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THE APPLICATION OF FULL SPECTRUM ANALYSIS TO NaI(Tl) GAMMA SPECTROMETRY FOR THE DETERMINATION OF BURIAL DOSE RATES SUPPLEMENTARY MATERIAL

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1. SUPPLEMENTARY TEXT

S1 Uncertainty analysis

In this supplementary material, we demonstrate how we derive systematic and random uncertainties on the activities of ^{40}K, ^{238}U and ^{232}Th in the unknown sample, and sum them up in the final step.

S1.1 Systematic uncertainty

The systematic uncertainties in our system depend mainly on the standards we use to calibrate the ^{40}K, ^{238}U and ^{232}Th detection efficiencies; these have two different sources. First, the ores (for ^{238}U and ^{232}Th) and chemicals (for ^{40}K) we used to make these calibration standard cups have associated uncertainties assigned by the original manufacturers (see section 2.2 in the main text). The manufacturer's uncertainties (*MU_r*, relative values) on radioactivity in all ^{40}K, ^{238}U and ^{232}Th calibration cups are derived from these associated uncertainties and the dilution ratio during sample preparation. The overdispersion (*OD*) in the spectra of the three cups of each calibration nuclide presumably arises from mixing and other preparation uncertainties, and is a further (independent) contribution to the systematic calibration uncertainty.

This *OD* is derived as follows – ^{40}K is used as an example and ^{238}U and ^{232}Th are treated in the same way. First, we obtain the count rates $CR_{K,j}(i)$ and their uncertainties $Un\_CR_{K,j}(i)$ in each channel i of the drift-corrected spectra $S_{K,j}$ within the ROI from three ^{40}K calibration cups (j = 1, 2, 3) with counting time $t_{K,j}$, respectively, while, i = 1, 2, …, M (M is the total channel number in ROI):

$$CR_{K,j}(i) = S_{K,j}(i)/t_{K,j} \quad (1)$$

$$Un\_CR_{K,j}(i) = \sqrt{S_{K,j}(i)}/t_{K,j} \quad (2)$$

Secondly, the count rates $CR_{Bg,j}(i)$ and their uncertainties $Un\_CR_{Bg,j}(i)$ in each channel i of three drift-corrected background spectra $S_{Bg,j}$ counted for $t_{Bg,j}$ were calculated (j = 1, 2, 3, and i = 1, 2, …, M):

$$CR_{Bg,j}(i) = S_{Bg,j}(i)/t_{Bg,j} \quad (3)$$

$$Un\_CR_{Bg,j}(i) = \sqrt{S_{Bg,j}(i)}/t_{Bg,j} \quad (4)$$

The average background count rate is obtained:

$$CR_{Bg}(i) = \left(\sum_{j=1}^{3} CR_{Bg,j}(i)\right)/3 \quad (5)$$

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Here we ignore any overdispersion in the three background spectra, so only the uncertainty from counting statistics is included:

$$Un\_CR_{Bg}(i) = \sqrt{\sum_{j=1}^{3}\left(Un\_CR_{Bg,j}(i)\right)^2}/3 \quad (6)$$

By subtracting averaged background count rates, we obtain net count rates and their uncertainties:

$$CR\_net_{K,j}(i) = CR_{K,j}(i) - CR_{Bg}(i) \quad (7)$$

$$Un\_CR\_net_{K,j}(i) = \sqrt{Un\_CR_{K,j}(i)^2 + Un\_CR_{Bg}(i)^2} \quad (8)$$

Then we normalize the net count rates to the activities $A_{K,j}$ contained in each ^{40}K calibration cup, respectively:

$$CR\_Norm_{K,j}(i) = CR\_net_{K,j}(i)/A_{K,j} \quad (9)$$

and their uncertainties:

$$Un\_CR\_Norm_{K,j}(i) = CR\_Norm_{K,j}(i) \times \sqrt{\left(\frac{Un\_CR\_net_{K,j}(i)}{CR\_net_{K,j}(i)}\right)^2 + \left(\frac{Un\_A_{K,j}}{A_{K,j}}\right)^2} \quad (10)$$

The uncertainties on activity $Un\_A_{K,j}$ come from the original manufacturer's relative uncertainty (MU_r_K):

$$Un\_A_{K,j} = A_{K,j} \times MU\_r_K \quad (11)$$

Since we define *OD* values as variations between three calibration cups generated only from calibration cup's fabrication process, here we deliberately strip the effect from $Un\_A_{K,j}$ away. However, $Un\_A_{K,j}$ will be taken into account during calculation of uncertainties on activities for the unknown samples. Therefore:

$$Un\_CR\_Norm_{K,j}(i) = Un\_CR\_net_{K,j}(i)/A_{K,j} \quad (12)$$

After obtaining the normalized net count rates from the three ^{40}K calibration standards, they are averaged to give the ^{40}K detection efficiency DE_K (counts·ks^{-1}·Bq^{-1}) and its uncertainty Un_DE_K, as discussed in section 2.4 in the main text.

$$DE_K(i) = \sum_{j=1}^{3} CR\_Norm_{K,j}(i)/3 \quad (13)$$

$$Un\_DE_K(i) = \sqrt{\sum_{j=1}^{3} Un\_CR\_Norm_{K,j}(i)^2}/3 \quad (14)$$

The channel-by-channel standard deviation $STD_K(i)$ in the detection efficiency of three ^{40}K spectra is calculated as:

$$STD_K(i) = \sqrt{\frac{1}{N-1}\sum_{j=1}^{3}\left(CR\_Norm_{K,j}(i) - DE_K(i)\right)^2} \quad (15)$$

Ideally, the differences between $STD_K(i)$ and $Un\_DE_K(i)$ should be close to 0. An unlimited counting time and a larger sample number N can partly reduce the differences caused by counting statistics. In this work, every spectrum of calibration standards or background was counted for 20 hours. Here we define their relative difference $D\_r_K(i)$:

$$D\_r_{K(i)} = \frac{STD_K(i)^2 - Un\_DE_K(i)^2}{DE_K(i)^2} \quad (16)$$

Theoretically $D\_r_K(i)$ should be identical for all channels, and the average of $D\_r_K(i)$ in M channels within ROI should be the best estimation of D_r_K. However, we found that the histogram of $D\_r_K(i)$ is not symmetric and there are outliers at high and low values. Because of this, we chose to use the centroid of the $D\_r_K(i)$ histogram after removing outliers as the best estimation of D_r_K.

Finally, we determine the relative overdispersion value for ^{40}K calibration standard:

$$OD\_r_K = \begin{cases} \sqrt{D\_r_K}, & if\ D\_r_K \geq 0 \\ -\sqrt{|D\_r_K|}, & if\ D\_r_K < 0 \end{cases} \quad (17)$$

The OD_r_U and OD_r_{Th} for the ^{238}U and ^{232}Th calibration standards are obtained in the same manner.

These two contributions to systematic uncertainties, *i.e.*, these from manufacturer's uncertainty and these from *OD* value for each nuclide are listed in **Table S1**, which shows the maximum total systematic uncertainty is <2% (for ^{238}U). The systematic uncertainties are fixed once the calibration standard cups are cast and counted for a certain time.

S1.2 Radom uncertainty

The random uncertainty includes the uncertainties contributed by the finite counts in each channel (counting statistics) and the fitting uncertainty caused by the fitting algorithm used to determine the activity concentrations. Counting uncertainty is essentially dependent on the detection efficiency (*DE*) of the spectrometer, the counting time and the activities of ^{40}K, ^{238}U and ^{232}Th contained in the unknown sample. Fitting uncertainty is the standard deviation of the fitting parameters. In order to assess the fitting uncertainty, we re-write the **Eq. (1)** in the main text to read:

$$\begin{bmatrix} DE_{K,1} \pm Un\_DE_{K,1} & DE_{U,1} \pm Un\_DE_{U,1} & DE_{Th,1} \pm Un\_DE_{Th,1} \\ \vdots & \vdots & \vdots \\ DE_{K,M} \pm Un\_DE_{K,M} & DE_{U,M} \pm Un\_DE_{U,M} & DE_{Th,M} \pm Un\_DE_{Th,M} \end{bmatrix} \times \begin{bmatrix} A_K \pm S_{K,fit} \\ A_U \pm S_{U,fit} \\ A_{Th} \pm S_{Th,fit} \end{bmatrix} = \begin{bmatrix} CR_{S,1} \pm Un\_CR_{S,1} \\ \vdots \\ CR_{S,M} \pm Un\_CR_{S,M} \end{bmatrix} \quad (18)$$

Where CR_S and Un_CR_S are counting rates and their statistical uncertainty of drift-corrected sample spectrum in ROI (M = 891, the number of channels in the ROI). From **Eq. (18)**, one can see that fitting uncertainties $S_{K,fit}$, $S_{U,fit}$ and $S_{Th,fit}$ on the ^{40}K, ^{238}U and ^{232}Th activities, respectively, are dependent on the counting statistics. By solving **Eq. (18)**, all statistical uncertainties are subsumed by the fitting uncertainties.

Eq. (18) was solved by iterative reweighted least-square regression as described in section 2.5 in the main text. The calculation of the activity (A_K, A_U and A_{Th}) of the ^{40}K, ^{238}U and ^{232}Th nuclides in the unknown sample and their corresponding uncertainties were carried out in our in-house developed DoseRateAnalyzer software, which employs a generalized uncertainty analysis tool *Metas.UncLib* (Zeier *et al.*, 2012, reference in the main text).

S1.3 Total uncertainty

After obtaining the fitting uncertainty $S_{K,fit}$, $S_{U,fit}$, and $S_{Th,fit}$, they are combined with the systematic uncertainties to give the total uncertainty:

$$\begin{bmatrix} Un_{K,Total} \\ Un_{U,Total} \\ Un_{Th,Total} \end{bmatrix} = \begin{bmatrix} A_K \times \sqrt{\left(\frac{S_{K,fit}}{A_K}\right)^2 + OD\_r_K{}^2 + MU\_r_K{}^2} \\ A_U \times \sqrt{\left(\frac{S_{U,fit}}{A_U}\right)^2 + OD\_r_U{}^2 + MU\_r_U{}^2} \\ A_{Th} \times \sqrt{\left(\frac{S_{Th,fit}}{A_{Th}}\right)^2 + OD\_r_{Th}{}^2 + MU\_r_{Th}{}^2} \end{bmatrix} \quad (19)$$

2. SUPPLEMENTARY TABLE S1

Table S1. *Systematic uncertainty contributed by ^{40}K, ^{238}U and ^{232}Th calibration standard cups. OD value for each nuclide was obtained by assessment on three cups of the same nuclide.*

Calibration standard	Cup	Activity concentration (Bq·kg^{-1})	Manufacturer's uncertainty *MU_r* (%)	Calibration standard *OD_r* value (%)
^{40}K	K1	14234	± 0.4	–0.5
	K2	14235		
	K3	14230		
^{238}U	U1	2622	± 0.2	1.3
	U2	2624		
	U3	2621		
^{232}Th	Th1	3150	± 1.0	–0.3
	Th2	3162		
	Th3	3161		