ESTIMATION OF RADIONUCLIDES IN SOILS - A COMPARISON OF METHODS FOR ANNUAL DOSE IN LUMINESCENCE DATING

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Abstract. A study was made in order to compare and test the performance of several methods for the annual radiation dose determination in luminescence dating. The following techniques were used: instrumental neutron activation, high resolution gamma ray spectrometry and alpha spectrometry. Detailed analysis was carried out through gamma spectrometry, the activities of different nuclides (^{234}Th, ^{226}Ra, ^{214}Pb, ^{214}Bi, ^{210}Pb, ^{228}Ac, ^{208}Tl) in the uranium and thorium series being measured, as well as ^{40}K. The potential of this method in checking the occurrence of radioactive disequilibrium in the series was investigated. The assumption that radium disequilibrium caused by the percolation of groundwater in soils can be encountered was supported by our finds. The consistency of the results obtained through the three different methods indicate the reliability of using high resolution gamma ray spectrometry as a fast and accurate method for measuring natural radionuclides concentrations in luminescence dating and as well for purposes of environmental monitoring.

Keywords: luminescence dating, annual dose, high resolution gamma spectrometry, alpha spectrometry, neutron activation

Introduction

Luminescence dating methods encompass a range of techniques which, based on a radiation produced charge population trapped within crystalline materials, are capable of determining the period of time which has elapsed since the last time the trapped charge population was reset. Ubiquitously occurring quartz and feldspars are the minerals used as dosimeters in the methods. For ceramic, fired, baked and volcanic materials, the resetting event is either the accidental or intentional firing of the materials or their crystallization and ejection from a magma body. For sedimentary materials the resetting event is the instant during which a sediment was exposed to daylight prior to deposition. The technique was firmly established in the 1970s and has undergone rapid development and enhancement [1, 2].

The age of the archaeological or geological material, expressed in years is obtained from [3, 4]:

$$age(years) = \frac{Palaeodose \quad (Gray)}{Annual \quad dose \quad (Gray/year)} \tag{1}$$

The palaeodose is build-up by the radiation from the naturally occurring radioelements U, Th and K (and to a lesser extent Rb) and by the cosmic radiation and can be evaluated from measurement of the natural luminescence signal and the sensitivity. From the age equation presented above it is clear that the assessment of the annual radiation dose is an important step in the dating process since it influences directly the final result and its uncertainty is linearly transferred to the age.

In natural environment, the major sources of radiation originate from naturally occurring radioactive chains and elements: ^{238}U, ^{235}U, ^{232}Th series ^{40}K, ^{87}Rb isotopes and from cosmic radiation. In evaluation of the rate at which ionization energy is deposited in a large sample of soil the 'infinite matrix' assumption is applied and consequently, the absorption of energy per unit mass is equal to the emission of energy per unit mass.

However, in the determination of the dose rate for luminescent dating it is important to distinguish between the dose absorbed by the soil matrix and by the grain showing luminescence. Therefore the annual dose rate of radiation has to be divided at least into three contributions to the varied absorption of alpha, beta and gamma radiation.

Thus, the determination of the dose rate in luminescent dating is a two step process. First, the activities of as many as possible nuclides from the uranium and thorium series have to measured together with the activity of ^{40}K and then the relevant activities have to be converted to the energy released per disintegration. This energy has to be related to the alpha, beta and gamma contribution. Conversion is performed using factors calculated from nuclear data tables, the most recent system being the one proposed by Adamiec and Aitken [5]. Finally, the contribution from cosmic radiation amounts to a few percent and can be calculated using the formula developed by Prescott and Hutton [6]. The present work aims to compare three of the most important methods available for natural radioactive isotope concentration measurement in soils for luminescence dating: instrumental neutron activation, high resolution gamma spectrometry and alpha spectrometry. The case study are chosen was the Neolithic archaeological site of Lumea Nouă, Romania. The analysis was carried out on five soil samples collected from the depths of : 0.8-1 m (sample 1), 0.4-0.5 m (sample 2), 1.5-1.7 m (sample 3), 1-1.2 m (sample 4), and 0.8-1 m (sample 5). All soil samples surrounded archaeological ceramic artifacts that will be dated using luminescence techniques.

Methodologies and experimental set-ups

High resolution gamma spectrometry

High resolution gamma ray spectrometry analysis was carried out on a ORTEC hiperpure germanium detector having the following characteristics: active volume of 181 cm^3, 0.878 keV FWHM at 5.9KeV, 1.92 keV FWHM and 34.2% relative efficiency at 1332.5 keV. The system was calibrated in energy using a standard Eu source. The detector is mounted in a lead castle and has a 0.5 mm beryllium window which makes it suited for measuring several U and Th decay products, down to ^{210}Pb with a gamma ray energy of 46.5 keV. This is important, because it is an indicator for possible radon escape in archaeological or geological times. In addition to this nuclide, other lines that were investigated are ^{234}Th (63.3 keV), ^{226}Ra (186.2 keV), ^{214}Pb (295.2 keV and 351 keV), ^{214}Bi (609 keV). The lines at 63.3 keV and 186.2 keV are moderately to heavily interfered by the 63.8 keV and 185.7 keV lines of ^{232}Th and ^{235}U, respectively, thus requiring proper corrections [7]. In the ^{232}Th decay chain we measured ^{228}Ac (338.3 keV and 911 keV) and ^{208}Tl (583.2 keV). Eventually, also the 1460.8 keV gamma ray of ^{40}K can be measured. Detection efficiencies were computed for the energies of interest using a Monte Carlo Code (GES-Gamma Electron Efficiency Simulator version 2.7 copyright 2006-2007 Dan Fulea). Moreover, in order to validate the procedure used we also determined the detection efficiencies experimentally, using radiometric reference materials RGU-1 (400 ± 2 µg/g) and RGTh-1 (800 ± 16 µg/g), measured in the same geometry as the soil samples, issued by the IAEA. In this standards the U and Th decay series are in equilibrium. A comparison of the values obtained by the two methods is represented (see figure 1). The differences that can be observed are to be expected due to the differences of chemical composition and packing density thus there is reason to have confidence in the values obtained by simulation.

As previously mentioned, ^{226}Ra 186.2keV is heavily interfered by the ^{235}U 185.7 keV line and a correction for this interference is needed to obtain unambiguous results. Correction for the interference was made following a suggestion of De Corte et al [8]. This is based on the calculation of ^{235}U 185.7 peak area from the rather intense ^{234}Th peak at 63.3 keV. Two assumptions have to be made in this case: that ^{238}U and ^{235}U are present in their isotopic natural ratio and that ^{238}U and its immediate daughter ^{234}Th are in equilibrium. Moreover 63.3 keV ^{234}Th peak is also spectrally interfered by a ^{232}Th peak at 63.8 keV. The correction for this interference is made using ^{228}Ac peak at 338.1 keV, obviously assuming equilibrium between ^{232}Th and ^{228}Ac.
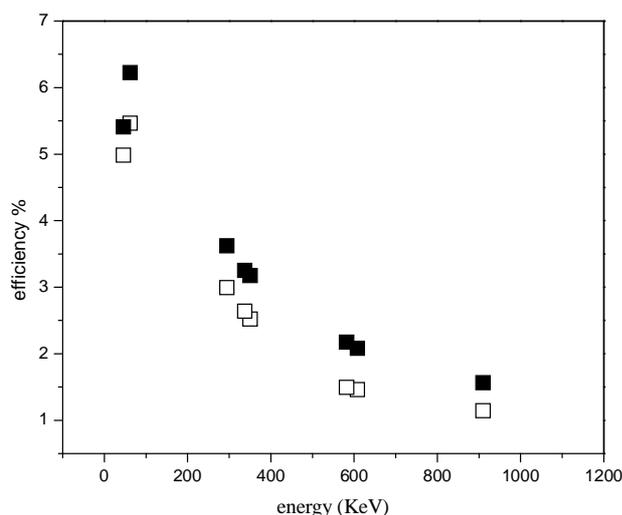
Fig. 1. Comparison between efficiency values determined experimentally using IAEA RGU-1 RGTh-1 ores (□) and Monte Carlo computed values for soil (■)

Instrumental neutron activation

For elemental concentration determination of ^{238}U, ^{232}Th and ^{40}K the Zirconium standardisation method was used [9]. Two of the five stable isotopes of zirconium (^{94}Zr and ^{96}Zr) generate the short live radioisotopes ^{95}Zr ($T_{1/2}$=64.02d) and respectively ^{97}Zr ($T_{1/2}$=16.9h) by neutron capture reactions. The zirconium monitor has a double utilization. The thermal to epithermal neutron flux ratio and the concentration of analysed element can be obtained from ^{95}Zr and ^{97}Zr. The elemental concentration is obtained according to:

$$\rho_i = \frac{A_{sp,i}}{S \cdot D \cdot C \cdot w} \cdot \frac{1}{k_{anal} \cdot A_{sp,c}} \qquad (2)$$

where ρ_i is elemental concentration; $A_{sp,i}$ are the photo peak count rates, representing the full-energy peak and counting time ratio; S is the saturation factor = 1 - exp($\lambda_i \cdot t_i$); λ is the decay constant = (ln2)/$T_{1/2}$; D is the decay factor = exp (- $\lambda_i \cdot t_d$), t_d is the cooling time; C is a "measurement" factor = (1-exp(-$\lambda_i \cdot t_c$)/($\lambda_i \cdot t_c$); w = mass of irradiated element and k_{anal} is a nuclear constant.

Before irradiation the samples were de-hydrated, weighed and then packed into Teflon cartridges. The samples were irradiated in a pneumatic rabbit in the D11 dry channel of the TRIGA-ACPR reactor. During irradiation time the ACPR reactor was operated in stationary mode (100 KW). The samples were irradiated together with Zr monitor, in order to determine the thermal neutron flux (E<0,5eV) to epithermal neutron flux ratio; the irradiation time was 2 hours. The samples were measured after 48 hours to allow ^{24}Na decay ($T_{1/2}$ = 15 h) which is formed by neutron capture in significant quantities in all the samples. Both the Zr monitor as well as samples induced activities were measured with a high-resolution gamma spectrometer with a 128 cm^3 HpGe detector type GEM-20180 and 20% relative efficiency. The system was calibrated for efficiency for certain source-to-detector distances with some sets of standard sources (^{241}Am, ^{133}Ba, ^{137}Cs, ^{60}Co and ^{152}Eu). The thermal to epithermal neutron flux ratio determined from the reaction rates induced in the two Zr nuclides is f = 10.56. The gamma spectra were processed using GENIE 2000 (® Canberra) software analysis package.

Alpha spectrometry

Measurements were performed using a Canberra 7410 alpha spectrometer with a PIPS detector having a resolution of 19 keV. The peaks of interest were the alpha emissions at 5.305 MeV for ^{210}Po and respectively 4.784 MeV for ^{226}Ra.

The first step in the chemical separation procedure implied was dissolving the soil samples. For this use was made of a Microwave Milestone ETHOS lab station, equipped with a Easy Wave Easy Control Software. For each 0.5g of samples 8ml of 65%NO$_3$, 5 ml of 37% HCl and 1.5ml of 40% HF were added. Then a three step heating treatment was performed up to 210°C.

In the case of ^{210}Po, samples with a thickness of 1-2 microns were prepared on 18.5 mm CrNi disks by spontaneous electrodeposition. As it is quite difficult to control the pH in the solutions before depositions and thus sometimes a low recovery is spotted. ^{209}Po was added as a tracer, its peak at 4.866 MeV being also analyzed in order to be able to make the necessary corrections. Ra samples were prepared using the Cathion exchange column method. This is a very effective method and the only correction that had to be implied was related to the filtering efficiency; for this the co precipitation of BaSO$_4$ was implied.

Results and discussions

Natural radionuclide concentrations were determined using three different methods in five soil samples that surrounded Eneolitical ceramics with the purpose of determining the annual gamma dose absorbed by coarse quartz grains inside the ceramic shreds. Specific activities of the nuclides of interest measured in the uranium series are presented (see table 1). They are clearly divided taking into consideration the possible cases of disequilibria (radium enrichment or depletion and radon loss).

Table 1
Specific activities of the nuclides in the uranium series measured by high resolution gamma spectrometry (^{234}Th, ^{226}Ra, ^{214}Pb and ^{210}Pb), neutron activation analysis (^{238}U) and alpha spectrometry (^{226}Ra and ^{210}Po). Errors quoted represents uncertainty and were obtained according to the classical laws of error propagation

Soil sample	Uranium specific activity (Bq/kg)						
	Pre- Ra		Ra		Rn daughters	^{210}Pb and ^{210}Po	
	Gamma Spect. ^{234}Th	Neutron activation ^{238}U	Gamma Spectr. ^{226}Ra	Alpha Spectr. ^{226}Ra	Gamma Spectr. ^{214}Bi	Gamma Spectr. ^{210}Pb	Alpha Spectr. ^{210}Po
1	24.8±6.9	23.3±2.1	18.1±2.0	-	23.8±1.9	31.1±10.1	20.4±3.6
2	23.1±7.7	22.7±1.9	40.3±10.6	36.0±6.0	26.0±2.1	14.6±7.0	23.1±4.1
3	16.8±9.5	19.8±1.7	35.0±15.7	30.0±6.0	24.3±2.2	24.5±8.1	26.7±4.5
4	31.9±8.2	24.1±1.5	21.1±11.2	17.0±5.0	23.0±2.2	31.9±7.3	27.7±4.1
5	22.1±7.4	21.6±2.0	33.5±8.8	-	22.6±8.1	21.2±8.7	29.2±8.8

Values obtained for ^{238}U by instrumental neutron activation are consistent within error limits with the values obtained for ^{234}Th through high resolution gamma spectrometry. As equilibrium between the above mentioned nuclides can be regarded as a fair assumption in the case of soils, we can conclude that the emission at 63 keV of ^{234}Th can be used with satisfying accuracy for gamma spectrometric measurement of ^{238}U. The assumption that radium disequilibrium is not unusual in soils was supported by the results obtained both through gamma spectrometry in the cases of sample 2 and sample 3, where a certain degree of radium enrichment can be noticed. Even though, the degree of disequilibrium is not sufficiently severe to have an important influence on the final age of ceramics taking into consideration the overall precision of the luminescence method (see figure 2). Nevertheless, taking into consideration the fact that gamma spectrometric data are supported by alpha spectrometric results for ^{226}Ra we do stress upon considering the detailed investigation on the concentration of this nuclide as a worthwhile procedure when performing gamma spectroscopic measurements.

Deriving the activity ^{210}Pb is also of major importance as this nuclide can serve as an indicator of radon loss throughout geological or archaeological time. Due to the low energy emission of this nuclide (46.5 keV) gamma spectrometric measurements are difficult to be performed with sufficient precision unless special detectors in ultra low background conditions are being used. Thus we consider data on [210]Po derived through alpha spectrometry to yield more reliable results.
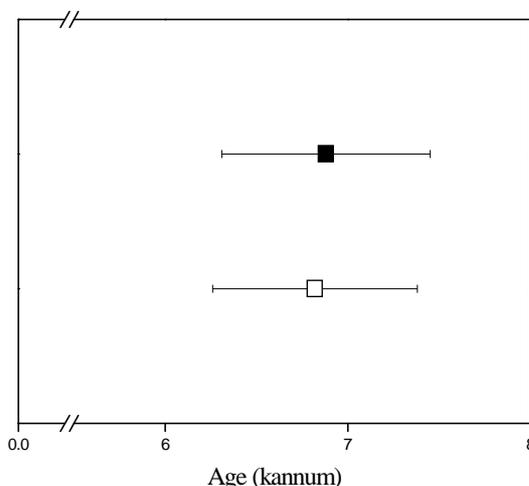
Fig. 2. Calculated ages for an Eneolitic shred collected from Lumea Nouă archaeological site taking into consideration the dosimetric information for soil sample 2 provided by gamma ray spectrometry (□) (taking into consideration radium enrichment) and by neutron activation analysis (■) (method that does not take into consideration the possible cases of disequilibrium in uranium series). All the other data related to the luminescence analysis of the shred can be found in [9]

In the case of thorium series equilibrium can be assumed and the specific activities measured are presented (see table 2) together with the measured concentrations for [40]K.

Table 2
Specific activities of [232]Th and [40]K measured in the investigated soil samples by high resolution gamma spectrometry (using [228]Ac and [208]Tl in the case of thorium series and [40]K for potassium) and instrumental neutron activation analysis.

Sample	Thorium specific activity (Bq/kg)		[40]K specific activity (Bq/kg)	
	Gamma Spectr. [228]Ac and [208]Tl	Neutron activation [232]Th	Gamma Spect. [40]K	Neutron activation [40]K
1	32.5±3.8	41.2±3.5	465±25	-
2	36.2±4.4	32.2±2.7	585±26	487±42
3	28.6±3.4	30.1±2.5	491±51	486±42
4	29.0±4.0	34.8±2.9	489±30	510±43
5	33.2±4.2	36.2±3.0	598±97	537±44

Conclusions
A relatively good agreement between the two methods (gamma spectrometry and instrumental neutron activation) can be seen thus both methods can be accurately used for dosimetric purposes.

Nevertheless, it can concluded that despite the better precision of instrumental neutron activation the method of choice for obtaining routine dosimetric information regarding natural nuclides in soils in luminescence dating can be considered to be gamma spectrometry due to the less

efforts involved in the experimental procedure and the advantages it offers on the possibility of checking for radioactive disequilibrium in uranium series.

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