Use of HPGe γ-ray spectrometry to assess the isotopic composition of uranium in soils

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Abstract

Gamma-ray spectrometry was used to determine uranium activity and investigate the presence of depleted uranium in soil samples collected from camping sites of the Greek expeditionary force in Kosovo. Assessment of 238 U concentrations was based on measurements of the 63.3 keV and 92.38 keV emissions of its first daughter nuclide, 234 Th. To determine the isotopic ratio of 238 U/235 U, secular equilibrium along the two radioactive series was first ensured and thereby the contribution of 235 U under the 186 keV peak was deduced. The uranium activity in the samples varied from 48 to 112 Bq kg$^{-1}$, whereas the activity ratio of 238 U/235 U averaged 23.1±4.3.

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1. Introduction

Radioanalytical methods such as α-spectrometry, liquid-scintillation counting and mass spectrometry have traditionally been used for the determination of low-level natural radioisotopes. These methods are indispensable for detecting low nuclide concentrations, i.e. below 10$^3$ pg/g, at the cost of labour-intensive radiochemical processing of the samples (Bickel et al., 2000). In cases where low detection limits
are not required, high-resolution $\gamma$-spectrometry provides the alternative of a non-destructive, multi-elemental and less time consuming technique. Its feasibility has often been illustrated in the quantitative analysis of uranium, thorium and their decay products in environmental samples (Bunzl et al., 1994; Pakou et al., 1994; Ioannides et al., 1997; Köhler et al., 2000).

In the work presented here, a high-purity germanium (HPGe) detector was employed to determine uranium activity in soil samples collected from the military installations of Greek peacekeeping troops in Kosovo. Due to the increased concern about possible health effects of depleted uranium ammunition in the area, the isotopic ratio of $^{238}\text{U}/^{235}\text{U}$ was also derived by analysing the decay schemes of the two radionuclides. Emphasis was placed on the selection of the proper $\gamma$-ray emissions and the thorough identification of all possible contributions under the spectral peaks used in the calculations.

2. Materials and methods

2.1. Analysis of the decay schemes of Uranium ($^{238}\text{U}$) and Actinium ($^{235}\text{U}$) series

The decay schemes of the naturally occurring uranium, actinium and thorium series are illustrated in Fig. 1. The energy and emission probability of the $\gamma$-rays (Firestone, 1996) usually recorded in environmental samples’ $\gamma$-ray spectra are also indicated. Because of the complexity inherent in the decay schemes, it is essential to disentangle overlapping emissions arising from separate radionuclides with caution to avoid ill-defined peaks. These subtleties are inclusively summarized in the following.

The activity of $^{238}\text{U}$ cannot be directly determined, since the isotope emits only a weak (0.064%) $\gamma$-ray at 49.55 keV. However, any of the $\gamma$-emitting daughter nuclides of $^{238}\text{U}$ could be used for this purpose, provided that they exist in secular equilibrium with their precursor. In most environmental samples, the above presumption is valid only for the first members of the $^{238}\text{U}$ series, up to $^{226}\text{Ra}$, whereas equilibrium along the rest of the series is disturbed, due to the loss of radon gas. The $\gamma$-emissions in the region of 63 and 93 keV, accompanying $^{234}\text{Th}$ decay have most commonly been employed for deriving $^{238}\text{U}$ concentrations (Joshi, 1987; Righi et al., 2000; García-Talavera et al., 2001). As depicted in Fig. 1, the peak recorded around 63 keV arises from the emissions of $^{234}\text{Th}$, $^{232}\text{Th}$ and $^{231}\text{Th}$. The contribution of the latter can be neglected unless the measured sample is highly enriched in $^{235}\text{U}$. Therefore, in the present analysis, the count rate under the 63 keV peak, was treated as the sum:

$$C(63) = C^{(234}\text{Th}, 63.3) + C^{(232}\text{Th}, 63.9)$$

where $C^{(\text{AX}, E_\gamma)}$ is the count rate arising from a $\gamma$-ray of energy $E_\gamma$ emitted by the nuclide $\text{AX}$.

The count rate of $^{232}\text{Th}$ may not be negligible in soils rich in natural thorium and it was, thus, deduced using the $^{228}\text{Ac}$ emission at 338.32 keV:
Fig. 1. Partial diagram of the uranium, actinium and thorium decay series. The energy (in keV units) and percent emission probability (quoted in parentheses) of the major $\gamma$-rays are indicated next to the corresponding nuclide, while emissions recorded in the same spectral peak are marked with superscripts. The nuclides used in the present calculations are enclosed in shadowed frames.

\[ C^{(232\text{Th}, 63.9)} = \frac{\epsilon(63.9) \times I^{(232\text{Th}, 63.9)}}{\epsilon(338.32) \times I^{(228\text{Ac}, 338.32)}} \times C^{(228\text{Ac}, 338.32)} \]  \hspace{1cm} (2)

where $I(^{\text{A}X}, E_{\gamma})$ and $\epsilon(E_{\gamma})$ are the emission probability and detection efficiency for the $E_{\gamma}$ keV $\gamma$-ray.

The peak at 93 keV consists of two $^{234}\text{Th}$ $\gamma$-rays, as well as an emission of $^{227}\text{Th}$:

\[ C(93) = C^{(234\text{Th}, 92.38)} + C^{(234\text{Th}, 92.8)} + C^{(227\text{Th}, 93.93)} \]  \hspace{1cm} (3)

The contribution at 92.38 keV may be isolated by substituting:
\[ C(^{234}\text{Th}, 92.8) = \frac{\varepsilon(92.8) \times I(^{234}\text{Th}, 92.8)}{\varepsilon(92.8) \times I(^{234}\text{Th}, 92.8)} \times C(^{234}\text{Th}, 92.38) \]  

(4)

and

\[ C(^{227}\text{Th}, 93.93) = f \frac{\varepsilon(93.93) \times I(^{227}\text{Th}, 93.93)}{\varepsilon(92.38) \times I(^{234}\text{Th}, 92.38)} \times C(^{234}\text{Th}, 92.38) \]  

(5)

In eq. (5), \( f \) stands for the activity ratio of \(^{238}\text{U}/^{235}\text{U}\), which may be calculated as:

\[
 f = \frac{A(^{238}\text{U})}{A(^{235}\text{U})} = \frac{m(^{238}\text{U}) \lambda(^{238}\text{U}) M(^{238}\text{U})}{m(^{235}\text{U}) \lambda(^{235}\text{U}) M(^{235}\text{U})}
\]  

(6)

where \( m(^{AX}) \), \( \lambda(^{AX}) \) and \( M(^{AX}) \) stand for the mass, half life and atomic mass of nuclide \(^{AX}\), respectively. The value assumed by ratio \( f \) is discussed later in the Results section.

It is noteworthy that an alternative approach to assess \(^{238}\text{U}\) activity has recently been proposed (Yücel et al., 1998), using the emission of \(^{234}\text{mPa}\) at 1001 keV. Although this \( \gamma \)-ray does not interfere with other emissions and is practically free from self-absorption effects, its low emission probability (0.835%) makes it inappropriate for the analysis of soil samples in which uranium activity typically amounts to less than 100 Bq kg\(^{-1}\).

Proceeding to the case of \(^{235}\text{U}\), its most probable \( \gamma \)-ray at 185.7 keV (57.2%) is recorded in the same peak as \(^{226}\text{Ra}\) emission at 186.2 keV (3.59%). The clean \(^{235}\text{U}\) photons emitted at 143.76 (10.96%), 163.3 (5.08%) and 205.3 (5.01%) keV should be avoided, as they suffer from summing-in effects due to the cascades of 19.6 with 143.76 and 185.7 keV, respectively (García-Talavera et al., 2001). Therefore, the peak at 186 keV was used in the present study, considering that:

\[ C(186) = C(^{235}\text{U}, 185.7) + C(^{226}\text{Ra}, 186.21) \]  

(7)

To deduce \(^{226}\text{Ra}\) contribution, equilibrium with its progeny had to be ensured first by sealing the samples for a period of at least 20 d, i.e. five to six times the half life of \(^{222}\text{Rn}\) (3.82 d). The intense \( \gamma \)-rays of \(^{214}\text{Pb}\) and \(^{214}\text{Bi}\) may be used subsequently to determine \(^{226}\text{Ra}\) activity. The clean 295.22 keV \( \gamma \)-ray of \(^{214}\text{Pb}\) was chosen for this purpose to yield:

\[ C(^{226}\text{Ra}, 186.21) = \frac{\varepsilon(186.21) \times I(^{226}\text{Ra}, 186.21)}{\varepsilon(295.2) \times I(^{214}\text{Pb}, 295.2)} \times C(^{214}\text{Pb}, 295.2) \]  

(8)

To cross-check the calculations, the 351.93 keV emission of \(^{214}\text{Pb}\) was also employed, after correcting for the \(^{214}\text{Bi}\) contribution:

\[ C(^{226}\text{Ra}, 186.21) = \frac{\varepsilon(186.21) \times I(^{226}\text{Ra}, 186.21)}{\varepsilon(351.9) \times I(^{214}\text{Pb}, 351.9)} \times \frac{C(351)}{1 + \frac{\varepsilon(351.06) \times I(^{214}\text{Bi}, 351.06)}{\varepsilon(351.9) \times I(^{214}\text{Pb}, 351.9)}} \]  

(9)

Finally, it should be noted that the use of the intense \( \gamma \)-ray of \(^{214}\text{Bi}\) at 609.3 keV
is rather inappropriate for analysing $^{226}$Ra, inasmuch as it suffers from coincidence summing-out effects, being emitted in cascade with a large number of other photons.

2.2. Sample preparation and radioactivity measurement

Seven soil samples, collected by a delegation of the Greek Atomic Energy Commission (EEAE) in January 2001 from the military installations of Greek peace keeping troops in the region of Uroševac, Kosovo, were received for uranium analysis. After oven drying, the samples were gently ground and passed through a 2 mm sieve. One hundred grams of each sample were placed in plastic vessels, 9 cm in diameter with a total capacity of 300 cm$^3$. The height of the samples was approximately 2 cm. The vessels were sealed for 30 days to allow equilibrium in the uranium, thorium and actinium series.

A 22% efficiency n-type HPGe detector (Princeton Gamma-Tech) was used for radioactivity measurements. The detector was situated in a well consisting of 5-cm-thick lead, to shield the measuring station against background radioactivity. Standard nuclear electronics were used and the spectra were stored for analysis in 2024 channels. A data collection period of 50,000 s was sufficient to provide good statistics. Background spectra were also collected for the same period of time. The net sample count rate at each energy peak was obtained after subtraction of the corresponding background rate. The latter was found to be at least four times lower than the sample count rate, depending on the peak under study.

To determine $^{238}$U activity, standards of three different uranium concentrations were prepared from the soil samples under study by adding aqueous uranyl nitrate ($\text{UO}_2(\text{NO}_3)_2$) solutions at a solid-to-liquid ratio equal to 1:1.5. After addition of the liquid, the soils were homogenised, dried at 100 °C and further processed as already described for the rest of the samples. Concentrations of uranium equal to 24, 56 and 80 mg per kg of dry soil were thus achieved, corresponding to $^{238}$U activities of 300, 700 and 1000 Bq kg$^{-1}$. The relative efficiency curve of the detector was determined from soil samples spiked with a $^{152}$Eu solution. Preparation of reference materials according to this protocol is strongly recommended when analysing environmental samples, as one has to consider the difference in the self-absorption properties between the sample and the calibration source. Such differences are particularly pronounced for photon energies below 200 keV and corrections may be circumvented by keeping the same dimensions, density and chemical composition between the sample and the calibration standard (Debertin and Jianping, 1989).

3. Results

3.1. Determination of $^{238}$U activity

Using the spectra collected for each soil sample both before (pristine-soil) and after labelling with the three standard uranyl salt concentrations (labelled-soil), $^{238}$U activity was determined as follows: the count rate of pristine-soil at the 63 and 93
keV peaks was subtracted from the corresponding count rate of the labelled-soils. After corrections for background, $^{238}\text{U}$ activity was determined through the decay of $^{234}\text{Th}$ as:

$$R(^{238}\text{U}) = R(^{234}\text{Th}) = \beta(E_\gamma) \times C(^{234}\text{Th}, E_\gamma)$$  \hspace{1cm} (10)

where $R(^{\text{A}}X)$ stands for the activity (Bq kg$^{-1}$) of the nuclide $^{\text{A}}X$ and the parameters $\beta(E_\gamma)$ were to be determined.

The count rates for the 63.3 keV and 92.38 keV $^{234}\text{Th}$ emissions were calculated using Eqs. (1), (2) and (3–6), respectively. After subtraction of the pristine- from the labelled-soil count rate, the ratio $f$ in Eq. (6) corresponds to the activity ratio in natural uranium. Using the isotopic composition given in Table 1 and substituting for the decay constants $\lambda(^{238}\text{U})=4.92 \times 10^{-18}$ s$^{-1}$ and $\lambda(^{235}\text{U})=3.12 \times 10^{-17}$ s$^{-1}$, as well as the atomic masses $M(^{238}\text{U})$ and $M(^{235}\text{U})$ of the two nuclides, $f$ acquires the value of 21.5. The parameters $\beta(E_\gamma)$ were determined for each set of one pristine- and three labelled-soils from the slope of Eq. (10), as exemplified in Fig. 2 and the

![Graph](image)

Fig. 2. To determine the activity of $^{238}\text{U}$, each soil sample was labelled with three different uranium activities (300, 700 and 1000 Bq kg$^{-1}$). The count rates of $^{234}\text{Th}$ at 63.26 (solid line) and 92.38 keV (segmented line) were averaged and extrapolated to yield uranium activity in pristine-soil.

### Table 1
Isotopic composition of uranium

<table>
<thead>
<tr>
<th>Uranium content (%)</th>
<th>$^{238}\text{U}$</th>
<th>$^{235}\text{U}$</th>
<th>$^{234}\text{U}$</th>
<th>$^{238}\text{U}/^{235}\text{U}$ activity$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural$^b$</td>
<td>99.274</td>
<td>0.720</td>
<td>0.0055</td>
<td>21.5</td>
</tr>
<tr>
<td>Depleted$^c$</td>
<td>99.797</td>
<td>0.202</td>
<td>0.0008</td>
<td>76.9</td>
</tr>
</tbody>
</table>

$^a$ Calculated from Eq. (7).


$^c$ From Dietz (1996).
238 U activity of the pristine-soil samples was subsequently deduced. Results obtained from the analysis of the two 234 Th emissions revealed that activity values acquired from the 92.38 keV γ-ray exceeded the 63.3 keV predictions by a factor of ~1.13 (Table 2). This finding may be attributed to the production of thorium Kα1 X-ray at 93.35 keV, which was not accounted for in the present calculations. However, a single factor analysis of variance performed to test the hypothesis that mean activity values obtained from the two peaks are equal, showed that the hypothesis is true at the 0.01 significance level ($F=0.84$, $F_{critical}=9.33$). Uranium activity is therefore considered to be the weighted average of the two measurements for each soil sample, ranging from 48±4 to 112±8 Bq kg⁻¹. Comparison with values reported in the literature is not always straightforward, as the concentrations of the naturally occurring radionuclides vary depending on soil composition. Results from various types of rock and soil furnished by NCRP (1988) report uranium activities between 7 and 60 Bq kg⁻¹, while the typical range given by UNSCEAR (1988) for different soil samples is 10 to 50 Bq kg⁻¹.

### 3.2. Calculation of uranium isotopic ratio

The concentration of 238 U assessed from the 63.3 keV 234 Th emission was used together with the concentration of 235 U calculated through Eqs. (7 and 9), to derive activity ratios of 238 U/235 U. The results given in Table 2 indicate that the ratios vary from 18.4±2.5 to 28.4±3.1 when 226 Ra was determined through the 295.2 keV 214 Pb γ-ray and from 17.2±2.4 to 26.8±2.9 when 226 Ra was determined through the 351.9 keV 214 Pb γ-ray. The US Department of Defense designates that depleted uranium contains approximately 0.2% of 235 U (Livingstone, 1995), a claim which is also supported by mass spectrometry measurements that specify a 235 U content between 0.2 and 0.3% (Camins and Shinn, 1989; Ebinger et al., 1990; Dietz, 1996). According to these specifications, 235 U in depleted uranium is lowered by ~72% as compared

**Table 2**

<table>
<thead>
<tr>
<th>Sample</th>
<th>238 U activity (Bq kg⁻¹)</th>
<th>238 U/235 U activity ratio</th>
<th>238 U activity (Bq kg⁻¹)</th>
<th>238 U/235 U activity ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$A_{63.3}$⁶</td>
<td>$A_{92.38}$⁹</td>
<td>Mean$^b$</td>
<td>$f_{a}^{c}$</td>
</tr>
<tr>
<td>S–1</td>
<td>97±12</td>
<td>124±11</td>
<td>112±8</td>
<td>18.4±2.5</td>
</tr>
<tr>
<td>S–2</td>
<td>84±15</td>
<td>111±13</td>
<td>99±10</td>
<td>27.3±3.8</td>
</tr>
<tr>
<td>S–3</td>
<td>79±9</td>
<td>82±12</td>
<td>80±7</td>
<td>28.4±3.1</td>
</tr>
<tr>
<td>S–4</td>
<td>76±7</td>
<td>82±5</td>
<td>80±4</td>
<td>28.0±3.2</td>
</tr>
<tr>
<td>S–5</td>
<td>99±15</td>
<td>101±13</td>
<td>100±10</td>
<td>27.8±2.6</td>
</tr>
<tr>
<td>S–6</td>
<td>101±10</td>
<td>112±7</td>
<td>108±6</td>
<td>19.2±2.7</td>
</tr>
<tr>
<td>S–7</td>
<td>46±7</td>
<td>48±4</td>
<td>48±4</td>
<td>21.4±2.7</td>
</tr>
</tbody>
</table>

$^a$ $A_{63.3}$ and $A_{92.38}$ are calculated from the 63.3 and 92.38 keV γ-rays of 234 Th, respectively.

$^b$ The mean values are calculated as the weighted average of the two measurements and the error is the uncertainty of the mean.

$^c$ $f_{a}$ and $f_{b}$ are calculated from the 295.2 and 351.9 keV γ-rays of 214 Pb, respectively.
to its content in natural uranium and $^{238}\text{U}/^{235}\text{U}$ activity ratio is increased to ~76.9 (see Table 1). The average of all measured activity ratios listed in Table 2 amounts to 23.1±4.4, very close to the value of 21.5 for natural uranium.

4. Conclusion

The use of HPGe $\gamma$-ray spectrometry permits the determination of uranium isotopic ratios in soils containing measurable uranium concentrations. In analyzing the decay schemes of the natural radioactivity series involved in the calculations, validity of secular equilibrium assumptions has to be ensured and overlapping $\gamma$-emissions from different nuclides have to be identified and resolved. Assessment of radioactivity from various photoemissions of the same nuclide offers a basis of cross-checking the accuracy of the results. The analysis of seven Kosovo soil samples carried out in the present study, showed that uranium isotopes are practically in their natural abundances, while the $^{238}\text{U}$ activity ranges within typically accepted levels, from 48 to 112 Bq kg$^{-1}$ with a mean value of 90±22 Bq kg$^{-1}$.

References


