Journal of Geoscience and Environment Protection, 2026, 14(4), 92-105
https://www.scirp.org/journal/gep
ISSN Online: 2327-4344
ISSN Print: 2327-4336

Accurate Determination of ^{232}Th through ^{208}Tl Using Ultra-Low Background Gamma Spectrometry in Environmental Matrices

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How to cite this paper: Khan, A. J., Syed, U.-F., & Costello, C. A. (2026). Accurate Determination of ^{232}Th through ^{208}Tl Using Ultra-Low Background Gamma Spectrometry in Environmental Matrices. *Journal of Geoscience and Environment Protection, 14,* 92-105.
https://doi.org/10.4236/gep.2026.144006

Received: March 14, 2026
Accepted: April 5, 2026
Published: April 8, 2026

Abstract

Accurate measurement of thorium-232 (^{232}Th) in environmental samples is essential for geochemical research, ecological monitoring, and radiological safety. Because ^{232}Th emits gamma radiation at a low probability, its activity is often estimated from short-lived daughter isotopes such as ^{228}Ac, ^{212}Pb, ^{212}Bi, and ^{208}Tl, assuming secular equilibrium. This study used ultra-low-background high-purity germanium (HPGe) gamma spectrometry to measure the ^{232}Th activity in certified reference materials and environmental sediment and soil samples. The 2614.5 keV gamma line of ^{208}Tl provided the most accurate and consistent results, although corrections for true coincidence summing (TCS) effects were necessary. Gamma lines from ^{228}Ac and ^{212}Pb exhibited minimal summing losses, which helped verify equilibrium-based measurements. Statistical analysis confirmed consistency across all daughter nuclides, validating the use of ^{208}Tl and related decay products for ^{232}Th determination. This method proves effective for routine environmental analysis and regulatory compliance.

Keywords

^{232}Th, ^{208}Tl, Soil, Sediment, Ultra-Low Background Gamma Spectrometry, True Coincidence Summing

1. Introduction

^{232}Th is a naturally occurring, long-lived radioactive element essential in environmental radioactivity, geochemistry, and nuclear fuel research. Measuring it directly via gamma spectrometry is difficult because of its low gamma emission. In-

stead, gamma rays emitted by decay products like ^{228}Ac, ^{212}Pb, ^{212}Bi, and ^{208}Tl are used for indirect detection under the assumption of secular equilibrium. The activity of ^{232}Th is determined by analyzing characteristic gamma-ray peaks from these decay products, such as the prominent 238.6 keV peak from ^{212}Pb, the 338.3 keV, 911.2 keV, and 968.97 keV peaks from ^{228}Ac, the 727.3 keV peak from ^{212}Bi, and the 583.2 keV and 860.6 keV peaks from ^{208}Tl (Khan et al., 2023). These peaks can be influenced by other radioactive elements like ^{226}Ra, ^{235}U, and ^{238}U, which are often present in samples containing ^{232}Th. While these decay series peaks are generally reliable in gamma spectrometry, spectral interference and true coincidence summing (TCS) corrections are often necessary (Yücel et al., 2011). In environmental samples with low activity, positioning the source close to the detector improves counting statistics but increases TCS, which impacts accuracy. Corrections for TCS are significant in near-geometry detection due to cascading decay transitions (García-Talavera et al., 2001). Studies show that the 338.3 keV peak of ^{228}Ac is least affected by interference, making it a preferred marker for ^{232}Th.

^{208}Tl is particularly useful because of its intense 2614.5 keV gamma emission (~99.8%), which is easily detectable and less affected by matrix effects. However, relying solely on this marker can be problematic if secular equilibrium is not established or if interference corrections are insufficient. Its presence also contributes to natural background radiation. Monitoring its levels helps assess radiation risks to humans and ecosystems, particularly in areas with high natural radioactivity, such as monazite-rich soils and uranium mines (Abbasi et al., 2022; González-Fernández et al., 2012).

Thorium is relatively immobile in the environment, making it a useful tracer for geochemical processes such as sediment sourcing, weathering, erosion, and particle transport in waterways. ^{232}Th and its decay products, such as ^{228}Ra and ^{228}Ac, are used for sediment dating, particularly short-lived radionuclides in the ^{232}Th decay series, to estimate recent sedimentation over decades to centuries. Thorium also plays a key role in monitoring nuclear materials and non-proliferation efforts. Although not fissile itself, thorium can be converted into fissile ^{233}U in reactors. Tracking it in environmental samples helps detect illegal nuclear activities or contamination. Elevated thorium levels in soils may indicate industrial pollution or phosphate fertilizer use. The activity concentration of ^{232}Th ranged from 15.3 ± 2.24 to 58.3 ± 4.92 Bq·kg^{-1} in topsoil and river sediments from the Jinding Pb-Zn mine catchment in Southwest China (Wang et al., 2023). In sediment samples from Novaya Zemlya in the Russian Arctic, ^{232}Th activity ranged from 21.11 ± 1.27 to 46.15 ± 3.61 Bq·kg^{-1} (Yushin et al., 2023). ^{232}Th measurement supports environmental cleanup near mines, waste sites, or nuclear facilities (Souza et al., 2025). Agencies such as the EPA and IAEA monitor radionuclides like ^{232}Th in drinking water, soil, and building materials to ensure safety standards. This paper discusses correction methods for accurately measuring ^{208}Tl activity to reflect ^{232}Th levels in low-background gamma spectrometry, comparing these results with other decay products such as ^{228}Ac, ^{212}Pb, and ^{212}Bi.

The novelty of this study lies in the systematic metrological evaluation of multiple gamma emissions within the ^{232}Th decay series under ultra-low background conditions, with particular emphasis on the analytical performance of the 2614.5 keV emission of ^{208}Tl. While this high-energy line is often avoided in close-geometry measurements due to true coincidence summing (TCS), the present work demonstrates that, when rigorous summing corrections are applied using GESPECOR (Sima et al., 2001) simulations, the ^{208}Tl line provides superior statistical precision and analytical reliability for environmental thorium determination. This study therefore establishes a practical methodology for reliable ^{232}Th quantification in environmental matrices using ultra-low background HPGe gamma spectrometry.

The primary objective of this study is to establish a metrologically robust methodology for the determination of ^{232}Th in environmental matrices using ultra-low background HPGe gamma spectrometry. The analytical performance of selected gamma emissions from ^{228}Ac, ^{212}Pb, ^{212}Bi, and ^{208}Tl is systematically evaluated based on 1) agreement with certified reference values, 2) inter-line consistency within the decay series under secular equilibrium, and 3) statistical precision following correction for true coincidence summing (TCS). These criteria provide a quantitative framework for identifying the most reliable gamma-ray indicators for routine environmental analysis.

2. Theory

^{232}Th decays into stable ^{208}Pb through a series of alpha and beta emissions involving various short-lived isotopes, as shown in **Figure 1**. ^{208}Tl is produced via beta decay of ^{212}Bi (~36% branch) and has a short half-life. Its presence and activity strongly depend on upstream equilibrium, especially involving ^{228}Th and ^{212}Bi. ^{208}Tl decays through a cascade of photon emissions over picoseconds or nanoseconds as given in **Figure 2** (Martin, 2007). Some excited states of ^{208}Pb, populated during ^{208}Tl decay, can de-excite by internal conversion (IC) rather than gamma emission. During IC, inner-shell electrons (usually K or L shell) are ejected, resulting in characteristic X-ray emissions as outer-shell electrons fill the vacancies, such as Pb Kα (~74 keV) and Kβ (~85 keV) X-rays. These events are often accompanied by a β^- particle and/or gamma photon, notably the 2614.5 keV gamma line. When a γ-ray or β particle triggers a coincidence in a surrounding or coupled detector (like a scintillator or plastic veto), and a low-energy X-ray is detected within the coincidence window, the system can veto the low-energy event.

Secular equilibrium occurs in a decay chain when the parent isotope's half-life is much longer than its daughters', and the system remains undisturbed for several half-lives, allowing activities to synchronize. Under these conditions, each daughter decays at the same rate at which it is produced, leading to equal activities across the chain. Achieving secular equilibrium in natural samples requires that the sample remain sealed for at least 5 - 6 half-lives of the intermediate daughters. To ensure secular equilibrium within the ^{232}Th decay chain, samples were sealed for

at least three weeks before counting. At this timescale, short-lived progeny such as ^{212}Pb ($T_{1/2}$ = 10.64 h) and ^{212}Bi ($T_{1/2}$ = 60.6 min) are fully equilibrated within 2 - 3 days, while longer-lived ^{224}Ra ($T_{1/2}$ = 3.66 d) and its progeny, including ^{208}Tl, approach equilibrium within 15 - 20 days.

3. Materials and Methods

At the Wadsworth Center of the New York State Department of Health (NYSDOH), we have been conducting low-background gamma spectrometry for over thirty years (Semkow et al., 2002). This technique is used for diverse applications, including environmental, food, air, and water monitoring, facility surveillance, as well as health physics and homeland security. Low-background gamma spectrometry is suitable for measuring samples with very low activity, such as water or chemically separated materials. Typical projects involve the mandated analysis of radium in drinking water (Khan et al., 2020) and the monitoring of cesium at nuclear sites. Additionally, we serve as a reference laboratory and participate in radiological exercises. In this study, we used high-purity Germanium coaxial detectors (HPGe) GX13023 XtRa, with 140% relative efficiency from Mirion Technologies (Canberra) Inc. The detector features a copper cryostat and end cap. Its top entry window is made of 0.62-mm-thick carbon composite, enabling sensitivity to photons down to about 10 keV. The detector is housed inside a three-layer lead shield: an outer 7.6 cm (3″) layer of Boliden lead with 20 Bq·kg^{-1} ^{210}Pb content; an inner 7.6 cm (3″) layer from Plombum Firma-Laboratorium (Kraków, Poland), <3 Bq·kg^{-1} ^{210}Pb, and <1 mBq·kg^{-1} ^{40}K; and a 2 cm-thick Alpha-grade lead inserts

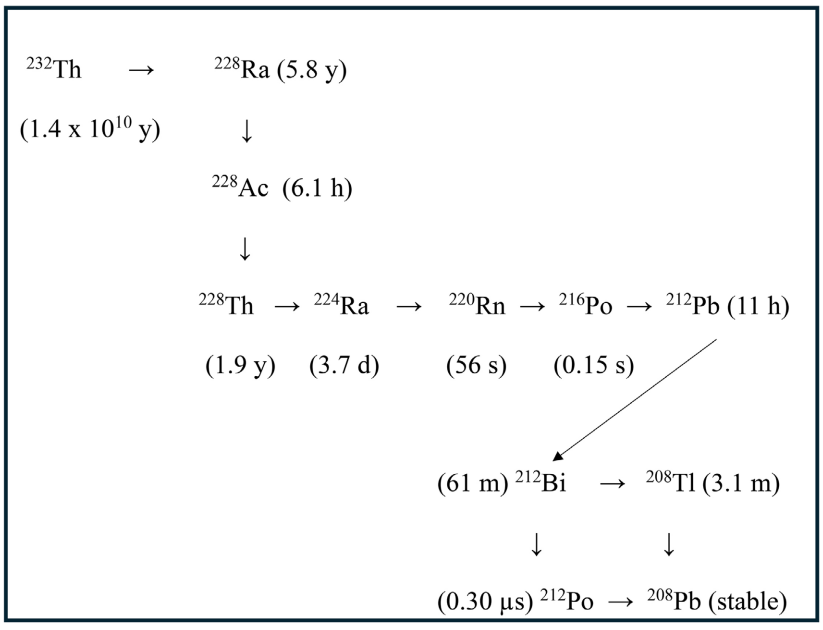

Figure 1. Thorium series (→alpha emission; ↓beta emission).

by Pure Technologies (Tequesta, FL, USA), with an alpha emission rate of 0.0007

counts/hr/cm^2 and 0.01 ppm ^{40}K. The Ge detector chamber is purged with boil-off nitrogen from its Dewar to limit radon ingrowth and its progeny. Details about the spectrometer's low background features are documented elsewhere (Khan et al., 2014). The lead shield is topped and flanked by a 6-panel plastic scintillator muon shield, each panel 5.1 cm (2") thick, one side divided into two for cryostat access. Made of BC-408 plastic scintillator (Saint-Gobain Crystals, Newbury, OH, USA), each panel contains two hemispherical photomultiplier tubes (Model 9900, ET Enterprises, Rockaway, NJ, USA). The entire setup is enclosed in a steel room with 15.2 cm (6") thick walls of pre-World War II steel (Dixie Manufacturing Co., Baltimore, MD, USA), situated beneath a 47-story building that provides approximately 33 meters of water-equivalent (mwe) shielding from cosmic muons. The signals from the scintillator panels are synchronized via high-voltage bias, then combined, preamplifier, amplified, and discriminated to produce a 40 μs TTL gate. This gate vetoes the Ge detector signals processed by the Lynx Digital Signal Analyzer (LYNX).

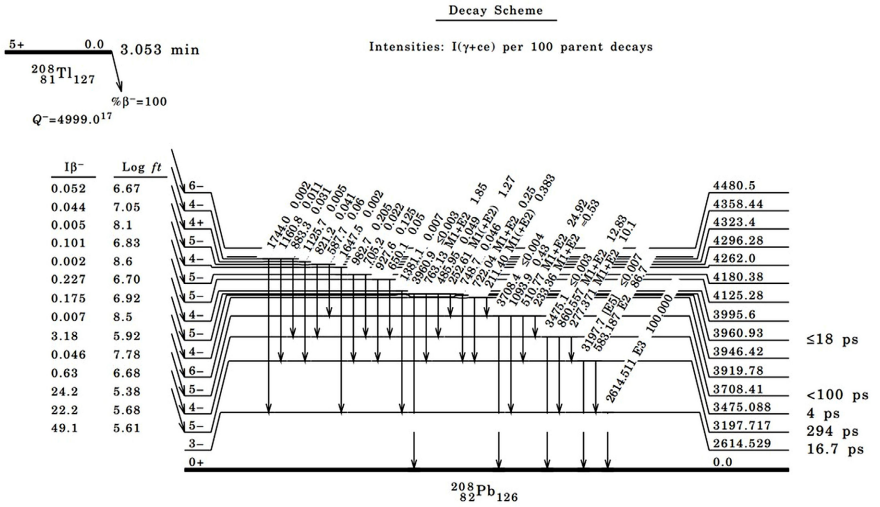

Figure 2. ^{208}Tl decay scheme (Martin, 2007).

Sediment samples (S1 - S4) were collected between 2018 and 2023 from the shoreline of the Lake Ontario boat launch, specifically at the water-land interface. At each location, approximately the upper 2 cm of surface material was collected and sieved in the field to remove coarse debris and stones. A topsoil sample (~500 g) was collected from a backyard site at a depth of approximately 15 cm (6 inches) and similarly sieved to remove gravel and larger particles. In addition, a soil sample from the IAEA-2006 proficiency testing (PT) exercise was included. This PT material was previously milled, sieved to <0.1 mm, and homogenized to ensure uniformity.

All environmental samples were air-dried, homogenized, and transferred into counting containers corresponding to two geometries: a 49 mL jar and an 800 mL Marinelli beaker. For the 49 mL geometry, approximately 50 - 60 g of sample was used, whereas for the 800 mL geometry, sample masses ranged from 1000 to 1200

g. Samples were hermetically sealed and stored for at least four weeks prior to counting to ensure the establishment of secular equilibrium within the ^{232}Th decay series.

Gamma spectrometric measurements were performed using an ultra-low background HPGe detector. Counting times ranged from 60,000 s to 240,000 s, depending on sample mass, geometry, and activity level. Each sample was measured in duplicate, and the reported activity values represent the mean of the two measurements to improve counting statistics and reproducibility. The relative difference between duplicate measurements was typically less than 5%, confirming good measurement reproducibility.

Secular equilibrium was verified experimentally by comparing activities derived from multiple daughter radionuclides (^{228}Ac, ^{212}Pb, ^{212}Bi, and ^{208}Tl). Equilibrium was considered established when the activities agreed within ±10% or within combined 1σ uncertainties. This criterion was satisfied for all samples analyzed. It should be noted that ^{208}Tl is produced via a branching decay of ^{212}Bi, with a branching ratio of approximately 36%. However, under conditions of secular equilibrium, the activity of ^{208}Tl is equal to that of its parent ^{232}Th, as the branching fraction is inherently accounted for in the decay constant governing its production and decay. Background spectra were acquired for 240,000 s under identical conditions.

Method validation and quality control were performed using certified reference materials (CRMs), including IAEA-447 (Moss Soil), IAEA-412 (Pacific Ocean Sediment), and IAEA-385 (Irish Sea Sediment), as well as the PT sample. These materials ensured traceability and accuracy of the analytical procedure. Detection limits were calculated following the formulation of Currie (Currie, 1968) for the critical level and detection limit, incorporating counting statistics of both sample and background spectra and accounting for unequal counting times, with modifications as described in (Rogers, 1970; Storm & Stansbury, 1992).

Efficiency calibration was performed for both counting geometries using a mixed gamma-ray standard traceable to the National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA) over the energy range of 50 - 1840 keV. Efficiencies outside this range were obtained by extrapolation. The total uncertainty of the efficiency calibration included contributions from the certified source activity and counting statistics. Sample-specific corrections for density and true coincidence summing were calculated using the Monte Carlo-based GESPECOR software (Sima et al., 2001; Sima & Arnold, 2002), and the resulting correction factors were applied to the measured peak areas prior to activity determination.

4. Results and Discussion

4.1. Understanding the ^{232}Th Decay Series and Measurement Strategy

The quantification of ^{232}Th by gamma-ray spectrometry is inherently indirect and relies on the accurate determination of its short-lived progeny under conditions

of secular equilibrium. Owing to its long half-life ($T_{1/2} = 1.4 \times 10^{10}$ y), ^{232}Th decays through a well-defined sequence of alpha and beta transitions terminating in stable ^{208}Pb. Within this decay chain, ^{228}Ac, ^{212}Pb, ^{212}Bi, and ^{208}Tl are of analytical importance due to their relatively intense and well-resolved gamma emissions. Under secular equilibrium, the activities of these daughter radionuclides are equal to that of the parent ^{232}Th. Consequently, reliable determination of ^{232}Th can be achieved through measurement of selected progeny gamma lines, if equilibrium conditions are verified and appropriate corrections such as coincidence summing are rigorously applied. This indirect approach constitutes the foundation of high-resolution gamma spectrometric analysis of thorium in environmental matrices.

4.2. Metrological Validation Using Certified Reference Materials

Method accuracy and traceability were assessed using three certified reference materials (IAEA-385, IAEA-412, and IAEA-447). Activities were determined independently from multiple daughter radionuclides (^{228}Ac, ^{212}Pb, ^{212}Bi, and ^{208}Tl) to evaluate internal consistency within the decay series. Across all reference materials, the measured ^{232}Th activity concentrations exhibited excellent agreement with the certified values as shown in Table 1. Deviations remained within one standard deviation of the reference uncertainties for all evaluated gamma lines, demonstrating both trueness and precision of the analytical protocol. The concordance among activities derived from different progenies further confirms the establishment of secular equilibrium in the reference matrices and validates the multi-line quantification strategy. Among the evaluated emissions, the 2614.5 keV gamma line of ^{208}Tl provided the highest metrological performance. Ratio analysis yielded a standard deviation of 0.0122 presented in Table 2, indicating superior reproducibility and minimal inter-matrix variability. Quantitative comparison between certified and measured activities based on this line demonstrated near-perfect agreement.

Table 1. ^{232}Th activity (Bq·kg^{-1}) in certified reference materials.

Parent Nuclide	Daughter Nuclide	Energy (keV)	Intensity (%)	IAEA-385 (33.8 ± 0.9)*	IAEA-412 (36.3 ± 3.5)*	IAEA-447 (37.3 ± 2.0)*	PT
^{232}Th	^{228}Ac	270.24	3.46	37.4 ± 6.1	36.3 ± 1.8	41.1 ± 4.1	438 ± 35
		338.32	11.3	33.7 ± 2.8	37.9 ± 1.2	34.6 ± 1.7	472 ± 18
		911.20	25.8	34.0 ± 4.6	36.4 ± 0.9	35.5 ± 1.0	446 ± 23
		964.77	4.99	34.1 ± 4.6	35.6 ± 1.6	36.9 ± 2.3	428 ± 23
		968.97	15.8	33.6 ± 2.4	35.3 ± 1.0	35.4 ± 1.2	443 ± 15
	Mean ± 1σ			34.0 ± 0.6	36.3 ± 0.5	35.6 ± 0.7	448 ± 08
	^{212}Pb	238.63	43.6	34.9 ± 2.0	37.7 ± 1.8	36.4 ± 1.1	460 ± 14
	^{212}Bi	727.33	6.67	33.9 ± 4.1	36.1 ± 1.5	36.6 ± 2.1	435 ± 20
	^{208}Tl	583.19	85.0	34.4 ± 2.0	36.0 ± 1.0	35.0 ± 1.2	439 ± 14
		860.56	12.5	32.1 ± 4.4	35.0 ± 1.6	32.2 ± 2.1	409 ± 23
		2614.5	99.8	33.7 ± 2.0	36.6 ± 0.9	36.7 ± 1.1	ND
	Mean ± 1σ			34.3 ± 0.7	36.2 ± 0.6	35.5 ± 0.8	431 ± 11

*Certificate value.

Table 2. Significant test for the gamma energy line for ^{232}Th measurement.

Gamma line	Mean ratio	Std Dev	t-Statistic	p-Value	($p < 0.05$)*
2615 keV	0.9964	0.0122	−0.5107	0.6604	No
583 keV	1.0394	0.0239	2.8571	0.1038	No
861 keV	0.9793	0.0487	−0.7365	0.5381	No
727 keV	1.0513	0.0425	2.0901	0.1718	No
239 keV	1.075	0.0415	3.1315	0.0886	No
338 keV	1.0473	0.0654	1.2532	0.3368	No
911 keV	1.0444	0.0359	2.1429	0.1654	No

*Statistical test of gamma-line-derived activity ratios (n = 5 environmental samples).

Quantitative comparison between certified and measured activities derived from the ^{208}Tl (2614.5 keV line) demonstrated excellent agreement within the combined measurement uncertainties for all investigated reference materials. To further illustrate the internal consistency of the gamma spectrometric determinations, the activities of ^{232}Th derived from individual daughter radionuclide gamma lines are presented graphically in **Figure 3** for the certified reference materials IAEA-385, IAEA-412, and IAEA-447. The figure compares activities calculated from the gamma emissions of ^{212}Pb (238.6 keV), ^{228}Ac (338.3 keV), ^{212}Bi (727.3 keV), and ^{208}Tl (583.2 and 2614.5 keV) with the certified ^{232}Th values for each material. The measured activities from all daughter radionuclides agree closely with the certified values within their respective uncertainties, demonstrating the absence of significant systematic bias and confirming the validity of the efficiency calibration and coincidence summing corrections applied in this study. In particular, the results obtained from the high-energy ^{208}Tl 2614.5 keV emission remain consistent with those derived from lower-energy gamma lines, despite the larger coincidence summing corrections required for close-geometry measurements. The graphical comparison highlights the validity of the multi-line approach and further supports the use of corrected ^{208}Tl emissions as reliable indicators for the determination of ^{232}Th activity in environmental matrices. For IAEA-385, the measured value (33.7 ± 2.0 Bq·kg^{-1}) was statistically indistinguishable from the certified value (33.8 ± 0.9 Bq·kg^{-1}). Similarly, IAEA-412 yielded 36.6 ± 0.9 Bq·kg^{-1} compared with the certified 36.3 ± 3.5 Bq·kg^{-1}, while IAEA-447 showed 36.7 ± 1.1 Bq·kg^{-1} relative to 37.3 ± 2.0 Bq·kg^{-1}. The agreement between the measured and certified activities derived from the ^{208}Tl 2614.5 keV gamma emission is illustrated in **Figure 4**. The figure compares the activities obtained for the certified reference materials IAEA-385, IAEA-412, and IAEA-447 with their corresponding certificate values. The results demonstrate excellent agreement within the reported uncertainties, confirming the reliability of the efficiency calibration and the accuracy of the coincidence summing corrections applied to the high-energy ^{208}Tl emission. This comparison further supports the suitability of the 2614.5 keV gamma line as a valid analytical indicator for the determination of ^{232}Th in environmental matrices.

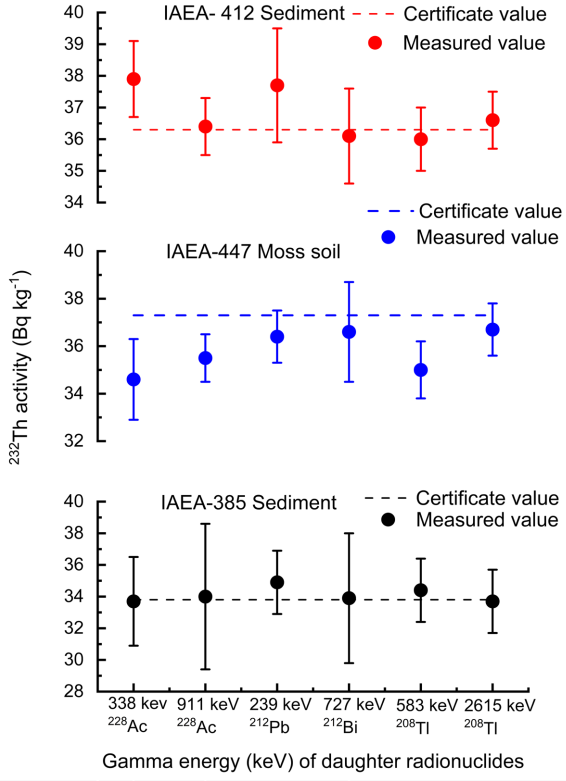

Figure 3. Comparison of ^{232}Th activity concentrations determined from individual daughter gamma line in certified reference materials.

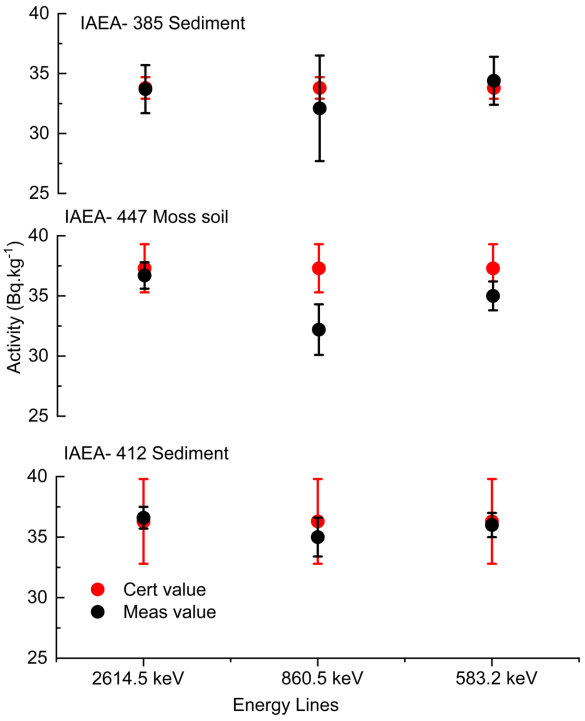

Figure 4. Comparison between measured and certified ^{232}Th activity concentrations derived from the ^{208}Tl 2614.5 keV gamma emission for the certified reference materials IAEA-412, IAEA-4447, and IAEA-385.

In all cases, the differences between measured and certified values were well within the combined standard uncertainties, indicating the absence of significant systematic bias. The relative deviations were below ~2%, confirming the trueness of the method and the adequacy of efficiency calibration and coincidence summing corrections.

These results substantiate the metrological reliability of the applied gamma-spectrometric protocol for accurate ^{232}Th determination in environmental matrices. The negligible bias observed across distinct matrices demonstrates the validation of the calibration and efficiency correction procedures. Although the ^{208}Tl 2614.5 keV line requires coincidence summing correction due to cascade emissions, the corrected results confirm its suitability as a primary analytical indicator for ^{232}Th. Its high emission probability and low spectral interference make it particularly advantageous for trace-level environmental analysis.

4.3. Application to Environmental Sediment and Soil Samples

The validated methodology was subsequently applied to shoreline sediment and soil samples (S1 - S4 and BS) to assess natural ^{232}Th activity under environmental conditions. Activities derived from ^{228}Ac, ^{212}Pb, ^{212}Bi, and ^{208}Tl were internally consistent, ranging from 20 to 26 Bq·kg^{-1} presented in Table 3. The close agreement among daughter-derived activities provides strong evidence for secular equilibrium within the decay chain in all investigated samples. The absence of systematic discrepancies between low- and high-energy gamma lines further indicates that matrix-dependent self-attenuation and efficiency corrections were appropriately accounted for.

Table 3. ^{232}Th activity (Bq·kg^{-1}) in sediment and soil samples.

Parent Nuclide	Daughter Nuclide	Energy (keV)	Intensity (%)	S1	S2	S3	S4	BS
^{232}Th	^{228}Ac	270.24	3.46	24.0 ± 0.7	22.5 ± 0.9	22.8 ± 0.7	24.5 ± 0.7	30.8 ± 2.5
		338.32	11.3	24.2 ± 0.5	20.2 ± 0.5	21.3 ± 0.5	24.4 ± 0.5	24.7 ± 1.1
		911.20	25.8	24.9 ± 0.4	21.1 ± 0.4	23.0 ± 0.4	24.0 ± 0.4	22.9 ± 0.8
		964.77	4.99	23.4 ± 0.6	20.2 ± 0.7	22.2 ± 0.5	22.9 ± 0.5	23.6 ± 0.7
		968.97	15.8	24.5 ± 0.5	20.6 ± 0.5	22.3 ± 0.5	23.2 ± 0.5	22.9 ± 0.9
	Mean ± 1σ			24.3 ± 0.2	20.7 ± 0.2	22.4 ± 0.2	23.8 ± 0.2	23.5 ± 0.5
	^{212}Pb	238.63	43.6	23.6 ± 0.4	20.7 ± 0.3	22.4 ± 0.5	23.9 ± 0.5	23.6 ± 0.7
	^{212}Bi	727.33	6.67	23.4 ± 0.5	21.0 ± 0.5	22.8 ± 0.5	22.7 ± 0.4	21.1 ± 1.6
	^{208}Tl	583.19	85.0	24.0 ± 0.3	20.4 ± 0.2	22.4 ± 0.3	22.8 ± 0.3	22.0 ± 0.7
		860.56	12.5	20.1 ± 0.5	18.7 ± 0.6	20.3 ± 0.4	20.2 ± 0.4	27.6 ± 2.0
		2614.5	99.8	26.2 ± 1.8	ND	27.4 ± 2.3	24.1 ± 1.7	24.1 ± 0.8
	Mean ± 1σ			24.0 ± 0.5	20.1 ± 0.2	21.8 ± 0.2	22.1 ± 0.2	23.3 ± 0.5

Sample S1 exhibited the highest mean ^{232}Th activity (24.3 ± 0.2 Bq·kg^{-1}),

whereas S2 showed the lowest (20.7 ± 0.2 Bq·kg^{-1}). The relatively narrow activity range suggests limited spatial variability and reflects natural geochemical heterogeneity rather than anthropogenic enrichment.

Overall, the measured concentrations fall within typical background levels reported for uncontaminated soils and sediments, supporting the interpretation that thorium in these samples is of lithogenic origin.

4.4. Statistical Assessment of Gamma Line Consistency

To quantitatively evaluate internal consistency within the ^{232}Th decay chain, activity ratios were defined for each gamma line as the ratio of the activity derived from an individual gamma emission to the mean activity obtained from all evaluated gamma lines for the same sample:

$$R_i = \frac{A_i}{\bar{A}} \tag{1}$$

where A_i is the activity determined from gamma line *i*, and $\bar{A}$ is the arithmetic mean activity derived from all gamma lines for that sample.

For each gamma energy, the distribution of ratios across all environmental samples (S1 - S4 and BS, $n = 5$) was analyzed. A two-sided Student's *t*-test was applied to test the null hypothesis:

$$H_0 : \mu_R = 1 \tag{2}$$

against the alternative hypothesis:

$$H_1 : \mu_R \neq 1 \tag{3}$$

where μ_R represents the mean ratio for a given gamma line. A significance level of $\alpha = 0.05$ (95% confidence level) was adopted.

As summarized in Table 3, none of the evaluated gamma lines exhibited statistically significant deviation from unity ($p > 0.05$), confirming the absence of systematic bias among activities derived from daughter radionuclides and supporting the assumption of secular equilibrium. Although the 238.6 keV (^{212}Pb) and 727.3 keV (^{212}Bi) lines approached the significance threshold ($p = 0.0886$ and 0.1718, respectively), the deviations remained within expected analytical uncertainty and do not indicate disequilibrium or methodological deficiency.

Among the evaluated emissions, the 2614.5 keV gamma line of ^{208}Tl exhibited the lowest standard deviation as shown in Table 2, indicating superior precision and minimal inter-sample variability. This statistical behavior reinforces its reliability and supports its preferential use in high resolution, ultra-low background gamma spectrometric determination of ^{232}Th, provided that appropriate coincidence summing corrections are applied.

4.5. Influence and Correction of Coincidence Summing

True coincidence summing effects were systematically evaluated using GESPECOR simulations as presented in Table 4. Significant summing losses were observed for the 2614.5 keV and 583.2 keV emissions of ^{208}Tl, with correction factors

decreasing to 0.7733 in the 49 mL geometry. This corresponds to potential count losses of up to 22.7% for close detector-sample configurations.

Table 4. Coincidence summing corrections calculated by GESPECOR in gamma energy lines.

Nuclide	Energy (keV)	Intensity (%)	49 ml	800 ml
^{228}Ac	338.32	11.3	0.95158	0.95886
^{228}Ac	911.20	25.8	0.96099	0.97248
^{212}Pb	238.63	43.6	0.99974	0.99990
^{208}Tl	583.19	85.0	0.80062	0.84460
^{208}Tl	2614.5	99.8	0.77330	0.82323

In contrast, emissions from ^{228}Ac (338.32 and 911.20 keV) and ^{212}Pb (238.63 keV) exhibited minimal summing effects, with correction factors exceeding 0.95, indicating negligible cascade interference. These results emphasize the critical importance of rigorous summing corrections for high-energy cascade emitters, particularly in close-geometry measurements. When accurately corrected, the 2614.5 keV peak retains its analytical superiority, combining high emission probability, minimal background interference, and excellent counting statistics.

Although the 2614.5 keV gamma emission of ^{208}Tl provides superior statistical precision and minimal spectral interference, its application may be limited in low-activity samples where the peak is not detectable or when strong coincidence summing corrections introduce additional uncertainty. In such cases, lower-energy emissions from ^{228}Ac (e.g., 338 keV) or ^{212}Pb (238 keV), which exhibit negligible summing effects, may provide more reliable estimates. Therefore, a multi-line approach remains essential for robust ^{232}Th quantification under varying measurement conditions.

5. Conclusion

This study highlights the effectiveness of ultra-low background high-purity germanium (HPGe) gamma spectrometry in accurately measuring ^{232}Th in environmental samples. By analyzing various gamma-emitting daughter radionuclides such as ^{228}Ac, ^{212}Pb, ^{212}Bi, and especially ^{208}Tl under secular equilibrium, ^{232}Th activity can be reliably determined even at low levels typical of natural soils and sediments. Of all the gamma lines studied, the 2614.5 keV emission from ^{208}Tl yielded the most accurate and consistent results, with minimal variation across certified reference materials and environmental samples. Although this line is affected by true coincidence summing (TCS), applying proper correction factors restored measurement accuracy without reducing sensitivity. Other lines, particularly from ^{228}Ac and ^{212}Pb, showed trivial summing effects and supported the activity estimates, further confirming the equilibrium assumption. The consistent activity measurements of ^{232}Th across multiple gamma lines, combined with statistical analysis and summing corrections, demonstrate the validity of this method for

routine environmental radioactivity evaluations. The results endorse using ^{208}Tl, alongside other thorium progeny, as a dependable tracer for ^{232}Th in soil and sediment samples, with applications in geochemical tracing, environmental monitoring, and radiological safety assessments. This method therefore provides a reliable analytical approach for routine environmental monitoring and regulatory compliance applications.

Authorship Contribution Statement

Abdul J. Khan: Project Design, Conceptualization, Methodology, Data Analysis, Data curation, Writing-Original Draft, Literature Survey, Supervision; Umme-Farzana Syed: Sample Preparation, Review and Editing; Cynthia A. Costello: Sample Collection and Distribution, Review and Editing.

Conflicts of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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