

A New Procedure for Multiple Isotope Analysis in Liquid Scintillation Counting

A. Grau Carles and A. Grau Malonda

INTRODUCTION

Double and triple labeled radiative samples are interesting in biological tracing work. The procedures to obtain the activity of each one of the components in a multilabeled sample are: double or triple window measurements,¹ spectral shift by quench variation,² rate counting at different times,³ different counting methods,⁴ different decay modes.⁵

All these procedures are based on the counting rate of the whole or part of the pulse height spectra. It seems interesting to look for new counting procedures in order to overcome some of the very known restrictions. This procedure could be based on using the differential shape of the pulse height spectra.

The aim of this chapter is to develop a procedure, based on spectra fitting, that obtains the activity of each one of the radionuclides in the sample.

The procedure will be applied to mixtures of pure beta-ray emitters, $^3\text{H} + ^{14}\text{C}$, and $^{35}\text{S} + ^{14}\text{C}$. The application to other kinds of decay schemes is possible, but they will not be studied here.

A code named DILATA has been developed in order to compute the spectral components and activities of radionuclides mixtures. In this chapter, only the mathematical procedure will be described.

FITTING PROCEDURE

The spectral issue of a liquid scintillation counter for beta-ray emission depends on the quenching degree of the sample. Two of the eight ^{14}C spectra obtained with a logarithmic amplifier have been plotted in Figure 1. The shape and pulse height of the spectra depend very strongly on the quenching of the samples.

The first problem to be solved is how to obtain the spectrum which corresponds to a given quench level. A direct interpolation can not be applied

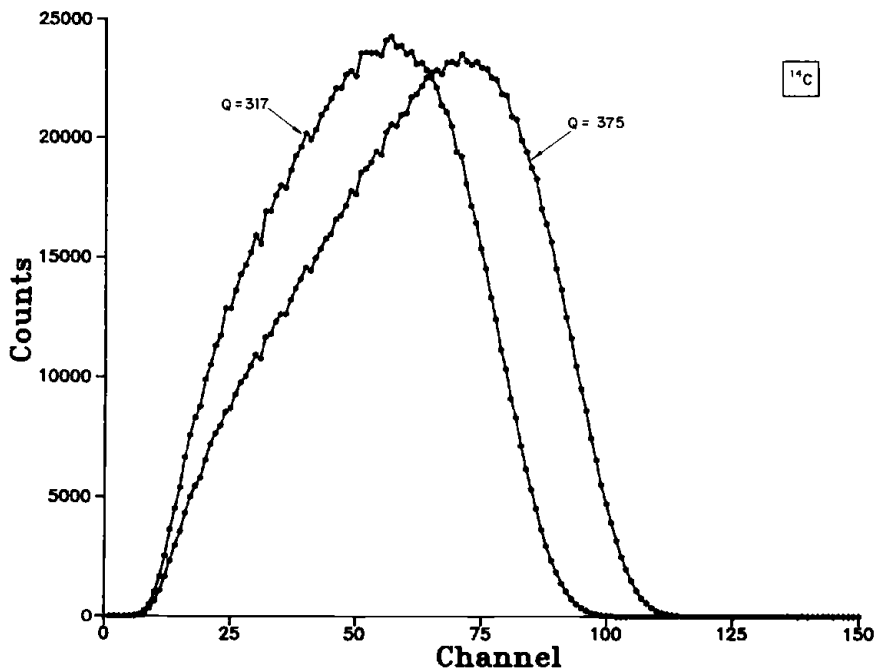


Figure 1. Experimental beta-ray spectra of ^{14}C for two different quenching values.

because of the dispersion of the spectra. One possible interpolation method could be the interpolation by spectral dilatation.

The general procedure has the following steps:

1. A set of spectra with different quench is obtained for each nuclide.
2. The interpolation procedure is applied to each nuclide, to obtain the spectra corresponding to the quench level of the experimental double labeled sample.
3. A least square fitting is done with the interpolated spectra and the double labeled spectrum in order to compute the activities of each one of the nuclides.

The procedure can be applied to multilabeled samples, but for simplicity and clarity we only discuss double labeled samples.

Special Functions

The experimental spectra, see Figure 1, are histograms and have the inconvenience of being defined for discrete values of the channel spectra. It is interesting, from a mathematical point of view, to have a continuous function defining the spectra.

The spectral function has been obtained by fitting Fourier series to the experimental spectra. The spectral function $f(w)$ is obtained from:

$$f(w) = \begin{cases} a + bw + \sum_{k=1}^N C_k \sin \frac{k\pi w}{M-1} & 0 \leq w < w^* \\ 0 & w > w^* \end{cases} \quad (1)$$

where N is the number of Fourier harmonics and M is the number of experimental points of the spectrum. The first and last spectral points are $w = 0$ and $w = M - 1$. w^* is the end of the spectrum.

The constants a , b and C_k can be obtained from the following equations:

$$a = y_0 \quad (2)$$

$$b = \frac{y_{M-1} - y_0}{M - 1} \quad (3)$$

$$C_k = \frac{2}{M - 1} \sum_{j=0}^{M-1} \bar{y}_j \sin \frac{\pi k w_j}{M - 1} \quad (4)$$

where y_j the number of counts in channel j , and

$$\bar{y}_j = y_j - (a + bw_j) \quad (5)$$

$$w_j = j = 0, 1, 2, \dots M - 1. \quad (6)$$

The calculation of the spectral function $f(w)$ is interesting for two reasons: it can eliminate very properly the statistical fluctuations of the spectra and permits a continuous function that allows application of the spectral dilatation interpolation method.

The first problem is defining the number of harmonics to be taken in the Fourier series. It is known that if the number of harmonics is equal or close to the number of experimental points of the spectrum, the function $f(w)$ will follow all the experimental points. In this case the statistical fluctuations will be included. We are interested in having a certain smoothing of the spectrum in order to attenuate the effects of statistical fluctuations. However, if we take a very low value for N , the function $f(w)$ can loose interesting or essential structures of data. That will produce a modification of the real shape of the spectrum.

Different values of N have been tried. $N = M/2$ seems to be a good compromise to obtain a moderate smoothing without losing essential structures.

Spectral Dilatation-interpolation Method

The spectral dilatation-interpolation method is interesting in the case of logarithmic spectra, nevertheless it is also applicable to linear spectra.

The spectral function $f(w)$ can be separated into two regions. Region 1 ranges from zero to the value that corresponds to the maximum of the spectrum. Region 2 is the remainder of the function.

The spectral dilatation method consists of applying a shift to region 1 of all

the spectra that makes all the maxima coincide in the same point. The same procedure can be applied to region 2, however, the common point is w^* in this case.

The transformation applied is a linear dilatation defined by:

$$w' = \frac{w_1}{w_k} w \quad (7)$$

where w_1 is the value of the common point after doing the dilatation and w_k is the position of this common point for each spectral function before carrying out the dilatation ($k = 2, 3 \dots v$), where v is the number of spectra for each nuclide.

We see in Figure 2 that the common point for region 1 is the maximum position of the less quenched spectrum. The w value of the less quenched spectrum is the common point for region 2.

It is proved that the choose of the position of the inflexion in the spectra or the point y/r as the common point for region 2 also gives good results.

Once the dilatation is computed it is not difficult to obtain the interpolated spectrum which corresponds to a given value of the quench parameter. First of all, we carry out a channel by channel interpolation between the dilated regions of the spectral functions. Then we calculate a new spectral function for

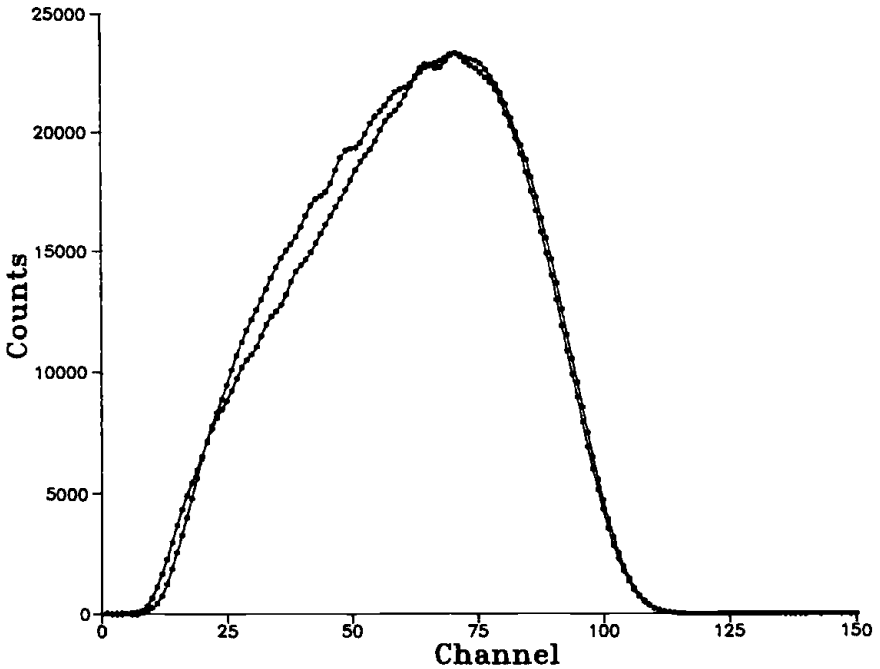


Figure 2. Fourier spectra after shifting.

these points as we have done before for the experimental spectra. Finally, we apply the contraction:

$$w' = \frac{\bar{w}_2}{w_1} w \tag{8}$$

where w_1 and \bar{w}_2 are the positions of the common point before and after the contraction is applied respectively. The next section shows how to calculate w_2 .

Spectral Parameters Depending on the Quench

In the previous section we associated the maxima and the ends of the spectral functions with the common points that correspond to the maximum and the end of the least quenched spectrum.

It is interesting to see the variation of these quantities as a function of the quench parameter. A straight line can be obtained by least square fitting of the data. The maximum and the end of the spectral function for a given value of the quench is calculated from this fitting.

Special Fitting

Once the radionuclide spectra, corresponding to the quench parameter of the experimental mixture have been interpolated, obtaining the activity of each component of a radionuclide mixture is a problem of least square fitting.

Let y_i be the number of counts in the channel i of the mixture spectrum and y_{ij} be the number of counts in the channel i for the spectral component j . The intensities p_j for each nuclide are related to the spectral components by the equation:

$$y_i \simeq \bar{y}_i = \sum_{j=1}^{j=n} p_j y_{ij} \tag{9}$$

where \bar{y}_i is the number of counts of channel i in the computed spectrum and n is the number of spectral components. The values for p_j are obtained from the condition of minimum for the quantity:

$$G(p_1, \dots, p_N) = \sum_{i=1}^{i=M} w_i [y_i - \bar{y}_i(p_j)]^2 \tag{10}$$

where w_i is the weight for channel i . These weights have been taken inversely proportional to the statistical variance of the count number in each channel:

$$w_i = \frac{1}{y_i} \tag{11}$$

Table 1. Activity Discrepancies for ^{14}C + ^3H mixtures

Q	$^{14}\text{C}/^3\text{H}$	$\Delta^{14}\text{C}$ (%)	$\Delta^3\text{H}$ (%)
326.6	6.3	0.16	0.57
216.2	14.2	0.55	7.1
326.0	0.6	7.0	2.2

different quench and proportions give a great number of possible combinations to be checked. In this chapter the procedure will be applied only to some particular mixture in order to show its possibilities.

Three radionuclides have been used in our experiment: ^3H and ^{14}C (both as n-hexadecane), and ^{35}S (dioctyl sulphide).

All the solutions were standardized by LMRI (France) and dispersed homogeneously into 10 mL of toluene or dioxane based scintillator. The standard solutions were added gravimetrically to each vial using a Sartorius microbalance. Carbon tetrachloride was used as a quencher.

A LKB 1219 Rackbeta Spectral liquid scintillation counter has been used to obtain the spectra.

RESULTS AND DISCUSSION

Four different situations have been considered:

- Mixture of ^{14}C and ^3H with middle quench and 6.3 times more counting rate of ^{14}C than ^3H
- Mixture of ^{14}C and ^3H with high quench and 14.2 times more counting rate of ^{14}C than ^3H
- Mixture of ^{14}C and ^3H with moderate level of quench and very poor counting statistics.
- Mixture of ^{14}C and ^{35}S with moderate level of quench and similar counting rates for both radionuclides.

Figure 3a shows the experimental spectrum of the ^{14}C and ^3H mixture. The quench parameter for this sample is $Q = 326.6$, this corresponds to a counting efficiency for ^3H of about 0.29%. The counting ratio relationship between ^{14}C and ^3H was about 6. The spectrum of residuals Figure 3b shows a balanced dispersion. Table 1 shows that the discrepancies between experimental and computed activities are 0.16% for ^{14}C and 0.57% for ^3H .

Figure 4a shows the experimental spectrum of a ^{14}C and ^3H mixture with a quench parameter $Q = 216.2$, the corresponding counting efficiency is 0.11%. The counting ratio relationship between ^{14}C and ^3H is 14.2. The spectrum of residuals, Figure 4b, shows some predominant positive values due to the oscillations of the experimental spectrum close to the maximum. Table 1 shows that the discrepancies between computed and experimental activities are 0.55% for ^{14}C and 7.1% for ^3H . A better stability of the experimental spectrum would improve the discrepancies.

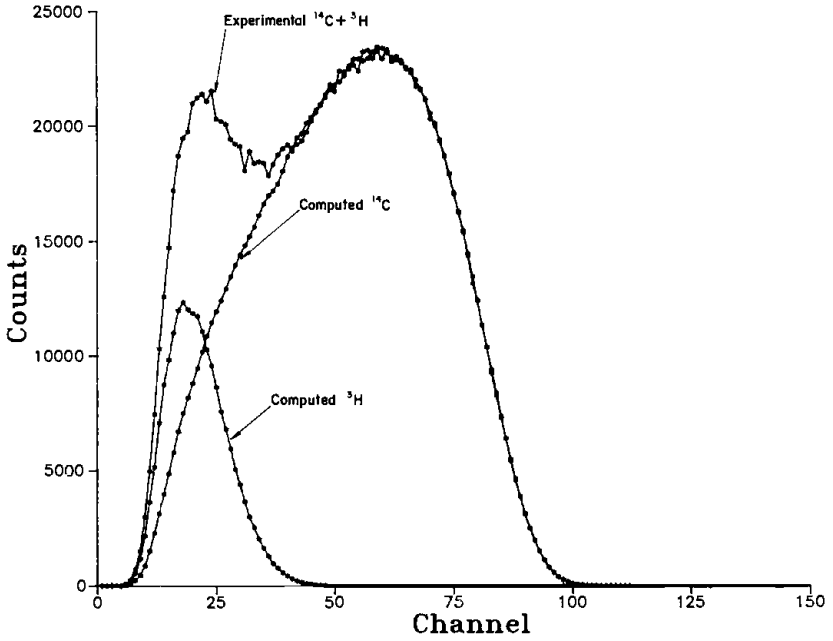


Figure 3a. Experimental spectrum of a mixture of ¹⁴C + ³H and spectral decomposition for middle quenching.

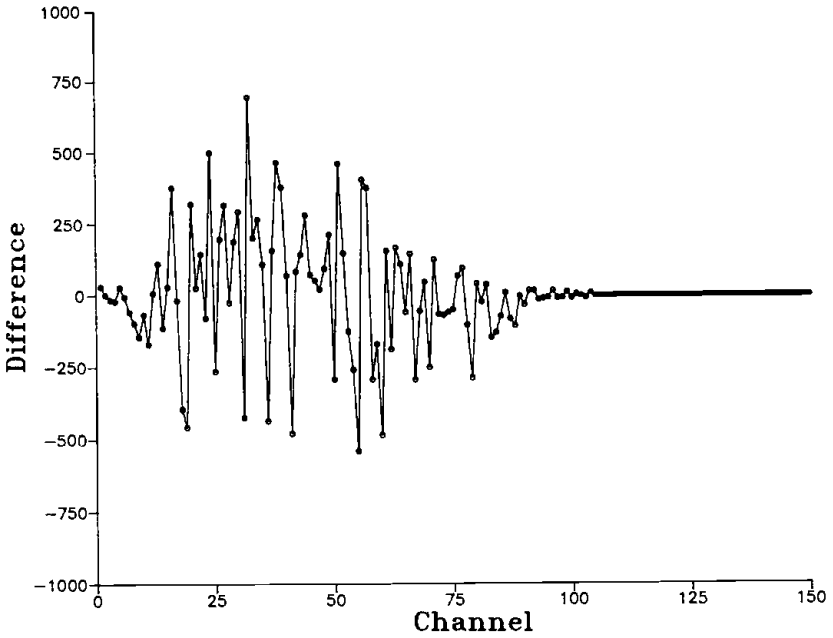


Figure 3b. Residual spectrum for the fitting of Figure 3a.

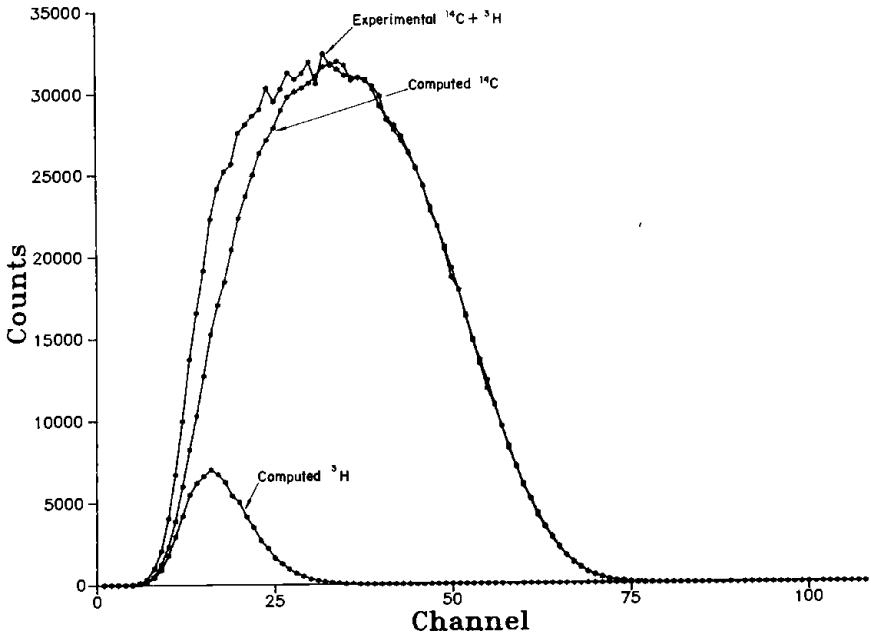


Figure 4a. Experimental spectrum for a high quenched mixture of $^{14}\text{C} + ^3\text{H}$.

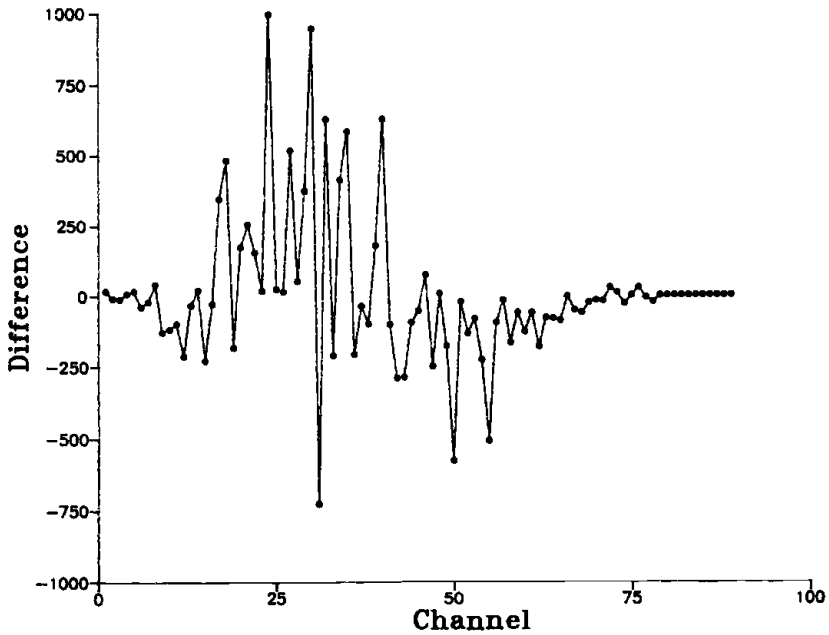


Figure 4b. Residual spectrum for the fitting of Figure 4a.

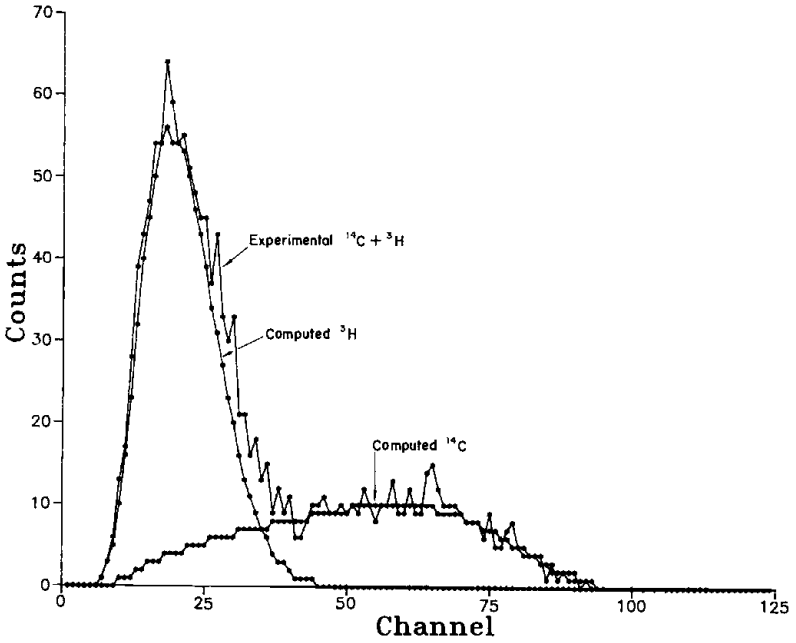


Figure 5a. Experimental spectrum of a mixture of ^{14}C and ^3H with very poor statistics and spectral components.

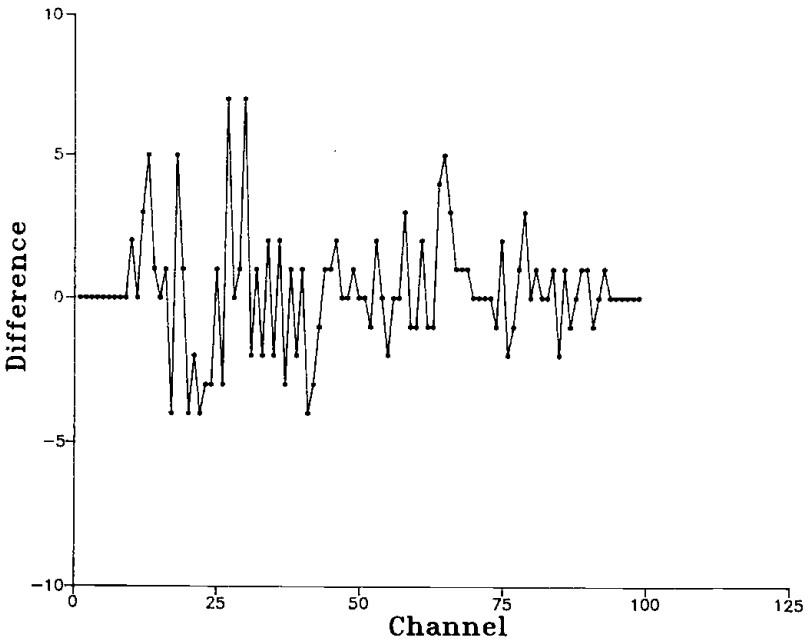


Figure 5b. Residual spectrum for the fitting of Figure 5a.

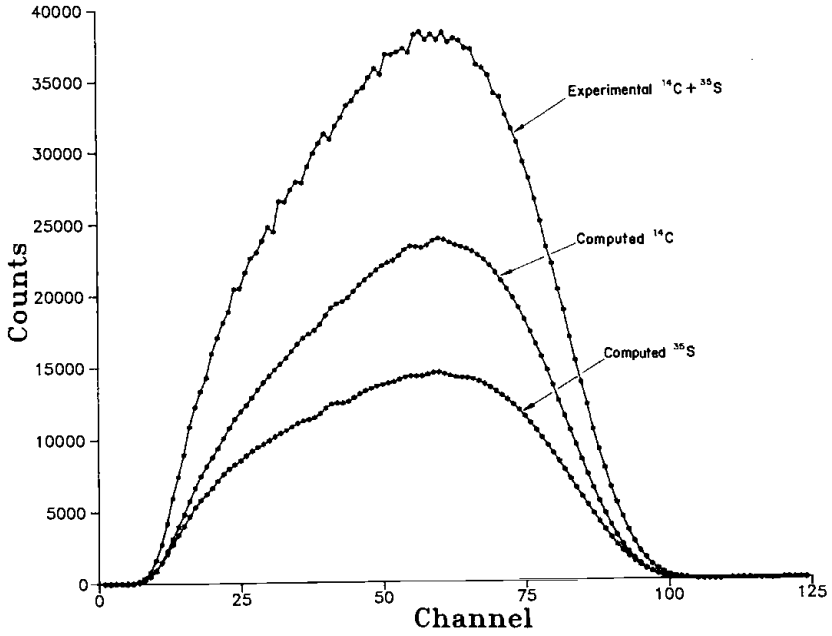


Figure 6a. Experimental spectrum and spectral components for a mixture of ^{14}C and ^{35}S .

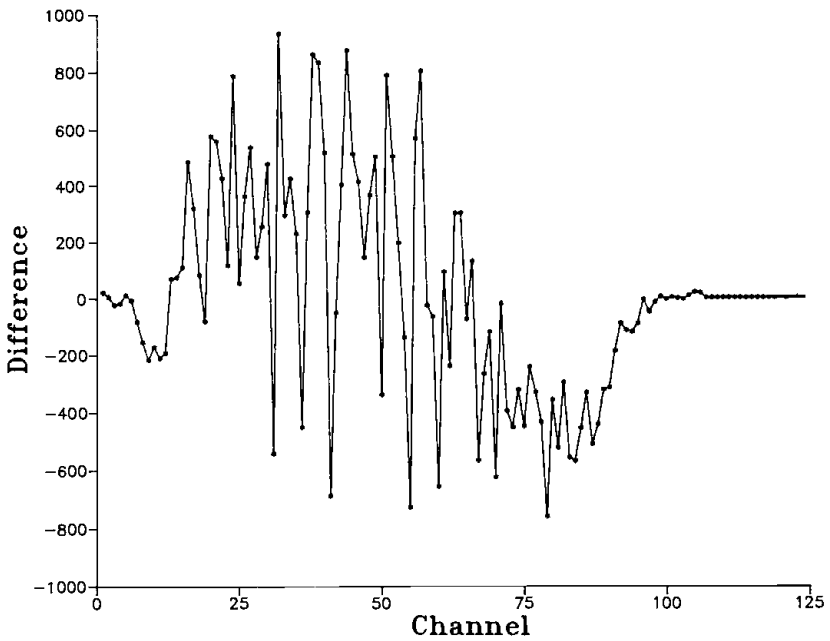


Figure 6b. Residual spectrum for the fitting of Figure 6a.

Figure 5a shows the experimental spectrum of ^{14}C and ^3H mixture with a quench parameter $Q = 326$. The measurement time was very short (1.5 seconds). That means that the counting rate is very low, like a low level activity sample, but without background. The counting rate between ^{14}C and ^3H is about 0.6. Figure 5b shows the residuals of the fitting. Systematic positive or negative values are clearly obtained, but the balance between both is quite acceptable. Table 1 shows that the discrepancies between computed and experimental activities are 7.0% for ^{14}C and 2.2% for ^3H .

Figure 6a shows the experimental spectrum of ^{14}C and ^{35}S . The quench is $Q = 330$, and the counting ratio relationship is $^{14}\text{C}/^{35}\text{S} = 1.5$. The discrepancies for ^{35}S and ^{14}C are 3.4% and 2.2%, respectively. Figure 6b shows the residuals of the fitting. It can be seen that for the low and high region of the spectrum there are several residuals unbalanced. The analysis of ^{35}S and ^{14}C is a very difficult problem because the maximum beta-ray energies for both radionuclides are very close, but the differences in the spectral shape permit the activities of each one of the radionuclides.

CONCLUSION

A computer code DILATA has been developed which is applicable to the analysis of radionuclide mixtures. The method is based on a new procedure to interpolate spectra and has been applied to obtain the activity of ^{14}C and ^3H mixtures in different conditions. The application to a mixture of ^{14}C and ^{35}S has shown the power of the method.

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