Ra --- 214Bi ; $P_\gamma = 0.0494(6)$						
ηm	ε_{exp}	$\sigma(\varepsilon_{exp})$	$k\eta m$	$f(k\eta m)$	ε_0^{exp}	$\sigma(\varepsilon_0^{exp})$
0.11989	0.062	0.002	0.01627	0.98393	0.063	0.002
0.15143	0.0590	0.0010	0.02055	0.97976	0.0603	0.0010
0.20922	0.0570	0.0006	0.02839	0.97220	0.0586	0.0006
0.3543	0.0618	0.0013	0.04808	0.95361	0.0648	0.0014
0.37702	0.0567	0.0011	0.05116	0.95075	0.0596	0.0012
0.39575	0.0510	0.0011	0.05370	0.94840	0.0537	0.0012
0.41426	0.0516	0.0013	0.05622	0.94608	0.0546	0.0014
0.43502	0.0582	0.0013	0.05903	0.94350	0.0616	0.0014
0.45752	0.0484	0.0013	0.06209	0.94071	0.0515	0.0014
0.48286	0.0529	0.0012	0.06552	0.93758	0.0564	0.0013
0.50122	0.058	0.002	0.06802	0.93533	0.062	0.002
0.53381	0.056	0.003	0.07244	0.93134	0.061	0.003
0.57259	0.0556	0.0007	0.07770	0.92664	0.0600	0.0008
0.59522	0.0500	0.0004	0.08077	0.92391	0.0541	0.0004
0.61501	0.0478	0.0006	0.08346	0.92153	0.0519	0.0007
0.6496	0.0553	0.0003	0.08815	0.91740	0.0603	0.0003
0.67119	0.0494	0.0003	0.09108	0.91484	0.0540	0.0003
0.73945	0.0488	0.0008	0.10034	0.90680	0.0538	0.0009
0.84724	0.0498	0.0003	0.11497	0.89434	0.0556	0.0003
0.87261	0.0483	0.0005	0.11841	0.89144	0.0541	0.0006
0.92639	0.0483	0.0005	0.12571	0.88535	0.0546	0.0006
1.06052	0.0459	0.0008	0.14391	0.87045	0.0527	0.0009
1.21481	0.0514	0.0007	0.16485	0.85378	0.0602	0.0008
1.45553	0.0494	0.0006	0.19752	0.82877	0.0597	0.0007
1.69032	0.0496	0.0008	0.22938	0.80549	0.0616	0.0010

1120.2 KeV ----- 226Ra --- 214Bi ; $P_\gamma = 0.151(2)$						
ηm	ε_{exp}	$\sigma(\varepsilon_{exp})$	$k\eta m$	$f(k\eta m)$	ε_0^{exp}	$\sigma(\varepsilon_0^{exp})$
0.09628	0.039	0.003	0.01307	0.98706	0.039	0.003
0.12306	0.0392	0.0013	0.01670	0.98351	0.0399	0.0013
0.17209	0.0355	0.0008	0.02335	0.97705	0.0363	0.0008
0.29373	0.0377	0.0016	0.03986	0.96131	0.0393	0.0017
0.31257	0.0366	0.0014	0.04242	0.95890	0.0382	0.0015
0.32809	0.0356	0.0014	0.04452	0.95693	0.0372	0.0015
0.34344	0.0365	0.0017	0.04660	0.95498	0.0382	0.0018
0.36065	0.0373	0.0016	0.04894	0.95281	0.0392	0.0017
0.3793	0.0352	0.0016	0.05147	0.95046	0.0371	0.0017
0.40031	0.0359	0.0015	0.05432	0.94783	0.0379	0.0016
0.41553	0.034	0.003	0.05639	0.94592	0.036	0.003
0.44255	0.034	0.003	0.06005	0.94256	0.037	0.003
0.47407	0.0359	0.0009	0.06433	0.93866	0.0383	0.0010
0.49012	0.0327	0.0005	0.06651	0.93669	0.0349	0.0005
0.50277	0.0337	0.0009	0.06823	0.93514	0.0360	0.0010
0.52633	0.0354	0.0004	0.07142	0.93226	0.0379	0.0004
0.53905	0.0320	0.0004	0.07315	0.93071	0.0344	0.0004
0.58375	0.0337	0.0011	0.07921	0.92529	0.0364	0.0012
0.65775	0.0317	0.0004	0.08926	0.91643	0.0346	0.0004
0.67192	0.0322	0.0007	0.09118	0.91475	0.0351	0.0008
0.70759	0.0320	0.0007	0.09602	0.91054	0.0351	0.0008
0.79733	0.0314	0.0011	0.10820	0.90008	0.0349	0.0012
0.89937	0.0322	0.0008	0.12204	0.88840	0.0363	0.0009
1.06154	0.0328	0.0008	0.14405	0.87034	0.0377	0.0009
1.21488	0.0321	0.0011	0.16486	0.85378	0.0376	0.0013
1377.67 KeV ----- 226Ra --- 214Bi ; $P_\gamma = 0.0400(6)$						
ηm	ε_{exp}	$\sigma(\varepsilon_{exp})$	$k\eta m$	$f(k\eta m)$	ε_0^{exp}	$\sigma(\varepsilon_0^{exp})$
0.08641	0.068	0.002	0.01173	0.98838	0.069	0.002
0.11056	0.0639	0.0009	0.01500	0.98516	0.0649	0.0009
0.15476	0.0658	0.0006	0.02100	0.97933	0.0672	0.0006
0.26442	0.0609	0.0012	0.03588	0.96506	0.0631	0.0012
0.28138	0.0664	0.0012	0.03818	0.96289	0.0689	0.0012
0.29536	0.0630	0.0012	0.04008	0.96110	0.0656	0.0012
0.30917	0.0612	0.0012	0.04195	0.95934	0.0638	0.0013
0.32466	0.0618	0.0012	0.04406	0.95736	0.0645	0.0013
0.34146	0.0665	0.0012	0.04634	0.95523	0.0696	0.0013
0.36036	0.0629	0.0012	0.04890	0.95284	0.0661	0.0013
0.37407	0.056	0.002	0.05076	0.95112	0.059	0.002
0.39839	0.061	0.003	0.05406	0.94807	0.064	0.003

0.42617	0.0611	0.0006	0.05783	0.94460	0.0646	0.0006
0.43998	0.0580	0.0003	0.05971	0.94288	0.0615	0.0003
0.45049	0.0551	0.0006	0.06113	0.94158	0.0585	0.0006
0.4705	0.0610	0.0003	0.06385	0.93910	0.0650	0.0003
0.48076	0.0545	0.0003	0.06524	0.93784	0.0581	0.0003
0.51823	0.0540	0.0006	0.07032	0.93324	0.0579	0.0006
0.58125	0.0538	0.0003	0.07888	0.92559	0.0581	0.0003
0.59242	0.0553	0.0005	0.08039	0.92425	0.0598	0.0005
0.62246	0.0569	0.0005	0.08447	0.92064	0.0618	0.0005
0.69823	0.0521	0.0009	0.09475	0.91164	0.0571	0.0010
0.78407	0.0452	0.0006	0.10640	0.90161	0.0501	0.0007
0.92132	0.0509	0.0005	0.12502	0.88592	0.0574	0.0006
1.04975	0.0495	0.0009	0.14245	0.87163	0.0568	0.0010
1764.49 KeV ----- 226Ra --- 214Bi ; $P_\gamma = 0.154(2)$						
ηm	ε_{exp}	$\sigma(\varepsilon_{exp})$	$k\eta m$	$f(k\eta m)$	ε_0^{exp}	$\sigma(\varepsilon_0^{exp})$
0.07622	0.045	0.002	0.01034	0.98974	0.045	0.002
0.09746	0.0403	0.0010	0.01323	0.98690	0.0409	0.0010
0.13632	0.0413	0.0006	0.01850	0.98176	0.0421	0.0006
0.23273	0.0425	0.0012	0.03158	0.96915	0.0438	0.0012
0.24766	0.0406	0.0011	0.03361	0.96722	0.0420	0.0011
0.25996	0.0389	0.0011	0.03528	0.96564	0.0403	0.0011
0.27212	0.0403	0.0012	0.03693	0.96408	0.0418	0.0012
0.28575	0.0395	0.0012	0.03878	0.96233	0.0411	0.0012
0.30053	0.0407	0.0012	0.04078	0.96044	0.0424	0.0012
0.31718	0.0394	0.0011	0.04304	0.95832	0.0411	0.0011
0.32924	0.038	0.002	0.04468	0.95678	0.039	0.002
0.35065	0.038	0.002	0.04758	0.95407	0.040	0.002
0.37509	0.0393	0.0007	0.05090	0.95099	0.0413	0.0007
0.38723	0.0364	0.0004	0.05255	0.94946	0.0383	0.0004
0.39647	0.0358	0.0007	0.05380	0.94831	0.0377	0.0007
0.41407	0.0387	0.0003	0.05619	0.94611	0.0409	0.0003
0.42309	0.0349	0.0003	0.05741	0.94498	0.0369	0.0003
0.45603	0.0347	0.0008	0.06188	0.94089	0.0369	0.0009
0.51145	0.0344	0.0003	0.06940	0.93407	0.0369	0.0003
0.52126	0.0345	0.0005	0.07073	0.93287	0.0370	0.0005
0.54767	0.0356	0.0005	0.07432	0.92966	0.0382	0.0005
0.6143	0.0340	0.0008	0.08336	0.92162	0.0369	0.0009
0.68977	0.0336	0.0006	0.09360	0.91264	0.0368	0.0007
0.81047	0.0331	0.0006	0.10998	0.89856	0.0368	0.0007
0.92338	0.0321	0.0008	0.12530	0.88569	0.0363	0.0009

Table B.9

Experimental efficiencies when the sample mass is not and is zero (ε_{exp} and ε_0^{exp} , whose uncertainties at 1 sigma level are $\sigma(\varepsilon_{exp})$ and $\sigma(\varepsilon_0^{exp})$, respectively) obtained for the different prepared Th-ORE standards. Then, E_γ and P_γ are the selected gamma emission energies and their emission probabilities, respectively, of the radionuclides belonging to the ^{232}Th -series. On the other hand, k , η , m and $f(k\eta m)$ are the geometric parameter, the sample mass attenuation coefficient, the sample mass and the self-absorption correction factor, respectively.

238.64 KeV ----- 228Th ---- 212Pb ; $P_\gamma = 0.433(4)$						
ηm	ε_{exp}	$\sigma(\varepsilon_{exp})$	$k\eta m$	$f(k\eta m)$	ε_0^{exp}	$\sigma(\varepsilon_0^{exp})$
0.195	0.340	0.004	0.02646	0.97406	0.349	0.004
0.27642	0.339	0.002	0.03751	0.96352	0.352	0.002
0.38366	0.3208	0.0011	0.05206	0.94991	0.3377	0.0012
0.58462	0.3087	0.0019	0.07933	0.92519	0.334	0.002
0.62074	0.2984	0.0017	0.08423	0.92085	0.3240	0.0018
0.65244	0.307	0.002	0.08854	0.91706	0.335	0.002
0.68174	0.297	0.002	0.09251	0.91359	0.326	0.002
0.71786	0.294	0.002	0.09741	0.90933	0.323	0.002
0.75362	0.287	0.002	0.10227	0.90515	0.317	0.002
0.7956	0.289	0.002	0.10796	0.90028	0.321	0.002
0.8255	0.279	0.003	0.11202	0.89683	0.312	0.003
0.8798	0.276	0.003	0.11939	0.89063	0.310	0.003
0.99511	0.2715	0.0013	0.13504	0.87767	0.3094	0.0015
1.12777	0.2578	0.0015	0.15304	0.86313	0.2987	0.0017
1.31015	0.2524	0.0013	0.17779	0.84375	0.2991	0.0015
1.54279	0.2528	0.0007	0.20936	0.82002	0.3083	0.0009
1.80947	0.2380	0.0014	0.24555	0.79411	0.2997	0.0018
2.36371	0.2277	0.0010	0.32076	0.74437	0.3059	0.0013
3.00006	0.2163	0.0010	0.40711	0.69340	0.3119	0.0014
3.42512	0.2123	0.0008	0.46479	0.66261	0.3204	0.0012
3.80667	0.1996	0.0008	0.51657	0.63696	0.3134	0.0013
4.96314	0.1787	0.0008	0.67350	0.56922	0.3139	0.0014
6.19994	0.1654	0.0007	0.84133	0.51048	0.3239	0.0014
7.69074	0.1486	0.0006	1.04363	0.45403	0.3273	0.0013
10.14847	0.1234	0.0009	1.37715	0.38514	0.320	0.002
338.42 KeV ----- 228Ra ---- 228Ac ; $P_\gamma = 0.113(19)$						
ηm	ε_{exp}	$\sigma(\varepsilon_{exp})$	$k\eta m$	$f(k\eta m)$	ε_0^{exp}	$\sigma(\varepsilon_0^{exp})$
0.16664	0.191	0.010	0.02261	0.97777	0.195	0.010
0.23753	0.202	0.004	0.03223	0.96853	0.209	0.004
0.33149	0.200	0.003	0.04498	0.95650	0.209	0.003
0.50787	0.195	0.006	0.06892	0.93451	0.209	0.006
0.53925	0.188	0.005	0.07318	0.93068	0.202	0.005

0.56679	0.190	0.007	0.07691	0.92734	0.204	0.008
0.59224	0.181	0.007	0.08037	0.92427	0.196	0.008
0.62362	0.185	0.008	0.08463	0.92050	0.201	0.009
0.65469	0.187	0.008	0.08884	0.91680	0.204	0.009
0.69116	0.181	0.007	0.09379	0.91248	0.198	0.008
0.71713	0.181	0.015	0.09731	0.90942	0.199	0.016
0.7643	0.177	0.012	0.10372	0.90391	0.196	0.013
0.81434	0.177	0.002	0.11051	0.89812	0.197	0.002
0.87694	0.161	0.003	0.11900	0.89095	0.181	0.003
0.96162	0.161	0.002	0.13049	0.88140	0.182	0.002
1.067	0.1648	0.0014	0.14479	0.86974	0.1895	0.0016
1.19163	0.158	0.003	0.16170	0.85626	0.184	0.004
1.44269	0.1535	0.0019	0.19577	0.83009	0.185	0.002
1.73067	0.153	0.002	0.23485	0.80162	0.191	0.002
1.93077	0.1494	0.0015	0.26201	0.78276	0.1909	0.0019
2.10236	0.1399	0.0015	0.28529	0.76716	0.107	0.002
2.64757	0.1350	0.0015	0.35928	0.72087	0.187	0.002
3.21503	0.1291	0.0014	0.43628	0.67752	0.191	0.002
3.89531	0.1212	0.0016	0.52859	0.63125	0.192	0.003
5.03891	0.112	0.003	0.68378	0.56525	0.198	0.005

583.19 KeV ----- 228Th ---- 208Tl ; $P_\gamma = 0.3037(3)$

ηm	ε_{exp}	$\sigma(\varepsilon_{exp})$	$k\eta m$	$f(k\eta m)$	ε_0^{exp}	$\sigma(\varepsilon_0^{exp})$
0.13067	0.071	0.003	0.01773	0.98250	0.072	0.003
0.18659	0.0712	0.0014	0.02532	0.97515	0.0730	0.0014
0.26086	0.0702	0.0008	0.03540	0.96552	0.0727	0.0008
0.40034	0.0669	0.0015	0.05433	0.94782	0.071	0.002
0.42507	0.0684	0.0014	0.05768	0.94474	0.0724	0.0015
0.44678	0.0695	0.0017	0.06063	0.94204	0.074	0.002
0.46685	0.0680	0.0016	0.06335	0.93956	0.072	0.002
0.49158	0.0662	0.0019	0.06671	0.93651	0.071	0.002
0.51607	0.0626	0.0019	0.07003	0.93351	0.067	0.002
0.54482	0.0650	0.0019	0.07393	0.93000	0.070	0.002
0.56529	0.063	0.003	0.07671	0.92752	0.068	0.003
0.60248	0.063	0.003	0.08176	0.92304	0.068	0.003
0.6187	0.0626	0.0010	0.08396	0.92109	0.0680	0.0011
0.64365	0.0618	0.0013	0.08734	0.91811	0.0673	0.0014
0.67623	0.0610	0.0011	0.09176	0.91424	0.0667	0.0012
0.71449	0.0631	0.0005	0.09696	0.90973	0.0693	0.0005
0.76315	0.0592	0.0013	0.10356	0.90404	0.0654	0.0014
0.85431	0.0608	0.0009	0.11593	0.89353	0.0681	0.0010
0.95863	0.0615	0.0009	0.13009	0.88173	0.0697	0.0010

1.038	0.0610	0.0007	0.14086	0.87292	0.0698	0.0008
1.0992	0.0604	0.0007	0.14916	0.86622	0.0697	0.0008
1.31614	0.0579	0.0007	0.17860	0.84311	0.0687	0.0008
1.52859	0.0587	0.0007	0.20743	0.82141	0.0714	0.0009
1.78002	0.0571	0.0006	0.24155	0.79687	0.0716	0.0008
2.22218	0.0534	0.0011	0.30155	0.75649	0.0705	0.0015
727.17 KeV ----- 228Th ---- 212Bi ; $P_\gamma = 0.0658(5)$						
ηm	ε_{exp}	$\sigma(\varepsilon_{exp})$	$k\eta m$	$f(k\eta m)$	ε_0^{exp}	$\sigma(\varepsilon_0^{exp})$
0.11806	0.094	0.009	0.01602	0.98417	0.095	0.009
0.16858	0.095	0.004	0.02288	0.97751	0.097	0.004
0.23569	0.094	0.002	0.03198	0.96877	0.097	0.002
0.36172	0.093	0.005	0.04909	0.95267	0.097	0.005
0.38406	0.091	0.005	0.05212	0.94986	0.095	0.005
0.40368	0.092	0.006	0.05478	0.94740	0.097	0.006
0.42181	0.086	0.006	0.05724	0.94514	0.091	0.006
0.44415	0.086	0.007	0.06027	0.94236	0.092	0.007
0.46628	0.093	0.007	0.06327	0.93963	0.099	0.007
0.49225	0.082	0.006	0.06680	0.93643	0.088	0.006
0.51075	0.072	0.005	0.06931	0.93416	0.077	0.005
0.54435	0.074	0.004	0.07387	0.93006	0.080	0.004
0.55547	0.084	0.003	0.07538	0.92871	0.090	0.003
0.5743	0.085	0.004	0.07793	0.92643	0.092	0.004
0.59854	0.079	0.003	0.08122	0.92351	0.086	0.003
0.62629	0.0813	0.0016	0.08499	0.92018	0.0884	0.0017
0.66271	0.081	0.004	0.08993	0.91584	0.089	0.004
0.72882	0.082	0.003	0.09890	0.90805	0.090	0.003
0.80441	0.083	0.003	0.10916	0.89926	0.092	0.003
0.86419	0.082	0.002	0.11727	0.89240	0.092	0.002
0.90821	0.078	0.002	0.12324	0.88740	0.088	0.002
1.07182	0.078	0.002	0.14545	0.86921	0.090	0.002
1.22803	0.075	0.002	0.16664	0.85238	0.088	0.002
1.41185	0.078	0.002	0.19159	0.83322	0.094	0.002
1.74144	0.067	0.003	0.23631	0.80056	0.084	0.004
860.56 KeV ----- 228Th ---- 208Tl ; $P_\gamma = 0.0446(4)$						
ηm	ε_{exp}	$\sigma(\varepsilon_{exp})$	$k\eta m$	$f(k\eta m)$	ε_0^{exp}	$\sigma(\varepsilon_0^{exp})$
0.10905	0.075	0.004	0.01480	0.98536	0.076	0.004
0.1558	0.0753	0.0015	0.02114	0.97919	0.077	0.002
0.21792	0.0735	0.0009	0.02957	0.97107	0.0757	0.0009
0.33461	0.0700	0.0019	0.04541	0.95610	0.073	0.002
0.35528	0.0642	0.0016	0.04821	0.95349	0.067	0.002
0.37342	0.076	0.002	0.05067	0.95120	0.080	0.002

0.39019	0.072	0.002	0.05295	0.94909	0.076	0.002
0.41087	0.062	0.002	0.05576	0.94651	0.065	0.002
0.43133	0.064	0.002	0.05853	0.94396	0.067	0.002
0.45536	0.067	0.002	0.06179	0.94098	0.071	0.002
0.47248	0.080	0.004	0.06412	0.93886	0.085	0.004
0.50355	0.056	0.004	0.06833	0.93504	0.059	0.004
0.51209	0.0675	0.0012	0.06949	0.93400	0.0723	0.0013
0.52766	0.0641	0.0016	0.07160	0.93209	0.069	0.002
0.5475	0.0625	0.0013	0.07430	0.92968	0.0672	0.0014
0.56979	0.0642	0.0006	0.07732	0.92698	0.0693	0.0006
0.59974	0.0612	0.0015	0.08138	0.92337	0.066	0.002
0.65283	0.0619	0.0010	0.08859	0.91702	0.0674	0.0011
0.71348	0.0586	0.0010	0.09682	0.90985	0.0644	0.0011
0.76286	0.0620	0.0008	0.10352	0.90407	0.0686	0.0009
0.798	0.0584	0.0007	0.10829	0.90000	0.0648	0.0008
0.93327	0.0552	0.0007	0.12664	0.88458	0.0624	0.0008
1.06002	0.0597	0.0008	0.14384	0.87050	0.0686	0.0009
1.20855	0.0522	0.0006	0.16400	0.85445	0.0610	0.0007
1.47875	0.0494	0.0012	0.20067	0.82642	0.0598	0.0015

911.07 KeV ----- 228Ra ---- 228Ac ; $P_\gamma = 0.258(4)$

ηm	ε_{exp}	$\sigma(\varepsilon_{exp})$	$k\eta m$	$f(k\eta m)$	ε_0^{exp}	$\sigma(\varepsilon_0^{exp})$
0.10608	0.065	0.003	0.01440	0.98576	0.066	0.003
0.15153	0.0660	0.0013	0.02056	0.97975	0.0673	0.0013
0.21192	0.0660	0.0008	0.02876	0.97185	0.0679	0.0008
0.32535	0.0636	0.0015	0.04415	0.95728	0.067	0.002
0.34545	0.0613	0.0012	0.04688	0.95473	0.0642	0.0013
0.36309	0.0626	0.0017	0.04927	0.95250	0.066	0.002
0.37939	0.0616	0.0016	0.05148	0.95045	0.065	0.002
0.3995	0.0596	0.0019	0.05421	0.94793	0.063	0.002
0.4194	0.0628	0.0018	0.05691	0.94544	0.066	0.002
0.44276	0.0589	0.0018	0.06008	0.94254	0.062	0.002
0.4594	0.064	0.003	0.06234	0.94048	0.068	0.003
0.48962	0.061	0.003	0.06644	0.93675	0.065	0.003
0.49747	0.0586	0.0009	0.06751	0.93579	0.0626	0.0010
0.51216	0.0565	0.0012	0.06950	0.93399	0.0605	0.0013
0.5308	0.0569	0.0010	0.07203	0.93171	0.0610	0.0011
0.55161	0.0587	0.0004	0.07485	0.92918	0.0632	0.0004
0.57979	0.0569	0.0012	0.07868	0.92577	0.0615	0.0013
0.62938	0.0573	0.0008	0.08541	0.91981	0.0623	0.0009
0.68603	0.0595	0.0009	0.09309	0.91308	0.0652	0.0010
0.73255	0.0604	0.0006	0.09941	0.90761	0.0666	0.0007

0.7653	0.0606	0.0006	0.10385	0.90379	0.0671	0.0007
0.89278	0.0588	0.0006	0.12115	0.88915	0.0661	0.0007
1.01156	0.0598	0.0006	0.13727	0.87584	0.0683	0.0007
1.15057	0.0587	0.0006	0.15613	0.86066	0.0682	0.0007
1.40455	0.0555	0.0011	0.19060	0.83397	0.0666	0.0013
969.11 KeV ----- 228Ra ---- 228Ac ; $P_\gamma = 0.158(3)$						
ηm	ε_{exp}	$\sigma(\varepsilon_{exp})$	$k\eta m$	$f(k\eta m)$	ε_0^{exp}	$\sigma(\varepsilon_0^{exp})$
0.10288	0.06551	0.003	0.01396	0.98618	0.066	0.003
0.14695	0.06521	0.0015	0.01994	0.98035	0.0665	0.0015
0.2055	0.06615	0.0009	0.02789	0.97269	0.0680	0.0009
0.31546	0.06697	0.002	0.04281	0.95853	0.070	0.002
0.33495	0.06254	0.0018	0.04545	0.95606	0.0654	0.0019
0.35206	0.06404	0.002	0.04777	0.95389	0.067	0.002
0.36787	0.06165	0.002	0.04992	0.95190	0.065	0.002
0.38736	0.06295	0.003	0.05256	0.94945	0.066	0.003
0.40665	0.0614	0.003	0.05518	0.94703	0.065	0.003
0.42931	0.06144	0.003	0.05826	0.94421	0.065	0.003
0.44544	0.06245	0.005	0.06045	0.94220	0.066	0.005
0.47474	0.05661	0.004	0.06442	0.93858	0.060	0.004
0.48196	0.0563	0.0013	0.06540	0.93769	0.0600	0.0014
0.49578	0.05885	0.0017	0.06728	0.93599	0.0629	0.0018
0.51326	0.05619	0.0013	0.06965	0.93385	0.0602	0.0014
0.53268	0.05829	0.0006	0.07228	0.93148	0.0626	0.0006
0.55915	0.05513	0.0016	0.07588	0.92826	0.0594	0.0017
0.6054	0.05817	0.0011	0.08215	0.92269	0.0630	0.0012
0.65821	0.05914	0.0011	0.08932	0.91638	0.0645	0.0012
0.70198	0.06068	0.0009	0.09526	0.91120	0.0666	0.0010
0.73246	0.05808	0.0009	0.09939	0.90762	0.0640	0.0010
0.85241	0.05825	0.0008	0.11567	0.89375	0.0652	0.0009
0.96354	0.05808	0.0008	0.13075	0.88119	0.0659	0.0009
1.09343	0.05765	0.0007	0.14838	0.86685	0.0665	0.0008
1.3318	0.05264	0.0013	0.18073	0.84148	0.0626	0.0015
1620.73 KeV ----- 228Th ---- 212Bi ; $P_\gamma = 0.0149(3)$						
ηm	ε_{exp}	$\sigma(\varepsilon_{exp})$	$k\eta m$	$f(k\eta m)$	ε_0^{exp}	$\sigma(\varepsilon_0^{exp})$
0.07923	0.051	0.002	0.01075	0.98933	0.005	0.002
0.11318	0.0620	0.0008	0.01536	0.98482	0.0063	0.0008
0.1583	0.0511	0.0004	0.02148	0.97886	0.0052	0.0004
0.24304	0.0486	0.0010	0.03298	0.96782	0.0050	0.0010
0.25806	0.0472	0.0009	0.03502	0.96588	0.0049	0.0009
0.27124	0.0537	0.0012	0.03681	0.96419	0.0056	0.0012
0.28342	0.0563	0.0012	0.03846	0.96263	0.0058	0.0012

0.29844	0.0434	0.0014	0.04050	0.96070	0.0045	0.0015
0.3133	0.0493	0.0014	0.04251	0.95881	0.0051	0.0015
0.33076	0.0582	0.0014	0.04488	0.95659	0.0061	0.0015
0.34319	0.048	0.003	0.04657	0.95501	0.004	0.003
0.36576	0.044	0.002	0.04963	0.95216	0.004	0.002
0.37012	0.0452	0.0009	0.05023	0.95161	0.0048	0.0009
0.37951	0.0427	0.0012	0.05150	0.95043	0.0045	0.0013
0.39122	0.0464	0.0009	0.05309	0.94896	0.0049	0.0009
0.40386	0.0522	0.0003	0.05480	0.94738	0.0055	0.0003
0.42169	0.0459	0.0012	0.05722	0.94516	0.0049	0.0013
0.45181	0.0470	0.0007	0.06131	0.94141	0.0050	0.0007
0.48617	0.0496	0.0007	0.06597	0.93717	0.0053	0.0007
0.51584	0.0423	0.0005	0.07000	0.93354	0.0045	0.0005
0.5355	0.0444	0.0005	0.07267	0.93114	0.0048	0.0005
0.61692	0.0413	0.0005	0.08372	0.92130	0.0045	0.0005
0.69042	0.0439	0.0005	0.09369	0.91256	0.0048	0.0005
0.77578	0.0471	0.0004	0.10527	0.90257	0.0052	0.0004
0.93571	0.0496	0.0009	0.12698	0.88431	0.0056	0.0010

Table B.10

Experimental efficiencies when the sample mass is not and is zero (ε_{exp} and ε_0^{exp} , whose uncertainties at 1 sigma level are $\sigma(\varepsilon_{exp})$ and $\sigma(\varepsilon_0^{exp})$, respectively) obtained for the different prepared KCl standards. Then, E_γ and P_γ are the gamma emission energy and its emission probability, respectively, for ^{40}K . On the other hand, k , η , m and f ($k\eta m$) are the geometric parameter, the sample mass attenuation coefficient, the sample mass and the self-absorption correction factor, respectively.

1460.83 KeV ----- 40K ; $P_\gamma = 0.1067(6)$						
ηm	ε_{exp}	$\sigma(\varepsilon_{exp})$	$k\eta m$	$f(k\eta m)$	ε_0^{exp}	$\sigma(\varepsilon_0^{exp})$
0.29152	0.053	0.002	0.03957	0.96158	0.055	0.002
0.29464	0.0515	0.0016	0.03999	0.96118	0.0536	0.0016
0.29483	0.0487	0.0012	0.04002	0.96116	0.0507	0.0013
0.30220	0.0508	0.0011	0.04102	0.96021	0.0529	0.0012
0.30122	0.0496	0.0006	0.04089	0.96034	0.0517	0.0007
0.31021	0.0504	0.0008	0.04211	0.95919	0.0525	0.0008
0.31181	0.0478	0.0013	0.04233	0.95899	0.0498	0.0013
0.31765	0.0508	0.0012	0.04312	0.95824	0.0530	0.0013
0.31628	0.0487	0.0012	0.04293	0.95842	0.0508	0.0012

Table B.11

Average ε_0^{exp} values (ε_0 , whose uncertainty at 1 sigma level is $\sigma(\varepsilon_0)$) for each gamma emission energy (E_γ) of the radionuclides (RN) belonging to the ^{238}U - and ^{232}Th -series, as well as ^{40}K .

RN	E_γ (keV)	ε_0	$\sigma(\varepsilon_0)$
^{210}Pb	46.5	0.521	0.010
^{234}Th	63.29	0.602	0.014
	92.6	0.470	0.016
^{226}Ra	186.2	0.421	0.003
^{214}Pb	295.21	0.262	0.003
	351.92	0.219	0.002
	609.31	0.0712	0.0006
	768.36	0.0575	0.0008
^{214}Bi	1120.2	0.0370	0.0003
	1377.67	0.0621	0.0009
	1764.49	0.0396	0.0005
^{212}Pb	238.64	0.320	0.003
^{208}Tl	583.19	0.0699	0.0004
	860.56	0.0693	0.0013
	338.42	0.192	0.004
^{228}Ac	911.07	0.0650	0.0005
	969.11	0.0646	0.0005
^{212}Bi	727.17	0.0908	0.0011
	1620.73	0.0502	0.0012
^{40}K	1460.83	0.0523	0.0005

Table B.12

Comparison between the fittings done by different functions (*Function-i*, with “i” = 1, 2 and 3) for ε_{exp} versus ηm , where F_{ij} are the parameters (which have to be multiplied by a common factor of 10^{-3}) resulted from the fittings done by each function. Besides, the relative average residues ($\langle Res \rangle$) have been obtained after fittings provided for each function. Uncertainties given at 1 sigma level.

[illegible]

RN	E_γ (keV)	$-F_{31}$	$-F_{32}$	$-F_{33}$	$\langle \text{Res} \rangle$ (%)
^{210}Pb	46.5	709(7)	48.5(5)	128.6(1.3)	1.3
^{234}Th	63.29	655(7)	25.0(2)	126.0(1.3)	2.8
^{226}Ra	186.2	979(10)	164.8(1.6)	86.9(9)	0.4
^{214}Pb	295.21	1478(15)	197(2)	56.9(6)	0.23
	351.92	1665(17)	197(2)	49.4(5)	0.22
^{214}Bi	609.31	2800(30)	170.8(1.7)	33.6(3)	0.17
	1120.2	3450(40)	112.7(1.1)	8.94(10)	0.30
^{228}Ac	338.42	1779(18)	183.1(1.8)	48.1(5)	0.20
	911.07	2850(30)	50.7(5)	-6.28(10)	0.25
^{212}Pb	238.64	1285(13)	202(2)	50.1(5)	0.20
^{208}Tl	583.19	2810(30)	121.2(1.2)	15.2(2)	0.16

Table B.13

Comparison of the MDA (Bq) values calculated for different samples (Ilmenite, Scale-1, IAEA-326 and (RGU-1, RGTh-1, RGK-1) + 70 % PbS) considering both cases: With and without anti-Compton system (MDA^a and MDA , respectively). Besides, other two cases have been considered at 186 keV: Without and with secular equilibrium between ^{238}U and ^{226}Ra (No sec. eq. and Sec. eq., respectively).

RN	E_γ (keV)	Ilmenite			Scale-1		
		MDA (Bq)	MDA^a (Bq)	MDA^a/MDA	MDA (Bq)	MDA^a (Bq)	MDA^a/MDA
^{210}Pb	46.5	0.49	0.31	0.62	0.55	0.30	0.54
^{234}Th	63.29	0.30	0.28	0.92	0.10	0.06	0.59
^{226}Ra	186.2 (No sec. eq.)	0.27	0.19	0.71	0.64	0.45	0.70
	186.2 (Sec. eq.)	0.15	0.10	0.69	0.36	0.26	0.70
^{214}Pb	295.21	0.05	0.03	0.56	0.11	0.08	0.71
	351.92	0.03	0.02	0.53	0.08	0.04	0.52
^{214}Bi	609.31	0.05	0.03	0.50	0.13	0.07	0.49
	1120.2	0.18	0.11	0.61	0.52	0.32	0.62
^{212}Pb	238.64	0.02	0.01	0.68	0.05	0.03	0.66
^{208}Tl	583.19	0.09	0.04	0.50	0.21	0.10	0.46
^{228}Ac	338.42	0.10	0.06	0.64	0.29	0.17	0.58
	911.07	0.06	0.04	0.74	0.21	0.10	0.48
^{40}K	1460.83	0.16	0.10	0.66	0.12	0.08	0.66
RN	E_γ (keV)	IAEA-326			(RGU-1, RGTh-1, RGK-1) + 70 % PbS		
		MDA (Bq)	MDA^a (Bq)	MDA^a/MDA	MDA (Bq)	MDA^a (Bq)	MDA^a/MDA
^{210}Pb	46.5	0.10	0.06	0.60	2.44	1.45	0.59
^{234}Th	63.29	0.08	0.05	0.63	1.20	0.83	0.69
^{226}Ra	186.2 (No sec. eq.)	0.12	0.08	0.67	0.83	0.69	0.83
	186.2 (Sec. eq.)	0.07	0.03	0.43	0.46	0.35	0.76
^{214}Pb	295.21	0.03	0.01	0.33	0.10	0.07	0.70
	351.92	0.02	0.01	0.50	0.06	0.04	0.67
^{214}Bi	609.31	0.03	0.01	0.33	0.08	0.04	0.50

	1120.2	0.11	0.05	0.45	0.36	0.18	0.50
²¹² Pb	238.64	0.01	0.01	1.00	0.04	0.03	0.75
²⁰⁸ Tl	583.19	0.04	0.02	0.50	0.13	0.06	0.46
²²⁸ Ac	338.42	0.06	0.03	0.50	0.19	0.10	0.53
	911.07	0.04	0.02	0.50	0.08	0.06	0.75
⁴⁰ K	1460.83	0.11	0.08	0.73	0.13	0.11	0.85

Table B.14

Chemical compositions (in %) and apparent densities (ρ , in g cm⁻³) of all the samples used in this work. Besides, in this table the activity concentrations calculated for PR-1 and PbS samples using the XtRa detector have been shown. Uncertainties given at 1 sigma level.

	RGU-1	RGTh-1	KCl	RGK-1	IAEA-326	PR-1	PR-2	IAEA-434	CSN-PG	Scale-1	Ilmenite	PbS	Activated carbon
ρ	1.62(2)	1.62(2)	1.62(2)	1.57	1.40	1.56	1.43	0.80	1.23	1.36	2.74	4.61	0.50
H								2.21	2.21				25.0
C						1.4	1.4						75.0
O	53.354	53.5398		36.727	54.303	40.78	40.78	55.0	55.0	48.0	33.0	17.18	
F						4.0	4.0	1.2	1.2				
Na	0.03				0.59					3.0			
Mg		0.02			0.615	0.24	0.24			5.0			
Al	0.1	0.04			5.5	0.29	0.29	0.1	0.1	10.0			
Si	46.4	45.0			32.68	0.98	0.98	0.47	0.47	10.0		1.0	
P		0.129			0.075	14.4	14.4	0.7	0.7	0.7			
S				18.398		0.74	0.74	18.24	18.24	10.0		6.95	
Cl			47.7										
K			52.3	44.875	1.9					5.0			
Ca	0.03	0.42			1.16	37.0	37.0	22.08	22.08	7.3		1.48	
Ti	0.008				0.45						30.0		
Mn		0.014			0.06					1.0			
Fe	0.03	0.13			2.667	0.16	0.16				37.0		
Ba		0.6235											
Pb	0.008	0.003										73.39	
Th		0.081											
U	0.04					0.01	0.01						
	Distilled water					PR-1	PbS						
ρ	1.00	RN	E_γ (keV)			a (Bq kg ⁻¹)	a (Bq kg ⁻¹)						
H	11.2	²¹⁰ Pb	46.5			1226(26)	30(36)						
O	88.8	²³⁴ Th	63.29			1568(67)	20(23)						
		²²⁶ Ra	186.2 (Sec. eq.)			1802(57)	7(8)						
		²¹⁴ Pb	295.21			1606(19)	1.8(1.9)						
			351.92			1623(18)	1.7(1.7)						
		²¹⁴ Bi	609.31			1602(19)	1.7(1.6)						
			1120.2			1594(28)	2(2)						

SUPPLEMENTARY MATERIAL-C

Table C.1

Values of ar_i parameters (in $\text{cm}^2 \text{g}^{-1}$) obtained after fitting η ($\text{cm}^2 \text{g}^{-1}$) with the energy by Eq. 1 for low Z values (1-26).

ar_i	H	Be	C	O	Na
ar_0	9.1390(3)	27.5983(4)	199.861(2)	508.018(3)	1542.316(8)
$-ar_1$	16.7583(2)	42.5454(2)	319.7533(2)	804.5681(3)	2489.3429(3)
ar_2	14.13964(2)	29.73935(3)	227.44684(3)	565.55237(4)	1786.00243(10)
$-ar_3$	6.890586(2)	12.302126(2)	94.200294(2)	231.212643(3)	746.500881(6)
ar_4	2.1342803(2)	3.3186319(2)	25.0098707(3)	60.5299880(4)	200.1073501(11)
$-ar_5$	0.43524811(2)	0.60477049(2)	4.41095328(2)	10.51568521(2)	35.64572660(3)
ar_6	0.058333213(3)	0.074269508(3)	0.516470058(3)	1.211640538(5)	4.21670888(2)
$-ar_7$	0.0049483238(2)	0.0059081240(2)	0.0386934486(3)	0.0892494313(4)	0.319258610(2)
ar_8	0.00024098993(2)	0.00027534891(3)	0.00168246656(3)	0.00381247225(4)	0.0140329005(2)
$-ar_9$	(5.135086(8))E-06	(5.710859(11))E-06	(3.234113(2))E-05	(7.194369(2))E-05	(2.7275043(3))E-4
ar_i	Si	S	K	Ti	Fe
ar_0	3101.446(18)	4371.930(19)	7391.41(6)	10318.98(10)	14596.5956(19)
$-ar_1$	4922.0442(4)	6867.6878(5)	11749.760(10)	16386.114(15)	22824.328(19)
ar_2	3470.16657(18)	4791.81883(19)	8309.0242(7)	11588.9668(11)	15900.4544(16)
$-ar_3$	1425.597990(10)	1946.730915(14)	3426.69295(3)	4782.21140(4)	6467.30234(8)
ar_4	374.9125209(19)	506.436060(4)	907.118400(7)	1268.650760(12)	1690.51755(2)
$-ar_5$	65.54177132(4)	87.53674245(6)	159.7003893(2)	223.6011231(2)	294.2202468(3)
ar_6	7.60675099(2)	10.04206718(2)	18.68433863(3)	26.22383986(3)	34.06771058(4)
$-ar_7$	0.564922969(2)	0.736953585(2)	1.400007775(2)	1.970557761(3)	2.529107656(4)
ar_8	0.0243533005(3)	0.0313842522(4)	0.0609354609(5)	0.0860465437(9)	0.1091784802(12)
$-ar_9$	(4.6421522(3))E-4	(5.9081673(4))E-4	(1.17341007(11))E-3	(1.66287674(17))E-3	(2.0873262(2))E-3

Table C.2

ar_{ij} values (in $\text{cm}^2 \text{g}^{-1}$) obtained after the ar_i parameters regressions varying Z .

ar_i	ar_0	ar_1	ar_2	ar_3	ar_4
ar_i	195.7856(14)	-249.9353(18)	140.85748(8)	-46.011369(3)	9.6513895(13)
ar_i	-184.1828(13)	271.6789(19)	-179.65406(9)	69.866075(6)	-17.6019687(19)
ar_i	28.71897(2)	-44.51595(3)	30.795478(19)	-12.4606603(12)	3.24589393(18)
ar_i	ar_5	ar_6	ar_7	ar_8	ar_9
ar_i	-1.3622811(2)	0.131506360(18)	-0.0085463911(16)	0.00034566758(15)	(-6.677368(8))E-06
ar_i	2.9778960(4)	-0.338104367(19)	0.0248237941(2)	-0.00106851397(17)	(2.0523607(19))E-05
ar_i	-0.56389988(11)	0.0652764905(15)	-0.00485154483(18)	0.000209944285(19)	(-4.0281549(6))E-06

Table C.3

br_i and cr_i (in $\text{cm}^2 \text{g}^{-1}$) values that resulted after fittings of η data varying the energy by the exponential and polynomial functions, respectively, within the range of high Z values.

br_i	Co	Cu	Zn	Ge	Zr	Ru	Sn	Cs
br_1	10.652(6)	11.004(6)	11.170(6)	11.409(6)	11.855(6)	12.156(5)	12.478(5)	12.665(5)
$-br_2$	2.501(10)	2.545(10)	2.564(10)	2.593(10)	2.557(15)	2.574(6)	2.584(6)	2.577(5)
br_i	Nd	Yb	Hg	Rn	Ra	Th	U	
br_1	13.989(4)	13.046(4)	13.165(4)	13.208(3)	13.139(2)	13.118(2)	13.084(2)	
$-br_2$	2.604(15)	2.537(4)	2.497(4)	2.476(3)	2.450(3)	2.437(3)	2.421(3)	
cr_i	Co	Cu	Zn	Ge	Zr	Ru	Sn	Cs
cr_0	71.316(3)	89.910(4)	100.376(5)	68.461(4)	138.322(6)	186.715(7)	263.480(8)	340.181(9)
$-cr_1$	53.1364(4)	67.0779(6)	74.8951(6)	49.4060(5)	100.1265(6)	135.3990(8)	191.0612(9)	246.5853(9)
cr_2	15.87936(2)	20.05918(3)	22.39443(3)	14.31028(2)	29.04924(3)	39.34099(3)	55.50003(3)	71.59480(4)
$-cr_3$	2.372664(3)	2.998782(4)	3.347373(4)	2.073951(3)	4.215987(4)	5.717981(4)	8.064808(4)	10.399008(4)
cr_4	0.177049(2)	0.223895(3)	0.249887(3)	0.150210(2)	0.305848(3)	0.415451(3)	0.585906(3)	0.755218(4)
$-cr_5$	0.0052755(2)	0.0066756(4)	0.0074499(5)	0.0043468(4)	0.0088685(6)	0.0120668(7)	0.0170186(8)	0.0219309(8)
cr_i	Nd	Yb	Hg	Rn	Ra	Th	U	
cr_0	440.315(10)	648.396(13)	893.862(18)	1029.277(18)	1087.477(18)	1139.045(19)	1189.214(19)	
$-cr_1$	319.2363(9)	469.5393(10)	646.3555(13)	743.6263(15)	785.2678(16)	822.3036(16)	858.1802(17)	
cr_2	92.70422(4)	136.19361(4)	187.23095(5)	215.24270(5)	227.18670(6)	237.85314(6)	248.14273(6)	
$-cr_3$	13.467979(5)	19.765647(5)	27.140664(5)	31.180727(6)	32.896402(6)	34.435219(7)	35.913667(7)	
cr_4	0.978381(4)	1.434608(4)	1.967881(4)	2.259559(5)	2.382915(5)	2.494057(6)	2.600420(6)	
$-cr_5$	0.0284219(8)	0.0416449(10)	0.0570751(12)	0.0655044(13)	0.0690544(14)	0.0722678(14)	0.0753314(15)	

Table C.4

cr_{ij} (in $\text{cm}^2 \text{g}^{-1}$) and br_{ij} values obtained after cr_i and br_i fittings varying Z , respectively.

cr_{ij}	cr_0	cr_1	cr_2	cr_3	cr_4	cr_5
cr_{i1}	12548.11(44)	-9061.72(31)	2623.59(9)	-380.4162(1.3)	27.6101(1)	-0.802083(3)

cr_{i2}	-7162.82(25)	5170.563(18)	-1496.2647(5)	216.8369(8)	-15.72849(6)	0.456637(16)
cr_{i3}	1027.874(4)	-741.8165(3)	214.6026(8)	-31.08848(1)	2.254085(8)	-0.0654113(2)
br_{ij}	br_1	br_2				
br_{i1}	-19.99(8)	2.00(8)				
br_{i2}	14.62(6)	-2.42(10)				
br_{i3}	-1.613(6)	0.319(12)				

Table C.5

dr_i values obtained after $\eta(E_\gamma, Z)$ data regressions with the energy for the region before the shell change and dr_{ij} values obtained after dr_i parameters fittings varying Z .

dr_i	Cs	Nd	Yb	Hg	Rn	Ra	Th	U
dr_1	11.358(2)	11.578(2)	11.889(3)	12.133(4)	12.214(3)	12.246(3)	12.274(4)	12.303(3)
$-dr_2$	2.677(4)	2.662(4)	2.625(4)	2.584(6)	2.555(6)	2.544(6)	2.535(5)	2.526(5)
dr_{ij}	dr_1	dr_2						
dr_{i1}	-22.60(2)	1.61(16)						
dr_{i2}	14.37(14)	-2.28(2)						
dr_{i3}	-1.470(15)	0.301(3)						

Table C.6

Thicknesses (h in cm), densities (ρ in g cm⁻³) and chemical compositions (in %) of all the samples analyzed in this work.

	RGU	RGTh	RGK	IAEA-326	IAEA-327	SiO ₂	Scale-1	Scale-2	IAEA-PG	K ₂ CO ₃
h				2.51	1.51	0.90	1.22	1.39	1.81	4.64
ρ	1.63(2)	1.63(2)	1.63(2)	1.21	1.24	1.24	1.32	1.00	0.70	1.24
H									2.21	
C										8.7
O	53.354	53.5398	36.727	54.303	51.5	53.33	48.0	48.0	55.0	34.8
F									1.2	
Na	0.03			0.59	0.85		3.0	4.0		
Mg		0.02		0.615	0.46		5.0	9.0		
Al	0.01	0.04		5.5	5.07		10.0	12.0	0.1	
Si	46.4	45.0		32.68	36.82	46.67	10.0	9.0	0.47	
P		0.129		0.075	0.03		0.7	0.9	0.7	
S			18.398				10.0	12.0	18.24	
K			44.875	1.9	2.05		5.0	2.0		56.5

Ca	0.03	0.42	1.16	0.58	7.3	3.1	22.08
Ti	0.008		0.45	0.504			
Mn		0.014	0.06	0.05	1.0		
Fe	0.03	0.13	2.667	2.086			
Ba		0.6235					
Pb	0.008	0.003					
Th		0.081					
U	0.04						

	Furnace slag	Tionite	Sulfafer	Ilmenite
<i>h</i>	1.14	1.25	1.33	1.50
ρ	1.69	1.21	1.27	3.00
H			1.2	
O	30.0	33.0	47.1	30.0
Al	10.0			
Si	30.0			
S			18.8	
Ca	30.0			
Ti		30.0		30.0
Fe		37.0	32.9	40.0

Table C.7

Comparisons between different methods used to calculate η (WinXCOM, physical equations, ExS and $\eta(E_\gamma, Z)$), for the certified samples (IAEA-326, IAEA-327 and IAEA-PG), by obtaining relative residues and average relative residues, $\langle \text{Res} \rangle$. Besides, a ($\text{cm}^2 \text{keV}^{1.0001}$) and b ($\text{cm}^2 \text{keV}$) values, obtained after fittings provided by the physical equations, are shown for each certified sample. In the cases of ExS and $\eta(E_\gamma, Z)$, Rayleigh scattering has been considered, but not for the physical equations.

E_γ (keV)	IAEA-326					IAEA-327				
	WinXCOM η ($\text{cm}^2 \text{g}^{-1}$)		Relative residues (%)			WinXCOM η ($\text{cm}^2 \text{g}^{-1}$)		Relative residues (%)		
	Without Rayleigh scattering	With Rayleigh scattering	Physical equations	ExS	$\eta(E_\gamma, Z)$	Without Rayleigh scattering	With Rayleigh scattering	Physical equations	ExS	$\eta(E_\gamma, Z)$
46.54	3.76E-01	4.20E-01	-19.3	4.3	-6.3	3.70E-01	4.14E-01	-19.3	4.4	-6.1
59.54	2.56E-01	2.84E-01	9.0	0.6	-4.6	2.53E-01	2.81E-01	8.9	0.6	-4.6
63.29	2.37E-01	2.63E-01	14.7	2.3	-4.3	2.35E-01	2.60E-01	14.6	2.2	-4.3
88.03	1.77E-01	1.91E-01	32.1	1.3	-2.8	1.76E-01	1.90E-01	31.8	1.2	-3.1
163.3	1.32E-01	1.37E-01	23.8	0.3	-0.7	1.32E-01	1.37E-01	23.6	0.4	-1.1
186	1.26E-01	1.30E-01	19.5	0.4	-0.3	1.26E-01	1.29E-01	19.4	0.5	-0.6
238.6	1.15E-01	1.17E-01	11.0	1.4	0.1	1.15E-01	1.17E-01	10.9	1.4	-0.3
295.2	1.07E-01	1.08E-01	3.8	0.0	-0.1	1.07E-01	1.08E-01	3.9	0.0	-0.4
338.4	1.01E-01	1.02E-01	-0.6	0.7	-0.4	1.01E-01	1.02E-01	-0.6	0.7	-0.6
351.9	9.97E-02	1.01E-01	-1.9	0.3	-0.4	9.97E-02	1.01E-01	-1.8	0.3	-0.6
563.2	8.23E-02	8.27E-02	-15.5	0.4	-0.5	8.23E-02	8.27E-02	-15.3	0.4	-0.4
583.2	8.11E-02	8.14E-02	-16.5	0.7	-0.4	8.11E-02	8.14E-02	-16.2	0.7	-0.3
604.7	7.98E-02	8.01E-02	-17.4	-0.2	-0.3	7.98E-02	8.02E-02	-17.2	-0.2	-0.1
609.3	7.95E-02	7.99E-02	-17.6	0.2	-0.3	7.96E-02	7.99E-02	-17.3	0.2	-0.1
661.8	7.67E-02	7.70E-02	-19.7	0.1	-0.1	7.67E-02	7.70E-02	-19.4	0.0	0.1
727.3	7.35E-02	7.37E-02	-22.0	0.4	0.1	7.35E-02	7.37E-02	-21.7	0.4	0.4
795.8	7.05E-02	7.07E-02	-24.1	0.4	0.1	7.05E-02	7.07E-02	-23.8	0.4	0.6
801.9	7.03E-02	7.05E-02	-24.2	-0.7	0.1	7.03E-02	7.05E-02	-24.0	-0.7	0.6
834.8	6.90E-02	6.91E-02	-25.2	-0.2	0.1	6.90E-02	6.92E-02	-24.9	-0.2	0.6
911.2	6.62E-02	6.63E-02	-27.1	1.0	-0.1	6.62E-02	6.63E-02	-26.8	1.0	0.6
964.6	6.44E-02	6.45E-02	-28.3	0.8	-0.3	6.44E-02	6.45E-02	-28.0	0.7	0.4
969	6.42E-02	6.44E-02	-28.4	-0.6	-0.3	6.43E-02	6.44E-02	-28.1	1.0	0.4
1099	6.04E-02	6.05E-02	-30.9	0.9	-1.0	6.04E-02	6.05E-02	-30.6	0.8	0.0

1116	5.99E-02	6.00E-02	-31.2	-0.1	-1.1	5.99E-02	6.01E-02	-30.9	-0.1	-0.1
1120	5.98E-02	5.99E-02	-31.3	0.2	-1.1	5.98E-02	5.99E-02	-31.0	0.1	-0.1
1168	5.86E-02	5.87E-02	-32.1	0.6	-1.4	5.86E-02	5.87E-02	-31.8	0.6	-0.3
1173	5.84E-02	5.85E-02	-32.2	0.8	-1.4	5.85E-02	5.85E-02	-31.9	0.8	-0.3
1310	5.53E-02	5.53E-02	-34.2	-0.6	-2.1	5.53E-02	5.53E-02	-33.9	-0.6	-0.8
1333	5.48E-02	5.49E-02	-34.5	0.3	-2.1	5.48E-02	5.49E-02	-34.2	0.3	-0.8
1365	5.41E-02	5.42E-02	-35.0	-0.3	-2.3	5.41E-02	5.42E-02	-34.7	-0.3	-0.9
1461	5.23E-02	5.23E-02	-36.2	-0.6	-2.5	5.23E-02	5.23E-02	-35.9	-0.6	-1.0
1764	4.75E-02	4.75E-02	-39.5	1.1	-2.8	4.75E-02	4.75E-02	-39.2	1.1	-0.9
			<Res> =	<Res>	<Res>				<Res> =	<Res>
			25.6	=	=				25.4	=
				1.1	2.0					1.1
			Parameters:						Parameters:	
			-a =						-a =	
			3.0(3)E-23						1.59(16)E-	
			b =						22	
			3.6(4)E-20						b =	
									3.0(4)E-19	

IAEA-PG					
E_γ (keV)	WinXCOM η (cm ² g ⁻¹)		Relative residues (%)		
	Without Rayleigh scattering	With Rayleigh scattering	Physical equations	ExS	$\eta(E_\gamma, Z)$
46.54	4.86E-01	5.37E-01	-19.2	4.8	-4.8
59.54	3.09E-01	3.42E-01	10.2	0.6	-3.7
63.29	2.82E-01	3.11E-01	16.5	2.8	-3.4
88.03	1.95E-01	2.11E-01	36.8	1.9	-2.8
163.3	1.38E-01	1.43E-01	26.7	1.0	-1.4
186	1.31E-01	1.35E-01	21.5	1.0	-1.1
238.6	1.19E-01	1.21E-01	11.1	1.4	-0.7
295.2	1.10E-01	1.11E-01	2.7	0.6	-1.0
338.4	1.04E-01	1.05E-01	-2.4	0.7	-1.3
351.9	1.03E-01	1.04E-01	-3.8	0.4	-1.3
563.2	8.45E-02	8.50E-02	-19.1	0.0	-1.3
583.2	8.32E-02	8.37E-02	-20.1	0.4	-1.2
604.7	8.19E-02	8.23E-02	-21.1	-0.4	-1.1
609.3	8.17E-02	8.21E-02	-21.3	-0.1	-1.0
661.8	7.87E-02	7.91E-02	-23.6	-0.1	-0.8
727.3	7.55E-02	7.57E-02	-26.1	0.4	-0.6
795.8	7.24E-02	7.26E-02	-28.3	0.5	-0.5
801.9	7.21E-02	7.24E-02	-28.5	-0.5	-0.5
834.8	7.08E-02	7.10E-02	-29.5	0.0	-0.6
911.2	6.79E-02	6.81E-02	-31.5	-0.1	-0.8
964.6	6.61E-02	6.62E-02	-32.8	-0.4	-1.0
969	6.59E-02	6.61E-02	-32.9	-0.2	-1.0
1099	6.20E-02	6.21E-02	-35.5	-0.1	-1.6
1116	6.15E-02	6.16E-02	-35.8	0.6	-1.7
1120	6.14E-02	6.15E-02	-35.9	0.8	-1.7
1168	6.01E-02	6.02E-02	-36.7	-0.4	-2.0
1173	6.00E-02	6.01E-02	-36.8	-0.1	-2.0
1310	5.67E-02	5.68E-02	-39.0	0.3	-2.4
1333	5.62E-02	5.63E-02	-39.3	-0.6	-2.4
1365	5.55E-02	5.56E-02	-39.7	0.7	-2.5
1461	5.37E-02	5.37E-02	-41.0	0.5	-2.4
1764	4.87E-02	4.88E-02	-44.4	0.5	-2.1
			<Res> =	<Res>	<Res>
			29.4	=	=
				1.2	2.0
			Parameters:		
			-a =		
			7.5(8)E-23		
			b =		
			2.3(3)E-19		

SUPPLEMENTARY MATERIAL-D

Table D.1

pr_i values obtained after fitting the experimental *FEPE* values fixing the energy, E_γ , and varying the RGU-1 standard thickness, h .

E_γ (keV)	pr_1	$-pr_2(mm^{-1})$	pr_3
46.539	0.235(6)	0.064(4)	0.052(3)
63.288	0.234(5)	0.049(3)	0.052(3)
92.56	0.217(6)	0.049(3)	0.063(4)
185.96	0.152(3)	0.051(3)	0.049(2)
241.979	0.112(2)	0.043(3)	0.033(3)
295.224	0.0926(12)	0.047(2)	0.0303(11)
351.932	0.0775(6)	0.043(2)	0.0238(9)
609.312	0.0368(4)	0.039(2)	0.0133(6)
768.356	0.0292(15)	0.033(2)	0.0097(6)
934.06	0.0224(6)	0.040(3)	0.0110(7)
1120.285	0.0215(4)	0.028(2)	0.0059(3)
1238.11	0.0197(7)	0.032(2)	0.0067(4)
1764.494	0.0182(5)	0.041(3)	0.0068(3)

Table D.2

pr_i values obtained after fitting the experimental *FEPE* values fixing the energy, E_γ , and varying the thicknesses of the RGTh-1 and RGK-1 standards, h .

E_γ (keV)	pr_1	$-pr_2(mm^{-1})$	pr_3
129.03	0.122(5)	0.047(3)	0.041(3)
238.63	0.1195(7)	0.0505(19)	0.0396(18)
338.42	0.0857(7)	0.0442(17)	0.0237(12)
583.19	0.0364(7)	0.034(2)	0.0121(6)
727.30	0.0412(18)	0.037(2)	0.0125(8)
860.00	0.0305(12)	0.048(3)	0.0132(7)
911.16	0.0303(6)	0.0374(18)	0.0102(4)
968.97	0.0306(8)	0.033(2)	0.0082(5)
1460.83	0.0214(4)	0.0419(16)	0.0077(3)
1588.23	0.0194(8)	0.0279(18)	0.0049(3)

Table D.3

Gamma emission energies and their gamma emission probabilities, E_γ and P_γ , respectively, selected to fit each parameter, pr_i (with “i” = 1, 2, 3), in order to obtain the general $\varepsilon_c(E_\gamma > 150 \text{ keV}, h)$ function.

RN	E_γ (keV)	P_γ	pr_1	pr_2	pr_3
234 Th	63.288	0.0375(8)	✗	✗	✗
	92.56	0.0215(19)	✗	✗	✗
226 Ra	185.96	0.0614(6)	✓	✓	✓
214 Pb	241.979	0.0727(2)	✓	✓	✓

	295.224	0.1841(4)	✓	✓	✓
	351.932	0.3560(7)	✓	✓	✓
	609.312	0.4549(19)	✗	✓	✓
	768.356	0.04892(16)	✗	✗	✗
214 Bi	934.06	0.0310(10)	✗	✓	✓
	1120.285	0.1491(3)	✗	✗	✗
	1238.11	0.05831(14)	✗	✓	✓
	1764.494	0.1531(5)	✓	✗	✗
210 Pb	46.539	0.0425(4)	✗	✗	✗
	129.03	0.0250(7)	✗	✗	✗
	338.42	0.114(4)	✓	✓	✓
228 Ac	911.16	0.262(8)	✓	✓	✓
	968.97	0.159(5)	✓	✓	✓
	1588.23	0.0306(12)	✓	✗	✓
212 Pb	238.63	0.436(5)	✓	✓	✓
212 Bi	727.30	0.0665(4)	✓	✓	✓
208 Tl	583.19	0.3058(11)	✗	✗	✗
	860.00	0.0446(4)	✓	✗	✗
40 K	1460.83	0.1055(11)	✓	✗	✓

Table D.4

Artificial radionuclides and their respective gamma energies, E_γ , chosen for this study. Besides, their gamma emission probabilities, P_γ , and half-lives, $T_{1/2}$, have also been given.

RN	E_γ (keV)	P_γ (%)	$T_{1/2}$ (years)
54 Mn	834.80	99.9752(5)	0.85530(8)
59 Fe	1099.25	56.5(3)	0.12190(3)
60 Co	1173.20	99.85(3)	5.2711(8)
65 Zn	1115.60	50.6(2)	0.6685(3)
133 Ba	356.00	62.05(19)	10.539(6)
134 Cs	795.80	85.47(9)	2.0644(14)
137 Cs	661.80	85.0(2)	30.05(8)
152 Eu	344.3	26.59(12)	13.522(16)
241 Am	59.54	35.92(17)	432.6(6)

Table D.5

Parameter values ($a_{Ti}^{low <Z>}$) resulted from fitting $f_g \times f_s$ versus d and fixing E_γ in the case of a low $<Z>$ - sample. Besides, the relative average residuals have been calculated for each E_γ value.

RN	E_γ (keV)	$10^{-1} a_{T1}^{low <Z>}$	$-10^{-2} a_{T2}^{low <Z>}$ (mm^{-1})	$10^{-2} a_{T3}^{low <Z>}$	$<Residual>$ (%)
210 Pb	46				
234 Th	63	10.8(2)	1.73(4)	-8.42(17)	2.0

226 Ra	186				
214 Pb	242, 295, 352				
	609	6.03(8)	1.79(3)	7.76(11)	1.4
	768	7.34(17)	1.55(4)	0.111(3)	2.3
214 Bi	934	6.06(15)	2.44(6)	14.8(4)	2.4
	1120	8.39(15)	1.61(3)	-3.20(6)	1.8
	1238	7.73(19)	1.95(5)	4.81(12)	2.4

Table D.6

Parameter values ($a_{Ti}^{high<Z>}$) resulted from fitting $f_g \times f_a$ versus d and fixing E_γ in the case of a high $<Z>$ - sample. Besides, the relative average residuals have been calculated for each E_γ value.

RN	E_γ (keV)	$a_{T1}^{high<Z>}$	$-10^{-2} a_{T2}^{high<Z>}$ (mm^{-1})	$-10^{-2} a_{T3}^{high<Z>}$	$<Residual>$ (%)
210 Pb	46	1.35(6)	2.89(13)	-6.8(3)	4.5
234 Th	63	1.28(3)	3.21(6)	-12.2(2)	2.0
226 Ra	186	1.42(3)	11.7(3)	36.3(9)	2.4
	242	1.55(5)	0.94(3)	54.8(1.9)	3.5
214 Pb	295	1.01(2)	1.96(4)	2.00(4)	2.0
	352	1.00(3)	1.94(5)	2.12(6)	2.7

Table D.7

Parameter values ($a_{Ti}^{high<Z>}$) resulted from fitting $f_g \times f_s$ versus d and fixing E_γ in the case of a high $<Z>$ - sample. Besides, the relative average residuals have been calculated for each E_γ value.

RN	E_γ (keV)	$10^{-1} a_{T1}^{high<Z>}$	$-10^{-2} a_{T2}^{high<Z>}$ (mm^{-1})	$10^{-2} a_{T3}^{high<Z>}$	$<Residual>$ (%)
	609	5.9(2)	2.13(8)	13.0(5)	3.6
	768	6.88(17)	1.95(5)	8.7(2)	2.5
214 Bi	934	6.23(17)	2.43(7)	15.6(4)	2.7
	1120	8.79(19)	1.59(3)	-4.62(10)	2.1
	1238	7.28(18)	2.35(6)	12.0(3)	2.5

Table D.8

Experimental $FEPE$ values (in %) corrected at each d value, these efficiency values having been calculated varying E_γ and fixing the RGU-1 standard thickness, h , at 25 mm.

RN	E_γ (keV)	d (mm)	0	25	35	45	55	65
210 Pb	46		9.98(18)	3.92(8)	2.96(6)	2.15(4)	1.96(4)	1.41(3)
234 Th	63		11.8(1.0)	4.3(4)	3.3(3)	2.4(2)	1.93(16)	1.49(12)
226 Ra	186		9.26(6)	3.6(2)	2.71(18)	2.15(14)	1.75(12)	1.31(9)
214 Pb	242		6.79(14)	2.79(6)	2.10(5)	1.61(3)	1.32(3)	0.979(19)

	295	5.87(8)	2.40(3)	1.76(3)	1.35(2)	1.106(17)	0.840(11)
	352	4.58(6)	2.04(3)	1.52(2)	1.16(16)	0.930(13)	0.699(9)
	609	2.15(3)	1.230(17)	0.926(13)	0.708(10)	0.593(9)	0.473(6)
	768	1.74(6)	0.99(3)	0.79(3)	0.59(2)	0.500(18)	0.388(11)
214 Bi	934	1.45(6)	0.77(4)	0.68(3)	0.53(2)	0.396(19)	0.354(13)
	1120	1.32(3)	0.749(18)	0.590(15)	0.451(11)	0.364(9)	0.293(6)
	1238	1.25(4)	0.67(3)	0.51(2)	0.424(16)	0.345(14)	0.275(9)

Table D.9

Parameter values (b_i) resulted from fitting $\ln(\varepsilon_c)$ versus $\ln(E_\gamma/E_0)$ and fixing the distance d , which is ranged from 0 to 65 mm. This efficiency calibration was carried out using the RGU-1 standard whose thickness was fixed at 25 mm. Furthermore, the relative average residuals and χ_R^2 values have been calculated for each d value, where the critical χ_R^2 is 2.01 at 0.05 significance level and 7 degrees of freedom.

d (mm)	$-b_0$	b_1	$-b_2$	b_3	<Residual> (%)	χ_R^2
0	34.7(1.2)	18.3(6)	3.28(11)	0.184(6)	3.8	3.07
25	22.9(5)	11.0(2)	1.94(4)	0.105(2)	3.6	1.57
35	20.9(2)	9.79(10)	1.73(2)	0.0933(9)	3.1	1.80
45	25.7(5)	12.3(3)	2.19(5)	0.121(3)	3.3	1.42
55	21.0(8)	9.6(4)	1.71(7)	0.092(4)	4.6	3.21
65	21.2(1.1)	9.6(5)	1.70(9)	0.092(5)	4.4	5.01

Table D.10

Parameter values (c_i) resulted from fitting dead time (t_d) versus distance (d), which is ranged from 0 to 65 mm. Furthermore, the relative average residues have been obtained for each chosen scale type.

Scale type	c_1	$-10^{-2} c_2$ (mm ⁻¹)	c_3	<Residual> (%)
Scale-A	28.9(6)	4.47(9)	2.91(6)	2.0
Scale-B	55.2(6)	3.45(4)	5.06(6)	1.1
Scale-C	41.6(7)	4.05(7)	3.91(6)	1.6

Table D.11

Chemical compositions (in %) and apparent densities (ρ , in g cm⁻³) of all the samples analyzed in this work.

	RGU-1	RGTh-1	RGK-1	IAEA-326	IAEA-327	IAEA-375	Sn-Sample	K ₂ CO ₃	Scale-A	Scale-B
ρ	1.63(2)	1.63(2)	1.63(2)	1.21	1.24	1.64	3.54	1.22	1.96	2.43
C								8.7		
O	53.354	53.5398	36.727	54.303	51.5	50.5	24.0	34.8	48.0	48.0
Na	0.03			0.59	0.85	0.33			4.0	3.0
Mg		0.02		0.615	0.46	0.36			9.0	5.0

Al	0.01	0.04		5.5	5.07	5.17	1.0		12.0	10.0
Si	46.4	45.0		32.68	36.82	37.22	1.0		9.0	10.0
P		0.129		0.075	0.03	0.02			0.9	0.7
S			18.398						12.0	10.0
K			44.875	1.9	2.05	2.04		56.5	2.0	5.0
Ca	0.03	0.42		1.16	0.58	1.58			3.1	7.3
Ti	0.008			0.45	0.504	0.604				
Mn		0.014		0.06	0.05	0.07	3.0			1.0
Fe	0.03	0.13		2.667	2.086	2.106	3.0			
Co							3.0			
Zr							5.0			
Sn							53.0			
W							7.0			
Ba		0.6235								
Pb	0.008	0.003								
Th		0.081								
U	0.04									

	Scale-C	Furnace Slag	Milk powder	Soil-1	Soil-2	IARMA- 097	IARMA- 098	IARMA- 099	IARMA- 100	Water-1 and Water-5
ρ	2.70	1.69	0.89	1.43	1.62	0.78	1.00	1.00	1.01	0.98
H			5.5			12.0	11.2	11.2	11.2	11.2
C			43.5			55.0				
N			1.6			10.0				
O	48.0	30.0	40.4	52.303	48.303	16.0	88.8	88.8	88.8	88.8
Na	2.0		1.0	0.59	0.59					
Mg	7.0		1.0	0.615	0.615	1.0				
Al	9.0	10.0		4.5	6.5					
Si	9.0	30.0		34.68	34.68					
P	0.9		3.0	0.075	0.075					
S	12.0									
K	2.0		1.0	2.9	3.9					
Ca	8.1	30.0	3.0	1.16	2.16	6.0				
Ti				0.45	0.45					
Mn	2.0			0.06	0.06					
Fe				2.667	2.667					

SUPPLEMENTARY MATERIAL-E

Table E.1

Experimental efficiencies obtained in the calibration procedure for slotted filters (SL), $\varepsilon_{exp}^{SL(j)}$, where $j = 1, 2$. Then, $m_{RGU-1}^{SL(j)}$ is the amount of RGU-1 added to each filter “j” in order to carry out the efficiency calibration. By using the $\varepsilon_{exp}^{SL(j)}$ values obtained for both filters, an average experimental efficiency was calculated, ε_{exp}^{SL} , for each E_γ , where $\sigma(\varepsilon_{exp}^{SL(j)})$ and $\sigma(\varepsilon_{exp}^{SL})$ are the uncertainties related to $\varepsilon_{exp}^{SL(j)}$ and ε_{exp}^{SL} , respectively, and Res (%) are the relative residuals resulted from fitting $\ln(\varepsilon_{exp}^{SL})$ versus $\ln(E_\gamma/E_0)$, being $E_0 = 1$ keV.

(*) In the case of the ^7Be , the efficiency value for slotted filters was obtained by using the fitting function given in Table E.2.

RN	E_γ (keV)	$m_{RGU-1}^{SL(1)} \text{ (g)} =$ 0.5115(2)		$m_{RGU-1}^{SL(2)} \text{ (g)} = 0.5014(2)$		ε_{exp}^{SL}	$\sigma(\varepsilon_{exp}^{SL})$	Res (%)
		$\varepsilon_{exp}^{SL(1)}$	$\sigma(\varepsilon_{exp}^{SL(1)})$	$\varepsilon_{exp}^{SL(2)}$	$\sigma(\varepsilon_{exp}^{SL(2)})$			
^{210}Pb	46.54	0.174	0.007	0.170	0.006	0.172	0.005	0.28
^{226}Ra	185.96	0.118	0.009	0.123	0.009	0.121	0.007	0.21
^{214}Pb	295.22	0.0697	0.0018	0.0732	0.0017	0.0715	0.0013	2.2
	351.93	0.0601	0.0012	0.0625	0.0012	0.0613	0.0009	-3.2
	609.31	0.0297	0.0007	0.0306	0.0007	0.0302	0.0005	3.1
^{214}Bi	1120.29	0.0179	0.0010	0.0179	0.0009	0.0179	0.0007	-1.7
	1764.49	0.0139	0.0008	0.0144	0.0008	0.0141	0.0006	0.78
^7Be	477.60					(*)0.0410	0.0010	

Table E.2

Parameters and their uncertainties, a_k^{SL} and $\sigma(a_k^{SL})$, respectively, being $k = 0, 1, 2, 3$, resulted from fitting the logarithm of the experimental efficiencies obtained in the case of the slotted filters (SL), ε_{exp}^{SL} , versus $\ln(E_\gamma/E_0)$, being $E_0 = 1$ keV.

Parameter	a_k^{SL}	$\sigma(a_k^{SL})$	R^2
a_3^{SL}	0.145	0.002	0.9995
a_2^{SL}	-2.58	0.04	
a_1^{SL}	14.2	0.2	
a_0^{SL}	-26.3	0.4	

Table E.3

Experimental efficiencies obtained in the calibration procedure for circular filters whose diameter is 150 mm (C-150), $\varepsilon_{exp}^{C-150(j)}$, where $j = 1, 2, 3$. Then, $m_{RGU-1}^{C-150(j)}$ is the amount of RGU-1 added to each filter “j” in order to carry out the efficiency calibration. By using the $\varepsilon_{exp}^{C-150(j)}$ values obtained for the three filters, an average experimental efficiency was calculated, $\varepsilon_{exp}^{C-150}$, for each E_γ , where $\sigma(\varepsilon_{exp}^{C-150(j)})$ and $\sigma(\varepsilon_{exp}^{C-150})$ are the uncertainties related to $\varepsilon_{exp}^{C-150(j)}$ and $\varepsilon_{exp}^{C-150}$, respectively, and Res (%) are the relative residuals resulted from fitting $\ln(\varepsilon_{exp}^{C-150})$ versus $\ln(E_\gamma/E_0)$, being $E_0 = 1$ keV.

(*) In the case of the ^7Be , the efficiency value for circular filters ($\varnothing = 150$ mm) was obtained by using the fitting function given in Table E.4.

RN	E_γ (keV)	$m_{RGU-1}^{C-150(1)}(\text{g}) = 0.5029(2)$		$m_{RGU-1}^{C-150(2)}(\text{g}) = 0.4898(2)$		$m_{RGU-1}^{C-150(3)}(\text{g}) = 0.5006(2)$		$\varepsilon_{exp}^{C-150}$	$\sigma(\varepsilon_{exp}^{C-150})$	Res (%)
		$\varepsilon_{exp}^{C-150(1)}$	$\sigma(\varepsilon_{exp}^{C-150(1)})$	$\varepsilon_{exp}^{C-150(2)}$	$\sigma(\varepsilon_{exp}^{C-150(2)})$	$\varepsilon_{exp}^{C-150(3)}$	$\sigma(\varepsilon_{exp}^{C-150(3)})$			
^{210}Pb	46.54	0.181	0.014	0.157	0.007	0.150	0.013	0.1619	0.007	-2.3
^{226}Ra	185.96	0.093	0.012	0.114	0.010	0.128	0.014	0.111	0.007	0.17
^{214}Pb	295.22	0.070	0.003	0.0684	0.0019	0.076	0.004	0.0715	0.0018	-4.1
	351.93	0.0615	0.0023	0.0561	0.0013	0.0637	0.0023	0.0603	0.0012	-7.3
	609.31	0.0296	0.0014	0.0280	0.0008	0.0332	0.0015	0.0302	0.0007	-2.3
^{214}Bi	1120.29	0.0146	0.0018	0.0172	0.0011	0.0180	0.0020	0.0165	0.0010	-2.2
	1764.49	0.0136	0.0017	0.0136	0.0009	0.0118	0.0016	0.0130	0.0008	-5.7
^7Be	477.60							(*)0.042	0.002	

Table E.4

Parameters and their uncertainties, a_k^{C-150} and $\sigma(a_k^{C-150})$, respectively, being $k = 0, 1, 2, 3$, resulted from fitting the logarithm of the experimental efficiencies obtained in the case of the circular filters whose diameter is 150 mm (C-150), $\varepsilon_{exp}^{C-150}$, versus $\ln(E_\gamma/E_0)$, being $E_0 = 1$ keV.

Parameter	a_k^{C-150}	$\sigma(a_k^{C-150})$	R^2
a_3^{C-150}	0.128	0.004	0.9993
a_2^{C-150}	-2.31	0.08	
a_1^{C-150}	12.8	0.4	
a_0^{C-150}	-24.0	0.8	

Table E.5

Experimental efficiencies obtained in the calibration procedure for circular filters whose diameter is 47 mm (C-47), $\varepsilon_{exp}^{C-47(j)}$, where $j = 1, 2, 3$. Then, $m_{RGU-1}^{C-47(j)}$ is the amount of RGU-1 added to each filter “j” in order to carry out the efficiency calibration. By using the $\varepsilon_{exp}^{C-47(j)}$ values obtained for the three filters, an average experimental efficiency was calculated, ε_{exp}^{C-47} , for each E_γ , where $\sigma(\varepsilon_{exp}^{C-47(j)})$ and $\sigma(\varepsilon_{exp}^{C-47})$ are the uncertainties related to $\varepsilon_{exp}^{C-47(j)}$ and ε_{exp}^{C-47} , respectively, and Res (%) are the relative residuals resulted from fitting $\ln(\varepsilon_{exp}^{C-47})$ versus $\ln(E_\gamma/E_0)$, being $E_0 = 1$ keV.

(*) In the case of the ^7Be , the efficiency value for circular filters ($\varnothing = 47$ mm) was obtained by using the fitting function given in Table E.6.

RN	E_γ (keV)	$m_{RGU-1}^{C-47(1)}(g) = 0.5029(2)$		$m_{RGU-1}^{C-47(2)}(g) = 0.4898(2)$		$m_{RGU-1}^{C-47(3)}(g) = 0.5006(2)$		ε_{exp}^{C-47}	$\sigma(\varepsilon_{exp}^{C-47})$	Res (%)
		$\varepsilon_{exp}^{C-47(1)}$	$\sigma(\varepsilon_{exp}^{C-47(1)})$	$\varepsilon_{exp}^{C-47(2)}$	$\sigma(\varepsilon_{exp}^{C-47(2)})$	$\varepsilon_{exp}^{C-47(3)}$	$\sigma(\varepsilon_{exp}^{C-47(3)})$			
^{210}Pb	46.54	0.291	0.015	0.25	0.02	0.305	0.011	0.2818	0.0281	-0.64
^{226}Ra	185.96	0.220	0.018	0.21	0.02	0.201	0.015	0.2096	0.0110	5.8
^{214}Pb	295.22	0.133	0.004	0.119	0.006	0.125	0.003	0.1254	0.0067	-0.82
	351.93	0.111	0.003	0.100	0.004	0.103	0.002	0.1045	0.0062	-6.5
	609.31	0.0505	0.0016	0.041	0.002	0.0456	0.0011	0.0458	0.0046	2.2
^{214}Bi	1120.29	0.023	0.002	0.023	0.003	0.0267	0.0015	0.0243	0.0021	5.0
	1764.49	0.0228	0.0019	0.020	0.003	0.0240	0.0013	0.0223	0.0020	-1.7
^7Be	477.60							(*)0.064	0.002	

Table E.6

Parameters and their uncertainties, a_k^{C-47} and $\sigma(a_k^{C-47})$, respectively, being $k = 0, 1, 2, 3$, resulted from fitting the logarithm of the experimental efficiencies obtained in the case of the circular filters whose diameter is 47 mm (C-47), ε_{exp}^{C-47} , versus $\ln(E_\gamma/E_0)$, being $E_0 = 1$ keV.

Parameter	a_k^{C-47}	$\sigma(a_k^{C-47})$	R^2
a_3^{C-47}	0.196	0.006	0.998
a_2^{C-47}	-3.47	0.10	
a_1^{C-47}	19.2	0.6	
a_0^{C-47}	-34.7	1.0	

Table E.7

Experimental efficiencies obtained in the calibration procedure for rectangular filters (R), $\varepsilon_{exp}^{R(j)}$, where $j = 1, 2, 3$. Then, $m_{RGU-1}^{R(j)}$ is the amount of RGU-1 added to each filter “j” in order to carry out the efficiency calibration. By using the $\varepsilon_{exp}^{R(j)}$ values obtained for the three filters, an average experimental efficiency was calculated, ε_{exp}^R , for each E_γ , where $\sigma(\varepsilon_{exp}^{R(j)})$ and $\sigma(\varepsilon_{exp}^R)$ are the uncertainties related to $\varepsilon_{exp}^{R(j)}$ and ε_{exp}^R , respectively, and Res (%) are the relative residuals resulted from fitting $\ln(\varepsilon_{exp}^R)$ versus $\ln(E_\gamma/E_0)$, being $E_0 = 1$ keV.

(*) In the case of the ^7Be , the efficiency value for rectangular filters was obtained by using the fitting function given in Table E.8.

RN	E_γ (keV)	$m_{RGU-1}^{R(1)} \text{ (g)} = 0.6018(2)$		$m_{RGU-1}^{R(2)} \text{ (g)} = 0.5913(2)$		$m_{RGU-1}^{R(3)} \text{ (g)} = 0.5914(2)$		ε_{exp}^R	$\sigma(\varepsilon_{exp}^R)$	Res (%)
		$\varepsilon_{exp}^{R(1)}$	$\sigma(\varepsilon_{exp}^{R(1)})$	$\varepsilon_{exp}^{R(2)}$	$\sigma(\varepsilon_{exp}^{R(2)})$	$\varepsilon_{exp}^{R(3)}$	$\sigma(\varepsilon_{exp}^{R(3)})$			
^{210}Pb	46.54	0.159	0.008	0.161	0.007	0.149	0.0085	0.1559	0.005	-0.47
^{226}Ra	185.96	0.121	0.011	0.107	0.009	0.133	0.011	0.1196	0.006	2.9
^{214}Pb	295.22	0.0770	0.0025	0.0729	0.0020	0.0780	0.0024	0.0759	0.0013	-0.85
	351.93	0.0676	0.0017	0.0623	0.0014	0.0639	0.0016	0.0646	0.0009	-5.3
	609.31	0.0326	0.0010	0.0311	0.0008	0.0319	0.0010	0.0319	0.0005	0.42
^{214}Bi	1120.29	0.0172	0.0013	0.0170	0.0011	0.0186	0.0013	0.0176	0.0007	1.8
	1764.49	0.0163	0.0012	0.0140	0.0009	0.0140	0.0011	0.0147	0.0006	-2.6
^7Be	477.60							(*)0.042	0.002	

Table E.8

Parameters and their uncertainties, a_k^R and $\sigma(a_k^R)$, respectively, being $k = 0, 1, 2, 3$, resulted from fitting the logarithm of the experimental efficiencies obtained in the case of the rectangular filters (R), ε_{exp}^R , versus $\ln(E_\gamma/E_0)$, being $E_0 = 1$ keV.

Parameter	a_k^R	$\sigma(a_k^R)$	R^2
a_3^R	0.150	0.003	0.9991
a_2^R	-2.70	0.05	
a_1^R	15.0	0.3	
a_0^R	-28.1	0.5	

Table E.9

Experimental efficiencies obtained in the calibration procedure for squared filters (SQ), $\varepsilon_{exp}^{SQ(j)}$, where j = 1, 2, 3. Then, $m_{RGU-1}^{SQ(j)}$, $m_{RGTh-1}^{SQ(j)}$ and $m_{RGK-1}^{SQ(j)}$ are the amounts of RGU-1, RGTh-1 and RGK-1, respectively, added to each filter “j” in order to carry out the efficiency calibration. By using the $\varepsilon_{exp}^{SQ(j)}$ values obtained for the three filters, an average experimental efficiency was calculated, ε_{exp}^{SQ} , for each E_γ , where $\sigma(\varepsilon_{exp}^{SQ(j)})$ and $\sigma(\varepsilon_{exp}^{SQ})$ are the uncertainties related to $\varepsilon_{exp}^{SQ(j)}$ and ε_{exp}^{SQ} , respectively, and *Res* (%) are the relative residuals resulted from fitting $\ln(\varepsilon_{exp}^{SQ})$ versus $\ln(E_\gamma/E_0)$, being $E_0 = 1$ keV.

(*) In the case of the ^7Be , the efficiency value for squared filters was obtained by using the fitting function given in Table E.10.

RN	E_γ (keV)	$m_{RGU-1}^{SQ(1)}, m_{RGTh-1}^{SQ(1)},$ $m_{RGK-1}^{SQ(1)} = 0.8337(2) \text{ g}$		$m_{RGU-1}^{SQ(2)}, m_{RGTh-1}^{SQ(2)},$ $m_{RGK-1}^{SQ(2)} = 0.8339(2) \text{ g}$		$m_{RGU-1}^{SQ(3)}, m_{RGTh-1}^{SQ(3)},$ $m_{RGK-1}^{SQ(3)} = 0.8302(2) \text{ g}$		ε_{exp}^{SQ}	$\sigma(\varepsilon_{exp}^{SQ})$	<i>Res</i> (%)
		$\varepsilon_{exp}^{SQ(1)}$	$\sigma(\varepsilon_{exp}^{SQ(1)})$	$\varepsilon_{exp}^{SQ(2)}$	$\sigma(\varepsilon_{exp}^{SQ(2)})$	$\varepsilon_{exp}^{SQ(3)}$	$\sigma(\varepsilon_{exp}^{SQ(3)})$			
^{210}Pb	46.54	0.085	0.005	0.094	0.005	0.099	0.005	0.092	0.007	-0.60
^{234}Th	63.29	0.103	0.011	0.123	0.012	0.106	0.011	0.112	0.011	1.4
^{226}Ra	185.96	0.081	0.007	0.090	0.007	0.080	0.007	0.083	0.006	0.026
^{212}Pb	238.63	0.068	0.002	0.075	0.002	0.069	0.002	0.067	0.004	-4.9
^{214}Pb	295.22	0.0472	0.0012	0.0564	0.0013	0.0582	0.0014	0.055	0.006	1.7
	351.93	0.0420	0.0008	0.0475	0.0009	0.0478	0.0009	0.046	0.003	-0.21
^{208}Tl	583.19	0.0253	0.0011	0.0270	0.0012	0.0240	0.0011	0.0268	0.0016	5.3
	609.31	0.0226	0.0005	0.0250	0.0005	0.0257	0.0006	0.0256	0.0017	5.0
^{214}Bi	1120.29	0.0142	0.0007	0.0166	0.0007	0.0144	0.0008	0.0151	0.0013	0.22
	1764.49	0.0114	0.0006	0.0132	0.0007	0.0116	0.0007	0.0121	0.0007	1.7
^{228}Ac	911.16	0.0185	0.0010	0.0203	0.0011	0.0194	0.0011	0.0176	0.0008	-9.2
^{40}K	1460.83	0.0132	0.0007	0.0132	0.0007	0.0123	0.0007	0.0129	0.0006	0.22
^7Be	477.60							(*)0.0330	0.0013	

Table E.10

Parameters and their uncertainties, a_k^{SQ} and $\sigma(a_k^{SQ})$, respectively, being k = 0, 1, 2, 3, resulted from fitting the logarithm of the experimental efficiencies obtained in the case of the squared filters (SQ), ε_{exp}^{SQ} , versus $\ln(E_\gamma/E_0)$, being $E_0 = 1$ keV.

Parameter	a_k^{SQ}	$\sigma(a_k^{SQ})$	R^2
a_3^{SQ}	0.134	0.007	
a_2^{SQ}	-2.43	0.12	0.998
a_1^{SQ}	13.7	0.7	

a_0^{SQ}	-26.6	1.3
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SUPPLEMENTARY MATERIAL-F

In order to obtain the activities of the parent radionuclides, that is, ^{212}Pb or ^{214}Pb , corresponding to the particulate matter deposited on the filters during the samplings, A_{ps} , the following equations were used:

$$\begin{aligned} dA_{ps} &= \phi a_p e^{-\lambda_p(t-t_s^{(1)})} dt \rightarrow A_{ps} = \int_{t_s^{(1)}}^{t_s^{(2)}} \phi a_p e^{-\lambda_p(t-t_s^{(1)})} dt \\ &= \phi a_p \lambda_p^{-1} (1 - e^{-\lambda_p \Delta t_s}) \end{aligned} \quad (\text{Eq. F1})$$

where λ_p is the decay constant of the parent radionuclide, ϕ is the flow resulted from each sampling, Δt_s is the time interval that lasts each sampling, $t_s^{(1)}$ and $t_s^{(2)}$ being the moments when each sampling starts and ends, respectively, and a_p is the activity concentration of the parent radionuclide in air at $t_s^{(1)}$.

Therefore, by using Bateman equation, it is possible to know the activity of the daughter radionuclides, that is, ^{212}Bi or ^{214}Bi , for the particulate matter deposited on the filters during the samplings, A_{ds} :

$$\begin{aligned} dA_{ds} &= \frac{\phi a_p \lambda_d}{\lambda_d - \lambda_p} \left(e^{-\lambda_p(t-t_s^{(1)})} - e^{-\lambda_d(t-t_s^{(1)})} \right) dt + \phi a_d e^{-\lambda_d(t-t_s^{(1)})} dt \rightarrow \\ \rightarrow A_{ds} &= \int_{t_s^{(1)}}^{t_s^{(2)}} \left[\frac{\phi a_p \lambda_d}{\lambda_d - \lambda_p} \left(e^{-\lambda_p(t-t_s^{(1)})} - e^{-\lambda_d(t-t_s^{(1)})} \right) + \phi a_d e^{-\lambda_d(t-t_s^{(1)})} \right] dt \quad (\text{Eq. F2}) \\ &= \frac{\phi a_p \lambda_d}{\lambda_d - \lambda_p} [\lambda_p^{-1} (1 - e^{-\lambda_p \Delta t_s}) - \lambda_d^{-1} (1 - e^{-\lambda_d \Delta t_s})] \\ &\quad + \phi a_d \lambda_d^{-1} (1 - e^{-\lambda_d \Delta t_s}) \end{aligned}$$

where λ_d and a_d are the decay constant and the activity concentration in air at $t_s^{(1)}$ of the daughter radionuclide, respectively.

Furthermore, to make the equations of A_{ps} and A_{ds} easier to handle, Eqs. F1 and F2 are rewritten in the following way:

$$A_{ps} = a_p \phi C_{ps} \quad (\text{Eq. F3})$$

$$A_{ds} = \frac{a_p \phi \lambda_d}{\lambda_d - \lambda_p} [C_{ps} - C_{ds}] + a_d \phi C_{ds} \quad (\text{Eq. F4})$$

where $C_{ps} = \lambda_p^{-1} (1 - e^{-\lambda_p \Delta t_s})$ and $C_{ds} = \lambda_d^{-1} (1 - e^{-\lambda_d \Delta t_s})$.

Thus, by using Eqs. F3 and F4, it is possible to obtain the activity ratio of the daughter and parent radionuclides for the particulate matter existing on the filters during the sampling:

$$\frac{A_{ds}}{A_{ps}} = \frac{\lambda_d}{\lambda_d - \lambda_p} + \frac{C_{ds}}{C_{ps}} \left(\frac{a_d}{a_p} - \frac{\lambda_d}{\lambda_d - \lambda_p} \right) \quad (\text{Eq. F5})$$

Then, once the samplings end, it is interesting to study the A_{ps} and A_{ds} dependence on the time elapsed between the sampling end and any other moment, that is, $A_{ps}(t)$ and $A_{ds}(t)$. Consequently, the evolution of the activities of the parent and daughter radionuclides present in the particulate matter on the filters can be known at any moment t after ending the samplings at $t_s^{(2)}$. Thus, this is possible making use of the following equations, which are analogous equations to the ones provided by F3 and F4:

$$A_{ps}(t) = A_{ps} C_{ps^{(2)}-t} \quad (\text{Eq. F6})$$

$$A_{ds}(t) = \frac{A_{ps} \lambda_d}{\lambda_d - \lambda_p} [C_{ps^{(2)}-t} - C_{ds^{(2)}-t}] + A_{ds} C_{ds^{(2)}-t} \quad (\text{Eq. F7})$$

where A_{ps} and A_{ds} were given by Eqs. F3 and F4, respectively, $C_{ps^{(2)}-t} = e^{-\lambda_p(t-t_s^{(2)})}$ and $C_{ds^{(2)}-t} = e^{-\lambda_d(t-t_s^{(2)})}$. Therefore, $A_{ds}(t)/A_{ps}(t)$ can also be completely determined:

$$\frac{A_{ds}(t)}{A_{ps}(t)} = \frac{\lambda_d}{\lambda_d - \lambda_p} + \frac{C_{ds^{(2)}-t}}{C_{ps^{(2)}-t}} \left(\frac{A_{ds}}{A_{ps}} - \frac{\lambda_d}{\lambda_d - \lambda_p} \right) \quad (\text{Eq. F8})$$

Once the samplings end and the filters are measured by gamma-ray spectrometry, it is possible to obtain N_p and N_d , which are the net counts corresponding to the full-energy peaks at the energies of the photons emitted by the parent and daughter radionuclides, respectively, and they can be determined by the following equations:

$$dN_p = P_{\gamma p} \varepsilon_p A_{ps}(t) dt \rightarrow N_p = \int_{t_c^{(1)}}^{t_c^{(2)}} P_{\gamma p} \varepsilon_p A_{ps}(t) dt = P_{\gamma p} \varepsilon_p A_{ps} C_{ps^{(2)}-c^{(1)}} C_{pc} \quad (\text{Eq. F9})$$

$$dN_d = P_{\gamma d} \varepsilon_d A_{ds}(t) dt \rightarrow N_d = \int_{t_c^{(1)}}^{t_c^{(2)}} P_{\gamma d} \varepsilon_d A_{ds}(t) dt \quad (\text{Eq. F10})$$

$$= P_{\gamma d} \varepsilon_d \left\{ \frac{A_{ps} \lambda_d}{\lambda_d - \lambda_p} [C_{ps^{(2)}-c^{(1)}} C_{pc} - C_{ds^{(2)}-c^{(1)}} C_{dc}] + A_{ds} C_{ds^{(2)}-c^{(1)}} C_{dc} \right\}$$

where $P_{\gamma p}$ and ε_p are the gamma emission probability and the full-energy peak efficiency referred to the full-energy peak selected to determine the parent radionuclide, $P_{\gamma d}$ and ε_d have the same definitions than the previous ones, but referred to the daughter radionuclide, $A_{ps}(t)$ and $A_{ds}(t)$ were given by Eqs. F6 and F7, respectively, $C_{ps^{(2)}-c^{(1)}} = e^{-\lambda_p(t_c^{(1)}-t_s^{(2)})}$, $C_{ds^{(2)}-c^{(1)}} = e^{-\lambda_d(t_c^{(1)}-t_s^{(2)})}$,

$C_{pc} = \lambda_p^{-1}(1 - e^{-\lambda_p \Delta t_c})$, $C_{dc} = \lambda_d^{-1}(1 - e^{-\lambda_d \Delta t_c})$ and $\Delta t_c = t_c^{(2)} - t_c^{(1)}$, being $t_c^{(1)}$ and $t_c^{(2)}$ the moments corresponding to the start and end of the filter measurements by gamma spectrometry.

Consequently, making use of the Eqs. F9 and F10, as well as of the Eqs. F3 and F4, it is possible to know the equations that allow us to calculate the activity concentrations of the parent and daughter radionuclides present in air aerosols at the beginning of the samplings, that is, a_p and a_d , respectively, at $t_s^{(1)}$:

$$a_p = N_p [P_{\gamma p} \varepsilon_p \phi C_{ps} C_{ps^{(2)}-c^{(1)}} C_{pc}]^{-1} \quad (\text{Eq. F11})$$

$$a_d = \frac{1}{\phi C_{ds}} \left\{ \frac{N_d (P_{\gamma d} \varepsilon_d)^{-1}}{C_{ds^{(2)}-c^{(1)}} C_{dc}} - \frac{N_p (P_{\gamma p} \varepsilon_p)^{-1} \lambda_d}{\lambda_d - \lambda_p} \left[\frac{1}{C_{ds^{(2)}-c^{(1)}} C_{dc}} - \frac{1}{C_{ps^{(2)}-c^{(1)}} C_{pc}} \right] - \frac{N_p (P_{\gamma p} \varepsilon_p C_{ps} C_{ps^{(2)}-c^{(1)}} C_{pc})^{-1} \lambda_d}{\lambda_d - \lambda_p} [C_{ps} - C_{ds}] \right\} \quad (\text{Eq. F12})$$

Thus, by using Eqs. F11 and F12, the activity concentration ratios of the parent and daughter radionuclides can be obtained:

$$\begin{aligned} \frac{a_d}{a_p} &= \frac{C_{ps} C_{ps^{(2)}-c^{(1)}} C_{pc} \left(\frac{P_{\gamma d} \varepsilon_d N_p}{P_{\gamma p} \varepsilon_p N_d} \right)^{-1}}{C_{ds} C_{ds^{(2)}-c^{(1)}} C_{dc}} - \frac{\frac{C_{ps} \lambda_d}{\lambda_d - \lambda_p} [C_{ps^{(2)}-c^{(1)}} C_{pc} - C_{ds^{(2)}-c^{(1)}} C_{dc}]}{C_{ds} C_{ds^{(2)}-c^{(1)}} C_{dc}} \\ &\quad - \frac{\lambda_d}{\lambda_d - \lambda_p} \left[\frac{C_{ps}}{C_{ds}} - 1 \right] \\ &= \frac{"a_d"}{a_p} - \frac{\frac{C_{ps} \lambda_d}{\lambda_d - \lambda_p} [C_{ps^{(2)}-c^{(1)}} C_{pc} - C_{ds^{(2)}-c^{(1)}} C_{dc}]}{C_{ds} C_{ds^{(2)}-c^{(1)}} C_{dc}} - \frac{\lambda_d}{\lambda_d - \lambda_p} \left[\frac{C_{ps}}{C_{ds}} - 1 \right] \end{aligned} \quad (\text{Eq. F13})$$

where " a_d " = $N_d [P_{\gamma d} \varepsilon_d \phi C_{ds} C_{ds^{(2)}-c^{(1)}} C_{dc}]^{-1}$, that is, the activity concentration of the daughter radionuclide in the case that it did not have any dependence on the evolution of its parent activity concentration.

Furthermore, by using propagation law of uncertainties, the uncertainties related to a_p , a_d and a_d/a_p , that is, $\sigma(a_p)$, $\sigma(a_d)$ and $\sigma(a_d/a_p)$, respectively, can be determined. Thus, they can be written by the following equations:

$$\sigma(a_p) = a_p \frac{\sigma_{N_p}}{N_p} \quad (\text{Eq. F14})$$

$$\begin{aligned}\sigma(a_d) &= \sqrt{(\beta + \gamma)^2 \sigma_{N_p}^2 + \alpha^2 \sigma_{N_d}^2} \\ &= \sqrt{(\beta + \gamma)^2 \sigma_{N_p}^2 + (a_d + (\beta + \gamma)N_p)^2 \left(\frac{\sigma_{N_d}}{N_d}\right)^2}\end{aligned}\quad (\text{Eq. F15})$$

$$\sigma\left(\frac{a_d}{a_p}\right) = \frac{a_d}{a_p} \sqrt{\left(\frac{\sigma(a_p)}{a_p}\right)^2 + \left(\frac{\sigma(a_d)}{a_d}\right)^2} \quad (\text{Eq. F16})$$

where σ_{N_p} and σ_{N_d} are the uncertainties of N_p and N_d , respectively, $\alpha = \frac{\partial a_d}{\partial N_d}$ and $\beta + \gamma = -\frac{\partial a_d}{\partial N_p}$.

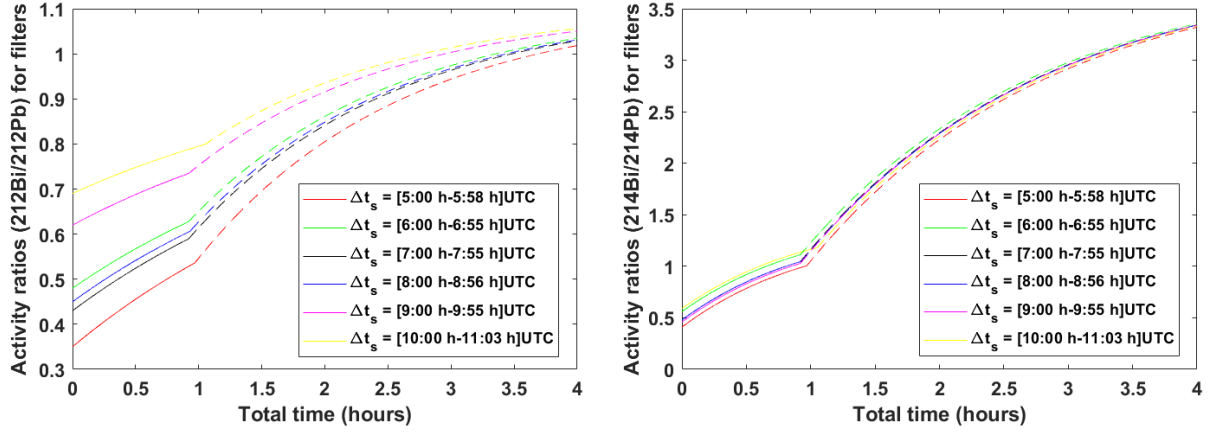


Figure F1. Activity ratios ($^{212}\text{Bi}/^{212}\text{Pb}$ and $^{214}\text{Bi}/^{214}\text{Pb}$) for the particulate matter deposited on the filters. The calculations of the activity ratios were done using Eqs. 3.6.3 (solid lines) and 3.6.6 (dashed lines) for each sampling carried out on July 22, 2021.

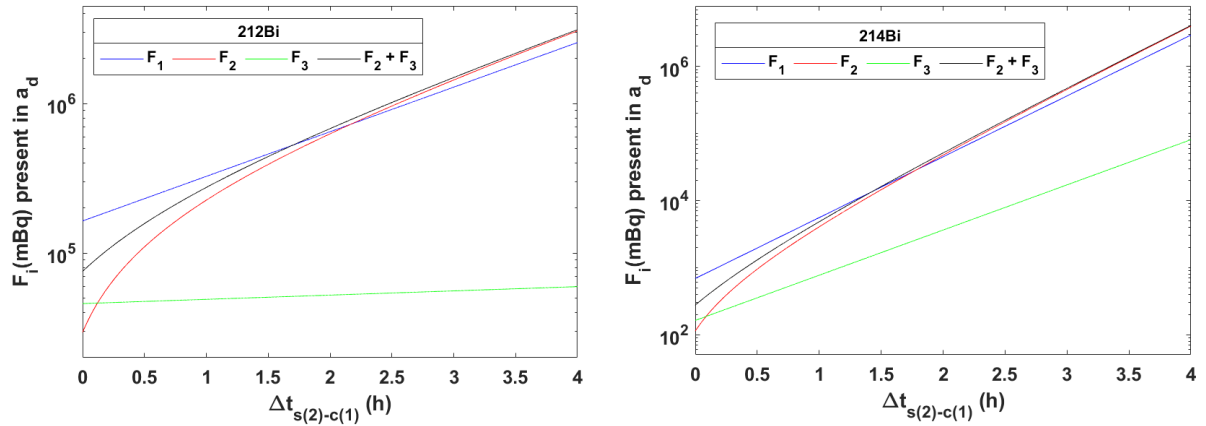


Figure F2. Behavior of the factors, F_i , present in the a_d equation for ^{212}Bi and ^{214}Bi , varying $\Delta t_{s(2)-c(1)}$ (sampling carried out on September 13, 2021, from 8:00 to 9:00 UTC).

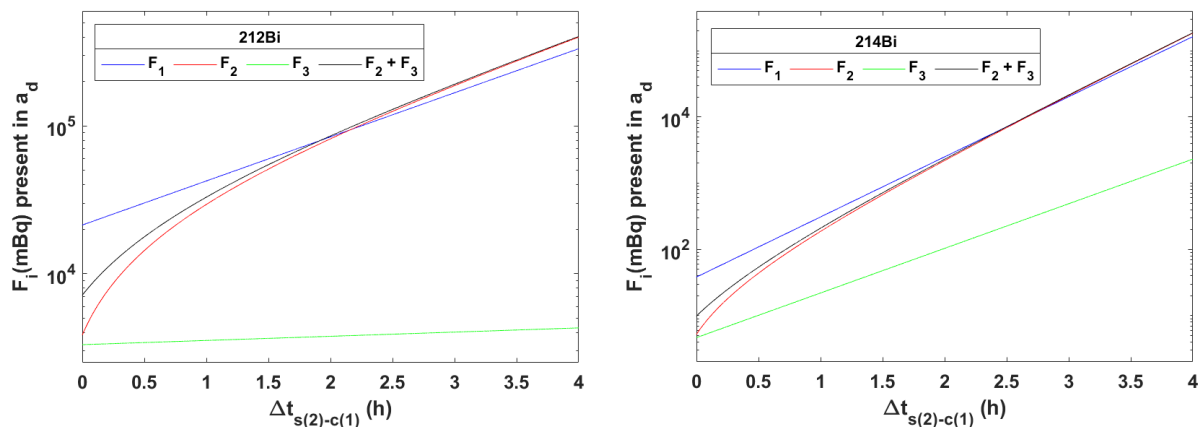


Figure F3. Behavior of the factors, F_i , present in the a_d equation for ^{212}Bi and ^{214}Bi , varying $\Delta t_{s(2)-c(1)}$ (sampling carried out on September 15, 2021, from 10:00 to 10:30 UTC).

Table F1

Comparison of the precisions calculating the activity concentrations of the ^{212}Pb and ^{212}Bi , as well as for their ratios, in air by using an ASS-500 and a PM_{10} samplers, where Δt_s , $\Delta t_{s(2)-c(1)}$ and Δt_c are the sampling duration, the time elapsed between sampling end and counting start and the counting duration, respectively, for each sampling carried out on July 22, 2021.*

Filter code	Δt_s (h)	$\Delta t_{s(2)-c(1)}$ (h)	Δt_c (h)	ASS-500			PM_{10}		
				^{212}Pb (mBq m $^{-3}$)	^{212}Bi (mBq m $^{-3}$)	$\frac{^{212}\text{Bi}}{^{212}\text{Pb}}$	^{212}Pb (mBq m $^{-3}$)	^{212}Bi (mBq m $^{-3}$)	$\frac{^{212}\text{Bi}}{^{212}\text{Pb}}$
A101	0.97 (5:00 UTC)	0.35	0.94	510(12)	179(17)	0.35(3)	510(14)	179(39)	0.35(8)
A102	0.92 (6:00 UTC)	0.42	0.94	583(14)	281(22)	0.48(4)	583(16)	281(46)	0.48(8)
A103	0.92 (7:00 UTC)	0.43	0.94	384(9)	164(17)	0.43(4)	384(12)	164(37)	0.43(10)
A104	0.93 (8:00 UTC)	0.40	0.94	331(8)	149(15)	0.45(5)	331(10)	149(34)	0.45(10)
A105	0.92	0.43	0.94	215(6)	134(14)	0.62(7)	215(8)	134(29)	0.62(14)

	(9:00 UTC)								
A106	1.05 (10:00 UTC)	0.25	1.00	102(3)	71(8)	0.69(8)	102(4)	71(17)	0.69(17)

(*) Numbers in parenthesis denotes uncertainty (1σ) associated with the data. Besides, for each Δt_s , the start times of each sampling are also specified in parenthesis.

Table F2

Comparison of the precisions calculating the activity concentrations of the ^{214}Pb and ^{214}Bi , as well as for their ratios, in air by using an ASS-500 and a PM_{10} samplers, where Δt_s , $\Delta t_{s(2)-c(1)}$ and Δt_c are the sampling duration, the time elapsed between sampling end and counting start and the counting duration, respectively, for each sampling carried out on July 22, 2021.*

Filter code	Δt_s (h)	$\Delta t_{s(2)-c(1)}$ (h)	Δt_c (h)	ASS-500			PM_{10}		
				^{214}Pb (Bq m ⁻³)	^{214}Bi (Bq m ⁻³)	$\frac{^{214}\text{Bi}}{^{214}\text{Pb}}$	^{214}Pb (Bq m ⁻³)	^{214}Bi (Bq m ⁻³)	$\frac{^{214}\text{Bi}}{^{214}\text{Pb}}$
A101	0.97 (5:00 UTC)	0.35	0.94	19.2(4)	7.8(3)	0.41(2)	19.2(5)	7.8(8)	0.41(4)
A102	0.92 (6:00 UTC)	0.42	0.94	17.1(4)	9.6(4)	0.56(3)	17.1(4)	9.6(8)	0.56(5)
A103	0.92 (7:00 UTC)	0.43	0.94	14.7(3)	7.0(3)	0.48(3)	14.7(4)	7.0(8)	0.48(5)
A104	0.93 (8:00 UTC)	0.40	0.94	11.5(3)	5.5(3)	0.48(3)	11.5(3)	5.5(7)	0.48(6)
A105	0.92 (9:00 UTC)	0.43	0.94	10.5(3)	4.8(3)	0.46(3)	10.5(3)	4.8(7)	0.46(7)
A106	1.05 (10:00 UTC)	0.25	1.00	5.96(14)	3.54(16)	0.59(3)	5.96(16)	3.5(4)	0.59(6)

(*) Numbers in parenthesis denotes uncertainty (1σ) associated with the data. Besides, for each Δt_s , the start times of each sampling are also specified in parenthesis.

Table F3

Flow (ϕ), counting duration (Δt_c), activity concentrations of ^{212}Pb and ^{212}Bi and $^{212}\text{Bi}/^{212}\text{Pb}$ activity ratio for different $\Delta t_{s(2)-c(1)}$ values (0.5 hour-sampling, September 15, 2021). The activity concentration obtained for ^{220}Rn at 10:00 UTC was less than its *mda*, that is, less than 50 mBq m^{-3} .*

Filter code	ϕ ($\text{m}^3 \text{ h}^{-1}$)	$\Delta t_{s(2)-c(1)}$ (h)	Δt_c (h)	^{212}Pb (mBq m^{-3})	^{212}Pb Z_{score}	^{212}Bi (mBq m^{-3})	^{212}Bi Z_{score}	$\frac{^{212}\text{Bi}}{^{212}\text{Pb}}$	$\frac{^{212}\text{Bi}}{^{212}\text{Pb}}$ Z_{score}
A108	610	0.43	0.50	75(3)	-1.1	56(10)	0.8	0.75(0.14)	0.9
		0.93	0.50	79(3)	0.1	40(15)	-0.3	0.51(0.19)	-0.3
		1.45	0.50	83(4)	1.0	39(22)	-0.3	0.5(0.3)	-0.6
		1.97	0.50	81(4)	0.5	-3(31)**	-	-	-
		2.47	0.50	74(3)	-1.4	-32(41)**	-	-	-
		2.98	0.50	80(4)	0.3	-25(63)**	-	-	-
		Average values		78.7(1.4)	0.7	45(10)	0.5	0.58(0.12)	0.6

(*) Numbers in parenthesis denotes uncertainty (1σ) associated with the data. (**) Activity concentrations not used in calculating the average values, where Z_{score} values are calculated with respect to the average values.

Table F4

Flow (ϕ), duration of counting (Δt_c), activity concentrations of ^{214}Pb and ^{214}Bi and $^{214}\text{Bi}/^{214}\text{Pb}$ activity ratio calculated for different $\Delta t_{s(2)-c(1)}$ values (0.5 hour-sampling, September 15, 2021). The activity concentration obtained for ^{222}Rn at 10:00 UTC was $4.6(0.4) \text{ mBq m}^{-3}$.*

Filter code	ϕ ($\text{m}^3 \text{ h}^{-1}$)	$\Delta t_{s(2)-c(1)}$ (h)	Δt_c (h)	^{214}Pb (Bq m^{-3})	^{214}Pb Z_{score}	^{214}Bi (Bq m^{-3})	^{214}Bi Z_{score}	$\frac{^{214}\text{Bi}}{^{214}\text{Pb}}$	$\frac{^{214}\text{Bi}}{^{214}\text{Pb}}$ Z_{score}
A108	610	0.43	0.50	2.54(0.07)	1.8	1.45(0.15)	0.7	0.57(0.06)	0.3
		0.93	0.50	2.34(0.08)	-0.2	1.3(0.4)	0.3	0.57(0.15)	0.3
		1.45	0.50	2.37(0.10)	0.1	0.9(0.8)	-0.3	0.4(0.3)	-0.3
		1.97	0.50	2.49(0.14)	0.8	0.8(1.8)	-0.2	0.3(0.7)	-0.3
		2.47	0.50	2.4(0.2)	0.2	0(4)**	-	-	-
		2.98	0.50	2.0(0.3)	-1.2	0(7)**	-	-	-
		Average values		2.36(0.07)	0.7	1.1(0.5)	0.4	0.5(0.2)	0.3

(*) Numbers in parenthesis denotes uncertainty (1σ) associated with the data. (**) Activity concentrations not used in calculating the average values, where z_{score} values are calculated with respect to the average values.

ANNEX II – REPORT ON THE IMPACT FACTOR OF THE PUBLICATIONS

Report on the impact factor (IF) of the publications

- Doctoral Thesis presented by D. Alejandro Barba Lobo, in the mode of “compendium of publication”.
- Number of published articles: 5
- Number of articles accepted for publication: 5

Impact factor (IF) of the publications according to the Journal Citation Reports of the year 2021

Journal	Number of publications	IF	Category	Quartile	Position in the category	Journals in the category
Measurement	3	5.131	Instruments and Instrumentation	Q1	11	64
			Engineering, Multidisciplinary	Q1	17	92
Radiation Physics and Chemistry	1	2.776	Nuclear Science and Technology	Q1	7	34
			Physics, Atomic, Molecular and Chemical	Q2	16	36
			Chemistry, Physical	Q3	110	165
Journal of Hazardous Materials	1	14.224	Engineering, Environmental	Q1	3	54
			Environmental Sciences	Q1	9	279

ANNEX III – PUBLICATIONS



An upgraded lab-based method to determine natural γ -ray emitters in NORM samples by using Ge detectors

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ARTICLE INFO

Keywords:

Gamma spectrometry
Ge detectors
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 ^{222}Rn losses

ABSTRACT

The regulation existing on NORM activities requires the accurate and quick measurement of natural radionuclides in a wide range of matrices by gamma spectrometry. The aim of this work has been to develop a comprehensive and accurate methodology to determine natural long-lived radionuclides (^{210}Pb , $^{228,226}\text{Ra}$, $^{234,228}\text{Th}$ and ^{40}K) by gamma spectrometry with Ge detectors in NORM samples. An exhaustive calibration method to obtain the full-energy peak efficiency (FEPE), for each gamma emission energy, as a function of the thickness, apparent density and matrix composition of the cylindrical sample, has been developed. The selected certified calibration standards contain only natural radionuclides belonging to the ^{238}U - and ^{232}Th -series as well as ^{40}K (codes RGU-1, RGTh-1 and RGK-1 from IAEA). Then, the obtained FEPE curves were validated using Genie 2000 simulations and Certified Reference Materials, for which the self-attenuation corrections were considered. Finally, a study on ^{222}Rn losses was done for several samples.

1. Introduction

In many problems related to the field of environmental radioactivity, the determination of long-lived gamma-ray emitting radionuclides such as $^{234, 228}\text{Th}$, $^{228, 226}\text{Ra}$, ^{210}Pb and ^{40}K is needed, in a wide variety of samples with different compositions and densities, as well as their geometry due to the available amount of sample is variable.

There are many industries (e.g., fertilizers, TiO_2 pigments, oil extraction, production of metals, mining) that generate intermediate materials, final products and wastes containing natural radionuclides at significant concentrations, and therefore they have to be considered as NORM (Naturally Occurring Radioactive Material) or TENORM (Technologically Enhanced NORM). The control of their potential radiological impact requires accurate methods for the measurement of natural radionuclides in industrial and environmental samples in a wide range of matrices with very different apparent densities, compositions and amount of sample, which requires different measuring geometries (thickness of sample) [1–3].

The Radiation Physics and Environment Group of the University of Huelva (Spain) has led many studies on radiological assessments of chemical NORM industries where a wide range of gamma-ray spectrometry measurements of TENORM samples is needed. TENORM

samples contain ^{238}U - and ^{232}Th -series radionuclides, which are not in secular equilibrium, and therefore the separate measurement of ^{238}U (via ^{234}Th), $^{230, 228}\text{Th}$, $^{228, 226}\text{Ra}$, ^{210}Pb and ^{40}K radionuclides is essential. The issue related to the secular disequilibrium is very important to be analyzed since there are many types of samples such as phosphogypsum materials, industrial wastes (like scales) and waters that present a clear disequilibrium between the radionuclides belonging to the ^{238}U - and ^{232}Th -series. The most common disequilibrium cases usually occur between ^{238}U and ^{226}Ra as well as between ^{226}Ra and ^{222}Rn . (See [4–6] for further information about studies on secular disequilibrium).

Nowadays, NORM samples are being very important because society is more committed to environmental sustainability. Among the samples of interest are industrial wastes, which are studied to evaluate their radiotoxicity levels, ensuring that they are within the limits allowed to guarantee the safety of the workers who are exposed to the radiation from these wastes. Besides that, other samples such as waters, which are used to irrigate farm products, are analyzed to assure that they are suitable for consumption (further information about NORM samples can be found in [7,8]).

On the other hand, exposure to NORM samples can lead to health problems when they have high levels of radioactivity. For this, lately radiological regulations for construction require the measurement of

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A general methodology to determine natural radionuclides by well-type HPGe detectors

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ARTICLE INFO

Keywords:

Gamma-Alpha-particle spectrometry
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Efficiency calibration
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NORM

ABSTRACT

This work aims to determine natural radionuclides (^{210}Pb , $^{228,226}\text{Ra}$, $^{234,228}\text{Th}$ and ^{40}K) in NORM samples by well-type HPGe detectors because they are of vital importance in studies on environmental samples. For this, a novel methodology has been developed, based on obtaining a general function for the full-energy peak efficiency (FEPE) versus the sample apparent density and composition, keeping the sample height constant. To obtain the general FEPE function, a calibration in efficiency has been accomplished using certified standards provided by IAEA (RGU-1 and RGTh-1), and KCl. Besides, different self-absorption correction functions were compared for cylindrical geometry, where chemical compositions need to be known. Then, a study on using an anti-Compton system was done, getting a lower detection limit and allowing to propose gamma spectrometry as an alternative technique to alpha-particle spectrometry. Finally, the followed methodology to calculate the FEPE was subjected to internal and external validations, checking its validity range.

1. Introduction

In the last decades, the natural radionuclides such as ^{210}Pb , $^{228,226}\text{Ra}$, $^{234,228}\text{Th}$ and ^{40}K are being of great interest due to their wide usage in many environmental fields. The knowledge and use of these radionuclides can be very useful in covering different problems present in the environment, such as the calculation of residence times of atmospheric aerosols [1]. Another example is marine scavenging where ^{234}Th is widely used [2]. ^{210}Pb determination is also interesting in order to date sediments or assess the erosion of a material [3,4].

When a material contains important concentrations of natural radionuclides, it has to be considered as a NORM sample (Naturally Occurring Radioactive Material) (for further information about NORM samples, see [5–10]). There are many industries that produce, for example, metals or fertilizers which generate industrial wastes with high concentrations of natural radionuclides. Consequently, spectrometric techniques need to be employed in order to assess the radiotoxicity to which the workers are exposed. Furthermore, materials related to building construction must be subjected to a radiological control [11].

On the other hand, in order to determine natural long-lived radionuclides by gamma spectrometry, an efficiency calibration of the detectors is necessary. Nowadays the calibration of detectors by Monte Carlo simulations has become generalized (for further information about

Monte-Carlo simulations carried out in HPGe detectors, see [12–16]). Thus, there are many cases for which old detectors are not characterized, and the laboratories have to send them into the factory to carry out the characterization procedure, involving high costs for the characterization and the new Monte Carlo software, and needing to wait some time without gamma measurements.

In contrast to Monte Carlo simulations, well-type Ge detectors can be calibrated relatively quickly and using calibration standards that do not imply so high costs. Besides, they have a high absolute efficiency which is about 40 % at low energies, that is, $E_\gamma \leq 150$ keV (where E_γ is the gamma emission energy). That efficiency value is approximately four times higher than the one obtained for any another coaxial detector for that same energy range, being this very important since self-absorption effects are more relevant for low energies. This agrees with many studies carried out on self-absorption corrections [3,17–24]. Regarding corrections related to self-absorption effects, in [25] a correction model was proposed, which is usually used in the case of coaxial well-type detectors. In the present study, the previous model has been employed and its validity has been checked, comparing it with other possible functions.

Furthermore, there are different techniques that are used to determine long-lived natural radionuclides, such as alpha-particle spectrometry with semiconductor detectors, Inductively Coupled Plasma Spectroscopy (ICP), Neutron Activation Analysis (NAA), Liquid

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A general function for determining mass attenuation coefficients to correct self-absorption effects in samples measured by gamma spectrometry

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ARTICLE INFO

Keywords:

Gamma spectrometry
Coaxial Ge detectors
Mass attenuation coefficient
Self-absorption
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ABSTRACT

This work is focused on obtaining a general function for calculating the mass attenuation coefficients of samples whose compositions are known such as waste, biota or NORM (Naturally Occurring Radioactive Materials) samples. After determining the general function, it is possible to assess the self-absorption effects by the self-absorption correction factor, which is really important to consider for samples measured by gamma spectrometry. In order to obtain a general function of the mass attenuation coefficients dependent on the gamma emission energy (E_γ) and the chemical elements (Z_i) with their respective concentrations (x_i), it was necessary to fit the tabulated values of the mass attenuation coefficients versus gamma energy in the range of 20 keV–2000 keV for each chemical element. This is the energy range for the majority of gamma emissions of natural radionuclides. Once those fittings for each chemical element, Z , from 1 (H) to 92 (U) were done, the parameters, that resulted from those fittings, were fitted versus the atomic number, Z . This provides a general function that allows to calculate the mass attenuation coefficient by knowing the gamma emission energy and the sample composition. Finally, both the general function for calculating the mass attenuation coefficient and the self-absorption correction factor, which is used in gamma spectrometry with coaxial Ge detectors, were validated by comparisons made with the values provided by databases for several samples with widely different known densities, compositions and activity concentrations.

1. Introduction

The determination of the mass attenuation coefficient of a sample, η , is very significant for obtaining the self-absorption correction factor, f , to be used in gamma spectrometry measurements, since it lets transform the full energy peak efficiency (FEPE) calculated in the calibrating matrix (ϵ_c) into the real sample one (ϵ). There are numerous studies carried out on gamma spectrometry that take this type of correction into account (Abbas, 2001; Abbas et al., 2001; Ajemigbitse et al., 2020; Bolívar et al., 1997; Bonczyk, 2018; Carrazana et al., 2010; Dhugosz-Lisiecka and Ziomek, 2015; Eke and Boztosun, 2014; Guerra, 2018; Jodłowski, 2016; Mantero, 2013; Mantero et al., 2015; Martínez-Ruiz et al., 2007; Montes et al., 2019; San Miguel et al., 2002; Suárez-Navarro et al., 2020; Xhixha-Kaçeli, 2013). These self-absorption corrections are more relevant in the lower energy range (20 up to about 150 keV), an effect proved in many studies on gamma spectrometry measurements (Bonczyk, 2018; Carrazana et al., 2010; Dhugosz-Lisiecka and Ziomek, 2015; Jodłowski, 2016; Martínez-Ruiz et al., 2007; Montes et al., 2019;

San Miguel et al., 2002; Suárez-Navarro et al., 2020).

On the other hand, the application of the self-absorption corrections to the calculation of the efficiency in the matrix of a real sample requires knowing the mass attenuation coefficient of both the reference and the real samples. Furthermore, if the composition of the real sample is very different from that of the reference sample and their densities are very different from each other, this may influence the validity of the method followed in this paper. This might happen because the correction introduced by the self-absorption factor would be very large, that is, it would have a very different value from 1 for energies that are within the range of low energies ($E_\gamma \leq 150$ keV). Consequently, if the corrections due to self-absorption effects are not considered, the values of calculated activity concentrations, for those radionuclides whose gamma emission energies are within the low energy range, can differ greatly from the expected values (up to 20 % of difference, or more). This can occur in this way because the activity concentration and the self-absorption factor are related by the next equation:

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A practical and general methodology for efficiency calibration of coaxial Ge detectors

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ARTICLE INFO

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Gamma-ray spectrometry
Efficiency calibration
Artificial and natural radionuclides
True coincidence summing
Self-absorption
Dead time

ABSTRACT

The correct determination of artificial and natural radionuclides like ^{152}Eu , ^{137} , ^{134}Cs , ^{60} , ^{57}Co , etc., and ^{234} , ^{228}Th , ^{228} , ^{226}Ra , ^{210}Pb and ^{40}K , respectively, is essential for many environmental science fields. For this, a general function was obtained for the full-energy peak efficiency (FEPE) by gamma-ray spectrometry using coaxial Ge detectors. Then, the experimental FEPE values, obtained fixing the energy, E_γ , were fitted varying the thickness, h , of cylindrical standards. The parameters resulted from these fittings were fitted, in turn, versus E_γ , obtaining a general efficiency function, $\epsilon_c(E_\gamma, h)$. $\epsilon_c(E_\gamma, h)$ was validated, obtaining very good z_{score} , except for E_γ affected by TCS effects. Consequently, a practical and general method was developed, recalibrating the detector by varying the sample-detector distance, d . $\epsilon_c(E_\gamma, h, d)$ was obtained, achieving very good z_{score} . Furthermore, this practical method was also employed to correct high self-absorptions and high dead times.

1. Introduction

There are several natural and artificial radionuclides of interest within the field of the environmental radioactivity, such as ^{234} , ^{228}Th , ^{228} , ^{226}Ra , ^{210}Pb and ^{40}K , as well as ^{241}Am , ^{152}Eu , ^{137} , ^{134}Cs , ^{133}Ba , ^{60} , ^{57}Co . In order to determine these radionuclides by gamma-ray spectrometry, it is of vital importance to use different types of detector efficiency corrections. Among the most important efficiency corrections, there are the following: true coincidence summing (TCS), self-absorption and dead time corrections.

Regarding the former correction type, they are often applied to determine artificial radionuclides, given that the majority of artificial radionuclides have TCS effects (^{152}Eu , ^{137} , ^{134}Cs , ^{60} , ^{57}Co , etc.). However, some natural radionuclides like ^{214}Bi and ^{208}Tl , which are daughters of ^{226}Ra and ^{228}Th corresponding to the ^{238}U - and ^{232}Th -series, respectively, also suffer TCS effects [1–3]. Therefore, this type of correction is indispensable to be considered in order to know the radionuclide activity concentrations in a proper way. Furthermore, it is necessary to clarify that there are two kinds of TCS effects: “summing in” and “summing out” effects. The former takes place when two photons are detected simultaneously and they are added to a specific full-energy peak, where those two photons have energies that do not belong to that specific peak. The second type consists in the opposite phenomenon, that is, one of those two simultaneous photons is taken away from that

specific peak and included in another peak.

In the case of the TCS corrections, nowadays the corrections provided by MCNP, GEANT4, PENELOPE or FLUKA simulation codes have become generalized [4–11]. However, in order to carry out these corrections by using simulation software, it is necessary to characterize the detector parameters and, consequently, expensive costs and several months are required, being the detector inoperative during the time taken to carry out the detector characterization procedure.

With respect to the self-absorption corrections, they are very useful to be employed due to the possible chemical composition and density differences between the samples used to calibrate the detectors and the other samples, which are called as problem samples. The reason is because when the composition and density of the calibration and problem samples are very different from each other, the photons are attenuated differently and, consequently, a self-absorption correction is required to introduce these differences in the detector efficiency calculation when this is obtained in the problem sample matrices [12–14]. Besides that, self-absorption corrections are essential in the cases of the radionuclides whose gamma emissions belong to the low energy range, that is, energies less than 150 keV, since the self-absorption effects are much more relevant for that energy range [15–17].

On the other hand, regarding the dead time corrections, they are usually employed in the cases for which samples, whose radionuclides have very high activity concentrations, are measured. In these cases,

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A methodology to determine ^{212}Pb , ^{212}Bi , ^{214}Pb and ^{214}Bi in atmospheric aerosols; Application to precisely obtain aerosol residence times and Rn-daughters' equilibrium factors

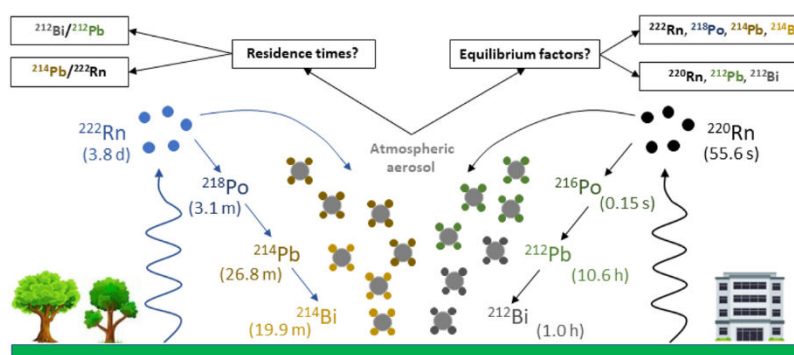
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HIGHLIGHTS

- A methodology to determine ^{212}Pb , ^{212}Bi , ^{214}Pb and ^{214}Bi in atmospheric aerosols was developed.
- Aerosol residence times and Rn-daughters' equilibrium factors were obtained by this method.
- Comparison between both ASS-500 and PM_{10} samplers was made.
- Optimum sampling and counting times were found to properly measure ^{212}Pb , ^{212}Bi , ^{214}Pb and ^{214}Bi .
- The methodology consistency was tested for several sampling and counting durations.

GRAPHICAL ABSTRACT



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ABSTRACT

Progeny of ^{222}Rn and ^{220}Rn , (^{212}Pb , ^{212}Bi , ^{214}Pb and ^{214}Bi) are essential to assess radiological hazard, external and internal doses, residence times and equilibrium factors. Precise measurements of these nuclides are quite complex due to their very short half-lives. This study outlines a new and precise methodology to measure these nuclides. Radon-222 and ^{220}Rn were measured using a radon monitoring system, while their respective progenies were collected in an atmospheric filter using an ASS-500 sampler and measured by gamma-ray spectrometry. The ^{212}Pb concentrations were very similar to the thoron ones, where all $^{212}\text{Bi}/^{212}\text{Pb}$ ratios were consistently less than 1. The relative uncertainties, σ_r , of the ^{212}Pb and ^{212}Bi activity concentrations, and $^{212}\text{Bi}/^{212}\text{Pb}$ activity ratio are generally less than 10%. Moreover, $^{214}\text{Pb}/^{222}\text{Rn}$ ratios were about 0.7, agreeing well with previous works. The σ_r for ^{214}Pb , ^{214}Bi and $^{214}\text{Bi}/^{214}\text{Pb}$ were generally less than 6%. This methodology was applied to estimate aerosol residence times using the $^{214}\text{Pb}/^{222}\text{Rn}$ and $^{212}\text{Bi}/^{212}\text{Pb}$ activity ratios, and to obtain equilibrium factors, achieving consistent results. Furthermore, the methodology consistency and validity range were studied with time elapsed between sampling end and counting start, and the sampling durations, finding the optimum times to precisely determine ^{212}Pb , ^{212}Bi , ^{214}Pb and ^{214}Bi .

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