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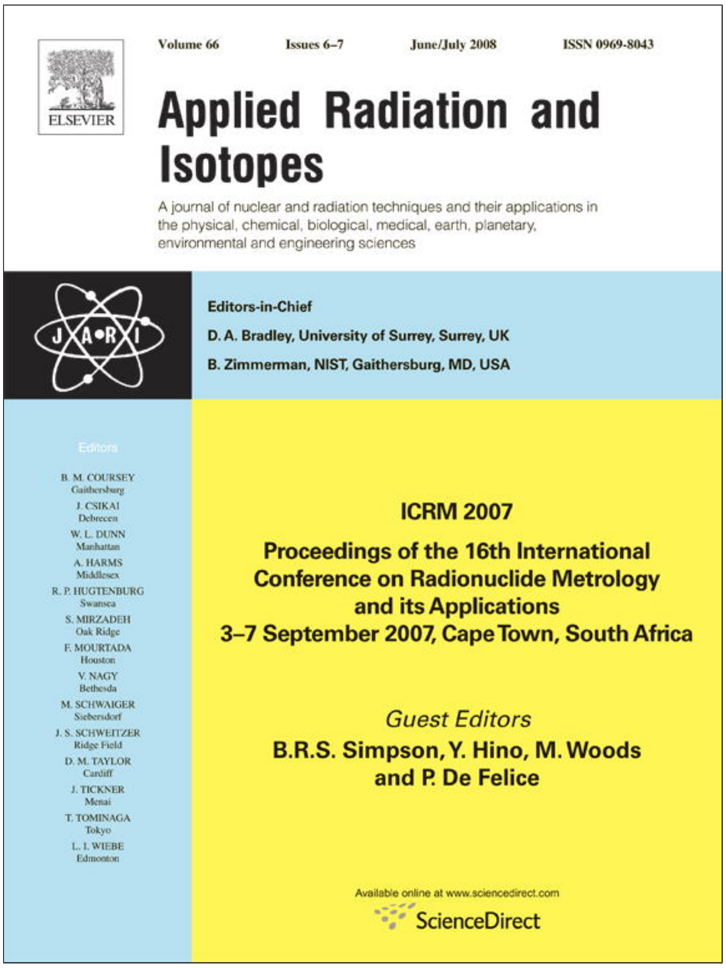

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Determination of soil, sand and ore primordial radionuclide concentrations by full-spectrum analyses of high-purity germanium detector spectra

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Abstract

The full-spectrum analysis (FSA) method was used to determine primordial activity concentrations (ACs) in soil, sand and ore samples, in conjunction with a HPGe detector. FSA involves the least-squares fitting of sample spectra by linear combinations of ^{238}U, ^{232}Th and ^{40}K standard spectra. The differences between the FSA results and those from traditional windows analyses (using regions-of-interest around selected photopeaks) are less than 10% for all samples except zircon ore, where FSA yielded an unphysical ^{40}K AC.

1. Introduction

Traditionally, windows analysis (WA) is used to determine, amongst other nuclides, primordial (^{40}K, ^{232}Th and ^{238}U) activity concentrations (ACs) in soil, sand and ore, from gamma-ray measurements. WA involves analysing individual gamma-ray lines in the spectrum by setting appropriate regions-of-interest ("windows") around the photopeaks of interest. By calculating the peak area, after correcting for the continuum and background, it is possible to extract ACs by making use of applicable gamma-ray branching ratios, measurement time, sample mass and the relevant photopeak detection efficiency. If the sample analysed has been sealed in order to achieve secular equilibrium in the ^{228}Th sub-series of the ^{232}Th series and the ^{226}Ra sub-series of the ^{238}U series, then activity concentrations are best determined by taking the weighted average of ACs calculated for each of the gamma-ray lines selected for analysis. However due to the volume, as opposed to point-source geometry used, some of these lines are significantly affected by coincident summing effects. These effects are more pronounced for specific lines, and are therefore a source of systematic error in the extraction of ACs. Unfortunately lines in the thorium and uranium series, which have significant branching ratios, often suffer coincident summing (in or out). In order to obviate these effects it is therefore best to omit these lines from the analyses, and rather include other lines (often having smaller branching ratios) associated with the respective decay series. Since the branching ratios are smaller the sample has to be counted for longer in order to achieve reasonable counting statistics. Furthermore, many gamma-ray lines associated with the primordial radionuclides are not resolved in energy and therefore form overlapping peaks. With the WA approach these overlapping peaks have to be deconvoluted by means of a peak-fitting procedure. Another problem encountered when using the WA approach to determine ^{40}K and ^{232}Th activity concentrations in a sample having elevated levels of thorium, is that the respective gamma-ray lines of 1461 and 1459 keV (from ^{228}Ac decay), are irresolvable even with a high-purity germanium detector (HPGe). By first calculating the sample ^{232}Th AC using other lines associated with the

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thorium series, it is possible but cumbersome to ascribe counts to ^{40}K and ^{228}Ac decay, respectively, by using the known branching ratios.

An alternative to the WA method approach is the full-spectrum analysis (FSA) technique (de Meijer, 1998; Hendriks et al., 2001). In the FSA method the measured gamma-ray spectrum (including the photopeaks, Compton distributions and escape peaks) is analysed using a chi-square minimisation procedure. To date FSA has been used to determine primordial ACs in conjunction with scintillator-based detectors (Hendriks et al., 2001). In order for a FSA to be performed it is necessary to have so-called standard spectra, where each spectrum represents the response of the detector system (for a specific volume-source geometry) to a sample containing an activity concentration of 1 Bq kg^{-1} (Hendriks et al., 2001, 2002). These spectra can be obtained by measurement (e.g. this work) or by Monte Carlo simulation (e.g., Hendriks et al., 2002). Below we report on the first use of the FSA method to analyse higher energy resolution soil, sand and ore spectra acquired with a germanium detector (low-background configuration).

2. Experimental methods

To compare the FSA and WA methods, soil, sand and ore samples having significantly different (relative) primordial activity concentrations were used. These samples were beach sand (from the West Coast (South Africa)), vineyard soil (from the Stellenbosch region), mine tailings (from Gauteng province) and zircon-rich ore (also from the West Coast). The samples were sieved through a mesh (2-mm diameter holes) to remove organic materials, stones and lumps. The samples (1000 cm^3) were then oven dried overnight at 105 °C and thereafter placed into polypropylene Marinelli beakers, which were sealed with silicone to achieve secular equilibrium between the gamma emitters in the uranium (mainly ^{226}Ra, ^{214}Bi and ^{214}Pb) and thorium (^{228}Ra measured by ^{228}Ac, ^{228}Th measured by ^{208}Tl and ^{212}Pb) decay series. In order to assess the accuracy of the WA and FSA methods, an IAEA reference soil sample (3 7 5) was also analysed. This soil has significant anthropogenic activity, in particular ^{137}Cs (5280 Bq kg^{-1} on 31 December 1991). Further details of the samples analysed are given in Table 1. After being sealed for at least 21 days the samples were each counted using a shielded (10 cm thick lead castle) HPGe detector (Canberra GC4520, p-type, 45% relative efficiency at 1.33 MeV, 2.2 keV FWHM energy resolution at 1332 keV). A standard Ortec 572 amplifier (gain $\leqslant \pm 0.0075\%/$ °C for 0–50 °C; DC level $\leqslant \pm 50\,\mu$V °C^{-1} for 0–50 °C) was used to shape the detector pulses such that they could be read by an Oxford PC-based multichannel analyser (MCA) system. A Marinelli beaker filled with tap water was used to measure the background spectrum used in the data analyses. The live time associated with this spectrum is 245,000 s (~3 days).

Standard spectra for the ^{238}U and ^{232}Th decay series; and ^{40}K were obtained by measuring IAEA reference materials RGU-1 (4940 Bq kg^{-1} uranium ore) and RGTh-1 (3250 Bq kg^{-1} thorium ore); and potassium chloride powder (16259 Bq kg^{-1} ^{40}K) from the company Merck (99.5% purity); respectively, using the same detector set-up and source geometry. Further detail of the IAEA reference materials are given in Tables 1 and 2. The measurement live times associated with HPGe spectra for sample and reference material are presented in Table 1. All spectra were energy calibrated using known gamma-ray lines (^{232}Th/^{238}U series, ^{40}K) and then transferred to a DEC Alpha machine (DS20-E Alpha server with 666 MHz dual processor).

3. Data analyses

To determine the activity concentrations, with the WA method, in a particular sample measured with the HPGe detector, the associated absolute photopeak detection efficiency response is required. In this work, this response was measured for each sample using gamma-ray lines associated with the decay of ^{238}U and ^{232}Th present in the sample, and the 1461 keV ^{40}K line as measured with the KCl source. Details of the lines used for this purpose are given in Table 3. This is similar to the approach described by Croft and Hutchinson (1999). A relative photopeak efficiency curve was generated for each sample. The absolute photopeak efficiency response was finally determined by scaling the relative curve to match the measured

Table 1
Sample and reference material descriptions, measurement times and densities

Sample	Live time (s)	Density (g cm^{-3})
Beach sand	43,192	1.63
Mine tailings	59,881	1.50
Vineyard soil	59,963	1.41
Zircon ore	50,235	2.24
IAEA soil	56,988	1.50
Uranium ore (RGU-1)	41,687	1.41
Thorium ore (RGTh-1)	42,011	1.36
KCl	3583	1.27

Table 2
Activity concentration (Bq kg^{-1}) (95% confidence interval) in IAEA reference materials used in this study

Reference materials	Certified reference values (95% confidence interval) (Bq kg^{-1})		
	^{40}K	^{232}Th	^{238}U
Uranium ore (RGU-1)	–	–	4910–4970
Thorium ore (RGTh-1)	3.1–9.5	3160–3340	72–84
Soil (3 7 5)	417–432	19.2–21.9	18–22(^{226}Ra)

Table 3
Gamma-ray lines and associated branching ratios (Firestone et al., 1996) used for photopeak efficiency and activity concentration determination

Series/radionuclide	Nuclide	Energy (keV)	Branching ratio
^{238}U			
	^{226}Ra[a]	186	0.0617
	^{214}Pb*	295	0.1850
	^{214}Pb*	351	0.3580
	^{234}Pa*	1001	0.0084
	^{214}Bi*	1238	0.0586
	^{214}Bi	1378	0.0392
	^{214}Bi	2204	0.0486
^{232}Th			
	^{212}Pb*	238	0.4330
	^{228}Ac*	338	0.1125
	^{208}Tl*	860	0.0450
	^{228}Ac*	911	0.2660
	^{228}Ac	965	0.0511
	^{228}Ac	969	0.1617
^{40}K	^{40}K*	1461	0.1067

[a] The186 keV branching ratio adjusted to correct for the contribution from ^{235}U.

*Denotes lines which are used for WA activity concentration calculations.

absolute photopeak efficiency at 1461 keV obtained using the KCl source which has a volume matching that of the sample. In order to account for the dependence of absolute efficiency at 1461 keV with sample bulk density, a power-law relationship was empirically established, namely

$$\varepsilon_k = a\left(\frac{\rho}{\rho_0}\right)^b,$$

where ε_k is the absolute photopeak detection efficiency at 1461 keV, ρ is the sample bulk density (g cm^{-3}), ρ_0 is a density of 1 g cm^{-3} and a and b are fit parameters. The values of a and b were found to be 0.8954 and −0.04788, respectively (Joseph, 2007). The average absolute photopeak efficiency curve obtained (for all except the zircon sample), and for only the zircon sample are shown superimposed in Fig. 1. It is seen that the latter efficiency is smaller at lower energies due to the ore having a larger effective Z, which results in relatively higher gamma-ray self-absorption due the photoelectric effect. So for example, the absolute photopeak efficiency for the zircon sample at 238 keV is 9% less than the average photopeak efficiency at the same energy.

The weighted average ACs in samples were then calculated using the absolute photopeak efficiency described above and the lines marked with a * in Table 3. The 609.3, 1120 keV (^{238}U series), and 583.2, 727.3, 795 keV (^{232}Th series), gamma-ray lines were omitted from the analyses since a sensitivity analysis showed that they yield activity concentrations that deviate significantly from the mean activity concentration by maximally, −14%, −6%, −11%, +15% and −10%, respectively (where “+” and “−” denotes activity concentrations which are, larger and smaller, respectively, than the mean), due to coincident summing.

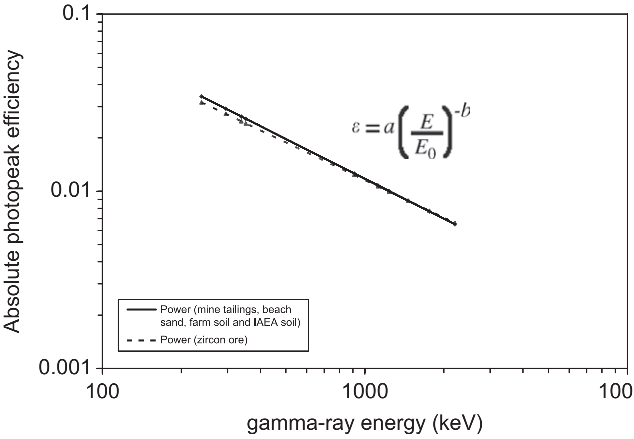

Fig. 1. Average (excluding the zircon-ore sample data) absolute photopeak efficiency as a function of gamma-ray energy. The corresponding curve as determined for the zircon-ore sample is shown as a dashed line. The photopeak efficiency ε was parameterized as shown, with E representing the gamma-ray energy (in keV) and E_0 set to 1 keV. The parameters a and b were found to be 2.0495 and 0.7473, respectively (corresponding to the solid line).

According to the FSA approach the sample spectrum Y' is analysed using a chi-square minimisation procedure, with reduced chi-square ($\chi^2{}_v$) defined by

$$\chi_v^2 = \frac{1}{n-m}\sum_{i=lec}^{i=hec}\left[Y'(i) - \sum_{j=1}^{3} C_j X_j'(i) - \alpha B'(i)\right]^2 \Big/ \sigma^2(i),$$

where i represents the ith spectrum bin (each 1 keV wide) and $Y'(i) = Y(i)/(m_s \times L_t)$, with m_s denoting the sample mass (kg) and L_t the spectrum measurement live time (s); X'_j ($j = 1,2,3$) represents the three standard spectra for the primordial radionuclides; $B'(i) = B(i)/(m_s \times L_{tb})$ with B and L_{tb}, representing the background spectrum and associated live time (s) respectively; C_j represents the respective sample activity concentrations (Bq kg^{-1}); lec and hec represents the lowest and highest energy bins used in the analysis; n represents the number of bins used and m is the number of parameters (C_j ($j = 1,2,3$), α) extracted from the analysis; and σ^2 represents the variance associated with the sample spectrum. The measured background spectrum was subtracted from each of the measured standard spectra X_j to obtain $X_{j'}$. The term $\alpha B'$ represents the background that would normally be subtracted from the sample spectrum, but which was included explicitly because the background as measured with a water-filled Marinelli does not adequately represent the background when soil is measured. The small difference occasionally causes problems in the FSA approach, especially in fitting the continuum part of the spectrum. The value of α would equal 1 if the background was correct. The obtained values given in Table 4 indicate that there are small changes from 1, indicating that the measured background does not

Table 4
The activity concentrations (Bq kg^{-1}) of ^{40}K, ^{232}Th and ^{238}U measured in the samples as determined by the WA and FSA methods

Sample	WA activity concentration (Bq kg^{-1})			FSA activity concentration (Bq kg^{-1})		
	^{40}K	^{232}Th	^{238}U	^{40}K	^{232}Th	^{238}U
Beach sand	33.5±0.9	4.8±0.1	4.0±0.1	37.1±0.7	5.3±0.1	4.0±0.1
Mine tailings	203±3	16.5±0.2	213±2	209±5	17.6±0.5	207±1
Vineyard soil	115±2	32.2±0.3	26.4±0.3	112±2	33.1±0.3	24.8±0.3
Zircon ore	20±60	8103±65	4817±33	−1108±53	8485±40	4362±34
IAEA soil	412±5	20.0±0.4	17.5±0.8	424±3	19.5±0.5	16.8±0.3

Note the unphysical ^{40}K activity concentration (FSA) for the zircon sample. The coefficients α multiplying the background spectrum were found to be 0.71 (±0.02), 0.54 (±0.11), 0.93 (±0.02), 576 (±9) and 1.23 (±0.06), for the beach, tailings, vineyard, zircon-ore and IAEA soil samples, respectively (see text for detail).

perfectly represent the true background for the sample and standard spectra. The chi-square minimisation was performed using the Physica software package (Chuma, 1994). Each FSA fit took less than 10 s on the DEC Alpha machine used.

The *lec* and *hec* values (keV) used for the final fits were 400 and 2800, respectively, for all spectra besides the one for the IAEA soil sample. For this spectrum the *lec* and *hec* values were set to 1000 and 2800, respectively, in order to exclude the significant contributions to the spectrum from anthropogenic sources present in the soil.

4. Results and discussion

The ACs derived using WA are given in Table 4. The uncertainties (1σ) quoted were obtained from the weighting averaging procedure and exclude type B uncertainties and covariances. It was found that the WA results for the IAEA soil sample fell near the lower bound of the 95% confidence intervals quoted for this sample (Table 2).

The FSA fits to a portion of the vineyard sample spectrum is shown in Fig. 2, while the derived ACs are also given in Table 4. The uncertainties quoted were obtained from the fits and exclude covariances and type B uncertainties. It is seen that the smallest and largest relative difference between the WA and FSA results (ignoring the zircon results) are 0.3% and 9.7%, respectively (relative to the FSA results). The FSA approach yields an unphysical value for the ^{40}K AC in the zircon ore due to poor decomposition of overlapping peaks near 1460 keV.This is primarily due to the large thorium AC present in this sample. The FSA results for the IAEA soil sample fall within the 95% confidence interval for ^{40}K and ^{232}Th, but just fall outside this interval for ^{238}U (^{226}Ra). The FSA-fit plots clearly show up gamma-ray lines that are not accounted for by the standard spectra used. So for example, the plot for the vineyard soil sample (Fig. 2) clearly shows the unaccounted for ^{137}Cs line (662 keV). The ^{137}Cs AC in this sample is ~1 Bq kg^{-1} and presumably stems from fall-out.

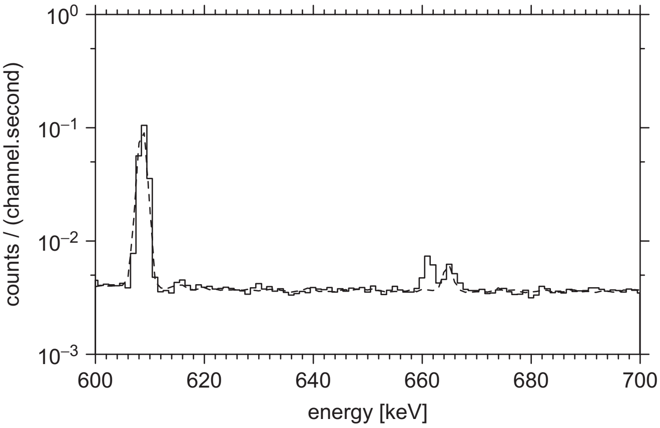

Fig. 2. The FSA fit (dashed line) to a portion of the vineyard soil sample spectrum (histogram).

5. Conclusion

We have demonstrated that it is feasible to use the FSA method to calculate ACs in soil, sand and ore sample spectra measured by an HPGe detector. The FSA results agree well with those obtained using the traditional WA method, except in the case of the zircon ore sample. For this sample the FSA method gives an unphysical ^{40}K AC due to the significant levels ^{232}Th-series activity present in the sample. At present we see no way of overcoming this problem by means of the FSA approach, except by decreasing the energy width of the spectra bins. This will however increase the analysis time. The FSA allows analysts to quickly (< 10 s per fit) obtain accurate ACs in typical soils and sand from measured HPGe gamma-ray spectra. Also, since FSA utilises the full spectrum and not only the photopeaks, it is possible to reduce sample measurement times. Any gamma-ray lines (e.g. due to anthropogenic sources) not accounted for in the standard spectra used are easily discernible when the FSA fit is superimposed on the sample spectrum. Another advantage of the FSA approach is that no corrections for coincidence summing are required. Care should however be taken with this approach when selecting the low-energy cutt-off energy since self-absorption of gamma-rays in samples can sometimes differ significantly from that in the standard samples.

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