

# DETERMINATION OF RADIONUCLIDE IMPURITIES IN PURE BETA RADIATION SOURCES BY SEMICONDUCTOR SPECTROMETRY

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**ABSTRACT.** In many applications, the radionuclidic purity of a radioactive substance is a crucial property. It involves, for example, the production of radiopharmaceuticals or reference standards used in metrology. However, the identification of admixtures is not straightforward for certain nuclides. The paper presents a technique for the determination of radionuclide impurities in the mixtures of pure beta-emitting nuclides. The proposed method is based on the comparison of measured beta spectra with the detector responses to individual radionuclides. These are obtained using a Monte Carlo calculation performed in the geometry corresponding to the accurate description of a measuring assembly.

**KEYWORDS:** Beta spectrometry, Monte Carlo simulation, Si(Li) detector.

## 1. INTRODUCTION

Beta-decaying radionuclides are used as sources of ionizing radiation in various industrial, medical, and scientific applications. In many of them, the key parameter of a radioactive substance is its radionuclidic purity, i.e. the absence of other radionuclides in the source. Usually, most of the potential impurities can be determined by gamma spectrometry. However, this analytical tool is not applicable if both the nuclide of interest and an admixture are pure beta radiation sources, i.e. no gamma ray is emitted. In addition, the impurity may be an isotope of the same element as the main nuclide, which precludes the use of any chemical analytical method.

The proposal of a method for the identification and quantification of radionuclide impurities in the mixtures of pure beta-emitting nuclides was one of the objectives of the recently completed MetroBeta project, which was supported by the European Metrology Programme for Innovation and Research (EMPIR) [1]. The research focused on the measurement of beta radionuclides was performed by several European national metrology institutes.

One procedure for identifying radionuclides from a mixed beta spectrum has been proposed by [2]. The authors demonstrated the application of the spectrum stripping method for the deconvolution of spectra measured using a magnetic spectrometer. The spectra belonging to individual nuclides were described by a function defined by the formula as follows

$$\sum_{i=1}^8 a_i \sin(b_i E + c_i), \quad (1)$$

where  $E$  stands for the energy of radiation. The Equation (1) is empirical in nature, which means that it describes the spectra shape well from a mathematical

point of view, but it has no deeper physical meaning. The parameters  $a_i$ ,  $b_i$ , and  $c_i$  were obtained by fitting the experimental data. The method was tested for the analysis of mixed spectra of three radionuclides  $^{32}\text{P}$ ,  $^{90}\text{Y}$ , and  $^{106}\text{Rh}$  with different mixing ratios. The accuracy achieved in determining the radionuclide activity ratios was better than 2%.

A different approach to solving the discussed problem is offered by the following procedure [3]. The mixed beta spectrum measured is divided into several regions. Considering a mixture of three radionuclides A, B, and C, the count rate  $n_i$  in each spectrum region can be expressed as

$$n_i = \eta_i^A A_A + \eta_i^B A_B + \eta_i^C A_C, \quad (2)$$

where the symbol  $\eta$  denotes a detection efficiency. The desired activity values  $A$  are calculated by minimizing the expression representing the variance using the least square method.

The procedures employed for the analysis of mixed beta spectra in this study partially utilize the principles mentioned above. However, values obtained from a precise Monte Carlo simulation were used to express the response to each single radionuclide instead of an empirical function. More details are given in the following section of the paper.

## 2. INSTRUMENTATION AND METHODS

### 2.1. DETECTOR AND MONTE CARLO MODEL

Beta spectra were measured at the Czech Metrology Institute spectrometry laboratory using a spectrometric system equipped with a lithium-drifted silicon detector. The detector was thoroughly characterized; therefore, its Monte Carlo model prepared for the MCNPX code [4] was available. A detailed description of the detector, its characterization, and the

model validation have been published in [5]. The source term for beta spectra calculations was defined as a histogram of electron energies derived from the Fermi theory of beta decay. The simulated detector response to a given radionuclide was obtained using a pulse-height tally (type F8). The computation time of the simulations was chosen to achieve the relative type A uncertainty of the histogram bin values at the level of tenths of a per cent. The efficiency of calculations was improved by the variance reduction techniques (i.e. cell-by-cell energy cutoff and source biasing).

All studied samples were prepared by drop deposition [6]. The droplet of a radioactive solution<sup>1</sup> was deposited on a 0.1 mm thick polyethylene terephthalate foil. The solvent was subsequently evaporated, resulting in the formation of a thin radioactive layer.

## 2.2. TWO-WINDOW METHOD

Suppose that the measured beta spectrum is a combination of contributions from two radionuclides A and B which differ in their beta decay endpoint energy. As the first step of an analysis using this method, two windows (regions of interest) are defined in the spectrum as indicated in Figure 1. Events originating from the radioactive decay of both components of a mixture are registered in region No. 1, whereas the detector response in region No. 2 is caused only by the radionuclide with a higher endpoint energy.

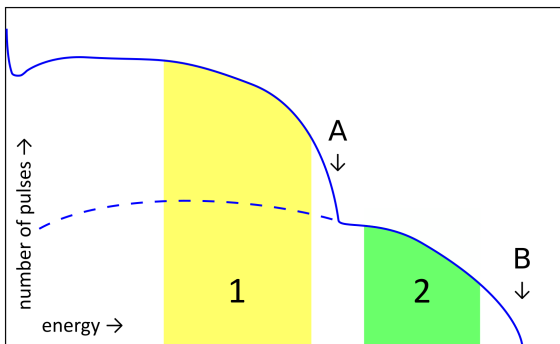


FIGURE 1. Illustration of the two-window method idea.

The following relations hold for the number of pulses  $N_1$  in region No. 1 and  $N_2$  in region No. 2

$$\begin{aligned} N_1 &= A_A \eta_1^A t + A_B \eta_1^B t, \\ N_2 &= A_B \eta_2^B t, \end{aligned} \quad (3)$$

where  $\eta_i$  stands for the detection efficiency in the  $i$ -th region of the spectrum for the radionuclide indicated by the superscript value and  $t$  is the live time of the measurement. By dividing the first expression in Equation (3) by the second one, a relation giving the ratio of radionuclide A and B activities is obtained

$$\frac{A_A}{A_B} = \frac{\eta_2^B}{\eta_1^A} \cdot \left( \frac{N_1}{N_2} - \frac{\eta_1^B}{\eta_2^B} \right). \quad (4)$$

<sup>1</sup>The aqueous solutions of  $\text{SrCl}_2$  (20 mg of  $\text{SrCl}_2$  per litre + 3 g of HCl per litre),  $\text{YCl}_3$  (50 mg of  $\text{YCl}_3$  per litre + 3 g of HCl per litre), and  $\text{H}_3\text{PO}_4$  (50 mg of  $\text{H}_3\text{PO}_4$  per litre) were used to prepare the samples analysed in this study.

The spectrum in Figure 1 corresponds to the situation where the endpoint energy value of an impurity is higher than the main nuclide endpoint. With a logarithmic scale on the vertical axis, its presence in a sample can be easily detected. On the other hand, if the impurity has an endpoint lower than the main nuclide, its identification may appear less clear, as the effect on the spectrum shape may not be visually apparent. Nevertheless, the procedure for the quantitative evaluation is identical for both variants.

## 2.3. SPECTRUM STRIPPING METHOD

An alternative approach to the analysis of pure beta radionuclide mixtures is the spectrum stripping method. Generally, this technique is based on the successive subtraction of the library spectra corresponding to individual nuclides present in a sample from the measured spectral response. The normalized library spectrum is subtracted channel by channel from the sample spectrum. This procedure proceeds from higher energies (i.e. for beta spectra from nuclides with a higher endpoint value) to lower ones.

When analysing a mixed beta spectrum using this method, one region of interest is defined at first. Its boundaries are chosen as follows. Considering the difficulties in modelling the detector response for low-energy electrons, it is advisable to choose the lower limit from approximately 500 keV upwards. The upper limit is restricted from above by the lowest value of an endpoint energy in the radionuclide mixture. In the selected region of interest, the integral of pulses is determined for both the measured and reference (i.e. admixture-free) spectra. For binary mixtures, the difference between these two values represents the number of pulses in the measured spectrum caused by the presence of an impurity in the sample  $N_I$ . The number of pulses corresponding to the main nuclide  $N_M$  is equal to the integral obtained from the reference spectrum. The activity ratio is then given by the following relation

$$\frac{A_I}{A_M} = \frac{N_I \eta^M}{N_M \eta^I} \quad (5)$$

with  $\eta^I$  and  $\eta^M$  being the detection efficiencies for radionuclides I and M respectively.

## 3. RESULTS

Both methods of spectra deconvolution described above in Sections 2.2 and 2.3 were tested on data from the measurement of samples with varying amounts of  $^{89}\text{Sr}$  and  $^{90}\text{Sr}$ . This mixture is commonly formed during the production of  $^{89}\text{Sr}$  radionuclide due to parasitic reactions [7]. The samples also contained  $^{90}\text{Y}$ , which is a radioactive decay product of  $^{90}\text{Sr}$ . As the parent nuclide has a much longer half-life than the daughter nuclide<sup>2</sup>, it can be assumed that secular (long-term) radioactive equilibrium between these

<sup>2</sup>The half-lives of radionuclides  $^{90}\text{Sr}$  and  $^{90}\text{Y}$  are 28.80(7) a and 2.6684(13) d respectively [8].

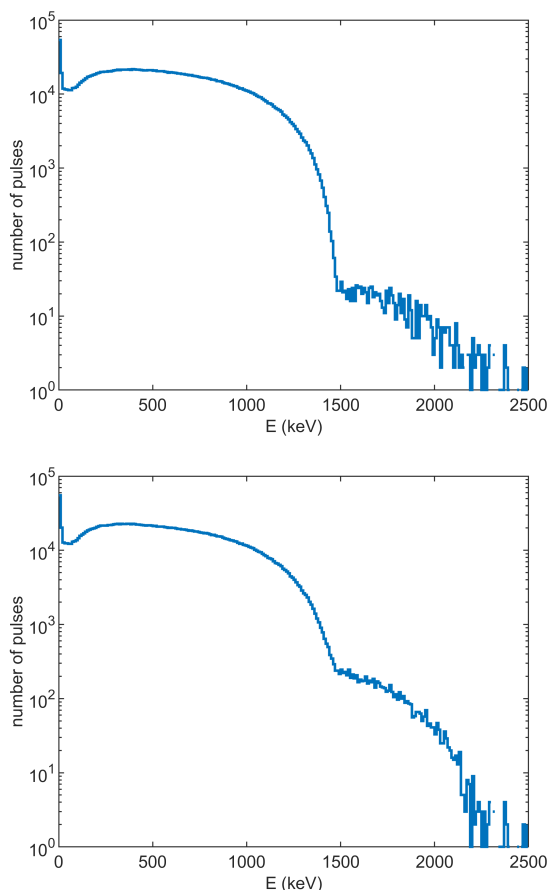


FIGURE 2. Beta spectra of  $^{89}\text{Sr}$  samples containing different amount of  $^{90}\text{Sr}/^{90}\text{Y}$  impurity (top 0.3 %, bottom 3.0 %).

nuclides was established in the sample. Therefore, the activity of  $^{90}\text{Sr}$  can be determined by the measurement of  $^{90}\text{Y}$ . Compared to  $^{89}\text{Sr}$ , the endpoint energy of  $^{90}\text{Y}$  is higher, which is favourable for the spectrum shape analysis because the high-energy part ( $> 500$  keV) of beta spectra is not significantly distorted by self-absorption [9].

### 3.1. TWO-WINDOW METHOD

The beta spectra of six samples were recorded using the Si(Li) detector. An example of two of these spectra is shown in Figure 2. The ratio of the  $^{90}\text{Sr}/^{90}\text{Y}$  impurity activity to the  $^{89}\text{Sr}$  main nuclide activity was calculated using Formula (4). The detection efficiencies were obtained from the Monte Carlo model of the detector. The regions of interest were defined in the energy range<sup>3</sup> of (700–1400) keV and (1500–1700) keV. The results obtained are summarized in Table 1. The standard uncertainty of the measured values was calculated as the uncertainty of an indirectly measured quantity (see [10]).

<sup>3</sup>The endpoint energy of  $^{90}\text{Sr}$  equals 549.5(14) keV [8]. It implies that the radionuclide does not contribute to the detector response in the selected regions of interest.

Declared [%]	Measured [%]
0.100(1)	0.15(1)
0.300(3)	0.35(2)
0.500(5)	0.52(2)
1.00(1)	1.04(3)
2.00(2)	2.07(4)
3.00(3)	3.08(5)

TABLE 1. Ratio of the  $^{90}\text{Sr}/^{90}\text{Y}$  impurity activity to the main nuclide  $^{89}\text{Sr}$  activity (two-window method).

A second set of samples was analysed in the same way. These samples were also composed of strontium isotopes; however,  $^{89}\text{Sr}$  was the impurity in  $^{90}\text{Sr}/^{90}\text{Y}$  in this case. The calculated activity ratios are summarized in Table 2.

Declared [%]	Measured [%]
1.00(1)	1.1(5)
2.00(2)	2.1(5)
5.00(5)	5.4(5)
8.00(8)	8.7(5)

TABLE 2. Ratio of the  $^{89}\text{Sr}$  impurity activity to the main nuclide  $^{90}\text{Sr}/^{90}\text{Y}$  activity (two-window method).

### 3.2. SPECTRUM STRIPPING METHOD

The spectrum stripping method was tested on four spectra corresponding to different concentrations of the  $^{89}\text{Sr}$  impurity in  $^{90}\text{Sr}/^{90}\text{Y}$ . An example of one measured spectrum compared with the response to a  $^{90}\text{Sr}/^{90}\text{Y}$  source of an older production date (i.e. virtually free of impurities<sup>4</sup>) is shown in Figure 3. The ratio of  $^{89}\text{Sr}$  to  $^{90}\text{Sr}$  activity was calculated according to formula (5), with  $^{90}\text{Sr}$  determined via  $^{90}\text{Y}$  (assuming radioactive equilibrium between these two nuclides). The evaluation was performed in the energy interval of 1000 to 1490 keV. A comparison of the measured values with the declared ones is shown in Table 3. The standard uncertainty of the results was calculated in accordance with the law of uncertainty propagation for an indirectly measured quantity [10].

Declared [%]	Measured [%]
1.00(1)	1.0(4)
2.00(2)	2.1(4)
5.00(5)	5.2(4)
8.00(8)	8.3(4)

TABLE 3. Ratio of the  $^{89}\text{Sr}$  impurity activity to the main nuclide  $^{90}\text{Sr}/^{90}\text{Y}$  activity (spectrum stripping method).

<sup>4</sup>The half-life of  $^{89}\text{Sr}$  is 50.57(3) d [11], whereas it is equal to 28.80(7) a for  $^{90}\text{Sr}$  [8].

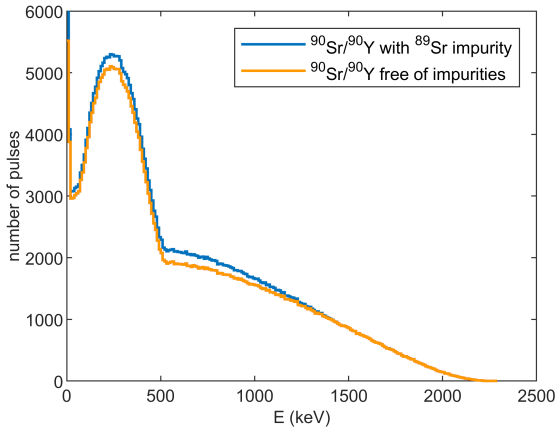


FIGURE 3. Beta spectra of two  $^{90}\text{Sr}/^{90}\text{Y}$  samples (with and without  $^{89}\text{Sr}$  impurity).

#### 4. DISCUSSION

Specifically, the spectra of mixtures consisting of  $^{89}\text{Sr}$  and  $^{90}\text{Sr}/^{90}\text{Y}$  nuclides in various ratios were studied. It is easier to analyse a mixed beta spectrum if the admixture has a higher endpoint energy value than the main nuclide. The presence of the impurity is well evident in the spectrum, even for low concentrations of the order of tenths of a per cent. The measured and the declared activity ratios of the impurity to the main nuclide agree within the uncertainty for values greater than 0.5 %. The results are slightly overestimated for the lower concentrations.

On the other hand, if the admixture endpoint energy is lower compared to the main nuclide, the analysis is more complicated. If only because the effect of the impurity on the spectrum shape is not obvious at first sight. Moreover, the typical achievable uncertainties are larger due to the subtraction of close values in Equation (4), which is used for the evaluation via the two-window method. The alternative evaluation of the same data set using the spectrum stripping technique provided slightly more accurate results (in terms of both measurement trueness and measurement precision). Either way, both mentioned methods allow the activity ratio to be determined only at a level of a few per cent under these conditions. Therefore, the sensitivity is about ten times lower in comparison with the situation mentioned in the previous paragraph.

Both proposed methods of beta spectra analysis are comparable in terms of instrumentation requirements or the complexity of calculations. However, the two-window method seems to be slightly more universal. The spectrum stripping method is not suitable when the impurity has a higher endpoint energy than the main nuclide because the response from the admixture in the high-energy part of the spectrum is low and its statistics is poor. This fact complicates the normalization of reference spectra, which is crucial for the correct calculation of the impurity concentration.

The advantage of the proposed method for the analysis of mixed beta spectra lies in its simplicity in terms of instrumentation. It requires only the equipment that is commonly available in radiometric laboratories. However, the results and the measurement repeatability are strongly dependent on the quality of measured samples. It is a limiting factor for the analysis of samples containing radionuclides with an endpoint energy value lower than circa 500 keV prepared by the universal drop deposition technique.

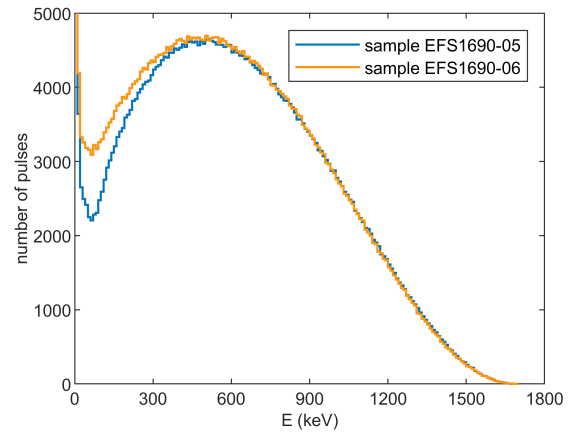


FIGURE 4. Beta spectra of two  $^{32}\text{P}$  samples of the same design.

The above-mentioned issue is demonstrated by the spectra in Figure 4. Both studied samples contained the same radionuclide  $^{32}\text{P}$  free of impurities and were of the same design. Nevertheless, the measured spectra differ significantly from each other in shape in the low-energy part. As a result of the crystallization, the radioactive layer formed is not homogeneous and its thickness varies locally [9]. Therefore, the level of self-absorption in the samples also varies, which influences the low-energy part of the beta spectra. Generally, there are two approaches how to overcome this limitation. The first relies on a change in the technology of samples production to improve their properties in terms of measurement repeatability. The second is based on the detailed characterization of each sample prepared by drop deposition, which is used to improve the accuracy of the Monte Carlo calculation of reference spectra. As part of the research on beta spectra metrology, the suitability of high-resolution X-ray fluorescence 2D scanning for this purpose was studied in detail and the results obtained have been presented in [12].

#### 5. CONCLUSION

The experiments performed showed that the analysis of beta spectra shape is a technique suitable for the quantification of radionuclide impurities. The method is promising, especially for the assay of mixtures consisting of pure beta minus emitters that are isotopes of one chemical element, i.e. other analytical tools,

such as gamma spectrometry or chemical analysis, are not applicable. The findings are of direct practical relevance, and the proposed method can be easily implemented in radiometric laboratories where the radionuclide purity of substances is determined.

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