

Determining ^{234}Th and ^{238}U in Rocks, Soils, and Sediments via the Doublet Gamma at 92.5 keV

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Efficient and accurate measurements of uranium (U) and U-series radionuclides in earth's materials are needed to assess its environmental impact, reconstruct geochemical histories, and quantify heat production in the crust. To date, measurements of ^{234}Th and ^{238}U by gamma spectrometry have relied on the quantification of ^{234}Th gamma emissions at ~63 keV (absolute intensity = 3.7%) and the $^{234\text{m}}\text{Pa}$ gamma at 1001 keV (absolute intensity = 0.84%). However, use of the 63 keV emissions can be hampered by ^{232}Th interferences and self absorption, and the 1001 keV photon has a very low yield. Here we describe the effective use of the ^{234}Th doublet gamma emission at ~92.5 keV (total absolute intensity = 4.8%) for ^{234}Th and ^{238}U measurements. This doublet has been largely ignored because of its proximity to the Th $K_{\alpha 1}$ (93.3 keV) and thus its vulnerability to a Th self-fluorescence interference. We demonstrate that additions of U and ^{40}K to a Th ore sample do not increase the count rate at 92-93 keV above that which would be expected from the associated additions of U and ^{234}Th . We also show that the Th self-fluorescence interference appears to be an anomaly associated only with the analysis of relatively thick (>1 mm) Th minerals, and suggest that fluorescence will not complicate the 92-93 keV region in most environmental samples. A review of decay data reveals that Th $K_{\alpha 1}$ X-rays associated with the decay of ^{235}U and ^{228}Ac can significantly interfere with quantification of the 92.5 keV ^{234}Th doublet. We show that simple experimentally-derived correction factors for these X-rays can be used to accurately determine ^{234}Th using its strongest gammas, resulting in higher count rates and smaller self-absorption corrections relative to the traditional analytical lines. Total 1-sigma analytical error associated with U measurements at 92.5 keV ranged from 1 to 9% and is dominated by the relative size of the ^{228}Ac interference. Detection limits for U in environmental samples using this technique are on the order of 50 ppb.

Introduction

^{238}U ($T_{1/2} = 4.468 \times 10^9$ years) and its short-lived daughter nuclide ^{234}Th ($T_{1/2} = 24.1$ days) are ubiquitous in the earth's crust, soils, and surface and ground waters, and have become important tracers of chemical, biological, and physical processes occurring in the environment. ^{238}U - ^{234}Th equilibria is used to quantify the residence times and sources of colloids in oceans and estuaries¹⁻³, and to trace the fate of particle-reactive contaminants in surface waters^{4, 5}. U and Th series nuclides are used to characterize and determine rates of chemical weathering processes and to identify erosion timescales⁶⁻¹⁰. U series radionuclides are also useful for tracing magmatic processes¹¹, and for dating minerals and fossils^{12, 13}. Most recently, the ^{234}Th isotope has been employed to trace the feeding activity of deep sea megafauna^{14, 15}.

Gamma-spectrometry has advantages over other analytical techniques commonly used to measure radionuclides: (1) no prior chemical treatment is needed before analysis, (2)

analysis is nondestructive, (3) large amounts can be analyzed (typically 1 to 250 g), which is particularly useful for samples with low radionuclide activities, and (4) gamma-spectrometry provides simultaneous quantitative information on a host of radionuclides, including many in the ^{238}U , ^{235}U , and ^{232}Th series, ^{40}K , cosmogenic nuclides (e.g., ^7Be), and anthropogenic radionuclides (e.g., ^{137}Cs , ^{241}Am). The fact that gamma-spectrometry is non-destructive is particularly useful in the analysis of valuable archeological finds¹³. Furthermore, since U is commonly found in very resistant minerals (e.g., zircons) which are not always thoroughly dissolved by chemical fusions and digestions¹⁶, gamma-spectrometry offers a simple whole-sample analysis that circumvents the common problem of incomplete sample dissolution. Gamma-spectrometry has found applications in the rapid discrimination between natural and depleted U in contaminated soils¹⁷, and in geophysical studies requiring the quantification of heat-generating nuclides in the earth's crust¹⁸. Although gamma-spectrometry is not adequate on its own for quantifying certain useful isotopic ratios (e.g., $^{234}\text{U}/^{238}\text{U}$), it can be very useful for measuring $^{226}\text{Ra}/^{238}\text{U}$, $^{210}\text{Pb}/^{226}\text{Ra}$, and for quantifying the relatively rare case of $^{234}\text{Th}/^{238}\text{U}$ disequilibrium².

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Direct measurement of ^{234}Th by gamma-ray spectrometry is possible because semiconductor-based detectors can be used to quantify gamma-ray emissions of ^{234}Th as it decays to the short-lived $^{234\text{m}}\text{Pa}$ ($T_{1/2} = 1.17$ min), or the emission of $^{234\text{m}}\text{Pa}$ as it decays to ^{234}U . Because ^{234}Th has a short half-life and is relatively insoluble, secular equilibrium typically exists between ^{238}U and ^{234}Th in soils, rocks and sediments¹⁹. It can also be guaranteed by >4 months of storage. Therefore, quantification of ^{234}Th can give immediate information on ^{238}U (and thus total U in any soils not contaminated with enriched ^{235}U). Gamma spectrometry is based on the identification and quantification of nuclide-specific emission lines, and uses emission probabilities and detector efficiencies to relate peak area to total activity or concentration. There have been some discrepancies over the emission probabilities of the 63.3 keV and the 92.5 keV doublet gammas^{20, 21}. However, in recent years, emission probability evaluations seem to be coming into better agreement, perhaps because of improvements in detector resolution and radiochemical separation techniques. An average of the most recent evaluations, along with the standard deviations on this average and associated references are given in Table 1.

Thorium-234 quantification based on the 63.3 and 92.5 keV emission lines is highly advantageous for gamma spectrometry because Ge detectors are typically at highest detection efficiency in the 40 to 120 keV energy region, often more than 5-fold higher than for emissions above 600 keV. The higher detector efficiencies, combined with higher emission probabilities make the ^{234}Th gammas the optimal choice for routine gamma analysis on most environmental samples^{19, 22-24}. While these advantages are partially offset by the fact that the Compton Continuum background is typically much greater in the 60-120 keV range than at higher energies, the determination of background levels is generally a manageable problem. The 1001 keV photon from $^{234\text{m}}\text{Pa}$ decay has a low emission probability and detector efficiencies are generally low in this energy region. Thus, analysis at this emission line requires long (>2 day) integrated count times. If long counting times are employed, quantification at this emission line is very straight-forward, since an emission probability of 0.839% is well agreed upon for this photon, and gammas at >200 keV generally require minimal self-absorption corrections. Furthermore, the Compton Continuum is quite low in the region of 1001 keV. Thus, measurement of ^{234}Th at 1001 keV can be considered a "standard" which may be compared to other quantification techniques²⁵.

Numerous researchers have demonstrated that the 63.3 keV decay emissions of ^{234}Th are useful for routine analysis of ^{238}U and ^{234}Th in soils and sediments, although some complications exist for this particular line. Murray et al.¹⁹ cautioned that an "unassigned" Th series radionuclide can interfere with ^{234}Th measurements at 63.3 keV. Work by Saha and Sahakundu²⁶ and Roy et al.²⁷ demonstrate the existence of a ^{232}Th gamma at 63.8 keV with an absolute intensity of 0.26%. This interference from ^{232}Th is not always trivial, and must be corrected for when analyzing samples high in thorium²⁸. ^{232}Th can also be quantified by gamma spectrometry via the strong emissions of ^{228}Ac and ^{212}Pb if secular equilibrium exists. Such measurement could permit a

relatively simple ^{232}Th interference correction at the 63 keV line²³. However, secular equilibrium between ^{232}Th and its daughters is frequently not achieved in soils and other environmental samples because of Ra solubility²⁹. Therefore, a reliable correction for ^{232}Th at 63 keV would require alpha-spectrometry or another analytical method.

A larger potential source of error associated with ^{234}Th and ^{238}U measurements at 63 keV is the need for a sample self-absorption correction^{23, 24}. The absorption of low energy photons (<100 keV) by the sample can introduce significant errors to the determination of radionuclide concentrations by gamma spectrometry³⁰. This correction can vary from sample to sample, as it will be a function of both density and composition. Numerous theoretical and experimental (e.g., point-source transmissions) techniques have been developed to correct for self-absorption phenomena^{31, 32}. While these procedures are effective at accounting for self absorption, it introduces an uncertainty to the measurement that is proportional to the self-absorption correction factor itself.

The doublet gamma at 92.5 keV from ^{234}Th decay offers a superior means of quantifying ^{234}Th and ^{238}U because of its relatively high emission probability (33% higher yield than the 63.3 keV photon) and its higher sample transmission probability. This will result in a smaller self-absorbance correction and thus lower uncertainties and potentially shorter counting times. However, several authors have noted that Th has $K_{\alpha 1}$ X-rays at 93.3 keV^{19, 23}, which would lead to a significant complication when analyzing ^{234}Th at this energy. If present, Th $K_{\alpha 1}$ "self-fluorescence" X-rays, and thus the interference at 93.3 keV would be a function of total Th content and the overall radioactivity of the sample. Such interference would be very difficult to correct for, and render the 92.5 keV gamma emissions essentially useless for ^{234}Th (and U) determination. If fluorescence exists here as a result of excitation from natural radionuclides, it should be possible to quantify total Th content on intrinsic Ge detectors using these Th $K_{\alpha 1}$ X-rays and a natural source of radioactivity such as U.

Here we demonstrate that the photopeak interfering with ^{234}Th gamma measurements at 92.5 keV is not a function of overall sample radioactivity. We suggest that the interference comes from another source, and is most likely associated with the decay of a specific nuclide. Our review of the literature revealed a detailed study of the decay of radiochemically-pure ^{228}Ac (^{232}Th series, $T_{1/2} = 6.15$ h) by Dalmasso et al.³³, which demonstrates that Th $K_{\alpha 1}$ X-rays at 93.3 keV accompany the decay of ^{228}Ac . This Th $K_{\alpha 1}$ X-ray has a reported absolute intensity of 3.2%³⁴ (presumably 3.2% of the ^{228}Ac decay rate) and results perhaps from an internal conversion process. We show that by using experimentally-derived interference corrections for Th $K_{\alpha 1}$ (via ^{228}Ac) and ^{235}U X-ray contributions to the 92-94 keV region, ^{234}Th (and U) can be accurately and efficiently quantified by gamma spectrometry at this energy.

Methods

Gamma Spectrometry Instrumentation and Efficiency Calibration

Emission spectra were collected using a Canberra “Broad Energy” High Purity Intrinsic Ge (HPGe) detector, which is surrounded by a 3600 lb low-background lead shield. The detector is 3 cm thick and has an active surface area of 50 cm². Resolution is 700 eV at 122 keV. The efficiency of the detector for measuring U-series nuclides was calculated using certified Uranium Ore (Canadian Reference Materials Project BL-5 U ore) diluted with high purity quartz. This allowed for the evaluation of the detector efficiency for U X-rays and ²³⁴Th gammas at 63 keV and 93 keV, using the emission probabilities in Tables 1 and 2. Samples and standards were counted in an identical geometry: a 105 ml plastic container (1.7 cm high; 8.9 cm dia.). The samples varied slightly in composition and density from the calibrating matrix, so self-absorption corrections at 63 keV and 93 keV were performed using a standard point-source transmission method³¹. Peak areas at 63 keV and 911 keV were calculated by the least-squares summation method in the Canberra *Genie2k* software package. The spectrum in the 70-110 keV region is crowded with X-rays and gammas from many nuclides, so we used the program *Peak Fit* to interpret this part of the spectrum. We fitted Gaussian-shaped peaks in this region, and the background was modeled with a hyperbolic function.

Th Fluorescence Experiments

In the first batch of experiments, 2 grams of Th ore (monazite, (Ce,La,Th,Nd,Y)PO₄, with 5.5% Th) was crushed and diluted with a) quartz, b) a potassium-matrix: KCl + Potassium Feldspar. Spectra of these mixes were collected for 4000 sec. U ore (in secular equilibrium with its daughters) was also measured in a quartz matrix in the same geometry as the Th ore. The Th ore sample was then spiked with measured amounts of U ore, and the spectra of these mixes were collected.

Interference Correction for Analysis of Unknowns

Interferences from the ²³²Th γ at 63 keV and the Th K _{α} X-rays at 93 keV (accompanying ²²⁸Ac decay) were determined by spiking a quartz sample with a small amount of crushed Th ore in the same geometry as the unknowns (Figure 2) and using the ratio of the 911 keV ²²⁸Ac γ to the 63 keV ²³²Th γ peak and the 911 keV ²²⁸Ac γ peak to the Th K _{α} X-ray at 93 keV. Again, since the samples were slightly different in composition from the calibrating matrix, self-absorption corrections at 63 keV and 93 keV were performed using the point-source transmission method.

Independent Measurements of U

To establish the accuracy of our new method and experimentally-derived interference correction, we analyzed a range of soil, sediment, and rock samples collected from a variety of locations. Our U and Th analyses were compared

to an established independent analytical method: instrumental neutron activation analysis. Since this technique is not readily available in most academic settings, these analyses were performed by an accredited private laboratory, Activation Laboratories Ltd (ACTLABS).

Results and Discussion

Figure 1 gives a partial emission spectrum for the Th ore measured in a quartz matrix and for the Th ore measured in a ⁴⁰K rich matrix. Additions of ⁴⁰K to the Th ore sample did not affect the emission spectrum at all, as is evident by the residuals plot also given in Figure 1. Figure 2 gives a partial emission spectrum of a U ore samples. The Th and U in quartz spectra were normalized to counts/sec/g ore counted, and are used to calculate theoretical spectra for different U and Th mixes. The differences between the theoretical spectra and the measured spectra in the 70-110 keV energy range for the U and Th mixes are plotted as residuals in Figure 3. If U-series nuclides excite the Th into fluorescence, then it should be evident by comparing the theoretical and measured spectra, as we would expect additional peaks at 90 and 93 keV in the measured spectra (Th K _{$\alpha 2$} & Th K _{$\alpha 1$} , respectively).

Our additions of U-series radionuclides and ⁴⁰K to a Th sample did not cause any fluorescence at the Th K _{$\alpha 2$} or Th K _{$\alpha 1$} energies of 90 and 93 keV, respectively. The peak increases at those energies were entirely a function of added U, and the theoretical U-Th mixes matched the analyzed U-Th sample for a range of U/Th ratios (Figure 3). This lack of observed Th fluorescence is consistent with the 109.7 keV binding energy of the Th 1s shell. Specifically, the energy region nearest the Th 1s binding energy (105-140 keV) is generally free of photons from U, Th, and K series nuclides in environmental samples (Figures 1 and 2).

It does appear that Th fluorescence can interfere with the 90-93 keV region in unique cases when relatively thick Th-rich minerals (e.g., thorite, monazite) are analyzed. We found that the intensity of the Th K _{α} and Th K _{β} emissions are higher relative to other gamma lines (that can be used as a relative scale to normalize for total Th and radioactive decay) when analyzing a relatively thick pure Th phase vs. a sample where Th is fine-grained and more dispersed (Figure 4). However, in most natural samples of rock, sediments, and soils, Th is typically dispersed in trace amounts. From our experiments, we conclude that Th fluorescence is unlikely to interfere in the measurement of the ²³⁴Th doublet gamma in most environmental samples.

Quantifying ²³⁴Th (and ²³⁸U) at 92-93 keV

Although the above experiments suggest that Th X-ray fluorescence is probably not significant in natural samples, the 70-100 keV energy range of rock and sediment emission spectra collected by intrinsic Ge detectors is crowded with gammas and X-rays emitted by the U and Th decay series. At least 18 major emission lines contribute to the spectra in the region (Table 2). Many of these lines, however can be separated using high resolution (FWHM < 800 eV) measurements. For high resolution measurements of the 92.5

300 keV ^{234}Th doublet, only a few known emissions could directly interfere. These include a gamma-ray from ^{227}Th (^{235}U series), PaK $_{\alpha 2}$ X-rays emitted from ^{231}Th decay (^{235}U series), Th K $_{\alpha}$ X-rays produced during the decay of ^{235}U , PoK $_{\beta}$ X-rays emitted by ^{214}Bi decay (^{238}U series), and Th K $_{\alpha}$ X-rays produced during the decay of ^{228}Ac (^{232}Th series). Of these, the ^{214}Bi is fairly weak, and unlikely to significantly interfere with the ^{234}Th doublet photopeak. If ^{214}Bi is a concern, its contribution can easily be subtracted by monitoring one of the many other ^{214}Bi lines, and using the recent data by Delgado et al.³⁵ or Morel et al.³⁶ on Ra-series X-ray and gamma-ray emission probabilities. In some situations, the ^{227}Th gamma-ray at 93.9 keV may contribute counts to the 92-93 keV photopeak. However, considering the $^{235}\text{U}/^{238}\text{U}$ activity ratio of 0.04605 (except at sites contaminated with unusual amounts of ^{235}U -enriched U), the ^{227}Th gamma-ray at 93.9 keV is likely to produce only a small interference (on the order of 1% of the total counts of ^{234}Th).

We establish the ability to discriminate between nearby photopeaks using the spectrum and Gaussian fit of a certified U-Th-containing sandstone ore emission spectrum (Figure 5). This sample shows a peak near 94.5 keV, most likely resulting from Rn X-rays (^{223}Ra) and ^{227}Th gammas that interferences with the 92-93 keV peak. Fortunately, we are able to resolve and fit these two peaks effectively using PeakFit, where the 1-sigma error on the baseline-subtracted 92-93 keV peak was generally 3 to 4% (Figure 5).

The resolved 92-93 keV peak shown in Figure 5 results from a combination of ^{234}Th gammas, Th K $_{\alpha 1}$ X-rays (from ^{228}Ac decay), ^{235}U X-rays, and a minor contribution from a Pa X-ray (from ^{231}Th , the immediate daughter of ^{235}U). The K $_{\alpha 1}$ X-rays associated with ^{228}Ac decay can be very significant, particularly in soils and rocks because of the low mobility of Th. Fortunately, ^{228}Ac has several strong, interference-free emissions which can be used to correct for its Th K $_{\alpha}$ X-ray at 93.3 keV. Using a sample of Th dispersed in quartz to experimentally obtain the 93/911 keV correction factor is probably more reliable than using the ^{228}Ac decay data and an efficiency correction to predict the interference. Decay data are not always reliable²¹ and ^{228}Ac decays in a cascade so coincidence summing for this radionuclide is common³⁷. In our study, the interference at 92-93 keV was consistent with an ^{228}Ac decay emission with an absolute emission probability of 3.5%, which is very close to the documented value of 3.2% (Table 2). In soils where secular equilibrium between U isotopes and their immediate Th daughters can be assumed, and where the $^{235}\text{U}/^{238}\text{U}$ activity ratio of 0.04605 applies, the contributions of ^{235}U X-rays and ^{231}Th X-rays can easily be related to the total amount of counts in the Th K $_{\alpha 1}$ -corrected 92-93 keV photopeak. When experimentally-deriving the correction factor for the 93 keV interference, it is important to use a finely dispersed (and diluted) Th sample to avoid the fluorescence effects that can occur with a thick pure Th mineral (Figure 4). We mixed crushed monazite (that had very low U) with crushed quartz in a ratio of 1:25.

Using this method, we are able to effectively measure the concentration of Th and U in a variety of natural samples. Analyses results for 16 soil, rock and sediment samples, with a range of Th and U concentrations determined by neutron

activation and gamma-spectrometry are given in Table 3. Our results agree well with those obtained by INAA, and offer improved analytical errors in many cases.

It is evident that quantification of U at 63 keV without a correction for a ^{232}Th gamma-emission consistently results in an overestimation of ^{234}Th and U (an average +11% bias). Although the uncorrected 63 keV results often come within 1-sigma of the neutron activation determinations, this bias could limit accuracy in samples with a high Th/U ratio. We found that in our samples, ^{228}Ac was generally in equilibrium with its parent ^{232}Th , so using the 911 keV peak to correct for its presence was valid, and the corrected results were in better agreement with the INAA technique. However, care should be used when performing the correction, as ^{232}Th is not always in equilibrium with its daughters in soils and sediments, so the photopeak at 911 keV is not always a perfect proxy for ^{232}Th .

Analytical uncertainties on U determinations using the 63 keV and 93 keV ^{234}Th gammas arise from a number of sources, including (a) the total number of counts at each energy, (b) uncertainties in the peak fitting and baseline-subtraction at each energy, and (c) uncertainties in the correction for ^{232}Th (0.26% intensity gamma at 63 keV) and ^{228}Ac (Thk $_{\alpha}$ x-rays at 93 keV). Cutshall et al.³¹ demonstrated that uncertainties in the calibration (and absorption correction for sample matrix effects) are lower than the statistical counting error using the point-source absorption correction. In these geological samples, the correction for ^{232}Th at 63 keV was fairly small, thus peak-fitting, baseline subtraction, and absorption-correction errors were most significant. In contrast, the ^{228}Ac correction at 93 keV is often on the order of half the total counts. Consequently, the uncertainties in U measurements determined using 93 keV were between 1 and 9%, and dominated by the relative size and fitting of the ^{228}Ac interference.

By analyzing several background spectra collected by counting an empty shield, we can estimate a detection limit (D_L) of U using the 92-93 keV doublet gamma:

$$D_L = \overline{bkg} + 3\sigma_{blk} \quad (1)$$

where bkg is the determination of U on an empty shield, and σ is the standard deviation (of the U determination on multiple background counts). Using this technique, we calculate a detection limit ~50 ppb U for a 150 g theoretical sample counted for 150,000 seconds.

Measurements of U by quantifying 63 keV and 93 keV gamma-emissions, when both are corrected for interferences, are in good agreement. These results contrast with a recent paper by El-Daoushy et al.²² who reported on a wider range of samples, concluding that the 93 keV peak interferences (the peak area in excess of ^{234}Th contributions) was variable when compared to the 63 keV peak for their dataset, and likely a result of Th X-rays. Our two studies appear to have slightly different measurement protocols, where El-Daoushy et al.²² used a Monte-Carlo simulation to determine absorption-corrections for 63 keV, and we experimentally determined the absorption correction for each sample at both the 63 keV and

93 keV peaks using the transmission technique. Although there is a fair amount of scatter in their data, the “excess peak area” they reported at 93 keV appears to be better correlated with ^{228}Ac than with ^{238}U .

Conclusions

Measurements of ^{234}Th (and ^{238}U) at 93 keV will be advantageous over analysis at 63 keV in many cases, and advantageous over the 1001 keV photopeak in nearly all cases. Some detectors, particularly well-type detectors have highest efficiency near 93 keV, sometimes higher by a factor of 2 than for 63 keV. If such detector efficiency advantages are combined with the higher gamma intensity at this energy, this would result in an increase in total sensitivity to ^{234}Th decay by up to a factor of 3 at the 92-93 keV gamma doublet. This would be particularly important for samples at or near ^{234}Th detection limits. Both detection lines also have different interferences, and the relative significance of either may be defined by sample composition. In the event that self-absorption corrections at 63 keV are large, measurements at 93 keV may provide lower uncertainties in addition to higher count rates. The most accurate usage of the 63 keV peak relies on the measurement of ^{232}Th . If ^{228}Ac cannot be a reliable indicator of ^{232}Th activity, and very accurate measurements of ^{234}Th or ^{238}U are required, then other analytical methods will be necessary (e.g., alpha spectrometry). Last, if samples contain little to no ^{228}Ac (such as U ores or peats) the 93 keV line will be the best choice emission for analysis, as the size of the ^{228}Ac interference dominates the measurement error at 93 keV. El-Daoushy et al. (2002) noted that the agreement between 63 keV and 93 keV-determined ^{234}Th was in good agreement for samples collected from ombrotrophic bogs, where ^{228}Ac was naturally low. In conclusion, it is probably best to collect data at both energies, as our results agreed best with the U analyses run by INAA when we averaged the data collected from 63 keV and 93 keV emissions (Table 3).

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Parent	Gamma Energy (keV)	Emission Probability %	References
^{234}Th	62.9+63.3 doublet	3.75 ± 0.21	20, 25, 38-40
^{234}Th	92.4+92.6 doublet	4.83 ± 0.07	25, 40, 41
$^{234\text{m}}\text{Pa}$	1001.0	0.838 ± 0.002	20, 38, 40

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Table 1. Gamma emissions useful for direct ^{234}Th quantification and indirect ^{238}U quantification (if secular equilibrium is established, then ^{238}U disintegrations/second = ^{234}Th disintegrations/second).

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Energy (keV)	Source	Emission Probability %	References
87.2	^{214}Pb X-ray (Bi $K_{b3,1,5}$)	3.18	35
89.6	^{214}Bi X-ray (Po $K_{b3,1,5}$)	0.35	35
89.9	^{214}Pb X-ray (Bi $K_{b2,4,0}$)	0.99	35
89.9	^{231}Th γ	0.94	34
89.95	^{228}Ac X-ray (Th $K_{\alpha 2}$)	1.96	33, 34
89.95	Th $K_{\alpha 2}$ fluorescence		34
92.3	^{231}Th X-ray (Pa $K_{\alpha 2}$)	0.42	34
92.4	^{214}Bi X-ray (Po $K_{b2,4}$)	0.083	35
92.5	^{234}Th doublet γ	4.83 ± 0.05	25, 40, 41
93.35	^{228}Ac X-ray (Th $K_{\alpha 1}$)	3.19	33, 34
93.35	Th $K_{\alpha 1}$ fluorescence		34
93.35	^{235}U X-ray (Th $K_{\alpha 1}$)	5.56	41
93.9	^{227}Th γ	1.37	34
94.3	^{223}Ra X-ray (Rn K_{b3})	3.01	34
94.65	$^{234\text{m}}\text{Pa}$ X-ray (U $K_{\alpha 2}$)	0.143	34
94.7	U $K_{\alpha 2}$ fluorescence		34
94.7	^{226}Ra X-ray (Rn $K_{b3,1,5}$)	0.1	34, 35
94.7	^{223}Ra X-ray (Rn $K_{b3,1,5}$)	8.94	34

Table 2. Significant (emission probability $>0.05\%$) emitters in the energy region of 88-95 keV. Emissions which might contribute directly to the ^{234}Th doublet peak on emission spectra collected by high-resolution Intrinsic Ge Detectors (resolution at 122 keV < 900 eV) at 92.5 keV are in bold.

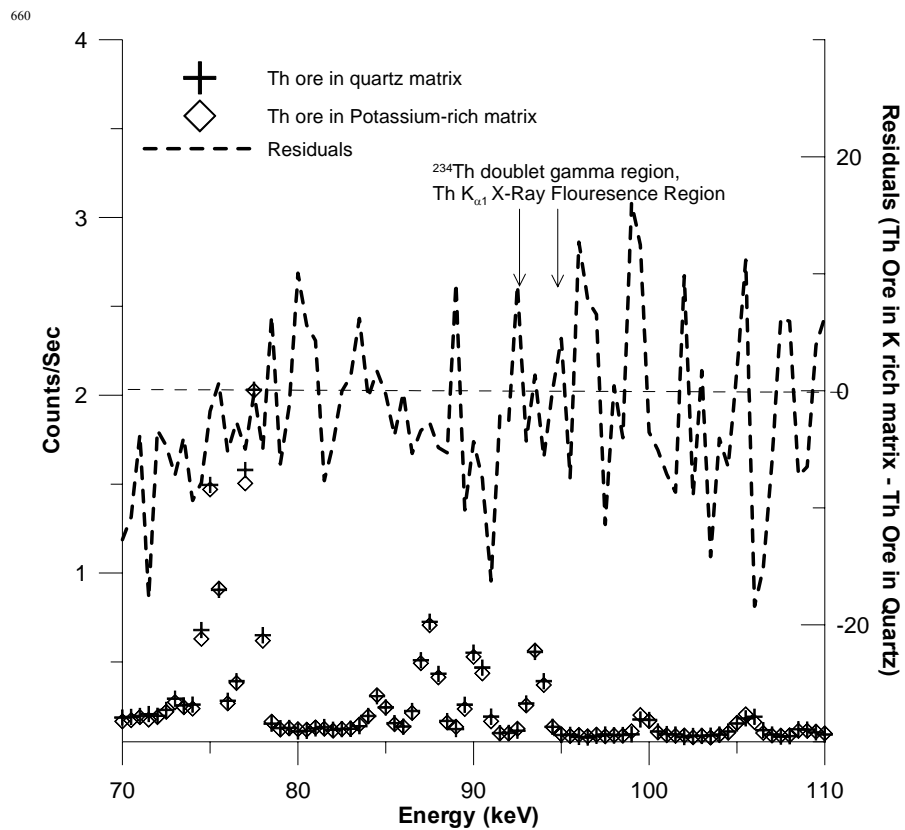
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665 **Figure 1.** Emission spectrum collected from a Th ore sample diluted (25 x) with quartz (+) and mixed with a
 670 potassium-rich mixture (◇). The quartz-matrix had $70 \text{ Bq } ^{40}\text{K kg}^{-1}$; the potassium-rich mixture had $11,200 \text{ Bq } ^{40}\text{K kg}^{-1}$.

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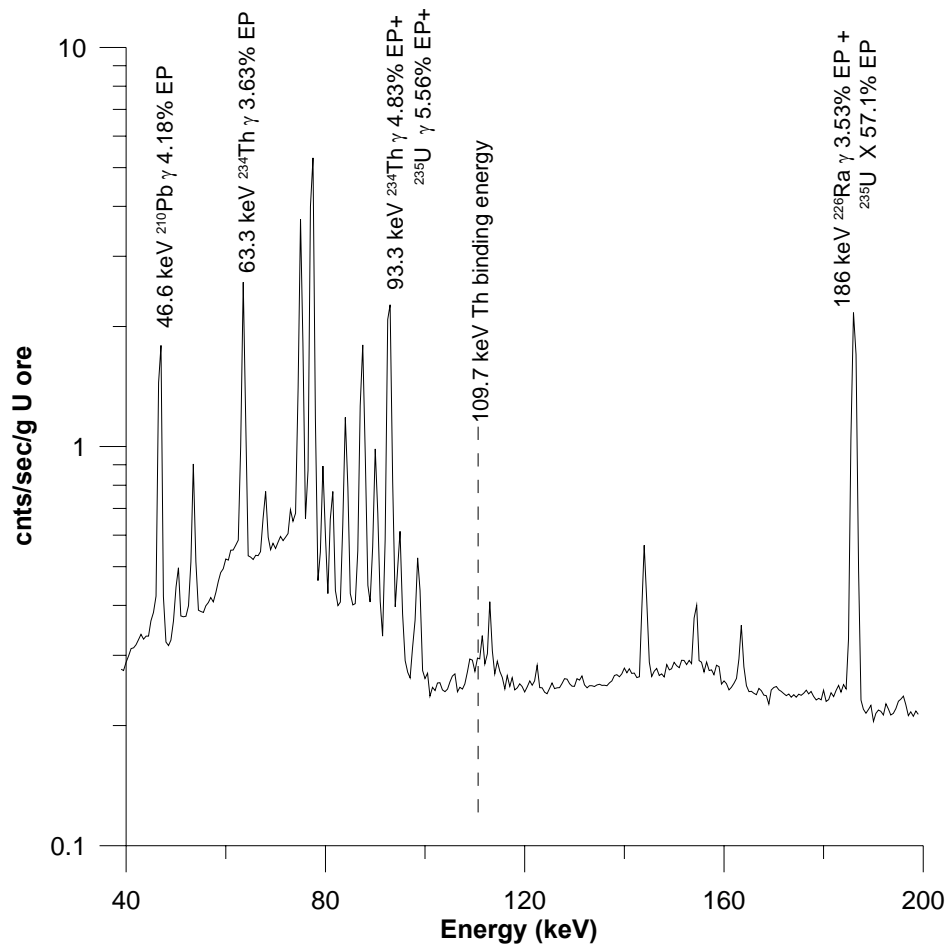


Figure 2. Emission spectrum collected from a U ore sample (diluted with quartz).

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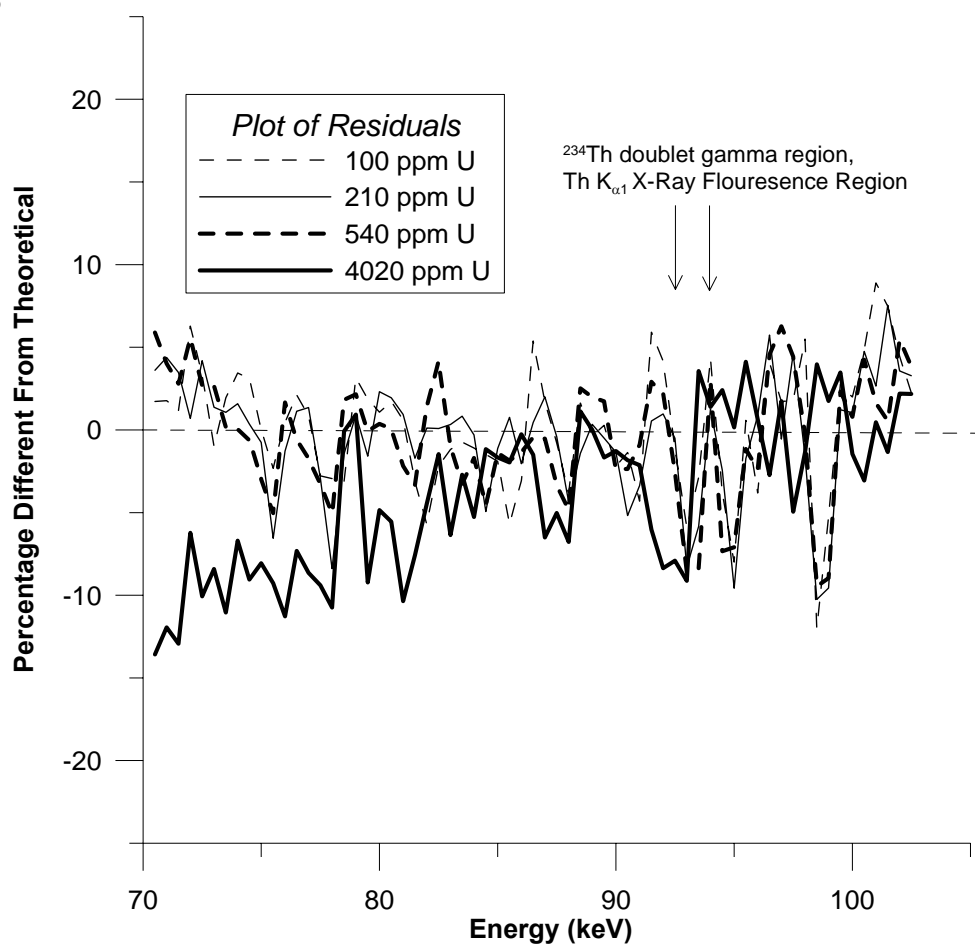
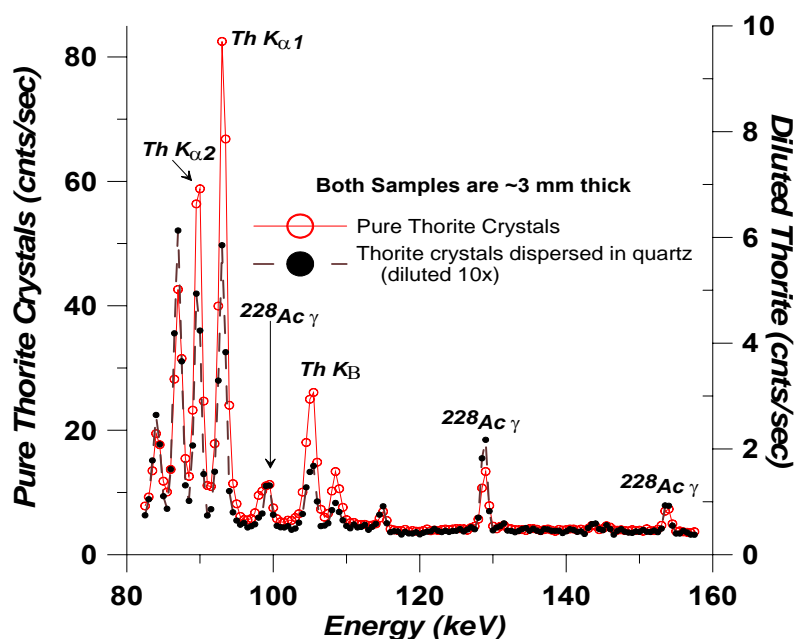


Figure 3. Plot of residuals in the 70-105 keV range for Th and U mixtures: [measured spectra – theoretical spectra]. The amount of Th in the samples remained constant at 0.12 g (all mixtures = 732 ppm Th). Theoretical spectra were calculated by summing the appropriate fractions of the spectra of the U and Th parts given in Figures 1 (plot +) and 2).

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Figure 4. A comparison of emission spectra collected from concentrated and diluted Th samples. When pure thorite crystals are analyzed (sample thickness = ~3 mm), the intensity of the Th K α and Th K β emissions are higher relative to the amount of Th or total radioactive decay than for a sample where Thorite is diluted (10 x) and more finely dispersed. Further evidence that Th fluorescence contributions are significant in the more concentrated Th sample is given by the ratio of the 90 keV K α 2 line to the 93 keV K α 1, which approaches the more expected ratio ~0.6. In more diluted Th samples, the ratio of the 90 keV to 93 keV is closer to 1 (See also Figure 1), because the relative importance of typical decay emissions, particularly at 90 keV, dominates the spectra rather than fluorescence. In the case of the pure thorite spectrum, natural Th fluorescence could interfere with quantifying the 92-93 keV ^{234}Th gamma doublet.

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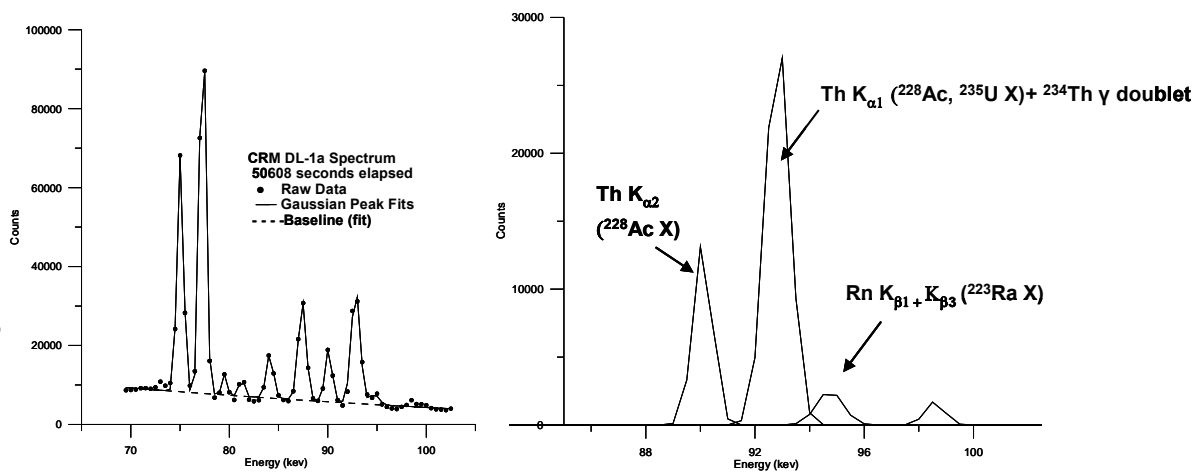


Figure 5. Raw spectral data, baseline fit, and Gaussian peak fits for an arkose sandstone U-Th ore reference material (left). Expanded view of the Gaussian peak fits from (left), baseline subtracted.

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Sample Type	Location	INNA	INAA	GS@ 63 kev	GS@ 63 kev	GS@ 93 kev	GS at 63,93
		U [†]	Th [†]	Uncorrected U [‡]	Corrected [‡] U	U	Average U
granite saprolite	Nunnock River Valley, SE Australia	6.2 ± 0.6	25 ± 2	6.3 ± 0.2	5.8 ± 0.2	5.9 ± 0.3	5.9
mineral soil	Nunnock River Valley, SE Australia	3.0 ± 0.4	12 ± 1	3.10 ± 0.2	2.8 ± 0.2	3.0 ± 0.2	2.9
mineral soil	Nunnock River Valley, SE Australia	3.7 ± 0.5	10.8 ± 1.0	3.9 ± 0.2	3.6 ± 0.2	3.7 ± 0.2	3.7
Haypress Pond upper sediment	Tennessee Valley Marin County, CA	1.8 ± 0.3	5.9 ± 0.6	2.2 ± 0.1	2.1 ± 0.1	1.9 ± 0.1	2.0
Haypress Pond deep sediment	Tennessee Valley Marin County, CA	2.5 ± 0.3	8.9 ± 0.8	2.8 ± 0.2	2.6 ± 0.2	2.6 ± 0.2	2.6
mineral soil	Tennessee Valley Marin County, CA	1.8 ± 0.3	6.6 ± 0.6	2.2 ± 0.1	2.0 ± 0.1	2.3 ± 0.2	2.2
mineral soil	Tennessee Valley Marin County, CA	4.0 ± 0.4	23.2 ± 2.1	4.2 ± 0.1	3.7 ± 0.1	4.0 ± 0.4	3.9
exposed, weathered lake sediments	Connecticut River Valley, New Hampshire	2.0 ± 0.3	8.8 ± 0.9	2.2 ± 0.1	2.0 ± 0.1	2.2 ± 0.2	2.1
upper 30 cm soil composite	Konza Prairie, Kansas	3.9 ± 0.4	13.3 ± 1.1	4.5 ± 0.2	4.2 ± 0.2	4.2 ± 0.2	4.2
upper 30 cm soil composite	Konza Prairie, Kansas	4.1 ± 0.4	13.3 ± 1.1	4.2 ± 0.2	3.8 ± 0.2	4.0 ± 0.2	3.9
upper 30 cm soil composite	Konza Prairie, Kansas	4.1 ± 0.4	12.8 ± 1.1	4.6 ± 0.2	4.2 ± 0.2	4.1 ± 0.3	4.2
upper 30 cm soil composite	Konza Prairie, Kansas	3.3 ± 0.4	12.9 ± 1.1	3.8 ± 0.1	3.4 ± 0.1	3.9 ± 0.3	3.6
upper 30 cm soil composite	Konza Prairie, Kansas	4.0 ± 0.4	13.5 ± 1.2	4.3 ± 0.2	3.9 ± 0.2	3.9 ± 0.2	3.9
upper 30 cm soil composite	Konza Prairie, Kansas	3.2 ± 0.4	8.9 ± 0.8	3.3 ± 0.2	3.1 ± 0.2	3.6 ± 0.2	3.4
upper 30 cm soil composite	Konza Prairie, Kansas	2.9 ± 0.4	11.5 ± 1.0	2.8 ± 0.1	2.5 ± 0.1	2.7 ± 0.1	2.6
sandstone U-Th Ore ^{##}	Denison Mines Ontario	116 ± 3	76 ± 4	119 ± 2	117 ± 2	111 ± 1	114

Table 3. U and Th concentrations (in ppm) of unknown samples analyzed in this study. [†]U and Th concentrations determined by Instrumental Neutron Activation (ACT Labs). [‡]Gamma-ray spectrometric measurement at 63 kev, not correcting for ²³²Th gamma-ray contributions. [#]Gamma-ray spectrometric measurement at 63 kev with a correction for ²³²Th gamma-ray contributions. ^{##}Canadian Certified Reference Materials Project U-Th ore DI-1a. Errors at the 1-sigma level are given.