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Comparing two efficiency calibration methods used in gamma spectrometry

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Abstract

The recent inter-laboratory comparison study revealed considerable differences between laboratories for activity concentrations of U, Th and K. One reason for these differences could be materials and methods employed for calibrating the detector's efficiency. To address this, we determined the activity concentrations of unknown samples originating from variable geochemical environments using two different efficiency calibration methods: one is based on the direct comparison with the non-certified Volkegem internal standard and the other one uses a certified multi-nuclide reference solution and correction factors for full-energy efficiency, emission probability, true coincidence summing and for sample density. The comparison is based on the hypothesis that consistency between the two methods raises the probability that the activity concentrations determined are accurate. We show here that agreement between the two methods is obtained when the Volkegem activity reference values of ⁴⁰K and ²³⁸U-series are raised by 9%. For the ²³²Th-series agreement is obtained for the two photon peaks at 338 keV and 911 keV when deploying the published activity reference value. We conclude that the efficiency calibration method should not account for more than 10% variability and cannot be the sole reason for the alarming differences revealed by the inter-laboratory comparison study.

Keywords: detector efficiency, calibration, internal standard, reference material

1. Introduction

Low-level gamma spectrometry is often used to determine the environmental radioactivity of samples. In fact, in the recent inter-laboratory comparison study (Murray et al., 2015) most laboratories determined the dose rate on the basis of γ -spectrometry. Yet, discrepancies appeared in the comparative dataset especially for the ²³²Th data, whereas the ⁴⁰K data showed reasonable agreement. While it is good to see reasonable agreement for ⁴⁰K activity concentrations which constitutes the largest proportion of the total dose rate, the overall discrepancy suggests that some dose rates determined by γ -spectrometry are significantly inaccurate.

A number of parameters govern the quality of the γ spectrometric data (e.g., measurement geometry, selection of photon peaks, etc), most of which are specific to the detector and the measurement procedure. The one parameter affecting all laboratories is the reference material and the associated efficiency calibration method and this may play an important role in dose-rate inaccuracies (e.g., Murray et al. 2018). Here we address this hypothesis through an empirical study that looks at the significance of the efficiency calibration method for obtaining accurate activity data for 40 K, 238 U and ²³²Th of unknown samples. The comparison is based on 81 samples arbitrarily selected from our laboratory's sample pool. Because the activities of these samples are not known independently, the study looks at the consistency of activity data derived from the two calibration methods. If the comparison shows systematic deviation from unity, one or the other method is likely inaccurate. If deviations are random, parameters other than the calibration method must be tested. We show that inaccuracy is not very likely for all photon peaks relevant for dose-rate estimation and for both methods tested. It is suggested that other laboratory parameters cause the discrepancies shown in the inter-laboratory comparison study (Murray et al., 2015).

	Resolution FWHM (keV)				Diameter	Length	Efficiency (%)	
					(mm)	(mm)	at 1332 keV	
Energy (keV)	60	122	662	1332				
	0.92	0.98	1.39	1.85	61.8	77.8	54	

Table 1. Properties of the coaxial (n) Ge detector (serial no 46-TN32165A) used in this study (ORTEC Quality Assurance Data Sheet, 2006). FWHM = full width half maximum of energy peak.

2. Methods and Materials

2.1. Detector and measurement details

The detector used in this study is a coaxial n-type high purity Germanium (Ge) detector (for details see Table 1) which sits in a castle composed of low-activity lead (10 cm), cadmium tin (1 mm), copper (2 mm) and perplex (6 mm). Dry and occasionally crushed samples were filled in cylinder-type sample holders which were subsequently sealed and stored for 4-6 weeks. The sample holder was filled with sample material up to a height of 12 mm and the remaining space in the holder was filled with 8 mm polythene. The latter replaces air in the holder and ensures a flat surface of the sample. This geometry was used for measuring the Volkegem internal standard and for measuring the background (empty sample holder). Each sample, weighing 60-80 g, was measured for around 80 hours.

	Photon	Activity	Photon		
Nuclide	energy	concentration	emission rate		
	(keV)	(Bq kg ⁻¹ *10 ⁶)	(s ⁻¹ *kg ⁻¹)		
¹³³ Ba	81	2.99	1.10		
⁵⁷ Co	122	3.00	2.57		
¹³⁹ Cer	166	2.99	2.39		
¹³³ Ba	356	2.99	1.85		
⁸⁵ Sr	514	15.00	14.8		
¹³⁷ Cs	662	6.11	5.20		
⁵⁴ Mn	835	5.93	5.93		
⁸⁸ Y	898	14.9	14.0		
⁶⁵ Zn	1116	14.8	7.44		
⁸⁸ Y	1836	14.9	14.8		

Table 2. The multi-nuclide solution QCYB41 (batch#16/1) in terms of photon energy, activity concentration, and yield certified in January 2016 (Eckert and Ziegler, 2016); $m = 2.014 \pm 0.001$ g; $\rho \sim 1.008$ g cm⁻³. The measurement uncertainty is 2% for all nuclides.

2.2. The efficiency calibration methods

Two materials were used for efficiency calibration: Volkegem loess (De Corte et al., 2007) and the multi-nuclide reference solution QCYB41 (Eckert & Ziegler (Deutsche Akkreditierungsstelle) 2016). The Volkegem sample, originating from a loess deposit in Belgium, has been analysed in several laboratories using different analytical techniques (e.g, ICP-MS, NAA). The QCYK multi-nuclide material is a 0.5 M HCl reference solution with a mass of ~2 g and a density of ~1 g cm⁻³. It is doped with 20 μ m/ml per nuclide (Table 2).

The calibration method associated with the Volkegem sample, henceforth denoted as cal#1, is a direct comparison with the standard material using the equation

$$A_{sample} = rac{[N/mT]_{sample}}{[N/mT]_{reference}} imes A_{reference}$$

where A is activity concentration (Bq kg⁻¹), N is the net number of counts, T is the count time and m is the mass of the sample. For $A_{reference}$ the values were taken from De Corte et al. (2007) and from the ICP-MS analysis (Geoff Duller, pers. com., June 2017). For values see Table 3.

The method associated with the multi-nuclide reference solution, henceforth denoted as cal#2, uses the equation

$$A = \frac{N}{mTP_{\gamma}\eta}$$

where P_{γ} is the gamma emission probability and η is a practical efficiency that takes account of the energy resolution, the density of the sample, the full-energy efficiency of the detector at that energy, and where necessary, true coincidence summing. In our lab η was approximated through (i) determining the full-energy peak efficiency, (ii) adopting coincidence summing factors from Debertin & Schoetzig (1990) for the energy peaks at 352 keV and 609 keV and, (iii) correcting the low-energy peaks for density. The approximation is based on participating regularly in IAEA-directed interlaboratory comparison studies which allow adjusting the values and, hence, optimise the parameter η .

2.3. Comparing the efficiency calibration methods

The photon peaks with the following energies (keV) were used for the comparison: (i) 46, 63, 352, 609 keV representing 226 Ra and 238 U, (ii) 238, 338, 911 keV representing 232 Th and (iii) 1460 keV from 40 K. With the exception of 40 K all radioisotopes emitting these energies have short half-lives and are therefore in radioactive equilibrium, that is, they all represent the corresponding parent nuclide with the same activity. Suitable for dose-rate estimation are peaks with the

Laboratory	Analytical technique	n	²³⁸ U	²³⁵ U	U	²²⁶ Ra	²³² Th	⁴⁰ K	Reference
Ghent	multiple	5	34.5 ± 1.5	1.59 ± 0.09	36.1 ± 1.7	34.1 ± 2.3	42.2 ± 2.5	497 ± 45	De Corte et al. (2007)
Liverpool	γ-spec; IAEA-375	1	38.8 ± 2.1	-	-	-	44.4 ± 0.7	571 ± 13	Abdualhadi et al. (2018)
Aberystwyth	ICP-MS	6	37.8 ± 0.5	-		-	44.3 ± 1.5	543 ± 6	Pers. com., Geoff Duller, June 2017
Dresden	Trans-mission	1	43 ± 5	-	-	42.2 ± 2.8	-	535 ± 56	Degering (2017)
Risø	γ -spec; BL-5, OKA-2 and K ₂ SO ₄	1	37.8 ± 0.7	-	-	42.8 ± 0.2	44.2 ± 0.5	570 ± 5	Murray et al. (2018)
Salzburg	γ-spec; QCYB41	1	38.4 ± 0.7	-	-		40.4 ± 1.5	556 ± 20	This study

Table 3. The Volkegem loess: activity concentrations (Bq kg⁻¹) determined in different laboratories using different analytical techniques; n=number of subsamples analysed.

energies 352, 609, 238, 338, 911 and 1460 keV, because they are the least affected by disturbances in the gamma spectrum such as Compton scattering, peak interference or true coincidence summing (see Gilmore 2008 for details). In addition, it is good practice to use several photon peaks for determining the parent activity because some disturbances depend on the sample's average atomic number (*Z*), chemical composition and density (e.g., Abdualhadi et al. 2018).

Three ways were used for comparing the two methods: (i) for the group of photon peaks representing ²³²Th or ²³⁸U the cal#1 to cal#2 ratio of activity data of each sample was used; (ii) for comparing the activity data obtained from individual photon peaks a plot of cal#1 versus cal#2 was used; (iii) to assess the performance of cal#1 and cal#2, the standard deviation of activities derived from photon peaks representing the corresponding parent nuclide was used.

2.4. Samples

The samples were arbitrarily selected from the pool of existing samples in our laboratory. They originate from central Africa, east and central north America, north and south Europe, central Asia, Mongolia and Arabia and represent, hence, variable geochemical environments and depositional settings. Some samples are inhomogeneous with regard to grain size (composed of clay, silt and sand), others are more or less homogeneous and the sampled environments suggest minor post-depositional disturbances. Exception to this are samples #5 and #81 which are from a carbonate-rich or evaporitic environment.

2.5. Uncertainties and consistency of activity data

The uncertainty of the activity concentrations is dominated by counting statistics, detection efficiency, nuclear decay data and geometry-defined true coincidence summing. For the activities measured here for ca 80 h the uncertainties are 2-4% where the one resulting from the cal#2 method is usually around 1% higher than the cal#1 uncertainty. The activity data are consistent if the deviation from unity does not exceed the sum of uncertainties calculated from the square root rule which is typically 4-5%.

3. Results

The activity data obtained from the peaks at 338 keV and 911 keV (Fig. 1A) and 46 keV (Fig. 2) are consistent. Deviations from unity that are >5% appear for 238 keV (Fig. 1A and B), 63 keV (Fig. 2), 352 keV and 609 keV (Fig. 3A) and 1460 keV (Fig. 4A). Using the higher cal#1 activity reference value for ²³²Th as indicated by the ICP-MS result (Table 3) raises the deviation at 911 keV from ~4% to ~9%, at 338 keV from unity to ~5% and reduces the deviation at 238 keV from ~15% to ~12% (Fig. 1B). Changing the cal#1 activity reference value for ²³⁸U (again according to the ICP-MS result; Table 3) brings the 352 keV and 609 keV ratios from 8% deviation to unity (Fig. 3B). Changing the cal#1 reference value for ⁴⁰K (again according to the ICP-MS result; Table 3) reduces the deviation from $\sim 10\%$ to $\sim 3\%$ (Fig. 4). Within each calibration method the deviations are similar for ²³⁸U, but not for ²³²Th: for the mean of 352 and 609 keV the standard deviation is 2-4% and for few samples it is 6-8% for both methods (Fig. 5A) where cal#1 tends to show smaller deviations. For 232 Th determined through the mean of 238, 338 and 911 keV the standard deviation of cal#1 is 6-12% and that of cal#2 is 2-6% (Fig. 5B).

4. Discussion

This empirical study looks for consistency between two efficiency calibration methods in order to infer the likelihood of data inaccuracy. Ideally, both methods deliver identical results within a given uncertainty which is typically 4-5% for the measurement procedure employed in this study. On the other hand, the two methods are considerably different: cal#2 accounts for nuclear parameters such as emission probability



Figure 1. The ratio of activity data obtained from the cal#1 and cal#2 methods plotted versus the sample number for the three photon peaks representing 232 Th. Each dot represents a sample's ratio and respective uncertainty. The red line indicates unity. The cal#1 activity reference value is A - 42.2 \pm 2.5 Bq kg⁻¹ following De Corte et al. (2007) and B - 44.3 \pm 1.5 Bq kg⁻¹ following Duller (pers. com.; see Table 3). See Section 2.2 for details about the cal#1 and cal#2 methods.



Figure 2. Comparing activity data (Bq kg⁻¹) for two radioisotopes (210 Pb: 46 keV, 234 Th: 63 keV) of the 238 U series derived from the cal#1 and cal#2 methods (for description see Section 2.2).

and detector-specific parameters such as full-energy peak efficiency while cal#1 assumes that these parameters are the same for internal standard and unknown sample. Differences between the results of the methods are therefore expected and these are likely energy- and, eventually, sample-dependent. However, the differences should not exceed the average uncertainty of activity data as long as each method is robust.

For ²³²Th consistent activity values are obtained when deploying the original Volkegem activity reference value given by De Corte et al. (2007) and when using the peaks at 911 keV and 338 keV (Fig. 1A). For the peak at 238 keV the two methods are not consistent (Fig. 1). This is most probably caused by the cal#1 method as it shows significant deviations for the activities of the ²³²Th radioisotopes (Fig. 5B). The interference with the ²¹⁴Pb peak at 242 keV requires manual peak and background analysis of the 238 keV peak in each spectrum, a procedure that we carried out in this study in the cal#2, but not in the cal#1 approach.

For ²³⁸U consistent activity values are obtained when raising the original Volkegem activity reference value by ~9% and using the 352 keV and 609 keV energy peaks (Fig. 3A). Even for the peak at 609 keV which is subject to substantial coincidence summing the data are in agreement after raising the value. For the low-energy peaks at 46 keV and 63 keV consistency is not expected owing to the sensitivity of these energies to the sample's Z and density. The apparent consistency at 46 keV (Fig. 2) suggest the influence of external (unsupported) ²¹⁰Pb which seem to dominate the activities determined and, thus, both calibration methods likely deliver inaccurate ²¹⁰Pb activities. The same applies to the peak at 63 keV where the inconsistency is more obvious suggesting minor reliability of this energy peak for determining the parent activity. For ⁴⁰K consistent activity values are obtained when raising the original Volkegem activity reference value by ~9% (Fig. 4).

Thus, this comparative study confirms the original activity reference values (De Corte et al., 2007) for 232 Th while for 238 U and 40 K consistency is achieved when the original value is elevated by ~9%. It confirms the usage of the peaks at 352, 609, 338, 911 and 1460 keV for robustly determining parent activity and, thereby, confirms the well-known: the energy peaks least affected by disturbances (e.g., Compton scattering) are perfectly suitable for direct comparison with the Volkegem and, eventually, other non-certified materials. There is therefore no reason to hypothesise inaccurate activity data resulting from the simple comparison with the Volkegem internal standard.

Photon peaks other than the ones listed above may be used in conjunction with the Volkegem material, but the issue with the 238 keV peak exemplifies the need for comparative studies to assess each peak's suitability. The low-energy peaks at 46, 63 and 93 keV and the one at 186 keV are not suitable for routine analysis owing to their sensitivity to differential



Figure 3. The ratio of activity data obtained from cal#1 and cal#2 for the two photon peaks representing 226 Ra and 238 U. The red line indicates unity. The cal#1 activity reference value is A - 34.5 ± 1.5 Bq kg⁻¹ following De Corte et al. (2007) and B - 37.8 ± 0.5 Bq kg⁻¹ following Duller (pers. com.; see Table 3). For description of cal#1 and cal#2 see Section 2.2



Figure 4. Comparing activity data (Bq kg⁻¹) for ⁴⁰K. The activity reference value for cal#1 is A - 497 \pm 45 Bq kg⁻¹ following De Corte et al. (2007) and B - 543 \pm 6 Bq kg⁻¹ following Duller (pers. com.; see Table 3).



Figure 5. The relative standard deviation (SD) of the mean of the photon peak data used to determine the parent activity. A – SD of 352 keV and 609 keV; B – SD of 238, 338, 911 keV.

self-absorption between unknown sample and standard or to peak interference (Mauz et al., 2021). Nonetheless, these peaks may provide insight into the sample's characteristics and, eventually, prompt additional quantitative analysis regarding the presence of secular disequilibrium (e.g. Abdualhadi et al. 2018).

The results for the ²³²Th photon peaks are surprising: two of these deliver consistent data straightaway suggesting that the considerable discrepancies revealed in the interlaboratory comparison do not arise from the Volkegem or other non-certified standard material. A number of other parameters should be screened instead, especially analytical procedures such as measurement geometry, background subtraction and photon-peak selection.

5. Conclusions

We agree with Murray et al. (2015) that the interlaboratory comparison results for ²³²Th "give the greatest cause of concern" (Murray et al. 2015, p.35). We think that the ~15% difference for ⁴⁰K is also alarming because the corresponding photon peak is easy to analyse even in lowactivity samples and regardless the detector type. Our results show that the choice of the efficiency calibration method generates minor inaccuracies only. We think therefore that the community should be committed to conducting intercomparison studies focusing on gamma-spectrometry. Initially, and for starting the process, individual laboratories may just compare data of a sample of their choice and develop best practice protocols for data analysis. This should be straightforward and may well provide hints to the origin of the discrepancies.

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Reviewer

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