TEST SPECTRA EXPERIMENTAL CONSTRUCTION FOR EVALUATING GAMMA-SPECTROMETRY COMPUTER CODES FOR THE ^{235}U DETERMINATION

by

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Scientific paper
DOI: 10.2298/NTRP140S0S1K

The determination of ^{235}U in environmental samples from its 185.72 keV photons may require the deconvolution of the multiplet photopeak at 186 keV, due to the co-existence of the 186.25 keV photons of ^{226}Ra in the spectrum. Successful deconvolution depends on many parameters, such as the detector characteristics, the activity concentration of the ^{235}U and ^{226}Ra in the sample, the background continuum in the 186 keV energy region and the gamma-spectrometry computer code used.
In this work two sets of experimental test spectra were constructed for examining the deconvolution of the multiplet photopeak performed by different codes. For the construction of the test spectra, a high-resolution low energy germanium detector was used. The first series consists of 140 spectra and simulates environmental samples containing various activity concentration levels of ^{235}U and ^{226}Ra. The second series consists of 280 spectra and has been derived by adding ^{137}Cs, corresponding to various activity concentration levels, to specific first series test spectra. As the ^{137}Cs backscatter edge is detected in the energy region of the multiplet photopeak at 186 keV, this second series of test spectra tests the analysis of the multiplet photopeak in high background continuum conditions.
The analysis of the test spectra is performed by two different γ-spectrometry analysis codes: (a) spectrum unix analysis code, a computer code developed in-house and (b) analysis of germanium detector spectra, a program freely available from the IAEA. The results obtained by the two programs are compared in terms of photopeak detection and photopeak area determination.

Key words: γ-ray spectrometry, test spectra, ^{238}U, multiplet photopeak

INTRODUCTION

In environmental samples, ^{235}U can be detected by its photons emitted at energies such as 143.767 keV (10.94%), 163.356 keV (5.08%), 185.720 keV (57.1%), and 205.316 keV (5.02%) [1]. However due to its long half-life ($704 \cdot 10^4$ years) [1] and to the low photon emission rates, in practice only photons at 185.720 keV can be used. The analysis of these photons is not always an easy task as ^{235}U in all environmental samples is detected together with the ^{238}U daughter isotope, ^{226}Ra, emitting photons at 186.25 keV giving rise to a multiplet photopeak at ~186 keV. The successful deconvolution of this multiplet depends on the detector characteristics, the activity concentration of the ^{235}U and ^{226}Ra in the sample, the background continuum in the 186 keV energy region and the γ-spectrometry computer code used for the analysis of the spectrum [2]. The influence of these parameters in the analysis of the ^{235}U-^{226}Ra multiplet photopeak is studied in the present work by the use of experimentally constructed test spectra.

The use of test spectra for examining the ability of gamma spectrometry computer programs to determine peak energies and areas with associated uncertainties has been reported in previous works [3-8]. Several test spectra sets are available on line, while several intercomparisons on the analysis of test spectra have been organized [3-7]. From the most recent intercomparisons can be concluded that most codes yield near optimum results for singlet peaks, but face difficulties with doublets/multiplets [7]. In addition, the conditions for constructing reliable test spectra are also defined in [4].

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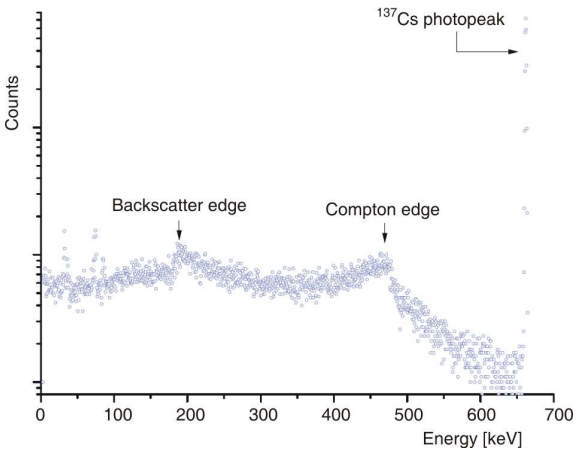

Figure 1. A typical ^{137}Cs spectrum

In [2] it is briefly described that two different series of experimental test spectra were constructed focusing on the deconvolution of the ^{235}U-^{226}Ra multiplet photopeak in different background continuum conditions. The first series, which consists of 140 spectra, simulates spectra of environmental samples containing only natural radioactivity, with various levels of ^{226}Ra and ^{235}U. The second series consists of 280 spectra simulating spectra of environmental samples containing various levels of ^{226}Ra and ^{235}U and contaminated with various levels of ^{137}Cs.

As it can be seen in fig. 1, in which a typical ^{137}Cs spectrum obtained by a high purity germanium detector is illustrated, the backscatter edge of the ^{137}Cs 661.66 keV photons lies on the 186 keV energy region making the analysis of the multiplet photopeak more demanding.

This work focuses on the description of the test spectra construction and the influence of the gamma spectrometry computer code used for the deconvolution of the multiplet photopeak.

MATERIALS AND METHODS

Test spectra construction

A method for the ^{235}U determination in environmental samples has been developed and described in [9] at the Nuclear Engineering Department of the National Technical University of Athens (NED-NTUA). Based on this method and on the conditions for constructing reliable test spectra described in [4], the parameters for the construction of the two test spectra are defined below.

For the construction of the test spectra a low energy germanium (LEGe) detector with a FWHM of 341 eV at 5.9 keV was used. The detector was calibrated in the energy region 20-200 keV. The constructed test spectra of both series simulate real spectra of volume cylindrical sources with a height of 69 mm and a volume of 282 mL and measured for 345600 s (equal to 4 days) in this detector. In this way, a typical measurement of an environmental sample in NED-NTUA is simulated.

The first series of test spectra corresponds to different ^{235}U-^{226}Ra activity concentration combinations. Five Ra activity concentration levels were defined in the region 15-1000 Bq/kg. Each of them was combined with seven ^{235}U activity concentration levels in the region 0.1-600 Bq/kg, creating a total of 35 different spectra. It should be noted that in each spectrum, the definition of the ^{226}Ra activity concentration levels was absolute, while the ^{235}U levels were defined relatively in terms of the photopeak ^{235}U/^{226}Ra area ratio. Table 1 shows the activity concentration combination used.

For the construction of the second series of test spectra, four ^{137}Cs activity concentration levels in the region 7.5-2300 Bq/kg were added to each of these 35 different spectra.

Volume sources for all these combinations were not available, therefore sources of different geometries were used to obtain equivalent spectra. In this way, a test spectrum derives by the superposition of four equivalent spectra:

– a 4d background spectrum of the LEGe detector,
– a ^{226}Ra equivalent spectrum,
– a ^{235}U equivalent spectrum, and
– a ^{137}Cs equivalent spectrum (for the test spectra of the second series).

The algorithm used for the superposition is described by eq. 1

$$C_{\text{test},i} \quad C_{\text{bk},i} \quad C_{\text{ra},i} \quad C_{\text{u},i} \quad C_{\text{cs},I} \tag{1}$$

Table 1. The ^{235}U-^{226}Ra activity concentration levels selected for the first test spectra series

^{226}Ra activity concentration [Bqkg^{-1}]	^{235}U activity concentration [Bqkg^{-1}]						
	^{235}U/^{226}Ra photopeak area ratio						
	10%	50%	75%	100%	150%	300%	1000%
15	9.09E-02	4.54E-01	6.82E-01	9.09E-01	1.36E+00	2.73E+00	9.09E+00
30	1.82E-01	9.09E-01	1.36E+00	1.82E+00	2.73E+00	5.45E+00	1.82E+01
100	6.06E-01	3.03E+00	4.54E+00	6.06E+00	9.09E+00	1.82E+01	6.06E+01
300	1.82E+00	9.09E+00	1.36E+01	1.82E+01	2.73E+01	5.45E+01	1.82E+02
1000	6.06E+00	3.03E+01	4.54E+01	6.06E+01	9.09E+01	1.82E+02	6.06E+02

where $C_{test,i}$ is the number of counts in the i-channel of the final test spectrum, $C_{bk,i}$ – the number of counts in the i-channel of the background equivalent spectrum, $C_{ra,i}$ – the number of counts in the i-channel of the ^{226}Ra equivalent spectrum, $C_{u,i}$ – the number of counts in the i-channel of the ^{235}U equivalent spectrum, and $C_{cs,i}$ – the number of counts in the i-channel of the ^{137}Cs equivalent spectrum.

As far as the background spectrum is concerned, it should be noted that a photopeak at the 186 keV energy region due to the background ^{226}Ra and ^{235}U was detected, as shown in fig. 2(a). The photopeak was replaced by its corresponding background continuum as shown in fig. 2(b). The following steps describe the procedure followed:

– the spectrum channels that belong to the photopeak are defined,
– a linear background continuum under the photopeak is determined by using the counts of the neighboring channels and by applying the least mean square algorithm, fig. 2(a), and
– the counts of the photopeak channels are replaced by counts derived by the use of a pseudo-random number generator following a Poisson distribution around the linear background continuum, fig. 2(b).

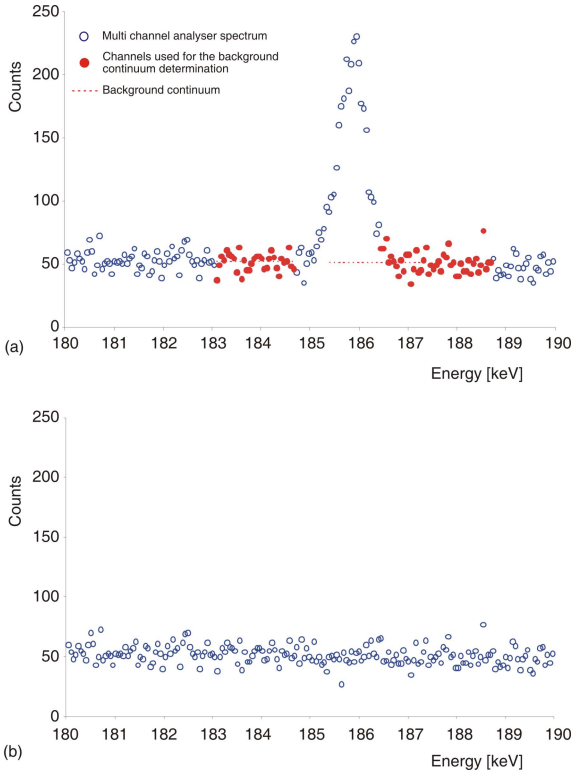

Figure 2. (a) part of the 4d LEGe detector background spectrum indicating the photopeak at 186 keV, and (b) the same part of the 4d LEG-e detectro background spectrum after the subtraction of the photopeak at 186 keV

For the ^{226}Ra equivalent spectra, a sealed point source was used. The various activity concentration levels were simulated by collecting spectra of different measuring time. For the ^{235}U equivalent spectra, foils of natural uranium were used in the same manner, while for the ^{137}Cs equivalent spectra, a volume source was used. For each ^{226}Ra-^{235}U combination four independent spectra were constructed, simulating repeated analyses of the same sample. Thus, the first series of test spectra consists of 4 35 = 140 spectra grouped in 4 groups, namely A, B, C, and D. Then, each ^{137}Cs activity concentration level was combined with the C and D test spectra group, leading to the second series of test spectra that consists of 35 2 4 = 280 spectra.

In fig. 3(a-c) three of the constructed spectra are presented. In each figure the concentration of the isotopes ^{226}Ra, ^{235}U, and ^{137}Cs are given for comparison purposes. Figure 3(a) presents a spectrum of the first series containing only ^{226}Ra (15 Bq/kg) and ^{235}U (14 Bq/kg). Figure 3(b, c) present spectra of the second series. The concentration of ^{226}Ra and ^{235}U are the same as in fig. 3(a), while ^{137}Cs concentration is 300 Bq/kg and 3000 Bq/kg, respectively. A gradual increase of the background continuum is apparent in fig. 3(b) and 3(c), taking into account the change in y-axis scale.

The gamma-spectrometry codes

The first gamma-spectrometry code used for the analysis of the test spectra was the spectrum unix analysis (SPUNAL) code. It is an in-house developed FORTRAN code on a UNIX system that allows, among other operations, for the:

– determination of the centroid, the area and the FWHM of the photopeaks in a gamma spectrum,
– deconvolution of multiplet photopeaks with up to 10 components, using a modified Marquardt algorithm,
– energy calibration and the qualitative determination of samples,
– efficiency calibration and the quantitative determination of samples, and
– application of corrections in the analysis of a gamma spectrum (*e. g.*, self-absorption corrections, decay/production corrections

The second gamma-spectrometry software used was (analysis of germanium detector spectra) (ANGES). ANGES has been developed in the Institute of Nuclear Research and Nuclear Energy, in Sofia Bulgaria and has been supported by the IAEA. The software is freely available [10]. It offers all the main features of a commercial software package except for control of the acquisition process. The program is able to perform automatic analysis of spectra but it is characterized as “user controlled” because it supplies all intermediate results and allows the user to modify

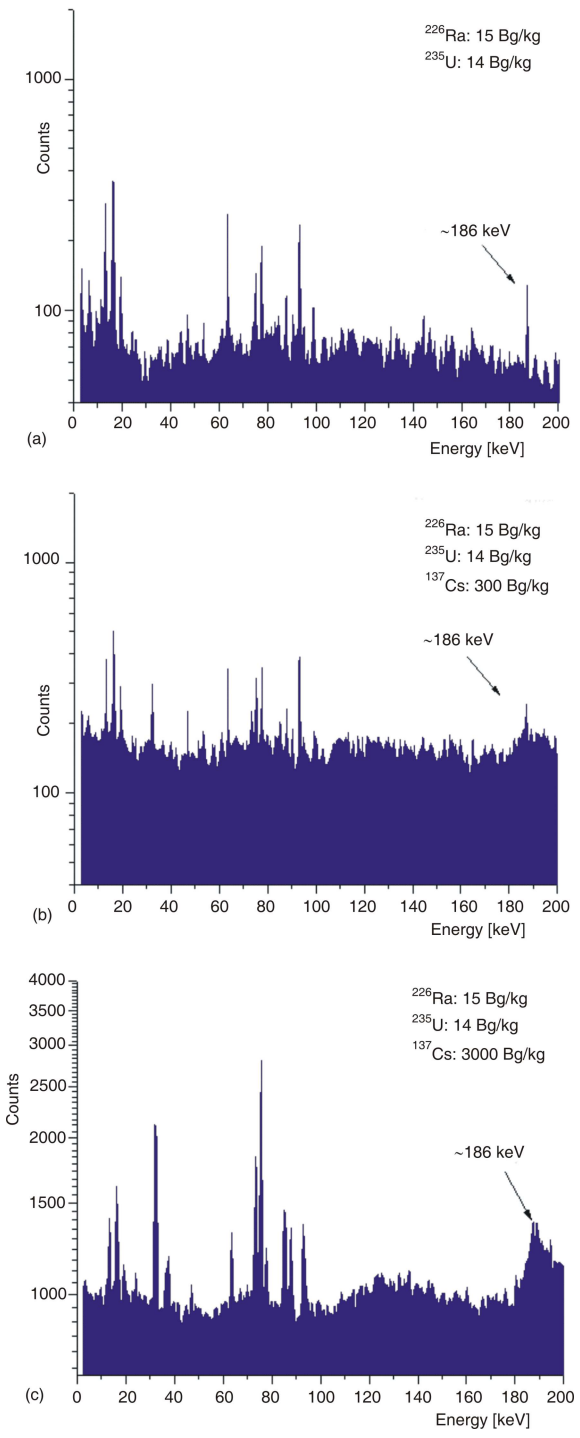

Figure 3. Examples of constructed test spectra: (a) test spectrum of the first series containing 15 Bq/kg ^{226}Ra and 14 Bq/kg ^{235}U, (b) test spectrum of the second series containing 15 Bq/kg ^{226}Ra, 14 Bq/kg ^{235}U, and 300 Bq/kg 137Cs, and (c) test spectrum of the second series containing 15 Bq/kg 226Ra, 14 Bq/kg ^{235}U, and 3000 Bq/kg ^{137}Cs

them. As an example it offers to the user the possibility to intervene in the peak location procedure performed automatically by the program, deleting or adding photopeaks in the analysis. This operation was used in this work for the analysis of the test spectra. More details on the ANGES operations can be found in [10, 11].

RESULTS AND DISCUSSION

After the analysis of each test spectrum, the peak area values and the corresponding uncertainties of the two components of the multiplet photopeak were collected. These values were compared with the theoretically expected values. For this purpose, the U-value (U) and relative bias (Rb) for each component were calculated by using eqs. 2 and 3, respectively,

$$U \quad \frac{Area_i \quad Area_{\text{ref}}}{\sqrt{Unc_i^2 \quad Unc_{\text{ref}}^2}} \tag{2}$$

$$Rb \quad \frac{Area_i \quad Area_{\text{ref}}}{Area_{\text{ref}}} \tag{3}$$

where $Area_i$ is the area of each component of the multiplet photopeak as defined by the software used, Unc_i – the uncertainty of the $Area_i$ as defined by the software used, $Area_{\text{ref}}$ – the theoretically expected value of the area of each component of the multiplet photopeak, and Unc_{ref} – the uncertainty of the $Area_{\text{ref}}$. For its calculation, the standard deviation of repeated measurements of the sources used for the construction of the equivalent spectra was estimated.

The following criteria were then applied to the analysis of each component:

– for |U| 1.96 (U-test, 95% confidence level): if |Rb| 10%, the analysis was considered accepted, and if |Rb| > 10%, the analysis was considered not accepted.

In this way, it was possible to reject results where the U-test was satisfied due to the big uncertainties of the measurement, despite the fact that the measurement values were significantly different (|Rb|>10%) from the theoretically accepted ones. This situation was mostly encountered in spectra with poor statistics, and

– for |U| > 1.96 (U-test, 95% confidence level): if |Rb| 5%, the analysis was considered accepted, and if |Rb| > 5%, the analysis was considered not accepted.

In this way, it was possible to accept results where the U-test was not satisfied, due to low uncertainties, while the measurement values did not differ significantly from the theoretically expected values. These cases mainly correspond to spectra with good statistics.

A result was considered as accepted, when the analysis of both components was judged as accepted. Analyses in which one or both components were not detected were rejected.

^{226}Ra [Bq/kg]	^{235}U/^{226}Ra area ratio						
	10%	50%	75%	100%	150%	300%	1000%
15	0%	0%	25%	0%	0%	0%	0%
30	0%	0%	0%	50%	0%	50%	25%
100	0%	100%	100%	75%	100%	100%	25%
300	0%	25%	100%	100%	75%	100%	75%
1000	25%	100%	100%	100%	100%	100%	50%

Figure 4. First test spectra series results – SPUNAL

^{226}Ra [Bq/kg]	^{235}U/^{226}Ra area ratio						
	10%	50%	75%	100%	150%	300%	1000%
15	0%	0%	75%	50%	25%	0%	0%
30	0%	50%	0%	25%	25%	0%	0%
100	0%	0%	75%	50%	0%	0%	0%
300	0%	0%	0%	50%	0%	0%	0%
1000	0%	0%	0%	25%	0%	0%	0%

Figure 5. First test spectra series results – ANGES automated analysis

Analysis of the first test spectra series results

Figures 4 and 5 illustrate the results of the analysis of the first test spectra series with the SPUNAL code and the ANGES program, respectively. As four spectra were analyzed for each ^{235}U-^{226}Ra combination, the percentage of accepted analyses is presented in each square of figs. 4 and 5.

The number of accepted analyses in the case of SPUNAL is 48.6%, while in the case of ANGES it is 12.9%. It should be noted however that the ANGES results correspond to the automated analysis mode, with no user intervention in the in the analysis. To examine the effect of user intervention, the analyses of this series test spectra with the ANGES program were repeated. This time the program was forced (by the user) to detect two components in the energy region of ~186 keV in cases that this was not achieved automatically. Figure 6 illustrates the results of these analyses.

The percentage of the accepted analyses in this case is 63.6%. This difference should be attributed to the user's intervention in the analysis. From figs. 4 and 6 it can be seen that the most accepted analyses correspond to spectra with higher photopeak areas and to spectra that the area ratio is neither big nor small enough.

^{226}Ra [Bq/kg]	^{235}U/^{226}Ra area ratio						
	10%	50%	75%	100%	150%	300%	1000%
15	0%	50%	100%	75%	50%	0%	50%
30	0%	50%	50%	75%	100%	50%	25%
100	25%	75%	75%	75%	75%	75%	0%
300	25%	100%	100%	100%	100%	100%	50%
1000	75%	100%	100%	100%	100%	100%	0%

Figure 6. First test spectra series results – ANGES with user's intervention

An interesting region in figs. 4 and 6 is bounded by the 100-1000 Bq/kg ^{226}Ra activity concentration and the 50%-300% ^{235}U/^{226}Ra photopeak area ratio. Most of the accepted analyses are concentrated in this region. This region corresponds to the most common ^{226}Ra-^{235}U combinations to be found in environmental samples, among those examined in this work. The percentages of accepted analyses in this region for both programs are equal to 91.7%. However, in the case of the SPUNAL code, rejected analyses are attributed to the fact that one of the components, usually the one with the lowest photopeak area, was not detected. In other words, whenever the SPUNAL code detected both components of the multiplet photopeak, the analysis was performed in an accepted way. On the other hand, between the rejected analyses of the ANGES program, there are cases in which both components have been detected but one or both corresponding areas significantly differ from the theoretically expected values. In this case there is no indication warning the user for an erroneous analysis.

As it was mentioned in Test spectra construction, for each ^{226}Ra-^{235}U combination, four independent test spectra were constructed. Figures 4-6 indicate that not all the analyses of the same ^{226}Ra-^{235}U combinations lead to accepted results. In terms of real samples, this means that, if initial analysis of the sample dos not yield results, deconvolution of the multiplet photopeak may be successful after repeated analyses of the sample.

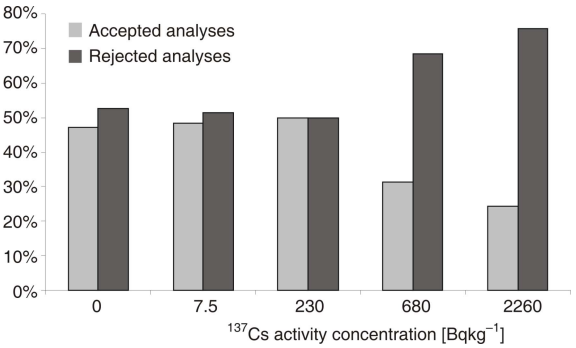

Figure 7. Second test spectra series results – SPUNAL

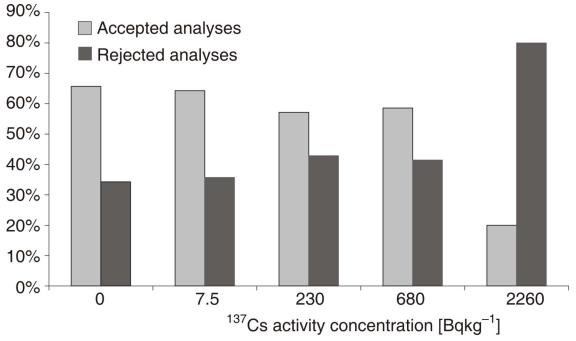

Figure 8. Second test spectra series results – ANGES

Analysis of the second test spectra series results

Figures 7 and 8 illustrate the results of the analysis of the second test spectra series with SPUNAL and ANGES respectively. Based on the conclusions of the automated analysis of first series spectra, ANGES analysis was performed with user intervention. Figures 7 and 8 present the percentage of accepted and rejected analyses, for the four ^{137}Cs activity concentration levels.

The effect of the ^{137}Cs presence in the deconvolution of the multiplet photopeak at ~186 keV is clear. The analysis becomes more difficult as the background continuum in the energy region of 186 keV increases, due to the presence of the ^{137}Cs backscatter edge. In the case of the SPUNAL code the percentage of accepted analyses remains practically unchanged provided that ^{137}Cs activity concentration is less than 230 Bq/kg. After this concentration level, there is a profound decrease at the percentage of accepted analyses. A similar effect, but for a higher ^{137}Cs activity concentration level (680 Bq/kg) is observed in the ANGES results. The user's intervention may again have a positive effect in ANGES analysis.

CONCLUSIONS

During this work, two series of test spectra were constructed for testing the ability of a gamma spectrometry computer code to deconvolute the multiplet photopeak at ~186 keV due to the presence of ^{235}U and ^{226}Ra in environmental samples. Two different computer codes were tested. The in house developed code SPUNAL and the freely available program ANGES. In each sample of the two series, different ^{235}U-^{226}Ra and ^{235}U-^{226}Ra-^{137}Cs combinations were examined, respectively. Each combination is examined more than one time, simulating multiplet analyses of the same sample and testing the repeatability of the analysis.

From the analysis of the two series it was concluded that, even if initial analysis is not successful, with repeated analyses of the same sample the deconvolution of the multiplet photopeak may finally succeed. The deconvolution depends on the ^{235}U and ^{226}Ra concentration in the sample and the presence of ^{137}Cs in it. More specifically, the number of successful analyses increases with the increase of the isotopes concentration in the samples and is more probable when the ratio of the photopeak area of the two components is neither too high nor too low. The increase of ^{137}Cs concentration makes the deconvolution of the multiplet photopeak more difficult as the ^{137}Cs backscatter photons increase the background continuum at the 186 keV energy region.

The ANGES program successfully analyzed more test spectra in both series, provided that the user intervenes in the analysis, forcing the program to detect the two components. However, for typical ^{235}U and ^{226}Ra environmental concentrations the two codes appear to have similar behavior. For these concentrations the SPUNAL code was found to be more reliable, as incorrect analysis can often be identified by the fact that one of the two components is not detected.

AUTHOR CONTRIBUTIONS

Theoretical analysis was carried out by K. L. Karfopoulos and M. J. Anagnostakis and experiments were carried out by K. L. Karfopoulos and D. J. Karangelos. The manuscript was written and the figures were prepared by K. L. Karfopoulos with the valuable contribution of all the authors.

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Received on September 25, 2013
Accepted on May 23, 2014

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ЕКСПЕРИМЕНТАЛНО КОНСТРУИСАЊЕ ТЕСТ СПЕКТАРА ЗА ПРОЦЕНУ ГАМА-СПЕКТРОМЕТРИЈСКИХ РАЧУНАРСКИХ КОДОВА ЗА ОДРЕЂИВАЊЕ ^{235}U

Одређивање ^{235}U у узорцима из природне средине преко његових фотона енергије 185.72 keV може захтевати деконволуцију мултиплет фотопика на енергији од око 186 keV, услед постојања и фотона ^{226}Ra енергије 186.25 keV у спектру. Успешност деконволуције зависи од више параметара, као што су карактеристике детектора, концентрација активности ^{235}U и ^{226}Ra у узорку, позадинско зрачење у области енергије од 186 keV и програмски код за гама-спектрометрију.

У овом раду пројектоване су две серије експерименталних тест спектара за проучавање деконволуције мултиплет фотопика различитим програмским кодовима. За конструкцију тест спектра коришћен је нискоенергетски германијумски детектор високе резолуције. Прва серија састоји се од 140 спектара и симулира узорке из животне средине који садрже различите нивое концентрације активности ^{235}U и ^{226}Ra. Друга серија састоји се од 280 спектара са придодатим ^{137}Cs, одговарајући различитим нивоима концентрације активности специфичних спектара из прве серије. Будући да је у области енергије мултиплет фотопика од 186 keV детектована доња граница расејања ^{137}Cs, другом серијом тест епектара анализиран је мултиплет фотопик у условима повишеног нивоа позадинског зрачења.

Проучавање тест спектара обављено је помоћу два програмска кода за гама-спектрометријску анализу: (а) програмског кода оригинално развијеног на UNIX систему и (б) програмског кода бесплатно доступног од стране IAEA за анализу спектара германијумског детектора. Резултати добијени овим програмским кодовима упоређивани су на детекцију фотопика и на одређивање области фотопика.

Кључне речи: гама-спектрометрија, тест спектар, мултиплет фотопик, ^{238}U