Determination of depleted uranium using a high-resolution gamma-ray spectrometer and its applications in soil and sediments

I.H. Saleh a,*, A.A. Abdel-Halim b

a Department of Environmental Studies, Institute of Graduate Studies and Research, Alexandria University, P.O. Box 832, EL-Shatby, Alexandria, Egypt

b Department of Basic and Applied Sciences, College of Engineering and Technology, the Arab Academy for Sciences and Technology and Maritime Transport, P.O. Box 1029, Alexandria, Egypt

Abstract

A high-resolution gamma-ray spectrometer based on a hyper-pure germanium detector has been used to determine the amounts of depleted uranium in ground features subjected to military operations during the Gulf War of 1991 and in beach sediment samples collected from the northern side of the Arabian Gulf. The determination of 235U/238U was evaluated using spiked samples with a series of depleted uranium solutions. According to this method, the levels of depleted uranium were found to exceed 6.5% of the total natural uranium required to achieve reasonable levels for detection. Soil results indicated that the average of the total radioactivity of 238U is 50.59 Bq/kg, with approximately 41.41% of this being represented by depleted uranium. For on-site and off-site individuals in an area of 10000 m², the RESRAD computer code was applied to calculate the annual radiological dose, which determined a level of 0.0031 mSv of total U; the code was also used to estimate the cancer risk, the level of which was determined to be 4.75 × 10⁻⁶ and 1.9 × 10⁻⁶ due to the total U and DU, respectively. © 2015 The Authors. Production and hosting by Elsevier B.V. on behalf of Taibah University. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

Keywords: Depleted uranium; Gamma spectrometer; Radiological dose; Risk; Sediment; Soil

1. Introduction

Depleted uranium (DU), a by-product of the uranium enrichment process, has been applied as armour-piercing ammunition in international military conflicts. DU is used in this way because of its high density, hardness, and pyrophoric properties [1,2]. The testing and use of such munitions has led to the release of DU into the environment at several locations around the world [3].

Natural uranium exists as three isotopes: 234U, 235U and 238U. Natural uranium is considered to be one of the most important radioactive elements in the environment because it represents the major source of environmental natural radiation that all forms of life are exposed to. Natural uranium exists in soil, air, and water as well as in materials of natural origin. The most abundant isotope is 238U (99.28%), which is known as the parent of a long radioactive decay chain that includes 16 radioactive elements.
In nuclear fuel production, natural uranium is isotopically enriched and increases the concentration of the fissile isotope $^{235}$U, usually to 3–5 atom%. The residue from this enrichment process is DU and a decreased proportion of both $^{234}$U and $^{235}$U, and hence, the proportion of $^{238}$U increases, as illustrated in Table 1 [4,5].

Large amounts of DU are produced annually from the enrichment process of nuclear fuel. The disposal of such wastes has been a problem facing the countries that use these industries for many years. Currently, one of the solutions is introducing DU into industrial applications.

The issue of the possible presence of DU in the environment has recently attracted considerable public interest. Utilizing DU in non-fission nuclear weapons results in the addition of $^{238}$U to the natural uranium in the environment. DU weapons are regarded as conventional weapons. The following amounts of ammunition containing DU were used in three recent conflicts: up to 321 tons in the Gulf War (2 August 1990–28 February 1991); approximately 3 tons in Bosnia-Herzegovina, 1995; and approximately 10 tons in Kosovo, 1999 [6–8].

DU is also involved in many civilian applications. DU is used as a cladding material in fast-breeder reactors, where its interactions with neutrons produce additional reactor fuel in the form of $^{239}$Pu. Moreover, DU has been used as a fluorescent additive in dental porcelain crowns (recently discontinued) and is used as a shield for X-ray radiation in hospitals. Furthermore, DU is used as a counterweight for rudders and flaps in commercial aircraft and forklifts as well as in the keels of sailing yachts [9].

Monitoring and assessing radioactive materials in the environment are very important for protecting the general public against ionizing radiation due to the radio-toxicities and the chemo-toxicities of uranium, as well as to protect environmental resources, such as fresh water, agricultural soil, foods, and resort areas, against ionizing radiation. Monitoring and assessing radioactive materials are also important for studying the environmental factors affecting the mobility of such materials in different environmental pathways [10]. Studies of environmental radioactivity have been conducted to investigate the weathering effects on the redistribution of uranium in the environment [11]. Such studies are also very important to investigate the radiological minerals of black sands [12] and to evaluate the radiation exposure due to different sources of natural radiation, such as agricultural fertilizers [13].

Comprehensive programs of radiation measurements and assessments have been established in different countries to assess the DU and general background radiation in the environment. In addition, several reports and articles have been published involving the characterization of the nature of uranium and DU munitions.

Several techniques have been published that involve determining the amount of DU in the environment and describing procedures to identify the uranium isotopic composition in solid uranium compounds [14,15]. An inductively coupled plasma-mass spectrometer (ICP-MS) was used to determine the isotopic composition based on ashing and chemical decomposition with mineral concentrated acids [16]. In addition, thermal ionization mass spectrometry (TIMS) was used for the quantification of DU [17]. Additionally, an alpha spectrometer was used to measure $^{234}$U/$^{238}$U ratio in the soil of a UK testing firing range [3].

Low-level high-resolution gamma-ray spectroscopy is a very convenient technique for determining the activity of uranium in environmental samples in which the activity of $^{238}$U exceeds 1 Bq/kg [18]. Determining the amount of DU using this method in soil is based on assuming an equilibrium of $^{238}$U up to $^{226}$Ra [19]. In addition, processing of uranium ore started approximately 200 years ago; therefore, $^{238}$U daughters (except $^{234}$Th and $^{234m}$Pa) do not exist in DU [20]. However, such conditions of equilibrium with $^{226}$Ra might no longer be sustainable due to the natural processes and technological activities in the environment, particularly in the surface soil. Additionally, the equilibrium of $^{226}$Ra is disturbed due to the leaching of radium or uranium from the soil by ground water.

This work aims to develop an experimental method for evaluating the gamma-ray spectrometry results to quantify DU by measuring two isotopes $^{238}$U and $^{235}$U as well as to investigate the DU that is present in the sediment and in soil samples collected from the northern area of the Arabian/Persian Gulf.

2. Experimental work

The measurements were performed using an extended energy range (24 keV–3 MeV), reverse electrode,
closed-end, coaxial gamma-ray spectroscopy apparatus that was based on a HPGe detector. The relative efficiency of the detector is 60%, and the resolution is 2.2 keV at 1.33 MeV. The detector is surrounded by a 20-cm thick lead shield and is concentric with a thin layer of copper. The gamma-ray spectra are collected and analysed using software (Genie-2000). A comprehensive quality control/assurance program is implemented in the radiation laboratory during the preparation stages for accreditation; the main steps were as follows:

1. The ambient background of radiation in the laboratory was periodically counted and evaluated.
2. Blank samples were measured periodically using an empty cleaned Marinelli beaker, and then, the results were subtracted from the gamma spectra of each sample.
3. The energy calibration of the counting system were conducted weekly using gamma-ray standards $^{137}$Cs, $^{241}$Am, $^{57}$Co, and $^{60}$Co. The gamma line at 1460.8 keV of $^{40}$K was used as a checkpoint for the energy calibration (because $^{40}$K is present in all environmental samples).
4. The absolute efficiency calibration was performed experimentally by using sets of radioactive mixed standards in a soil matrix packed in a 1-L Marinelli beaker.
5. Quality control soil samples$^1$ were measured in parallel with the analysed samples to ensure that the bias in the results is less than 5%, following the laboratory criteria.
6. Externally, the laboratory participates periodically in Proficiency Testing (PT) (MAPEP) for radiation measurements.

$^{235}$U radioactivity was determined using the gamma energy lines of 143.76 keV and 163.36 keV. However, the most intensive gamma line of 185.71 keV was excluded to avoid its interference with the 186.21 keV gamma line of $^{226}$Ra. $^{238}$U radioactivity was determined using its direct daughter $^{234}$Th(24d) at the gamma lines 63.39 keV, and both 92.38 keV and 92.80 keV were taken as one line, assuming that $^{238}$U and $^{234}$Th are in secular equilibrium. The radioactivities were calculated from the net photopeak areas of each gamma line according to Eq. (1):

$$\text{Specific activity} = \frac{\text{net photopeak area}}{T \times \text{Eff}(E) \times P_{\gamma}(E) \times M} \quad (1)$$

where $T$ is the counting time, $\text{Eff}(E)$ is the full-energy peak efficiency at photon energy $E$, $P_{\gamma}(E)$ is the emission probability of gamma-ray photons of energy $E$, and $M$ is the mass of the sample being measured.

Samples of approximately 1 kg each were measured for approximately 40 ks. To obtain reliable results for $^{238}$U and $^{235}$U, the minimum detectable activity (MDA) was calculated for each radionuclide according to Eq. (2) [21,22], with the obtained results listed in Table 2.

$$\text{MDA} = \frac{L_D}{T \times \text{Eff}(E) \times P_{\gamma}(E) \times M} \quad (2)$$

where $T$, $\text{Eff}(E)$ and $P_{\gamma}(E)$ are as identified above in Eq. (1). Finally, $L_D$ is the detection limit calculated using the following equation:

$$L_D = L_C + K\sigma_D \quad (3)$$

where $L_C$ is the critical level below which no signal can be detected, $\sigma_D$ is the standard deviation, and $K$ is the error probability.

### 3. DU determination

In this part, eight samples of uncontaminated sediment containing DU were selected from samples that had been collected before 1991 from the southern beach of the Arabian/Persian Gulf. These samples were dried and homogenized into 1-mm grain size particles and then measured for $^{235}$U and $^{238}$U. The percentage of $^{235}$U in total uranium $R_u\%$ was calculated for each sample from the mass concentration of $^{235}$U and $^{238}$U according to Eq. (4):

$$R_u\% = \frac{C_{235}}{C_{238}} \times 100\% \quad (4)$$

---

$^1$ Quality control soil samples were supplied through the proficiency testing Mixed Analyte Performance Evaluation Program (MAPEP), organized by the Department of Energy, United States.
where \( C_{235} \) and \( C_{238} \) are the concentrations in mg/kg for \( ^{235}\text{U} \) and \( ^{238}\text{U} \) in the sediments and are calculated using the Eqs. (5) and (6), respectively.

\[
C_{235} = \frac{A_{235}}{80.01}
\]

(5)

\[
C_{238} = \frac{A_{238}}{12.45}
\]

(6)

where \( A_{235} \) and \( A_{238} \) are the measured concentrations of the activities in the sediments in Bq/kg and 80.1 and 12.4 are the specific activities of \( ^{235}\text{U} \) and \( ^{238}\text{U} \), respectively, in Bq/mg of each isotope.

The results indicated that \( R_m \% \) ranges between 0.7384 and 0.872, with a mean of 0.77, which matches its parentage of \( ^{235}\text{U} \) in the natural uranium isotopic composition.

Uranylacetate solution of 500 Bq/L of DU was used to spike the previously measured sediment samples with a range of activities from 10 Bq to 260 Bq, as presented in Table 3. The DU spiked percentage of \( DUs \% \) was deduced from total \( ^{238}\text{U} \) via Eq. (7).

\[
DUs \% = \frac{DUs}{A_{238} + DUs} \times 100\%
\]

(7)

where \( DUs \% \) is the calculated total radioactivity percentage of \( ^{238}\text{U} \), \( A_{238} \) is the measured radioactivity of \( ^{238}\text{U} \) before the spiking process, and \( DUs \) is the spiked amount of DU radioactivity.

The spiked samples were dried and mechanically homogenized using a vibrate/Mixer and then measured for \( ^{235}\text{U} \) and \( ^{238}\text{U} \); subsequently, the ratio \( R_m \) was recalculated from the measured data of \( ^{235}\text{U} \) and \( ^{238}\text{U} \) and then used to determine the DU percentage \( DUm \% \) in the spiked samples using Eq. (8). The results are presented in Table 3.

\[
DUm \% = \frac{R_{U-\text{nat}} - R_m}{R_{U-\text{nat}} - R_{DU}} \times 100\%
\]

(8)

where \( R_{U-\text{nat}} (=0.00725) \) is the isotope ratio \( ^{235}\text{U}/^{238}\text{U} \) of natural U, \( R_{DU} (=0.002) \) is the isotope ratio \( ^{235}\text{U}/^{238}\text{U} \) of DU, and \( R_m \) is the measured isotope ratio \( ^{235}\text{U}/^{238}\text{U} \) of the samples after spiking. The obtained results are listed in Table 3.

For a comparison between the observed \( DUm \% \) and the expected \( DUs \% \), the chi squared \( (\chi^2) \) test was used to test the difference between the expected (spiked) \( DUs \% \) and the observed (measured) \( DUm \% \). The results of this comparison are as follows: \( \chi^2 = 0.851 \) with a \( p \)-value of 0.9969. Therefore, the results of this conditional experiment confirm the ability of high-resolution gamma-ray spectrometry to determine the DU in soil with reasonable accuracy.

Please cite this article in press as: I.H. Saleh, A.A. Abdel-Halim. Determination of depleted uranium using a high-resolution gamma-ray spectrometer and its applications in soil and sediments, J. Taibah Univ. Sci. (2015), http://dx.doi.org/10.1016/j.jtusci.2015.02.015
Fig. 1. The relationship between the spiked DU percentage ($DU_s\%$) and the determined DU percentage ($DU_m\%$).

Moreover, the best fitting shown in Fig. 1 between the spiked percentage of $DU_s\%$ and $DU_m\%$ results in the following linear relation in Eq. (9):

$$DU_m\% = 0.9221 \times DU_s\% + 6.5468 \quad (9)$$

Therefore, to reliably detect the DU in soil, its total percentage of uranium should be greater than 6.5% of the total uranium.

4. Results in the soil and the sediment

Seven soil samples were collected from contaminated military sites during the Gulf War, 1991, and 5 sediments samples were collected from the Gulf beach sediments. The collected samples were analysed to determine $(^{235}\text{U}/^{238}\text{U})\%$, and then, the DU percentage was estimated using Eq. (10) between $(^{235}\text{U}/^{238}\text{U})\%$ and $DU_m\%$, as shown in Fig. 2.

$$DU_m\% = -191.73 \times Rm\% + 138.34 \quad (10)$$

The detected levels are listed in Table 4. The total uranium activities in soil ranged from 38.89 Bq/kg to 61.95 Bq/kg, with an average value of 50.59 Bq/kg. The DU in the soil showed positive levels ranging from 15.67 Bq/kg to 27.57 Bq/kg, with an average of 20.95 Bq/kg. However, the results of the sediments showed underestimated levels of DU, which may be attributed to the dilution by sea water or may be affected by movements of sediment affected by tidal processes.

5. Radiological dose and risk

The total uranium in the soil showed an average value of 50.59 Bq/kg. Approximately 41.41% of this value is DU that originated from military operations during the Gulf War 1991. To assess the radiological sequences of the total U and its decay chain radionuclides on the

Table 4 The radioactivities of $^{235}\text{U}$, $^{238}\text{U}$ and DU in the investigated sediment and soil samples.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>$^{238}\text{U}$ (Bq/kg)</th>
<th>$^{235}\text{U}$ (Bq/kg)</th>
<th>$Rm%$</th>
<th>DU (Bq/kg)</th>
<th>$DU_m%$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MSED1</td>
<td>20.56 ± 2.34</td>
<td>0.97 ± 0.11</td>
<td>0.73</td>
<td>-0.33</td>
<td>-1.623</td>
</tr>
<tr>
<td>MSED2</td>
<td>12.67 ± 1.32</td>
<td>0.59 ± 0.06</td>
<td>0.74</td>
<td>-0.06</td>
<td>-0.473</td>
</tr>
<tr>
<td>MSED3</td>
<td>16.02 ± 1.65</td>
<td>0.746 ± 0.07</td>
<td>0.722</td>
<td>-0.01</td>
<td>-0.089</td>
</tr>
<tr>
<td>MSED4</td>
<td>16.48 ± 1.69</td>
<td>0.776 ± 0.08</td>
<td>0.73</td>
<td>-0.26</td>
<td>-1.623</td>
</tr>
<tr>
<td>MSED5</td>
<td>14.56 ± 1.50</td>
<td>0.68 ± 0.06</td>
<td>0.726</td>
<td>-0.12</td>
<td>-0.856</td>
</tr>
<tr>
<td>SOIL1</td>
<td>38.89 ± 2.98</td>
<td>1.28 ± 0.10</td>
<td>0.512</td>
<td>15.62</td>
<td>40.174</td>
</tr>
<tr>
<td>SOIL2</td>
<td>55.19 ± 4.36</td>
<td>1.85 ± 0.12</td>
<td>0.52</td>
<td>21.33</td>
<td>38.640</td>
</tr>
<tr>
<td>SOIL3</td>
<td>61.95 ± 4.98</td>
<td>2.01 ± 0.13</td>
<td>0.502</td>
<td>26.08</td>
<td>42.092</td>
</tr>
<tr>
<td>SOIL4</td>
<td>55.08 ± 5.02</td>
<td>1.89 ± 0.13</td>
<td>0.532</td>
<td>20.02</td>
<td>36.340</td>
</tr>
<tr>
<td>SOIL5</td>
<td>38.90 ± 2.67</td>
<td>1.19 ± 0.09</td>
<td>0.476</td>
<td>18.31</td>
<td>47.077</td>
</tr>
<tr>
<td>SOIL6</td>
<td>46.94 ± 3.91</td>
<td>1.59 ± 0.13</td>
<td>0.525</td>
<td>17.69</td>
<td>37.682</td>
</tr>
<tr>
<td>SOIL7</td>
<td>57.17 ± 5.28</td>
<td>1.73 ± 0.12</td>
<td>0.47</td>
<td>27.57</td>
<td>48.227</td>
</tr>
</tbody>
</table>

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area of 10000 m², the RESRAD (onsite) computer code “developed by Department of Energy and Nuclear Regulatory Commission for site-specific radiological dose and risk assessment for both on-site and off-site individuals” was used to evaluate the radiological dose to an individual exposed while residing and/or working in this area. For this purpose, the contaminated thickness of soil was set as 2 m and the soil density was set as 1500 kg/m³. The dose conversion factors in addition to the environmental transport factors were set according to the U.S. Federal Guidance Report FGR 11 [23] and the U.S. Federal Guidance Report FGR 12 [24]. The obtained total annual effective dose equivalent is 0.0031 mSv and ranged from 0.0013 to 0.0051 mSv. In addition, the average estimated cancer risk is $4.75 \times 10^{-6}$. From this risk, approximately $1.9 \times 10^{-6}$ is due to the DU, which represents approximately 41.41% from total uranium in the area.

6. Conclusions

The method used in this study indicated that the gamma-ray spectrometer is reliable and suitable for determining DU in contaminated soil based on the measurement of $^{235}$U/$^{238}$U. The lower threshold of the DU percentage that can be determined by this method was found to be 6.5% of U. The contaminated soil collected from military-affected land features from the Gulf War of 1991 exhibited average activities of 50.59 Bq/kg for total U and 20.95 Bq/kg for DU. However, the results in the sediments exhibited underestimated DU levels. The annual effective dose equivalent due to exposure to the total uranium and its decay chain radionuclides was found to be 0.0031 mSv. The estimation of the cancer fatal risk was found to have an average value of $4.75 \times 10^{-6}$. DU contributes approximately 41.41% of the total uranium detected in the investigated area.

References

and Air Concentration and Dose Conversion Factors for Inhalation, Submersion and Ingestion, Office of Radiation Programs, U.S. Environmental Protection Agency, Washington, DC 20460, 1989.