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Measurement of natural radioactivity: Calibration and performance of a high-resolution gamma spectrometry facility

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\textbf{A B S T R A C T}

Murray et al. (2015) described an international inter-comparison of dose rate measurements undertaken using a homogenised beach ridge sand from Jutland, Denmark. The measured concentrations for $^{226}\text{Ra}$, $^{232}\text{Th}$ and $^{40}\text{K}$ from different laboratories varied considerably, with relative standard deviations of 26\% ($n = 8$), 59\% ($n = 23$) and 15\% ($n = 23$), respectively. In contrast, the relative standard deviations observed internally within our laboratory were 9\%, 11\% and 7\%, respectively ($n = 20$), and in addition our mean values were consistent with the global $^{40}\text{K}$ mean, but significantly different from the $^{232}\text{Th}$ mean. These problems in both accuracy and precision have led us to examine both the long term performance of our analytical facility, and its calibration. Our approach to the preparation of new absolute $^{238}\text{U}$, $^{232}\text{Th}$ and $^{40}\text{K}$ standards is outlined and tested against international standards. We also report analyses of the Volkegem (De Corte et al., 2007) and Nussi (Preusser and Kasper, 2001) loess samples, for further comparison with other laboratories.

1. Introduction

Dose rate determination in luminescence dating is as important as dose determination, in terms of its contribution to the age. Uncertainties in dose rate are thus of considerable importance, and yet the quality of the input data used to derive these dose rates (such as radionuclide concentrations, or integral count rates) receives little or no systematic attention in the luminescence dating literature. Indeed many laboratories do not determine their own radionuclide concentrations, but rather buy analyses from other analytical facilities; this makes quality control more difficult. In 2006, a laboratory intercomparison study was initiated to investigate the coherence in measurement and analysis of the various parameters that are used to produce a luminescence age. The study was based around a homogenised beach ridge sand from Jutland, Denmark; 23 laboratories returned radionuclide analyses. The results of this intercomparison are now available (Murray et al., 2015) and our present study arises from the dose rate results in particular. As the host laboratory for this study, we had undertaken extensive measurements to test, \textit{inter alia}, homogeneity of radionuclide concentrations in the intercomparison sample; 20 different subsamples were analysed using 4 different gamma spectrometers. These analyses documented the reproducibility of our facility (RSD of 9\%, 11\%, 7\% for $^{226}\text{Ra}$, $^{232}\text{Th}$ and $^{40}\text{K}$, respectively) but of course could not give information about the accuracy. The radionuclide concentrations in the intercomparison study were considerably over-dispersed (up to 60\%), especially those for $^{232}\text{Th}$ (Fig. 1). Although our analyses lay within one standard deviation of the respective means, it was clear that independent testing of our calibration was desirable. This led to the present study.

The calibration standards chosen by high resolution gamma spectrometry facilities for the analysis of natural radionuclides have varied considerably across different laboratories, and unfortunately they are not always described at an appropriate level of detail. Murray et al. (1987) produced multiple independent U and Th standards by mixing, with a low activity sand, known quantities of uraninite ore BL-5 (certified reference material, CRM, produced by the now Natural Resources Canada, NRCAN), or thorium nitrate refined in 1906 (Amersham International). These pulverised mixtures were then in turn mixed with polyester resin to retain Rn and provide a constant counting geometry. For $^{40}\text{K}$ they mixed either reagent-grade K$_2$SO$_4$ or KCl directly with polyester resin and assumed stoichiometry. Guibert and Schvoerer (1991) also made their own standards by first diluting and fusing pitchblende (UO$_2$) and ThO$_2$ in di-lithium tetraborate glass; they did not discuss the possible effects of high temperature on volatile daughter radionuclides, or the age of the ThO$_2$ (important for confidence in the degree of secular equilibrium, since all gamma rays are emitted by $^{228}\text{Ra}$, $t_\beta\text{,} 6.7$ years, and its daughters). These glasses were then crushed and mixed with a silica powder to provide the final U and Th standards.

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The $^{40}$K standard was made from K$_2$SO$_4$. Preusser and Kasper (2001) produced their own standards based on material provided by the International Atomic Energy Authority (IAEA) but no further details were given. Mauz et al. (2002) used a soil material (“BFS ST2.3/Boden/V-98”) for which the concentrations were given by Schkade et al. (1998). De Corte et al. (2005) made use of certified IAEA gamma-spectrometry reference materials RGK-1, RGU-1 and RGTh-1 (IAEA, 1987). The first is based on reagent-grade K$_2$SO$_4$ and the latter two are derived by the IAEA from NRCAN’s CRM BL-5 (uraninite) and CRM OKA-2 (britholite).

All the calibrations above used known activity standards presented in the same geometry as the unknown samples to be analysed. Others, such as Oczkowski (2001), Al-Sulaiti et al. (2012) and Rihs et al. (2016, 2015) calibrated their detectors by determining the absolute efficiency as a function of energy and then used emission probabilities from the literature to calculate concentrations in the unknowns.

Two groups have used their calibrations to compare the analyses of loess samples with the results of other analytical techniques (Volkegem et al., 2007; and Nussi loess, Preusser and Kasper, 2001). These samples are of some importance because other laboratories have subsequently adopted them as internal reference materials (e.g. Jacobs and Roberts, 2015).

The overall aim of this work is to test the precision of our existing calibration, and if possible to improve on both its accuracy and precision. We first examine a 13 year time series measured using a single sample to determine the typical reproducibility of our spectrometer analyses. The dependence of calibration and analyses on sample presentation is examined using Monte Carlo modelling (MCNP) before the preparation of new standards based on internationally recognised calibrated U and Th mineral ores and an analytical-grade potassium salt. Minimum detection levels are derived, and the accuracy of the calibration is investigated as these minimum levels are approached. The new calibration is then tested using additional standard materials from the IAEA and NRCAN. Finally, the implications of this work for the analyses reported in the original intercomparison study are discussed.

2. Sample presentation and instrumentation

Samples were prepared for counting by grinding up to 800 g of material in an eccentric grinder fitted with a puck head (FDLSmith model LM2 and Essa bowl pulveriser). This homogenises the sample and reduces it to < 200 μm in only a few minutes. Loss on ignition on field samples was determined by heating the sample in air at 450 °C for 24 h – the most volatile of the longer-lived gamma-emitting nuclides ($^{210}$Pb) should not be lost at this temperature. All samples (unknowns and standards) were then mixed with a high viscosity wax (Bottle Wax, blend 1944, British Wax Refining Company) at a typical mass ratio of 1:2 (wax:sample) and cast in a fixed cup-shaped geometry of wall thickness 10 mm, to give a typical sample mass of 200–250 g; the high viscosity of the wax helps prevent settling during settling. This process presents the sample to the detector in a reproducible geometry, all $^{226}$Ra (and daughters) is retained within the mixture, and the sample can be stored indefinitely for recounting at a later date. All samples and calibration standards were stored for at least 20 days ($^{222}$Rn half-lives) before counting.

Analyses were undertaken using two similar Canberra closed-end coaxial ‘n’-type germanium detectors (laboratory codes J and K, sensitive diameters 55 mm, depth 45 mm, resolution 1.76 keV at 1332 keV, 810 eV at 122 keV, relative efficiency ∼ 20%) and one PGT closed-end coaxial ‘p’ type detector (code D, sensitive diameter 49 mm, depth 30 mm, resolution 1.9 keV at 1332 keV, relative efficiency ∼ 10%). Spectra were collected in 4k channels usually for ∼ 20 h, and analysed using proprietary software based on the procedures described by Murray et al. (1987) to give net peak areas from various daughter nuclides and, after calibration, activity concentrations in Bq kg$^{-1}$ of $^{238}$U, $^{226}$Ra, $^{210}$Pb (detectors J and K only), $^{232}$Th and $^{40}$K.

3. Analytical reproducibility

Since 2003 we have repeatedly measured the same sample on each of our detectors (note that this sample, lab. code 950509A, was prepared in 1997 using polyester resin rather than wax). Typical reproducibility for $^{226}$Ra, $^{232}$Th and $^{40}$K analyses are shown in Fig. 2 for detector D.

In general there are no clear signs of systematic changes in calibration when the detector was recalibrated and/or recommissioned after repair (usually after pumping). Only in the case of the $^{226}$Ra time series is there a significant (9%) systematic change after 3563 days, associated with a recalibration (but not with repair).

From these radionuclide data, the calculated relative standard deviation in our total dry dose rate is 2.5%. We conclude that our analyses have been acceptably stable over a period of ∼ 13 years.
chosen to use NRCAN’s high-activity primary material directly; 5
(IAEA, 1987) by NRCAN using their own high activity CRMs, we have
5. Preparation of new standards
tivities are correspondingly less certain.

Fig. 3. Modelled deviations in self-attenuation as a function of energy for differ-
tent wax-sample mixtures.

Fig. 2. Time series of radionuclide activity concentrations for one detector
beginning in 2003. Vertical lines indicate recommissioning. The solid hor-
izontal line is drawn at the mean value, the blue and pink dashed lines at one
standard error and one standard deviation, respectively. (For interpretation of
the references to colour in this figure legend, the reader is referred to the Web
version of this article.)

4. Sample presentation: effects of self-absorption

Before preparing new calibration standards, Monte Carlo modelling
(MCNP) was used to investigate the likely variation in self-attenuation
as a function of energy resulting from typical variations in the mass of
ground sample in a prepared wax/sample mixture (the simulations
were performed for a disc geometry, but the controlling factor, the
sample thickness, is the same (10 mm) for both the cup and the disc
gometry). The results of these calculations are summarised in Fig. 3,
normalised to a standard 66% sample by weight. For all mixtures the
maximum change in self-attenuation > 100 keV is 6%. For likely mix-
tures of both calibration standards and material to be analysed
(sample/wax ratio > 50%) the change is < 2%. However at 46 keV
(210Pb) the range in likely attenuation is considerable and 210Pb ac-
tivities are correspondingly less certain.

5. Preparation of new standards

Rather than use the low activity standards diluted for the IAEA
(IAEA, 1987) by NRCAN using their own high activity CRMs, we have
chosen to use NRCAN’s high-activity primary material directly; 5
independent dilutions were prepared and cast in wax to provide a
measure of the reproducibility of our preparation procedure. We base
our calibration on uranium ore (BL-5), thorium ore (OKA-2) (both with
well-known parent activities, and both confidently expected to be in
secular equilibrium - apart from radon isotopes and short lived
daughters) and analytical grade K$_2$SO$_4$ (Table 1). Secular equilibrium in
BL-5 has been tested by NRCAN; they found a $^{226}$Ra/$^{238}$U activity ratio
of 0.979 ± 0.022 (see Table 1). To provide relative gamma ray in-
tensities from $^{226}$Ra and $^{222}$Rn daughters (with negligible contribution
from U, especially $^{235}$U at 186 keV) two different $^{226}$Ra rich materials were
used: (i) an uncalibrated (i.e. not accurately known) solution of
$^{226}$Ra solution containing ~ 200 Bq.g$^{-1}$, and (ii) an IAEA oil field se-
diment (IAEA-448) with $^{238}$U/$^{226}$Ra activity ratio of 0.3%. The
standard ores and IAEA-448 were supplied to us crushed to < 100 µm
particle size and homogenised, and the purity of the K$_2$SO$_4$ requires that
it is completely homogeneous.

Different portions of the standards BL-5 and OKA-2 were diluted by
mixing with crushed low activity quartz rich sand (M32, Sibelco
Belgium; $^{226}$Ra 1.39 ± 0.08; $^{232}$Th 0.85 ± 0.06, $^{40}$K 6.8 ± 0.7
Bq.kg$^{-1}$). These mixtures were then ground to < 200 µm and cast in
standard cup geometry to give 5 independently diluted standards based
on each standard material; the notional activity of the U and Th cups
was each ~ 800 Bq, sufficiently low as to ensure that counting dead-
time was < 1%. All weighing was to a precision of < 0.1%. Because of
the high initial activities of the U and Th standards, it was necessary to
undertake dilution and crushing in two steps, introducing an extra
weighing uncertainty in the dilution. To provide the relative $^{226}$Ra
standards, the pure solution was dried onto a portion of low activity
sand, homogenised and cast to give 2 cups each of ~ 800 Bq. In
addition 3 cups were prepared from IAEA-448. Different portions of
K$_2$SO$_4$ were mixed directly with wax to give 20 cups.

The $^{40}$K standards received the least handling, and so should be
most reproducible. Fig. 4 shows a histogram of the analyses of the 20
cups; the relative standard deviation (RSD) is 0.8% (n = 20). Using the
Shapiro-Wilk test (Shapiro and Wilk, 1965), we cannot reject the hy-
pothesis that the sample is taken from a normally distributed popula-
tion (W = 0.962 > Wp = 0.905 for p = 0.05; n = 20). In contrast the
$^{238}$U and $^{232}$Th standards were manipulated more, and their RSDs are
1.5% (n = 5) and 1.2% (n = 5) respectively.

The uranium and thorium standards were heavily diluted in quartz
sand (respectively < 0.5% and < 2.5% of standard in the mixture by
weight) to ensure that counting dead-
time was < 1%. All weighing was to a precision of < 0.1%. Because of
the high initial activities of the U and Th standards, it was necessary to
undertake dilution and crushing in two steps, introducing an extra
weighing uncertainty in the dilution. To provide the relative $^{226}$Ra
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1.5% (n = 5) and 1.2% (n = 5) respectively.

The uranium and thorium standards were heavily diluted in quartz
sand (respectively < 0.5% and < 2.5% of standard in the mixture by
weight) to ensure that the attenuation characteristics of the cast mix-
ture are indistinguishable from those of the quartz sand matrix. To
confirm that this was also true of the potassium standard (pure K$_2$SO$_4$
mixed only with wax) the mass attenuation coefficients at 1.46 keV
(gamma energy from $^{40}$K) of a typical wax and K$_2$SO$_4$ mixture (1:3 by
weight) were compared with those of corresponding mixtures of quartz,
and typical granite and basalt in wax. For an attenuation depth of 5 mm
(i.e. average attenuation through ~ half cup wall thickness) the at-
tenuation loss of 3.4% is indistinguishable for all 4 materials.

Finally three cups of pure wax were prepared for determining
background count rates.

6. Accuracy as a function of activity concentration, and minimum
detection limits

After initial calibration, it was considered important to investigate
the size of any systematic deviation in analysis as a function of activity,
and incidentally to determine the minimum detection limits. To this
end we first prepared an additional mixed sample, containing ~ 2700
Bq $^{40}$K, and ~ 60 Bq each of $^{238}$U and $^{232}$Th, using K$_2$SO$_4$, BLS and OKA-
2. The three nuclides are in proportions typical of sediment (see e.g.
Ankjergaard and Murray, 2007). This mixture was then cast and
counted for various periods of time, from 30 s to 20 h. At the end of
each counting period, the sample was removed and the detector al-
lowed to continue counting background until a cumulative count time

A.S. Murray et al.

217
of 20 h was reached. The resulting spectra were then equivalent to those obtained from counting samples of very well-known relative activities, ranging from 4.2 × 10⁻²% to 100% of the mixed sample activity concentrations. The observed deviations from the expected activity concentrations are plotted as a function of expected activity concentrations in Fig. 5a. Any systematic deviations from expected values do not appear until very low concentrations; these probably reflect inaccurate background corrections. The analytical uncertainties also begin to increase significantly below a few Bq kg⁻¹. Fig. 5b shows these uncertainties plotted against expected activity concentrations for all the measured radionuclides. Minimum Detection Limit (MDL) values are a very useful way of characterising an analytical facility; here we define the MDL as the concentration at which the relative analytical uncertainties exceed 30% - this is shown as a horizontal dashed line in Fig. 5b, and the derived MDLs are summarised in Table 2.

With the possible exception of ²¹⁰Pb, these MDLs are much lower than all likely concentrations in real sediment samples. At low concentrations, our analyses are much more likely to be inaccurate (Fig. 5a) than imprecise (Fig. 5b). The likely systematic uncertainty at the MDL (taken from Fig. 5a) is listed in Table 2, column 3, together with the more useful likely uncertainty at 1 Bq kg⁻¹ (U series and Th series) and 20 Bq kg⁻¹ K (column 4).

7. Comparison with known and potential standards

To test our new calibration, various reference materials from IAEA and NRCAN were identified for measurement, together with two analytical-grade K salts. These are summarised in Table 3. Note that only the values labelled R (for Recommended) and C (for Certified) are considered reliable by the suppliers. The ratios of our analyses to the given values are also given in Table 3. In the discussion below, we do not consider sample preparation as a likely source of discrepancy, because we have shown that we are able to grind, mix and cast samples with a standard deviation of < 1.5% (see section 5 above). Note also that Nussi and Volkegem results are not included in average ratio calculations because the ‘given’ values are not considered sufficiently well known.

Uranium – Given the uncertainties, all our U analyses are considered acceptable, and the weighted average of the ratios of our analyses to the expected values is 1.029 ± 0.013 (n = 5).

Table 1
Summary of absolute calibration materials.

<table>
<thead>
<tr>
<th>²³⁸U, Bq kg⁻¹</th>
<th>²²⁶Ra, Bq kg⁻¹</th>
<th>²¹⁰Pb, Bq kg⁻¹</th>
<th>²³²Th, Bq kg⁻¹</th>
<th>⁴⁰K, Bq kg⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>BL-S⁴</td>
<td>875.4 ± 1.9  C</td>
<td>857 ± 19 C</td>
<td>866 ± 10 C</td>
<td>-</td>
</tr>
<tr>
<td>OKA-²</td>
<td>2.70 ± 0.05  C</td>
<td>-</td>
<td>-</td>
<td>117.4 ± 1.2 C</td>
</tr>
<tr>
<td>K₂SO₄</td>
<td>117.4 ± 1.2  C</td>
<td>0.108 ± 0.003 P</td>
<td>14.23 ± 0.03 S</td>
<td></td>
</tr>
</tbody>
</table>

⁴ Natural Resources Canada (NRCAN) concentration given as 7.09 ± 0.03 %U (95% confidence).
² NRCAN concentration given as 2.893 ± 0.058 %Th, 218.6 ± 8.2 μg g⁻¹ U, 0.34 ± 0.02 %K (95% confidence).
²² BDH AnalaR NORMAPUR, purity given as 100.4%.
²³ Weight concentrations converted to activity concentrations using data given in Guérin et al. (2011).
²⁴ C – certified, P - Provisional, S – stoichiometry.

Table 2
Minimum detection limits (MDL) and likely systematic uncertainty, for 250 g sample in wax/sample mix, 20 h count time.

<table>
<thead>
<tr>
<th>Element</th>
<th>MDL Bq kg⁻¹</th>
<th>Sys. uncert. (%) at MDL</th>
<th>Sys. uncert. (%) for U, Th: 1 Bq kg⁻¹</th>
<th>K: 20 Bq kg⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>²³⁸U</td>
<td>0.9</td>
<td>19</td>
<td></td>
<td>19</td>
</tr>
<tr>
<td>²²⁶Ra</td>
<td>0.04</td>
<td>140</td>
<td></td>
<td>5</td>
</tr>
<tr>
<td>²¹⁰Pb</td>
<td>2</td>
<td>15</td>
<td></td>
<td>15</td>
</tr>
<tr>
<td>²³²Th</td>
<td>0.03</td>
<td>100</td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>⁴⁰K</td>
<td>0.6</td>
<td>16</td>
<td></td>
<td>4</td>
</tr>
</tbody>
</table>

Fig. 4. Histogram of measured to calculated ⁴⁰K activity ratios in our new K₂SO₄ standards. Dashed vertical lines drawn at ± 1 σ and solid vertical line at the mean value.

Fig. 5. Minimum detection limits. a) Deviations from expected activity concentration plotted against the expected concentration. These data are geometry and spectrometer specific (here collected using a planar ‘n’ type hpGe detector, efficiency ~ 20%). b) Relative analytical uncertainty against expected concentration. The minimum detection limit is shown as a dashed horizontal line of 20 h reached. The resulting spectra were then equivalent to those obtained from counting samples of very well-known relative activities, ranging from 4.2 × 10⁻²% to 100% of the mixed sample activity concentrations. The observed deviations from the expected activity concentrations are plotted as a function of expected activity concentrations in Fig. 5a. Any systematic deviations from expected values do not appear until very low concentrations; these probably reflect inaccurate background corrections. The analytical uncertainties also begin to increase significantly below a few Bq kg⁻¹. Fig. 5b shows these uncertainties plotted against expected activity concentrations for all the measured radionuclides. Minimum Detection Limit (MDL) values are a very useful way of characterising an analytical facility; here we define the MDL as the concentration at which the relative analytical uncertainties exceed 30% - this is shown as a horizontal dashed line in Fig. 5b, and the derived MDLs are summarised in Table 2.

With the possible exception of ²¹⁰Pb, these MDLs are much lower than all likely concentrations in real sediment samples. At low concentrations, our analyses are much more likely to be inaccurate (Fig. 5a) than imprecise (Fig. 5b). The likely systematic uncertainty at the MDL (taken from Fig. 5a) is listed in Table 2, column 3, together with the more useful likely uncertainty at 1 Bq kg⁻¹ (U series and Th series) and 20 Bq kg⁻¹ K (column 4).
It also accumulated 228Ra (half life 6.7 years) in a similar manner to the suggestion that our calibration is accurate, but that there is true variability in the ‘known’ materials.

Thorium – Again we probably overestimate the IAEA-314 value (1.23 ± 0.08), and also the IAEA RGTh-1 (1.06 ± 0.02). The latter is surprising, because both our standards and the IAEA material are based on natural sediments and non ore-grade rocks (see e.g. Ankjærgaard and Murray, 2007), and so this result was omitted from the average ratio in Table 3. The weighted average of our analyses to the expected values is 1.017 ± 0.010 (n = 5).

Potassium – We are in good agreement with the two independent K-salts, and the low activity Gabbro. We overestimate the 40K in IAEA RG-Th-1, and this is probably at least in part the result of a normally weak Th series interference (1459 keV, 228Ac) in the 1461 keV line from 40K. The 232Th to 40K ratio in RG-Th-1 is very far from what is typical in natural sediments and non ore-grade rocks (see e.g. Ankjærgaard and Murray, 2007), and so this result was omitted from the average ratio in Table 3. The weighted average of our analyses to the expected values is 1.017 ± 0.010 (n = 5).

We conclude that our calibrations for the uranium series and 40K are consistent with the expected concentrations in the independent materials, but that this is not true for our Th analyses which are consistently higher than expected. In our view this deviation is most likely to originate with discrepancies between the independent reference materials, rather than in our sample preparation and counting procedures. The reproducibility of the independently prepared U, Th and K calibration cups (n < 1.5%) and the satisfactory U series and K analyses all indicate that the uncertainties in our preparation procedures are very much smaller than 10% (the size of the Th discrepancy). In addition, the IAEA RGTh-1 is prepared from the high level OKA-2 NRCAN Th ore, which is also the source of our Th calibration.

And yet, as pointed out above, our Th analyses which are consistently smaller than 10% (the size of the Th discrepancy). In addition, the IAEA RGTh-1 is prepared from the high level OKA-2 NRCAN Th ore, which is also the source of our Th calibration. And yet, as pointed out above, our Th analyses which are consistently smaller than 10% (the size of the Th discrepancy). In addition, the IAEA RGTh-1 is prepared from the high level OKA-2 NRCAN Th ore, which is also the source of our Th calibration. And yet, as pointed out above, our Th analyses which are consistently smaller than 10% (the size of the Th discrepancy). In addition, the IAEA RGTh-1 is prepared from the high level OKA-2 NRCAN Th ore, which is also the source of our Th calibration. And yet, as pointed out above, our Th analyses which are consistently smaller than 10% (the size of the Th discrepancy).

Radium – Our result underestimates the IAEA-448 certified value by 8%, but we estimate the IAEA RGU-1 by 3% (this material is manufactured by IAEA from the NRCAN Certiﬁed Reference Material (CRM) BL-5 used for our primary calibration). Either the given value for IAEA RGU-1 is wrong, or that for IAEA-448. Because these analyses are signiﬁcantly over-dispersed, the unweighted average is used to give the ratio of our analyses to the expected values of 1.01 ± 0.04 (n = 3). The primary source of our calibration (NRCAN BL-5) was derived by pulverising a solid rock sample, and so we can be conﬁdent that the 238U series in this material is in equilibrium down to and including 228Ra. This assumption is conﬁrmed by the certified values listed in Table 1, and it is also consistent with the average of the agreement NLL to ‘given’ ratios of 1.029 ± 0.013 (n = 5) and 1.01 ± 0.04 (n = 3) for 238U and 228Ra analyses, respectively, (see Table 3). These data support the suggestion that our calibration is accurate, but that there is true variability in the ‘known’ materials.

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(red data). Only $^{238}$U and $^{226}$Ra have moved significantly, but in opposite directions, which is surprising since they are based on the same calibration material. We have also analysed the Nussi and Volkegem loess samples using our new calibration and results are given in Table 3. Our analyses of these materials are on average between 10 and 15% higher than those published previously.

8. Conclusions

From the time series of radionuclide concentrations ($^{226}$Ra, $^{232}$Th and $^{40}$K) measured on one gamma detector, we conclude that our dose rate analyses have remained satisfactorily reproducible over at least 13 years. In order to test the accuracy of these measurements, we have prepared new calibration standards based on NRCAN U and Th ores, and analytical grade K$_2$SO$_4$. By independently preparing between 5 and 20 samples of each calibration material, it has been shown that uncertainties arising from preparation lead to an overall standard deviation of < 1.5%.

By counting a single mixed sample for different durations and then continuing to count background until all net measurement times are the same, the dependence of accuracy and precision on activity concentration has been measured on one of the three detectors. We observe that there are no significant systematic uncertainties in our analyses as the activity concentration decreases to well below those typical of unknown samples, and it is concluded that the minimum detection limits are not likely to be a limiting factor in the majority of these samples.

It has proved surprisingly difficult to obtain high quality samples with which to test our calibration, and even in the few we have used, there are significant inconsistencies in measured-to-known ratios between samples; these inconsistencies cannot be explained by our calibration procedure, unless they are attributed to sample preparation. However, since sample preparation has been shown to introduce uncertainties of < 1.5%, this is not considered a likely cause of these discrepancies.

Although the accepted ratios of our analyses to the given values are considered satisfactory for $^{238}$U, $^{226}$Ra and $^{40}$K, we overestimate the expected $^{232}$Th activity concentrations by ~10%, probably because of discrepancies in the values of independent materials. In general, however, this is not of major concern in most dose rate estimations, because, in our experience, $^{40}$K contributes around ~50% to the total dry dose rate in most coarse-grained samples, and the typical Th-series contribution is ~25%. In such a sample, a 10% uncertainty in a Th analysis resulting from a poor calibration corresponds to a dose rate uncertainty of 2.5%.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.radmeas.2018.04.006.

References


