PROCESSING OF COMPLEX ALPHA SPECTRA MEASURED USING LSC, PIPS, AND OTHER SPECTROMETERS

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ABSTRACT. This paper is devoted to the problem of radionuclide identification in multilabel samples by mathematically decoding the complex alpha spectra measured using liquid scintillation (LS), PIPS, and other alpha spectrometers. An algorithm is proposed that models the sample spectrum using elementary spectra of individual radionuclides. Each energy line of the radionuclide is modeled by a function representing a combination of asymmetric normal distribution, exponent and hyperbole, connected by the condition of the continuity of the function and its derivative. The algorithm is based on the minimization of the function characterizing the deviation between the model and the apparatus spectra. This minimization is carried out by a nonlinear optimization algorithm based on the exact penalty function method. We discuss the problems that have arisen when implementing the algorithm, and we propose methods for solving these problems. We also present methods for performing the correct estimation and minimization of measurement uncertainties. On the basis of this algorithm, the software SpectraDecAlpha was developed. This software allows for automatic, continuous processing of complex spectra, including spectra with poor statistics, bad resolution, and a high degree of overlapping. The areas of application include rapid analysis of radionuclide content in ecological and technological samples, processing of spectra of radiochemically separated fractions, precise determination of isotopic ratios in industrial uranium- and plutonium-containing materials, and many more. Some practical results of applying this software to decode the complex spectra are reported.

INTRODUCTION

When conducting radioecological monitoring, a major problem is the correct interpretation of the the α-β spectrometric measurements. If current methods for deconvoluting the γ spectra are investigated thoroughly, then in many cases it becomes clear that when deconvoluting the α spectra, and especially β spectra, the results are inadequate to fully map the radionuclide composition. This is mainly a consequence of overlapping the spectral contributions of the various radionuclides present in the sample. Examination of the algorithms and software has shown that it is nearly impossible to correctly decode the complex spectra using previous algorithms and software; therefore, we need to find a solution to this problem.

Our approach to decoding β spectra of liquid scintillation (LS) spectrometers and their realization are presented in the literature (Kashirin et al. 2000; Ermakov et al. 2002; Malinovsky 2002a,b). The increased precision requirements for analyses have led to the need for developing similar algorithms and software for decoding α spectra.

METHODS

Statement of the Problem

The deconvolution of LSC and PIPS spectra, as well as LS counting (LSC) spectra, is carried out by modeling the sample's apparatus spectrum (P_i) by elementary spectra of individual radionuclides. The model spectrum is created as a linear combination of the normalized spectra of individual radionuclides:

$$M_i = \sum_{j=1}^{J} c_j M_{ij}, \; i = 1, 2, \ldots N$$

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where M_i is the model spectrum, $M_{i,j}$ is the spectrum of the individual nuclide j, c_j is the proportion of radionuclide j in the model spectrum, and N is the number of channels. The c_j coefficients and the shape of the spectra of individual radionuclides are adjusted to get a model spectrum as close as possible to the experimental one.

Spectra of Individual Radionuclides

The spectrum of each radionuclide is represented as the sum of the separate energy lines E_{jl}:

$$M_{ij} = \sum_{l=1}^{L} \nu_{jl} G(i, E_{jl}) \tag{1}$$

where ν_l is the intensity of the energy line, L is the number of the energy line, and $G(i,E_{jl})$ is the function describing the energy line.

In the most cases, each energy line of a radionuclide is modeled by a function representing a combination of asymmetric normal distribution, exponent and hyperbole, connected by the condition of the continuity of the function and its derivative:

$$G(i, E_{jl}) = H\begin{cases} e^{-\frac{(i-\mu)^2}{2\sigma_2^2}}, \mu < i \\ e^{-\frac{(i-\mu)^2}{2\sigma_1^2}}, \mu - d_1 < i < \mu \\ e^{\frac{d_1(2i - 2\mu + d_1)}{2\sigma_1^2}}, \mu - d_2 < i < \mu - d_1 \\ e^{-\frac{d_1(2d_2 - d_1)}{2\sigma_1^2}} \left(\frac{a}{b-i}\right)^r, i < \mu - d_2 \end{cases} \tag{2}$$

where $\mu = k_0 + k_1 E_{jl} + k_2 E_{jl}^2 + k_3 E_{jl}^3$;

$$H = 1/\left(\sum_i G(i, E_{jl})\right);$$

$a = r\sigma_1^2/d_1$; $b = \mu + a - d_2$; μ, σ_1, σ_2, d_1, d_2, a, and r are parameters of the function; and k_0, k_1, k_2, and k_3 are coefficients of energy calibration. The function above can describe correctly not only an upper part of peak, but also its tail.

For individual spectrometers, the number of terms in the function can be less. For example, the spectrum of a single line in many LS spectrometers is modeled only by a normal distribution:

$$G(i, E) = \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{(i-\mu)^2}{2\sigma^2}} \tag{3}$$

where the μ and σ depend on the energy of the particle and the quench of the sample.

Minimization Algorithm

To solve the problem above, we must use the weighted least-squares method as well as the exact penalty function, which consists of the minimization of the "loss function" (Malinovsky et al. 2002a,b). Calculation of the contributions (c_j) and the parameters of the function (Equation 2) and correction of coefficients of energy calibration is carried out simultaneously during the minimization. Restrictions on the stability of the energy calibration and on the parameters of the modeling function, which depend on the quality of the spectrometer and of the sample preparation, are similarly added to the penalty function. Shor's r-algorithm (Kappel and Kuntsevich 2000), which realizes one of the variant gradient methods of optimization, is used to minimize the loss function.

Considering the Conversion Electrons

To correctly analyze the α spectra, it is necessary to consider the influence of internal conversion electrons on the shape of the spectrum. The probability of detecting the alpha particle and the conversion electron in coincidence increases when the detection solid angle is high (i.e. when the source is close to the detector). This causes a distortion of the spectrum shape.

The smaller the source-detector distance, the more dramatic the effect. The model spectrum (Figure 2a) shows what should be a ^{236}U spectrum without conversion electrons. When executing routine analyses, strict calculation of all conversion junctions for each radionuclide is inefficient. The conversion junction is related to the greater size of the preliminary investigations influencing the conversion spectra shape and to the much greater size of computations due to the increase in the number of radionuclide energy lines. As a consequence, more time is needed to decode each spectrum, complicating the computation automation and increasing of the measurement error.

Empirical investigations suggest a simple method to take into account the effect of conversion electrons for the majority of usual radionuclides ($^{232(4,6,8)}$U, $^{238(39,40)}$Pu, ^{x}Ra, ^{x}Th, etc.). If the decay path with the greatest intensity goes to the ground level (even-even nucleus, e.g ^{236}U in Figure 1), the distortion of the spectrum is compensated by a decrease in a part of the minor lines and their displacement in the higher energy area (Figure 2).

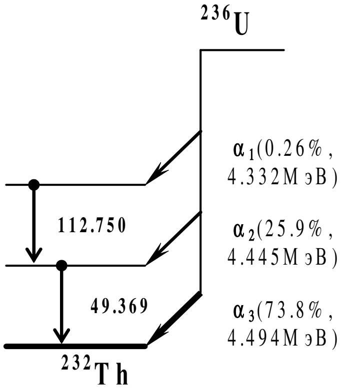

Figure 1 Decay scheme ^{236}U

The use of this method has considerably improved the quality of the decoded spectra (Figure 2b). Nevertheless, there are radionuclides, such as ^{241}Am, ^{243}Am, ^{235}U, for which this method is inaccurate. These are radionuclides for which the decay path of greatest intensity does not go to the ground

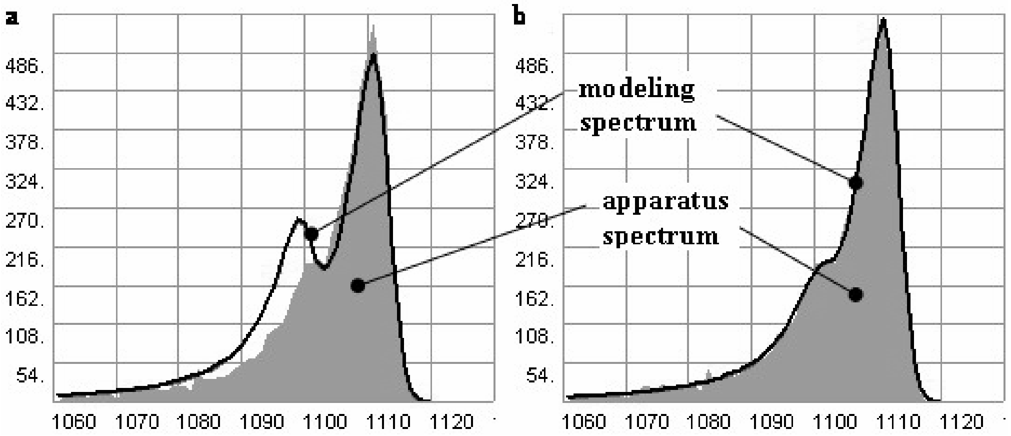

Figure 2 Spectra deconvolution of ^{236}U without (a) and with (b) taking into account conversion electrons

level (odd-even nucleon transitions). These are relatively rare and calculation of the conversion contribution is not difficult. To account for conversion in this case, we employ the following (see e.g. ^{243}Am, Figure 3). Based on a decay scheme, a spectrum is constructed for an additional (fictitious) radionuclide $^{243}Am^{ce}$, assuming 100% detection efficiency of the conversion electrons. Its spectrum has more energy lines than a spectrum of ^{243}Am (Table 1). Further, this radionuclide ($^{243}Am^{ce}$) together with ^{243}Am take part in decoding the spectrum, and its calculated activity is then added to the calculated activity of ^{243}Am.

Table 1 Spectrum of $^{243}Am^{ce}$, assuming 100% detection efficiency of the conversion electrons.

E (keV)	5348	5344	5336	5327	5313	5303	5296	5284	5275	5254	5242	5206
I (%)	4.4	1.75	3	12	6.8	2.6	15.82	12.07	24	12.8	4.28	0.48

As an example, the spectra of ^{243}Am measured at different distances between the detector and a source and their decoding on the specified method are shown in Figure 4.

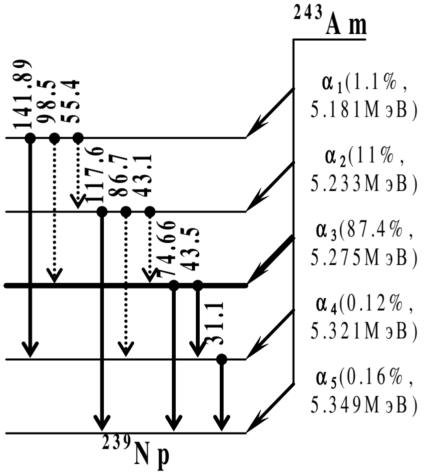

Figure 3 Decay scheme of ^{243}Am

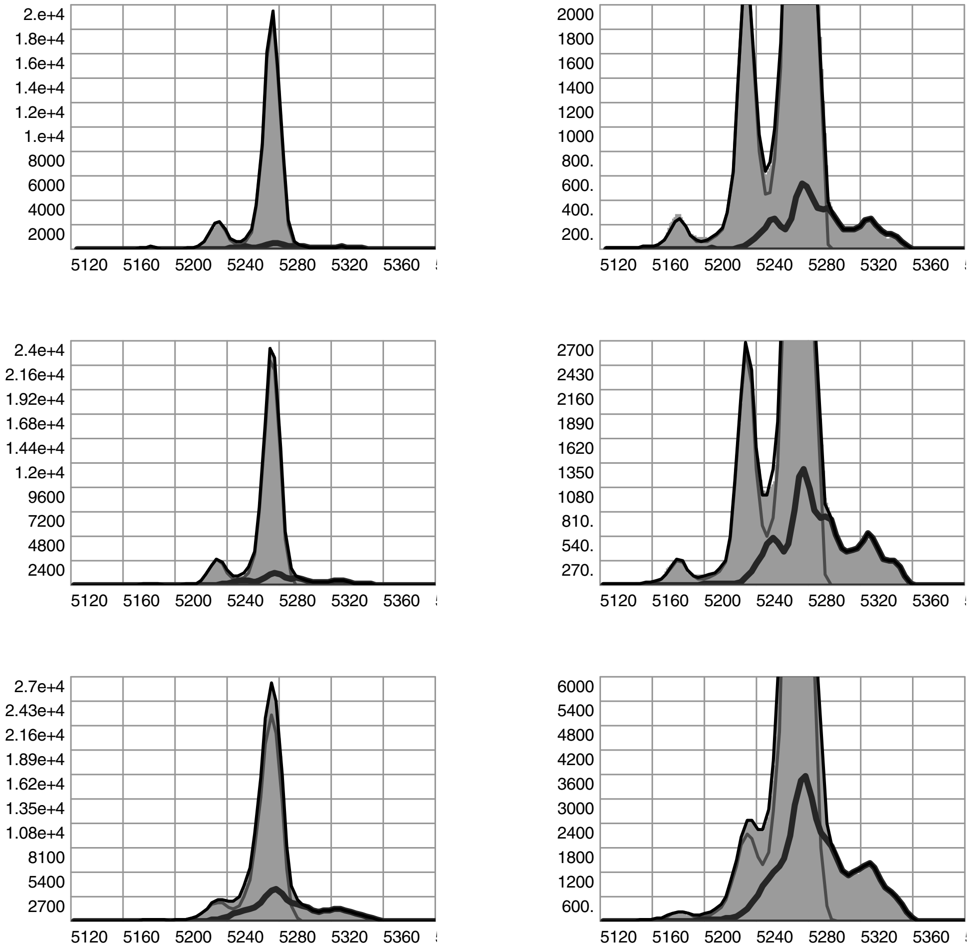

Figure 4 Spectra of ^{243}Am at different distances between the sample and the detector (13 mm - upper graph; 9 mm - middle graph; 5 mm - lower graph). The graphs on the right are enlarged. An Ultra Alpha Detector BU-012-150-500 and evaporation source were used. Gray shading - the measured spectrum; dark, thin line - the full model spectrum; thick, dark line - the part of a spectrum modified by the conversion electrons; light, thin line - unmodified part of the spectrum.

Final Result, Uncertainty, and Optimization of Uncertainty

The final content (activity) of individual radionuclides is calculated using the following formula:

$$A_j = \frac{(N - N_{bkg}) \times c_j}{t\varepsilon_j} = \frac{N_j}{t\varepsilon_j} = \frac{N - N_{bkg}}{t\varepsilon_j},\ j = 1, 2 \ldots J \tag{8}$$

where t is the measuring time; c_j is the contribution of the j-th isotope to the integrated spectrum counts; ε_j is the counting efficiency for the j-th isotope; N is the total counts integrated over all channels; N_{bkg} is the background counts integrated over all channels; N_j is the counts relating to the j-th radionuclide; and $N_{bkgj} = N - N_j$ is the total integral account of all radionuclides in the sample, including the background, after subtraction of the j-th radionuclide.

The combined standard uncertainty is thus:

$$\frac{u_c(A_j)}{A_j} = \sqrt{\left(\frac{u_c(N_j)}{N_j}\right)^2 + \left(\frac{u(\varepsilon_j)}{\varepsilon_j}\right)^2} \tag{9}$$

The uncertainty of the deconvolution process is set to be neglected in the software, hence:

$$u(N_j) = \sqrt{u(N)^2 + u(N_{bkg})^2} = \sqrt{N + N_{bkg}} = \sqrt{N + N - N_j} = \sqrt{2N - N_j}$$

In addition, for each radionuclide the optimized uncertainty is calculated. Optimization (Figure 5) consists of choosing a bounded channel region for which the statistical component of relative uncertainty (Equation 10) will be minimal:

$$\frac{u(N_j)}{N_j} = \frac{\sqrt{2N^{opt} - N_j^{opt}}}{N_j^{opt}} \tag{10}$$

where N^{opt}, N_{bkg}^{opt} are the count in the optimized bounded region of the sample and the background, respectively, and $N_j^{opt} = (N^{opt} - N_{bkg}^{opt}) \times c_j$ are the contributions of determined nuclide to the count of the sample in the bounded region.

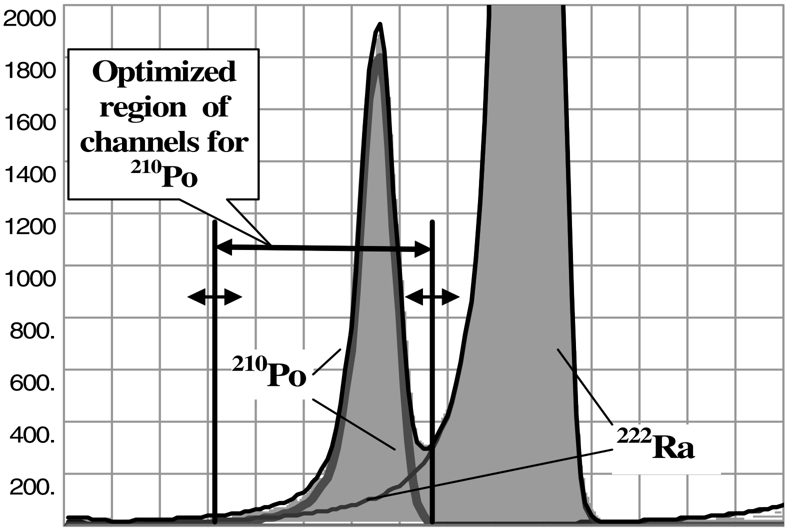

Figure 5 Illustration of optimization of uncertainty

REALIZATION

The proposed methods and algorithms are realized in the software SpectraDecAlpha. This software allows analysts to automatically process difficult spectra, including spectra with small statistics, with very good or very bad resolution, or with a high degree of imposing contributions from separate isotopes against each other. The complex can be used on a semiconductor, liquid scintillations, ionization, and any other alpha spectrometers. This method can be used to quickly analyze the isotope contents in ecological and technological samples, to process spectra of radiochemical fractions, to define the relative isotope composition in industrial uranium and plutonium, and many more applications. The program is written usingthe Microsoft® Visual Studio.Net® 7.1 development system and operates under Windows® 98/ME/NT/2000/XP/2003.

Examples of Use

By using the proposed approach for decoding α spectra, one can considerably simplify and increase the accuracy of many radiation measurements. The following are some examples that illustrate how the program works.

1. Definition of the isotope contents in the plutonium fraction of sample IAEA-784 after radiochemistry (Figure 6, Table 2).

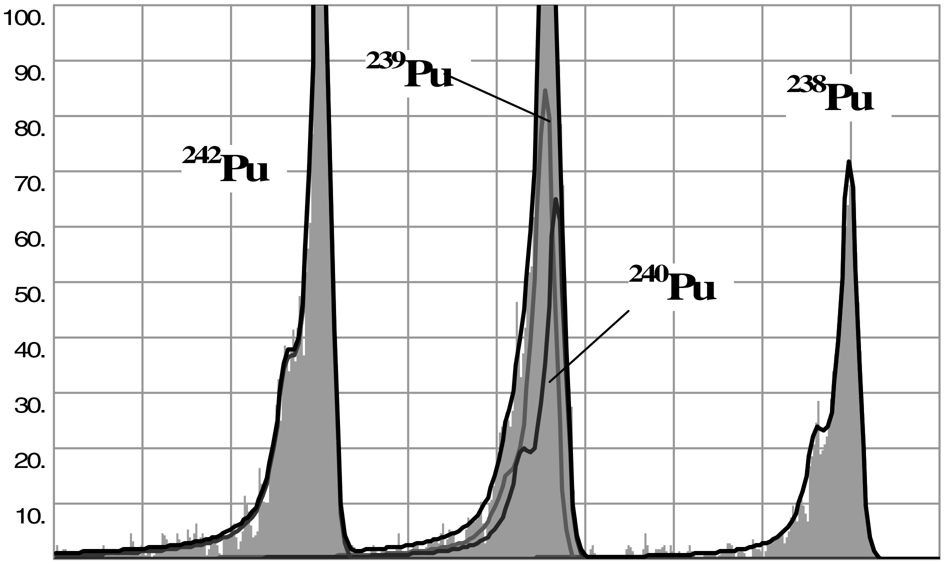

Figure 6 Definition of the isotope contents in the Pu fraction of sample IAEA-784

Table 2 Isotopic composition of sample IAEA-784 (Shakhashiro et al. 2005).

	Activity (Bq)			
	Obtained results		IAEA data	
^{242}Pu	0.209 ± 0.012 (tracer)			
^{238}Pu	0.114 ± 0.05		0.114 ± 0.023	
^{239}Pu	0.132 ± 0.015	0.239 ± 0.009 (sum)	0.144 ± 0.003	0.244 ± 0.005 (sum)
^{240}Pu	0.107 ± 0.015		0.100 ± 0.002	

The detection system consists of an Alpha spectrometer model 7401 (Canberra, Inc.) with PIPS detectors (600 mm^2), an ADC/mixer-router 1510, and a PC-based MCA S-100. The detector type and producer are PD-600-22-100 (Canberra-Nuclear). Distance to the detector surface is 3 mm.

Radiochemistry preparation includes chromatographic separation and purification of Pu in a column containing Dowex 1×4 (200–400 mesh) via 7.5M HNO_3 and 9M HCl, plutonium stabilization in Pu(IV) state, and extraction purification via 0.2M TTA solution in toluene, then electroplating plutonium from ammonia oxalate-chloride solution onto stainless discs. A characteristic feature of this method is the ability of the software to define the contents of all isotopes of plutonium, automatically separating ^{239}Pu and ^{240}Pu.

2. Decoding the spectrum of the sample of industrial uranium (Figure 7, Table 3). Here, it is essential that isotopes of uranium, together with daughter radionuclides and impurities (despite an essential overlap of their spectra) are all simultaneously defined. Comparison with mass-spectrometry measurements shows good agreement in the results.

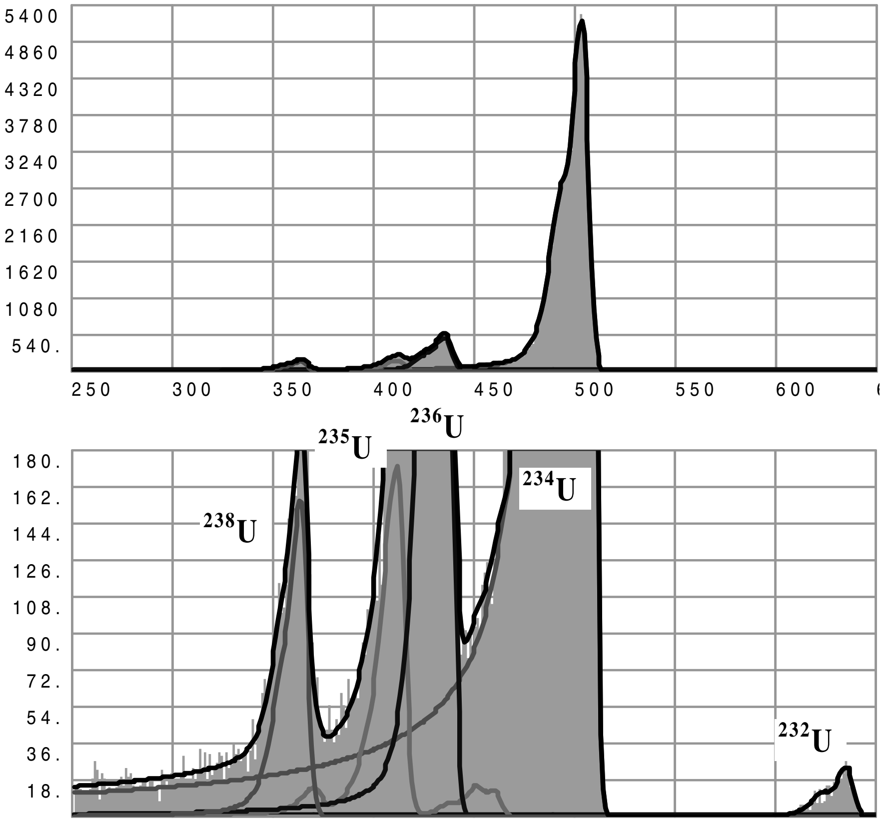

Figure 7 Decoding the spectrum of the industrial uranium sample

Table 3 Decoding the spectrum of a sample of industrial uranium.

	Abundance (% mass U)	
Isotope	Alpha spectrometry	Mass spectrometry
^{232}U	(2.2 ± 0.2) × 10^{-7}	—
^{234}U	0.157 ± 0.001	0.16 ± 0.05
^{235}U	17.4 ± 1.0	17.0 ± 0.2
^{236}U	1.46 ± 0.05	1.41 ± 0.06
^{238}U	81 ± 5	81.4 ± 0.2

3. Comparison of the decoding results of the test sample, measured in an ionization chamber, with and without taking into account the conversion effect (Figure 8, Table 4). Evidently, the inat-

tention to conversion electrons can often increase the measurement error, to the point where it would be impossible to define some isotopes in complex samples.

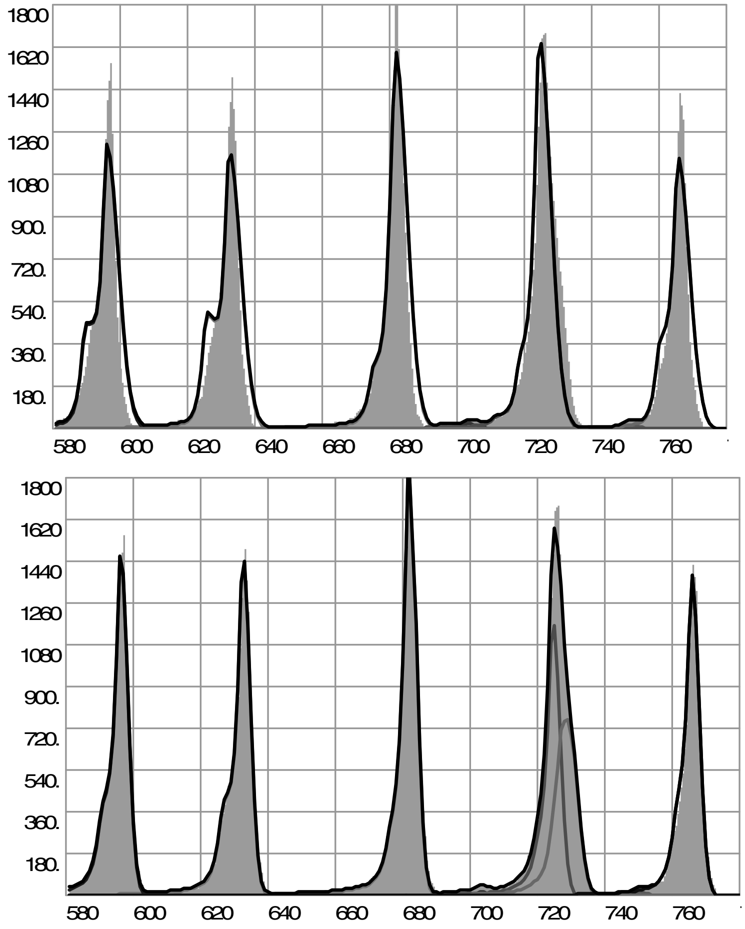

Figure 8 Decoding of the test sample, measured in an ionization chamber (above) and without account for the conversion effect (below).

Table 4 Decoding the spectrum of the sample of industrial uranium.

	Activity (Bq)			
Isotope	CE[a]	Without CE	2 σ (%)	Deviation (%)
^{224}Ra	0.26	0.42	55	62
^{226}Th	0.10	0.12	78	15
^{232}U	0.40	0.71	39	77
^{234}U	27	30	2	10
^{236}U	26	29	2	9
^{239}Pu	32	35	2	7
^{241}Am	39	36	2	9
^{244}Cm	25	27	2	8

[a] CE = conversion effect.

CONCLUSION

The proposed approach to α spectrometry makes it possible to determine the radionuclide composition of complex mixtures, irrespective of spectra quality. The proposed methods and algorithms are realized in software comprehensively tested on various spectrometers, including LS counters, PIPS detectors, ionization chambers, and others.

In particular, this method has produced good results in the Proficiency Test of the Analytical Laboratories for the Measurement of Environmental Radioactivity (ALMERA; Shakhashiro et al. 2005). At present, this software is the basic tool for decoding alpha spectra in the SIA Radon lab and at some nuclear power stations and radiochemical combines of Russia.

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