Determination of ^{235}U in the context of interference with ^{226}Ra for the study of the disequilibrium in the ^{238}U decay series

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Abstract. The compound peak from ^{235}U and ^{226}Ra at 186 keV has been used to study methods for the de-convolution of complex peaks in gamma-ray spectroscopy and hence to determine the state of radioactive equilibrium of geological and environmental materials. A uranium reference material known to be in equilibrium has been analysed by gamma-ray spectroscopy, using a broad energy, HPGe detector (BEGE by Canberra Electronics) with the sample in a Marinelli beaker geometry. The compound peak at 186 keV has been studied in detail. The energies of the ^{226}Ra and ^{235}U lines that contribute to this peak are accurately known from published data. Although these two lines are separated by only 0.5 keV it has been shown that it is possible to obtain reliable values for the two peak intensities by using this detector together with appropriate data manipulation strategies. The FWHM of the detector and its variation with energy were determined experimentally to reduce the free parameters in the fit; a least squares fit of a sum of the two Gaussians superimposed on a second degree polynomial background was then performed on the ^{235}U/^{226}Ra 186 keV compound peak using the MIGRAD minimizer in ROOT (an object oriented C++ data analysis platform developed at CERN). The free parameters in the fit were the heights of the two Gaussians and the background model parameters. A numerical method for determining the intensity of ^{235}U and hence its concentration in an environmental sample, independent of ^{226}Ra / ^{222}Rn equilibrium state has been established and the chi squared surface has been studied to determine the errors in the important intensity parameters and to compare these values with the case where the FWHM and peak positions are also free parameters.

1. Introduction

The accurate determination of ^{235}U in the environment is of great importance. Not only in the commercial exploration for uranium, but also in the assessment of the risk of radiation exposure due to naturally occurring radioactive material (NORM) [1,2] as well as many other applications.

Natural uranium is mainly composed of ^{238}U and ^{235}U with abundances of 99.27 % and 0.72 % respectively [3]; therefore the ratio of ^{238}U to ^{235}U in the environment is expected to be very close to 137.9 and accurate determination of ^{235}U can be used to deduce the total amount of uranium in a typical environmental sample. Any alteration of this ratio in the environment is due to human intervention, or as a remote possibility, to a natural nuclear process such as the Oklo reactor in Gabon, Africa.

In many gamma-ray spectroscopy procedures secular equilibrium in the uranium decay series is assumed. Uranium (^{235}U and ^{238}U) decay through these series to stable isotopes of lead. Many of these decays emit characteristic gamma-rays. Gamma-ray spectroscopy is a nuclear analytical technique that utilizes these emitted gamma-rays. It is non-destructive and makes use of the penetrating nature of gamma-rays emitted by specific isotopes to identify the isotopes present in a sample, as well as their concentrations. In most gamma-ray methods for NORM the peaks from the decay of ^{214}Pb and ^{214}Bi are used to infer the activity of ^{226}Ra [4,5]. These isotopes (of lead and bismuth) follow the gaseous ^{222}Rn, the daughter of ^{226}Ra, in the uranium decay series. It is relatively easy (through tight sealing of sample counting containers) to compensate for problem of radon escape so that, after ingrowth, these peaks are a direct measure of the ^{226}Ra content of the samples. However, the equilibrium between radium and uranium can be strongly affected by a number of geological processes. Because of the constant ratio between ^{235}U and ^{238}U in nature, as mentioned above, the 185.715 keV peak from ^{235}U can be used as a measure of the uranium content. In order to do this with good accuracy, it must be de-convoluted together with the 185.25 keV peak from ^{226}Ra. A HPGe detector is widely used for monitoring environmental radioactivity because of its good resolution [5,6]; in spite of this good resolution, it still fails to resolve these peaks, making extraction of vital information in this peak difficult. Procedures for determining ^{226}Ra from the ^{222}Rn daughters after ingrowth, followed by subtraction to determine ^{235}U from the compound peak can introduce errors. Therefore a direct method for ^{235}U determination is required.

2. Extraction of peak intensities in spectra from uranium decay

The gamma-ray spectra from the uranium (and thorium) decay series are complex (see figure 1). Certain of the peaks are well resolved and it is relatively straightforward to extract their intensities. On the other hand, many of the peaks do overlap, even using the best available high-purity germanium detectors and the extraction of the relevant intensities is much more challenging. In this work we focus on the extraction of the ^{235}U and ^{226}Ra peak intensities from the compound peak at 186 keV. The energies of the gamma lines are 185.715 keV from ^{235}U and 186.211 keV from ^{226}Ra [5]. These lines are only 0.496 keV apart and their relative intensity for a specimen in equilibrium is 0.4275:1. Their separation is significantly less than the resolution, expressed as the full-width at half maximum (FWHM), of modern high purity germanium (HPGe) detectors. The extraction of the individual intensities from this peak is therefore an important and interesting example in the analysis of

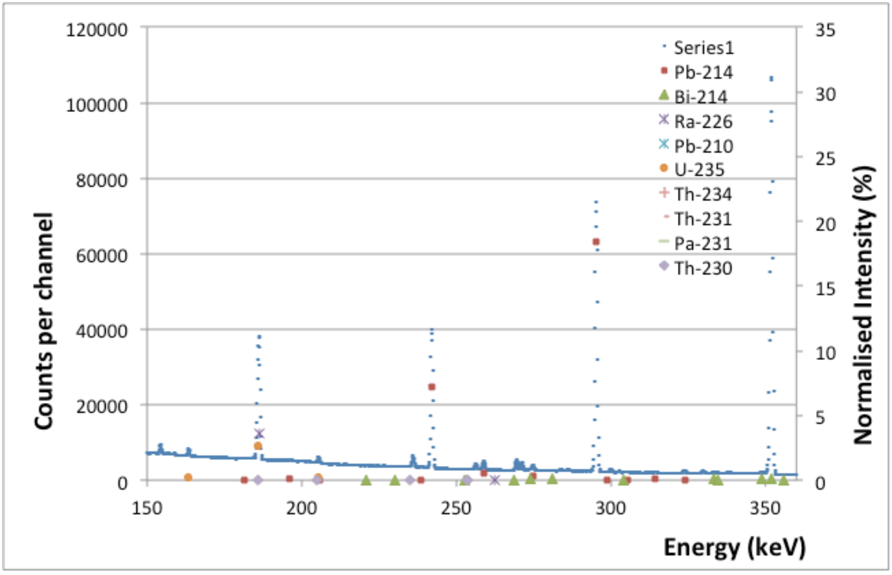

Figure 1: Energy region from 150 - 360 keV from gamma-ray spectrum from reference material (IAEA U) containing uranium in equilibrium with its daughters, The relative intensities of the principal gamma transitions are also shown

compound peaks. The techniques developed can be used in a number of other applications as well, in optically stimulated luminescence dating, for example.

The de-convolution of compound peaks depends on the application of peak fitting methods, particularly least squares or maximum likelihood techniques. Where the FWHM or the peak positions are included in the fit the method is essentially non-linear whereas if these are known, a linear method can be used.

The important parameters to extract from the procedure are the peak intensities and the fitting procedure should therefore minimise the errors in these quantities. This is a somewhat different problem from that of just obtaining the *best fit* to the data itself. These results (outcomes) are closely related but they are not the same. For example if the FWHM values and the peak positions can be established independently, that will both increase the number of degrees of freedom per estimated parameter and also allow the use of a linear LSSQ method with an exact algebraic solution instead of a numerical solution based on the minimum in the chi-squared surface. The effect of this on the errors, both systematic and statistical, in the peak intensity parameters will be studied in the present work.

In this approach the model used to describe the reality of the gamma-spectrum in the peak region is crucial. It must describe both the peak shape and the background shape accurately but with a minimum of estimated parameters. In our initial studies we have chosen to describe the peak shape by a simple Gaussian and the background by a second degree polynomial. So the initial model fitted was (Note FWHM = 2.3548 sigma):

$$N_i = aE_i^2 + bE_i + c + d\frac{2.355}{F_{235}\sqrt{2\pi}}\exp\left(\frac{-(E_i - E_{235})^2}{2\left(F_{235}/2.355\right)^2}\right) + f\frac{2.355}{F_{226}\sqrt{2\pi}}\exp\left(\frac{-(E_i - E_{226})^2}{2\left(F_{226}/2.355\right)^2}\right)$$

where i is the channel number for the gamma-ray spectrum in the region to be fitted, E_i is the energy equivalent of channel i and typically $170 < E_i < 195$ keV

N_i is the number of counts in channel i.

F_{235} is the FWHM of the ^{235}U peak;

F_{226} is the FWHM of the ^{226}Ra peak and these are essentially the same;

E_{235} is the energy of the ^{235}U peak;

E_{226} is the energy of the ^{226}Ra peak;

a, b, c, d and f are free parameters in the fit.

d and f are the intensities of the two peaks and the errors in these parameters are to be minimised.

The peak positions were determined by an accurate calibration over the energy region of interest and fixed for the fit while the FWHM's were determined by using an experimental determination with a standard source and an interpolation for the variation with energy and also fixed for the fit.

The shapes of the various gamma peaks (as well of course as their relative intensities) can depend on the structure of the particular detector and as well as the counting geometry. These experimental details are given in the next section. The fitting method chosen uses the CERN system ROOT [9]. This makes use of the MIGRAD and MINUIT procedures [9].

3. Experimental

3.1. Sample Preparation and Counting Geometry

Sample preparation and the choice of counting geometry are of great importance in the counting of environmental radioactive samples [10]. In this study, a sealed Marinelli beaker was used as a sample container. Counting in a Marinelli beaker increases the efficiency; and reduces counting times for low activity samples [10]. The sealing prevents the escape of ^{222}Rn from the specimen and establishes secular equilibrium between this gaseous radioisotope and its daughters. The sample mass was obtained and the typical count period was 24 hours in order to minimise the statistical uncertainty.

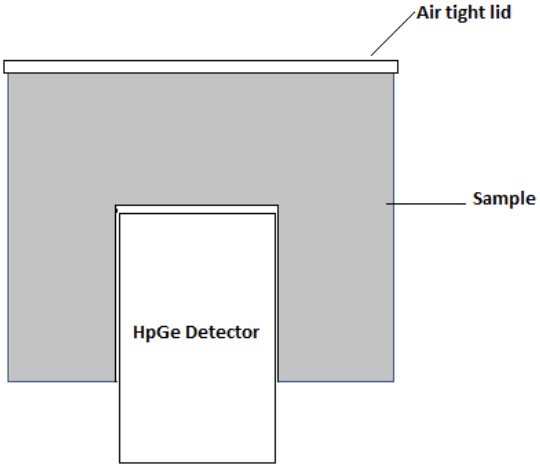

Figure 2: Schematic of the counting geometry with the sample in a Marinelli beaker

3.2. Gamma-ray spectroscopy

The gamma-ray spectroscopy system used in this study consisted of: lead castle, broad energy hyperpure germanium detector (Canberra HPGe), analog to digital converter (ADC), signal amplification systems (preamplifier and amplifier) and a Canberra DSA-1000 digital signal processing (DSP) system interfaced to a multichannel analyzer (MCA). The use of a DSP system with its greatly increased stability is of great importance in this approach.

3.3. Energy calibration

Energy calibration uses standard sources such as ^{60}Co and ^{137}Cs with well known transition energies to establish the equivalent energy of each channel A least squares fit of a polynomial function of second degree is often used [11].

In this work the peak positions must be very accurately known and a two stage procedure was adopted. An initial energy calibration utilised standard sources such as ^{60}Co and ^{137}Cs with well known transition energies together with a first degree polynomial.

This was refined in a second stage procedure using peaks from ^{214}Pb and ^{214}Bi present in the sample spectrum to obtain a highly accurate energy calibration over the region of interest.

3.4. FWHM and efficiency calibration

The variation of the full energy peak efficiency and the variation of the FWHM for the detector with energy were determined using a standard multi-isotope source from Eckert and Ziegler Isotope Products. The same source was used to determine the variation in the resolution as a function of energy. These results were all obtained for the specific counting geometry shown in figure 2.

4. Data analysis

Spectral raw data were collected with a typical count period of 24 hours (86400 seconds) using an electronic data acquisition system (Canberra DSA-1000 digital signal processing (DSP) system interfaced to a multichannel analyser (MCA), stored as an ASCII file and initially analysed using GENIE2000 software. The raw data were then read into the C++ programme for further analysis.

The C++ program has been written to read in the data and implement the routine MIGRAD in the ROOT platform. Since the region of interest is the 186keV ^{235}U/^{226}Ra compound peak, the C++ procedure read data in the range $130keV \le E_i \le 200keV$. To initiate the quest of finding the best parameters for the fit function, the user is prompted to supply the FWHM for the detector and then

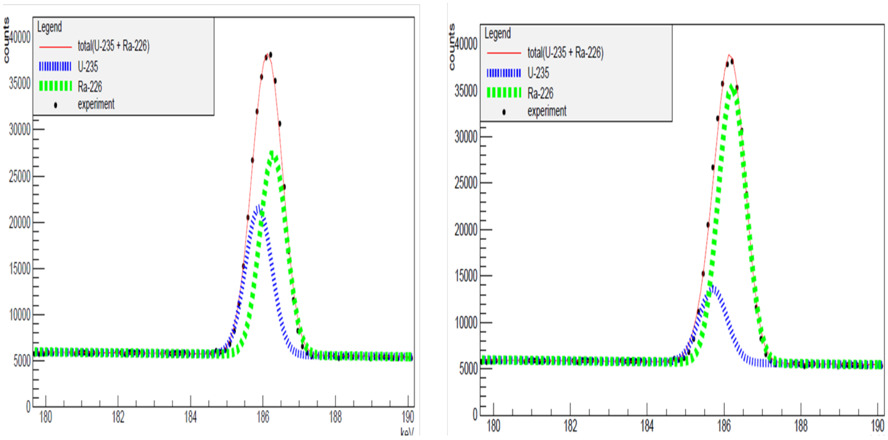

Figure 3. Data points together with fit of two Gaussians plus background using ROOT. Sample IAEAU reference material in equilibrium; detector: BEGe. (a) With a calibration slope of 0. 12553 keV per channel and (b) with a calibration slope of 0. 12531 keV per channel; FWHM 0.85 keV in both cases.

MIGRAD iterates, scanning the chi-square surface until a convergence criterion[1] is satisfied, thereby printing out the best fit parameters as well as the associated errors. Experimental data was then plotted together with the theoretical prediction.

5. Results and discussion

Values for the centroids of the ^{235}U and ^{226}Ra are known from published data to be 185.715 keV and 186.211 keV, respectively [12]. Initial results were used to test the sensitivity of the reduced parameter approach to the energy calibration. Figure 3b shows the results obtained from the de-convolution of the compound 186 keV peak in the spectrum from the IAEA uranium standard using a slope of 0. 12531 keV per channel for the energy calibration. With this value the best fit predicts an intensity that

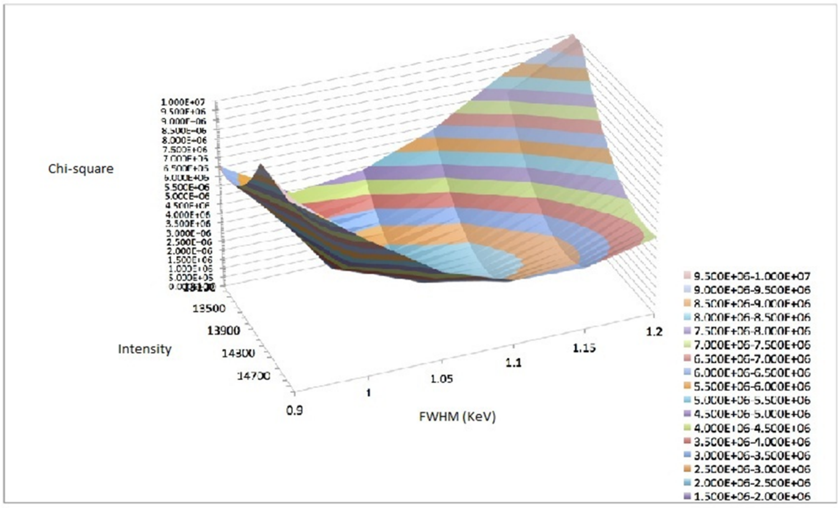

Figure 4. Chi-squared surface for co-axial detector illustrating how the surface varies with changes in the FWHM and the intensity of the ^{235}U peak. The value of the intensity at the minimum is a sensitive function of the value of the FWHM.

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[1] The iteration stops when the derivative of chi-square with respect to parameter(s) is zero or the maximum number of iterations is exceeded.

is close to the theoretical value of 0.74 for a sample in equilibrium. As is shown in Figure 3a, a slope of 0.12553 keV per channel gave a ratio that is much too small for the ^{235}U peak intensity. A common FWHM of 0.85 keV was used to obtain these results. These results demonstrate the need for a very high degree of accuracy in the energies of the transitions as well as the energy calibration when the reduced parameter approach is used.

To investigate the sensitivity of the parameters (intensities) to the choice of FWHM, chi-square was plotted against the peak intensity and the FWHM. Figure 4 shows the resulting chi-square surface and it is observed that a small change (of about 0.05 keV) in the FWHM results in a large variation in the local minimum of the chi-square surface.

6. Conclusion

This de-convolution method for a compound peak without the peak position as a free parameter requires a highly accurate energy calibration in the peak region. If this is not the case then there can be large errors in the peak intensities found even at the minimum chi squared value. The results show that the energy calibration slope should be accurate to at least four significant figures in the case of the compound 186 keV peak.

The chi-squared variation and thus the errors in the determination of the important intensity parameters are also sensitive to variations in the FWHM and this parameter must also be known with a high degree of accuracy for the linear least squares method to be successfully applied. If these two requirements can be met then the positions and widths of the peaks can be fixed and do not have to be used as parameters in the fit. This greatly reduces the statistical error. Further work will be carried out to assess the accuracy of this method for the simultaneous determination of the amounts of ^{235}U and ^{226}Ra and the use of this technique to assess the degree of disequilibrium in geological and environmental samples as well as to areas such as optically stimulated luminescence dating.

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