REAL TIME SPECTRUM ANALYSIS

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A method is described for the separation of a composite pulse-height spectrum into its unresolved component parts, which belong to a set of measured library spectra. The method allows real-time estimation giving running estimates during acquisition of the spectrum, minimises computation space, especially for a number of parallel calculations, estimates in advance the rms errors, and produces a significance measure for the hypothesis that the composite contains only the library spectra.

Least squares curve-fitting, and other methods, can be compared, with the formalism developed, allowing analytical comparison of the effect of detector energy resolution and detection efficiency. A rational basis for the choice between the various methods of spectrum analysis follows from the theory, minimising rms estimation errors. The method described is applicable for very low numbers of counts and poor resolution.

1. Introduction

A number of methods exist for the separation of the components of a composite spectrum, such as the pulse height spectrum due to the electromagnetic radiation from a mixture of different radionuclides. A standard approach and the one adopted here is to estimate the number of counts that would be attributed to each of a set of measured library spectra.

In this case, the particular objectives were to be able to carry out the calculation in real time, to minimize data storage requirements and to reduce estimation errors to the minimum.

The real time analysis has been effected by up-dating the estimates by a table look-up method as each count is acquired.

Storage space is required for the tables, a compressed form of the library spectra, and the running estimates, only. Thus no additional storage space is required to achieve real time analysis. Further, the method allows a number of different composites of the same library spectra to be analysed in parallel.

Error minimization involved a separate study of the accuracy of statistical methods such as χ^2, least squares and moments analyses. The most accurate method was determined by the calculus of variations. Adaptation for real time analysis and data compression does not produce a loss of accuracy.

A rigorous mathematical derivation of the results given here is provided in the appendices. Presented below is a line of argument which should allow the reader both to understand how the method works and to implement it with the use of a computer interfaced to a detector.

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2. Estimation of spectrum composition using the "window" method

If a radioactive sample is supposed to be a composite of an undetermined proportion of a certain set of components whose pulse height spectra are known in the form of a set of measured 'library' spectra, a real time estimation of the counts attributable to each component could be executed as follows.

1) At each energy channel the intensities of the spectra are compared.
2) The spectrum with the greatest intensity is selected.
3) A 'table' is created for each spectrum containing 1 in each channel where that component is the 'most likely' and 0 elsewhere, thus dividing the spectrum into a series of 'windows'.

A composite spectrum is acquired. As each count is acquired the energy is used as an index to select a 1 or a 0 from each table which is added to a total estimating the number of counts attributable to that component.

Thus each count is assigned to one or another of the components according to which is the most likely, considering each measurement independently of the others.

The estimation carried out in this way is erroneous, since each pure component in fact contributes counts, in a certain proportion, to each window, thus a 'blurred' resolution is obtained, unduly equalising the proportions of each component.

The estimate may, however, be 'corrected', after acquisition, as follows

4) A matrix is formed in which the i, jth element shows the proportion of counts in the ith spectrum which are assigned to the jth total. This is

determined by multiplying the ith spectrum by the jth table, summing the product at each channel and dividing by the total number of counts.

5) This matrix is inverted so that the jth row shows the composition corresponding to each table – a composition which must include negative values if the spectra overlap. The set of estimates is multiplied by this matrix.

The estimate resulting from this correction is a true estimate. That is with increasing total number of counts the estimate will converge to the true proportions.

However the corrected estimate is not longer 'real time' since a transformation of the estimate must be carried out in retrospect. Further, storage space will be increased since the matrix multiplication will introduce fractional counts which are essential to accuacy should we attempt to restore real time analysis by using the matrix after each count, or a batch of counts, is acquired.

The estimate can be made real time again as follows. Steps 1)–5) are carried out as above.

6) Instead of multiplying the estimates by the matrix after acquisition, the tables are multiplied by the matrix before acquisition.
7) A composite spectrum is acquired. As each count is

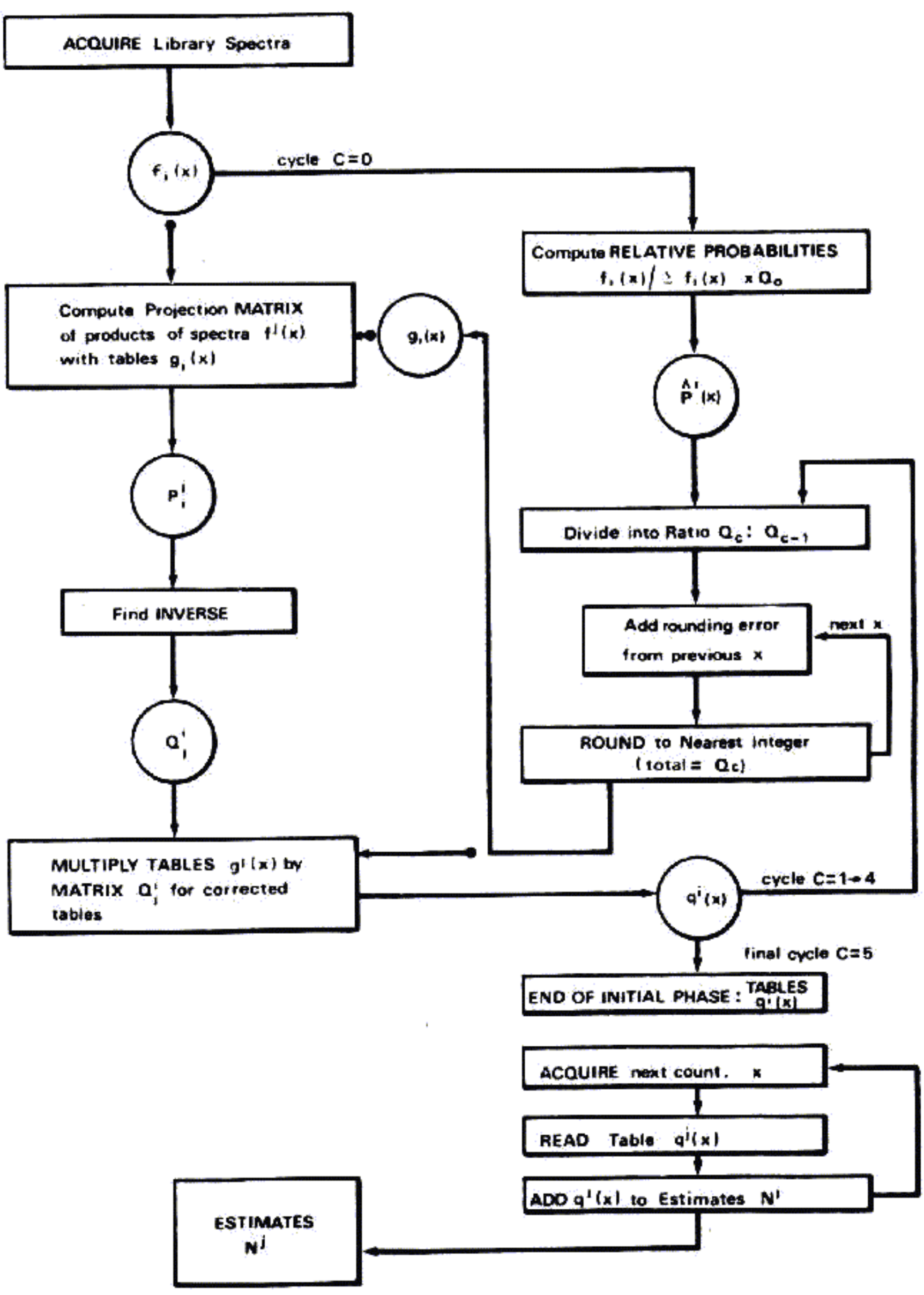

Fig. 1. Procedure-flow chart for implementation of the method.

acquired the corresponding value is read off the corrected tables and added to the totals to form real time running estimates.

This method still has the defect of requiring fractional counts to be accumulated with consequent increase in storage space and dead-time. This may be corrected as follows.

The corrected tables are calculated as above to a relatively high order of accuracy, say 1 part in 64.

8) The value in each channel of each table is rounded to a selected lower order of accuracy, passing the rounding error from each channel onto the next channel, maintaining a unit total in each channel across the set of tables.
9) The correction matrix is re-calculated as in steps 4) and 5) above. It will approximate to a unit matrix.
10) The truncated tables are corrected using this matrix as in step 6) above.
11) The cycle of truncation and re-correction is repeated until integer values are obtained.

A composite spectrum is acquired and use of the tables will add or subtract a whole number of counts to each estimate. This has the effect of incrementing just one total (as in the simple window method) but then compensating for the overlap of the spectra by transferring one or several counts from one estimate to another.

The last-mentioned method will produce true estimates in real time with no more storage space required for each estimation than the memory requirements of the estimate itself.

In appendix I a rigorous mathematical presentation of the above argument is given, while the flow chart in fig. 1 summarizes the implementation procedure.

3. Optimisation of the estimate – The 'relative window' method

While it is proved that the above window technique produces convergent estimates, it is not proved that these estimates converge at a faster rate than any other.

It would appear that the binary assignation which is used at the outset of the method is not optimal. Although the use of the correction matrix ensures that almost any tables can be used to derive tables which will give convergent estimates, the optimal selection of the tables is a different question. It has been proved (see appendix 2) that optimal estimation is achieved if the binary windows used in the initial set of tables are replaced by a set of tables in which a count is assigned to each component in proportion to the intensity of each spectrum in a given channel – that is, to its relative frequency at that energy. This measure is included in the procedure shown in fig. 1 and proof of the optimization, using calculus of variations in relation to arbitrary tables, is given in Appendix II.

It is remarkable that the method of reducing the tables back to integer form results in a loss of accuracy, relative to the optimum form of only a few per cent – more than compensated for by the increased count rate that results from the smaller dead-time integer arithmetic causes in the acquisition. This is provided that the spectra do not have extremely fine structure.

4. Estimation errors

The rms value of estimation errors arising from the statistical variation of the component spectra from their measured library forms may be calculated from the 'correction' matrix in advance of acquisition. The correction matrix is the matrix calculated as described in steps 4) and 5) of section 2. above, multiplied by the series of matrices calculated as in step 9) of the data compression process. Since these latter matrices approximate to the unit matrix it will be seen that they contribute only marginally to the estimation errors.

The estimation errors are estimated in rms as follows.

1) The mean of the diagonal elements of the correction matrix, minus 1, is calculated.
2) This value is multiplied by the total number of counts to be acquired and square rooted.
3) This value is the sum, in quadrature, of the errors corresponding to estimation of each of the different components. Not every component will be subject to equal error, but in many cases it will be sufficient to assume that they are. In this case, the 'unit error' in estimating the intensity of a single component is found by dividing the above value by the square root of the number of components.

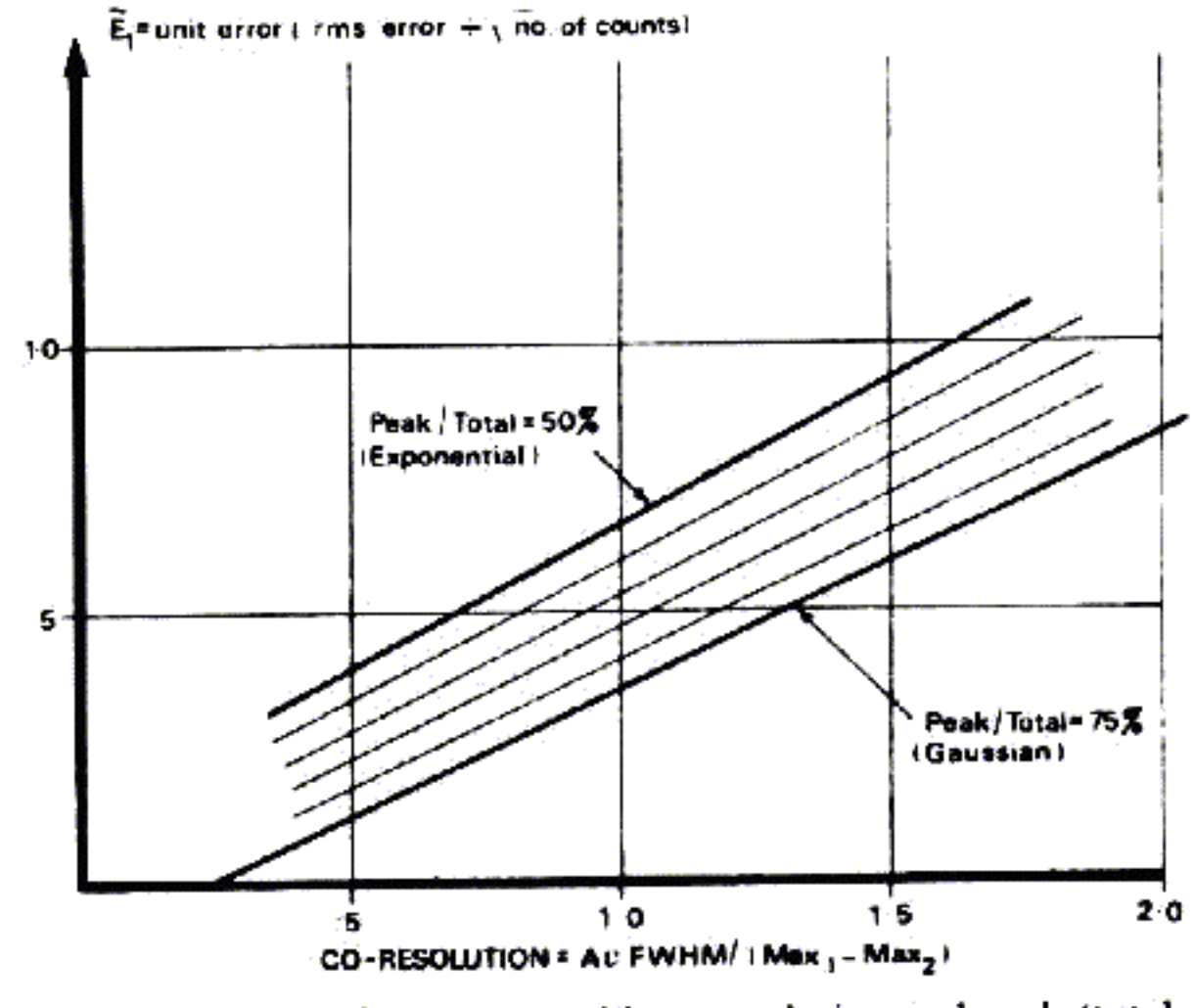

Fig. 2. Variation of rms errors with co-resolution and peak/total ratio of typical sets of component spectra.

Fig. 2 illustrates how this unit error varies with peak shape and separation, and some examples are given in appendix II. The estimates obtained will be true irrespective of the choice of a priori composition.

5. Significance of the estimate

This estimated error is valid only if the composite spectrum is acquired under the same conditions as the library spectra and contains no foreign elements. The hypothesis that this is so can be tested in retrospect, or, if desired, in real time during acquisition, by up-dating one additional total computed as follows. (see appendix 3 for proof)

1) The scalar product of each library spectra with each of a set of tables is calculated to form a matrix. The library spectra, or their derivatives, may be used for the tables.
2) This matrix is inverted and the elements in each column summed.
3) A linear combination of the library spectra is formed with the coefficients so obtained, and 1 is subtracted from each channel.
4) A 'significance measure' is calculated during acquisition using this table in the same way as already described for the estimation itself.
5) The rms of this total corresponding to a valid estimation is calculated as follows.
   The significance table is squared and the scalar product of this table with an 'average spectrum' composed of the library spectra in equal proportions is calculated. This value is multiplied by the number of counts and square root taken.
6) Comparison of the measured significance total with the known rms value will indicate the degree of confidence which may be assigned to the estimation. If it lies within the computed rms range, then the true composition may be assumed to lie within the range of the unit error of the estimation composition.

6. Experimental verification using simulated composites

A single wire proportional counter was connected to an analogue–digital converter via a sample-and-hold circuit and interfaced to a microcomputer programmed to implement the above method. X-ray fluorescence

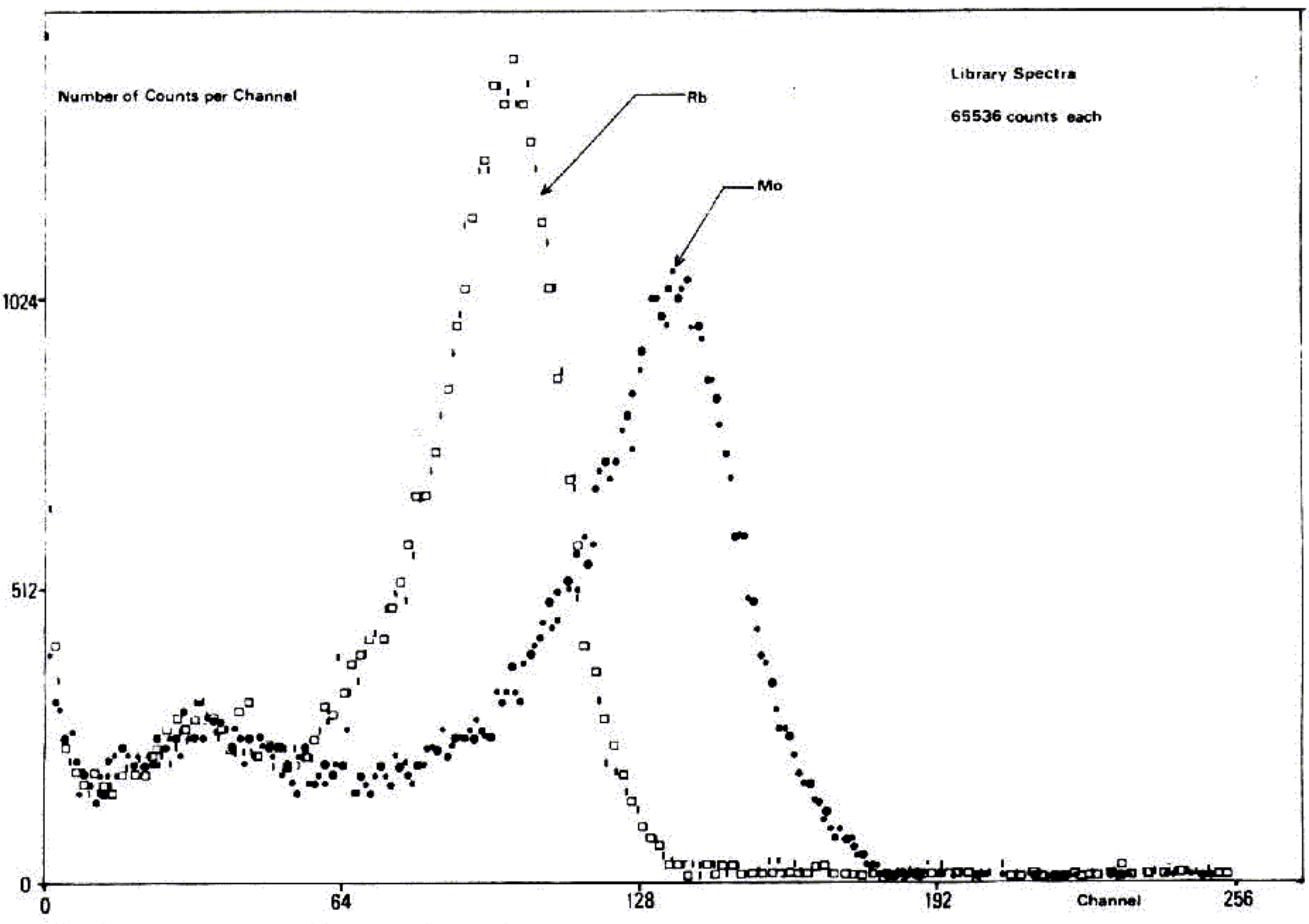

Fig. 3. Component spectra used in example of application of method.

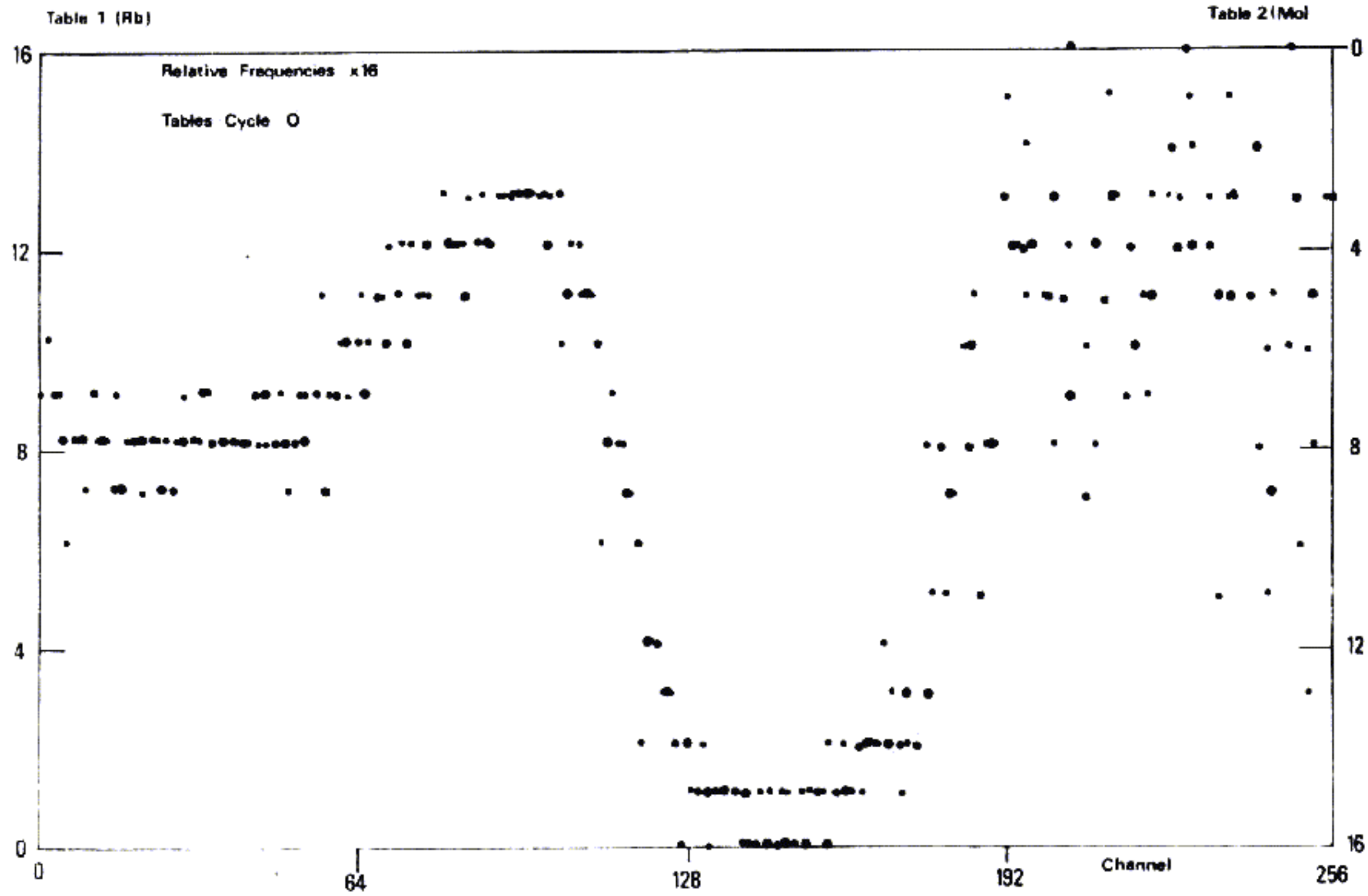

Fig. 4. Relative probabilities calculated from spectra shown in fig. 3.

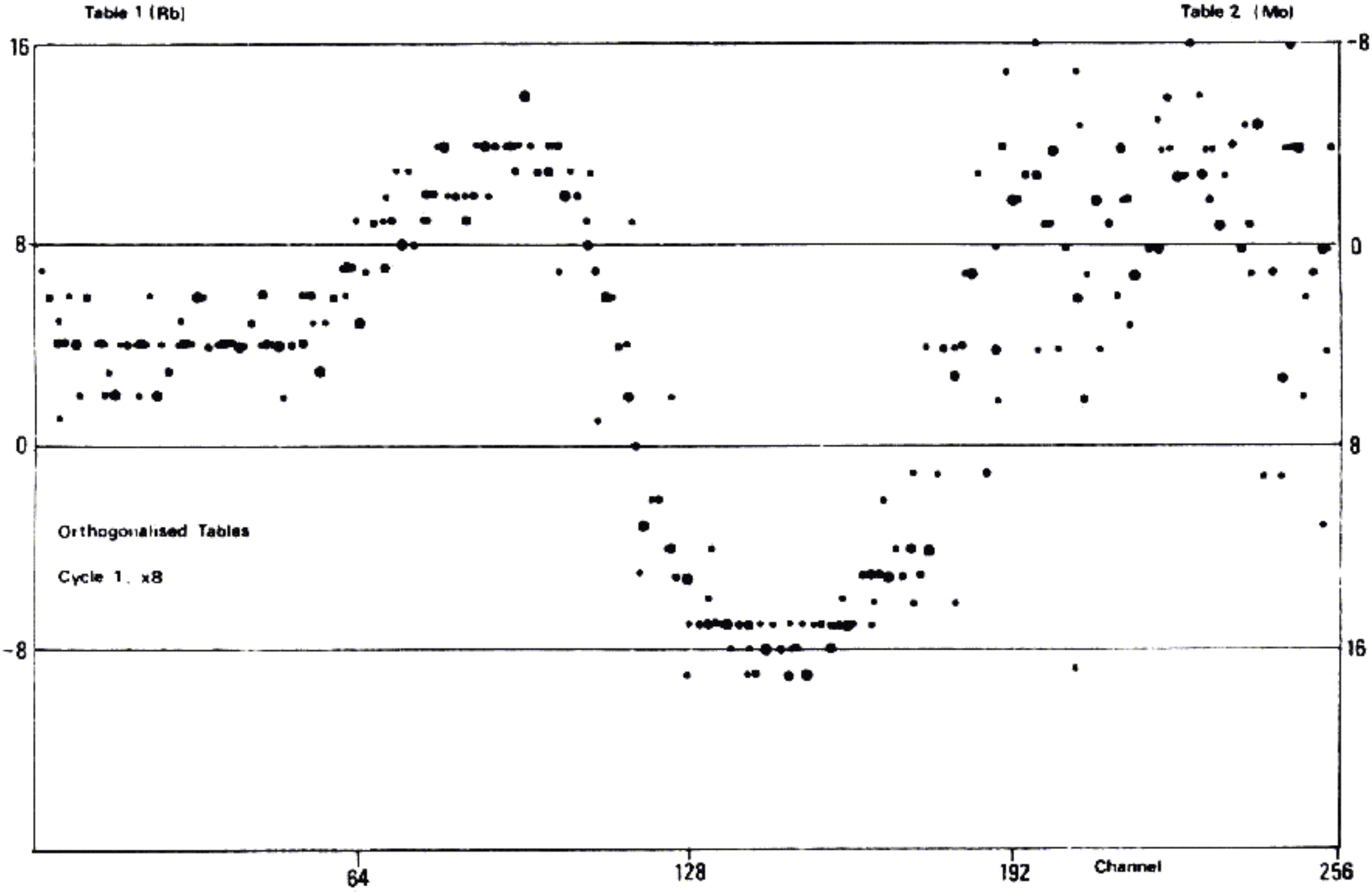

Fig. 5. Orthogonalised tables derived from relative probabilities in fig. 4.

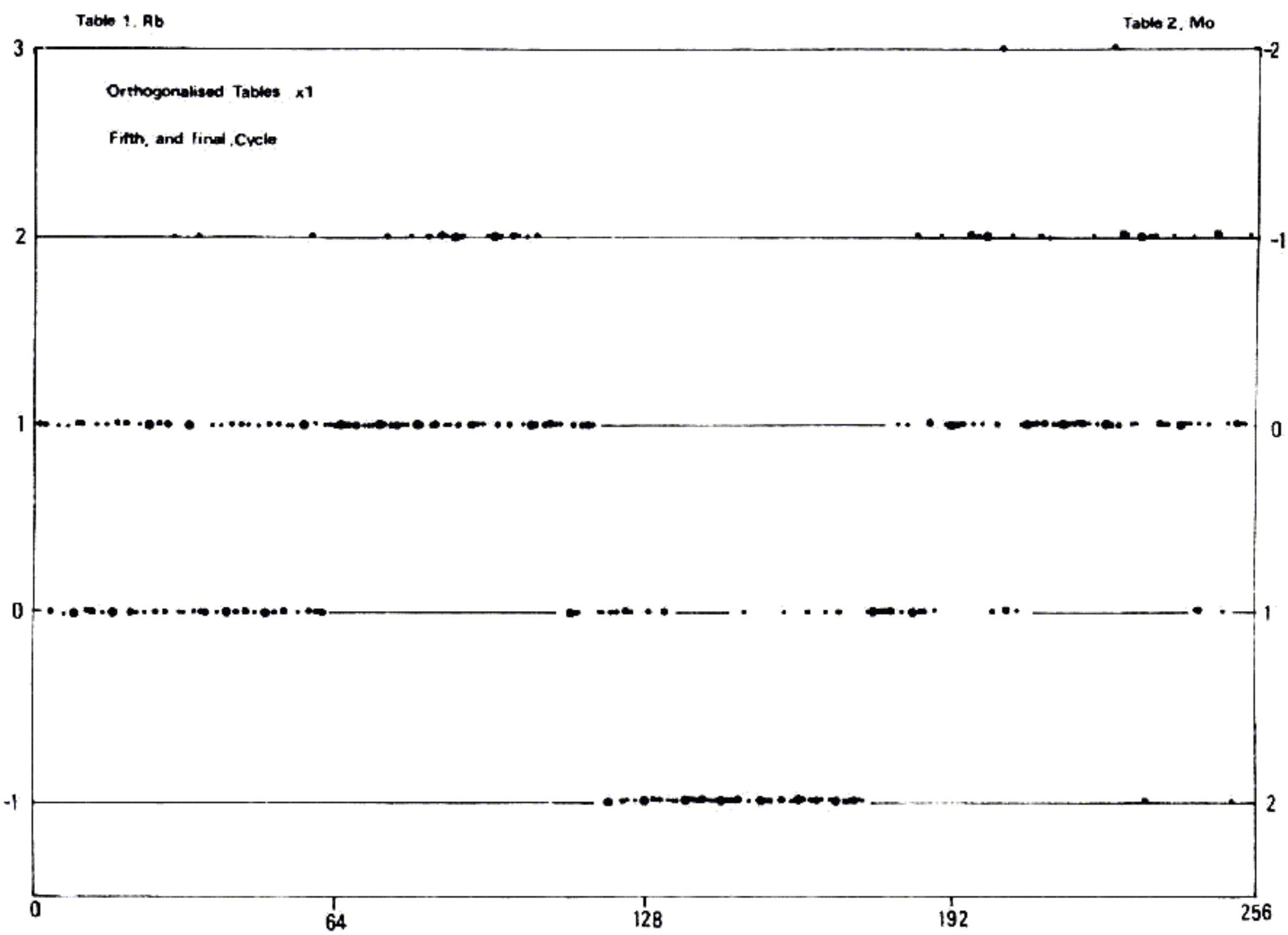

Fig. 6. Tables reduced to integer values.

spectra of Rb and Mo, obtained by irradiation with 60 keV ^{241}Am radiation, were used as two library spectra of 64k counts each. A series of 100 pairs of component spectra were acquired, and then combined to form a series of 100 composite spectra the true composition of which was thus known. The method of estimation described above was applied and the estimation errors measured. The spectra and incrementing tables used are illustrated in figs. 3 to 6.

In addition 20 composites were acquired by the same method and subject to a variation in gain by a numerical technique. Both estimation error and significance measure were computed for these samples. The results are shown in table 1, from where it can be seen that the errors measured experimentally closely approximate to the predicted values, and marked shifts in the significance measure were recorded when detector gain was varied sufficiently to cause a systematic error in estimation.

7. Comparison with other methods of separation [6, 7]

Composite spectra may be separated by comparing well-resolved peaks with the line-spectra of known radionuclides. Such methods may be manual or automated. Techniques of this kind are difficult to bring into comparison with the method described here. Although invaluable in certain areas of work they are unsuitable where the number of counts is very low, the peaks are unresolved or real-time analysis is required. It is these latter areas that we have been concerned with here. However, all methods depending on comparison of a composite spectrum with a set of whole measured library spectra – such as curve-fitting by the χ^2 method or least squares method, or using first derivatives of the spectra, as well as the window method mentioned above or comparison of the series of moments of the spectra – may be executed by the proposed method of real-time analysis. In each particular method however, the relative

Table 1
Results for experimental verification using simulated composites

Library spectra	Rb	Mo
No. of channels	256	256
No. of counts	64k	64k
Peak channel	100	135
FWHM	28	37
% cts within fwhm	47	45
% Coresolution = $(135-100)/\frac{1}{2}(28+37)\times 100 = 110$		
Spectrum overlap, A	0.68	

Various predictions of unit error $\tilde{E}_1$ = rms error/$\sqrt{\text{no. cts}}$

(1)	From spectrum overlap, A: $\frac{1}{2}\sqrt{A/(1-A)}$	0.73
(2)	From graph in fig. 2:	0.78
(3)	From eq. (39) and integered tables in fig. 6:	0.86
(4)	From eq. (39) and initial tables in fig. 4:	0.72
(5)	Estimate (3), weighted by fwhm for various compositions:	

Rb : Mo	0:4	1:3	2:2	3:1	4:0
Estimate	1.00	0.93	0.86	0.81	0.75

Experimental results: empirical measures of unit error
100 composites of various compositions of 1k cts ($\sqrt{N} = 32$)

Rb : Mo	0:4	1:3	2:2	3:1	4:0	all tests
rms/$\sqrt{N}$	1.00	0.99	0.83	0.82	0.69	0.88
5%ile/1.96 $\sqrt{N}$	1.03	1.04	1.14	1.09	0.73	1.03
Mean error × $\sqrt{\text{no. tests}}$ /$\sqrt{N}$	.	.	.	.	.	0.70

Experimental results: significance measure
20 composites of 2k cts, composition Rb : Mo = 2 : 2, with detector gain varied slightly from initial setting

Gain	1.00	0.99	1.01	0.98	1.02
Mean sig. measure. $\sqrt{\text{no. tests}}$ /rms	0.43	1.97	−4.61	2.61	−5.98
Mean error. $\sqrt{\text{no. tests}}$ /rms	−1.8	0.1	−6.96	6.83	−13.2

frequency tables used in the initial phase as described above, are replaced by tables having a form corresponding to that method. In all but the method proposed here these will not be of the optimal form. (See appendix IV for specific treatment.)

It should be pointed out that the χ^2 method as conventionally applied in this area of radiation science is in fact erroneous, since the values of the frequency of each channel in the acquired composite spectrum are used to weight the fitting misclosure to be minimised. In the true χ^2 method, the frequency of each channel in the mean expected composite spectrum should be used. In this latter case χ^2 is effectively identical to the method proposed. (See appendix IV for proof.) In the former case a systematic error in estimation results, especially for low count numbers [11].

8. Summary

The procedure for implementing the method described here is shown in fig. 1. The method involves an initial phase of processing of the library spectra, so that as the composite spectrum in question is acquired it is necessary only to read a value off a table of integers, using the energy of the acquired count as an index, and to add this to the total estimating the number of counts attributable to particular components while the next count is being acquired.

The advantages of the method may be listed as follows:

1) Estimation is real-time, current estimates being updated as each count is acquired.
2) Computer memory usage is minimised – being one byte per component per channel plus the memory space required to store the output estimate – a saving which becomes critical where a large number of parallel analyses are being carried out simultaneously.
3) The method is completely automatic.
4) The method is applicable for composites of one count upwards where peaks may be completely overlapping.

5) Dead-time will be small, and comparable to the dead-time of an integrated circuit ADC providing the digital input to the computer.
6) Rms estimation errors are known in advance of acquisition of the composite spectrum. The same error estimation formulae are applicable to other methods of spectrum analysis, such as least squares curve fitting.
7) The rms estimation errors are minimised.
8) A significance measure is obtainable, in real time, also applicable to other methods of separation.
9) Background stripping may be done automatically without additional computation during acquisition by including the background as an additional but undetermined component.

Not all the above advantages will be utilised since trade-off between the various factors has to be considered, viz. accuracy vs memory usage, acquisition rate vs real time analysis, reliability vs speed and space.

Appendix I

Formalism

A particular mathematical formalism is used which should be explained. All lower case letters represent functions of x (energy), with the exception of the indices $i, j, \ldots$ and x itself. All upper case letters represents constants, independent of x.

The product integral

$$f * g = \int f(x)g(x)\mathrm{d}x \tag{1}$$

is represented by the above shorthand, and plays a central role. If $f(x)$ is a frequency spectrum, ($g(x)$ may be any function) there are two possible ways of computing $f * g$:

1. Add g to total as each value of x is acquired (f times).
2. Multiply f times g for each value of x, and add.

Method (1) is implied here. That is, $g(x)$ is stored as a 'table', and acquired values of x will read values of $g(x)$ from the table, the value to be added to the total. Each of the analytical methods of spectrum analysis corresponds to using a particular set of functions for $g(x)$, (see appendix 4 below).

For instance, if we create a set of functions, $g(x)$, each corresponding to one of the component spectra, $f(x)$, such that $g(x) = 1$, where that component is the most likely, that is where its value of $f(x)$ is greater than that of the other components, and $g(x) = 0$ elsewhere, then a composite spectrum could be separated into its estimated components by calculating $f * g$, as above. This is called the 'window' method.

The (x) will be omitted in future.

Matrix operations are represented by using superscripts to denote column vectors and subscripts to denote row vectors. Matrix elements may be either constants or functions. Scalar products (ie. row × column = scalar) are indicated by using an identical index as both subscript and superscript (eg. $A^i B_i = C$), implying summation over the range of the index, which is always M, the number of component spectra. Other matrix notation will be used when required, such as $(A^i_j)^{-1}$. I^i_j is the unit matrix. 1^j represents a column of ones. Note that the use of the indices makes multiplication commutative and associative.

Further, a character is primed (eg. c') to indicate an actualised value as distinct from unprimed characters which would represent hypothetical or estimated values of the same quantity; a bar above a character (eg. $\bar{c}$) represents an average or mean value; a tilde above a character (eg. $\tilde{E}$) represents an rms value; a circumflex (eg. $\hat{c}$) represents an a priori value.

Estimation

c' is a composite spectrum, composed of M pure spectra, f'_i, with intensities N'', such that

$$c' = f'_i N''. \tag{2}$$

The total number of counts is

$$N' = c' * 1 = 1_i N''. \tag{3}$$

and f'_i are normalised so that

$$f'_i * 1 = 1_i. \tag{4}$$

In advance of acquiring the spectrum, c', a set of 'incrementing tables' g^i are created, and as c' is acquired the 'projections' P'' are computed as described above by

$$P'' = g^i * c'. \tag{5}$$

The object is to choose the g^i so that the P'' are good approximations to N'', namely N'.

To solve for g^i, substitute (2) into (5):

$$P'' = g^i * f'_j N''. \tag{6}$$

The $M \times M$ square matrix, $g^i * f'_j$ we call P''_j, so that

$$P'' = p''_j N''^j, \tag{7}$$

$$P''_j = g^i * f'_j. \tag{8}$$

The 'correction matrix' Q''^j_i is defined as the inverse of P''^j_i, so that

$$Q''^j_i = \left(P''^j_i\right)^{-1}, \tag{9}$$

$$N''^j = Q''^j_i P''. \tag{10}$$

The projection matrix is not known, since the actually realised spectra, f'_j, are 'hidden' within the composite, c'.

An estimate of P''_j may be made using the hypotheti-

cal, or ideal, library spectra, f_j:

$$P_j^i = g^i * f_j, \tag{11}$$

$$Q_i^j = \left(P_j^i\right)^{-1}. \tag{12}$$

Eq. (10) gives N'^j exactly. Estimates of N'^j, can be calculated from the library spectra using

$$N^j = Q_i^j P''^i, \tag{13}$$

$$i.e.\ N^j = Q_i^j P''^i_k N'^k. \tag{14}$$

Eq. (13) will allow us to make an estimate from P'' using arbitrary g^i [9]. Eq. (14) shows how estimates are related to the true values. The transformation matrix I'^j_k, which is required to approximate to a unit matrix, is defined by

$$I'^j_i = Q_i^j P''^i_k. \tag{15}$$

so

$$N^j = I'^j_k N'^k. \tag{16}$$

Substituting (8), (11) and (12) into (15)

$$I'^j_k = \left(g^i * f_j\right)^{-1}\left(g^i * f'^i_k\right). \tag{17}$$

If

$$q^j = Q_i^j g^i, \tag{18}$$

then

$$q^j = \left(g^i * f_j\right)^{-1} g^i \tag{19}$$

and (17) becomes

$$I'^j_k = q^j * f'^i_k. \tag{20}$$

q^j are the 'orthogonalised incrementing functions' [10]. Whereas the g^i have up till this point been arbitrary functions, the q^j have the special property that

$$q^j * f_k = I'^j_k. \tag{21}$$

That is, the q^j will, on average, increment only f_j, and not f_k, $k \neq j$. Thus, the projections, P''^i, resulting from the choice of q^i as g^i are estimates of N'^j. That is,

$$N^i = q^i * c^i = \left(q^i * f_j^i\right) N'^j. \tag{22}$$

Comparing eqs. (20) and (21), as $f_j^i \to f_j$, $I'^j_j \to I^j_j$, thus, from (22), $N^i \to N'^j$.

Henceforth, wherever incrementing functions q^i given by (19) are used, the projections will be referred to as N^i rather than the more general P''^i.

Appendix II

Optimisation of estimate

The issue now is to choose g^i such that the resulting orthogonalised incrementing tables, q^i, lead to the most rapid approach of N^i to N'^i. That is, to minimise the errors,

$$E'^i = N^i - N'^i. \tag{23}$$

Substituting (16) into (23), with

$$D'^i_j = I'^i_j - I^i_j, \tag{24}$$

$$E'^i = \left(I'^k_i\right)^{-1} \cdot D'^k_j \cdot N'^j. \tag{25}$$

The variation of the transformation matrix I'^k_i from its ideal form may be seen as originating from the variation of the actual spectra from their ideal, library forms

$$d_j^i = f_j^i - f_j, \tag{26}$$

$$d_j^i * 1 = 0_j, \tag{27}$$

$$D'^k_j = q^k * d_j^i. \tag{28}$$

As each count is acquired, an error in the estimate N^j is accumulated:

$$q^j, \text{ with probability } \frac{1}{M} f_i \cdot 1^i \qquad (i \neq j) \tag{29}$$

$$q^j - 1, \text{ with probability } \frac{1}{M} f_j$$

(Here we assume the different components have the same a priori probability.) Thus, the mean error, $\bar{E}^j$ is

$$\frac{1}{M}\left(1^i q^j * f_i - 1^j\right) \cdot N^i = \frac{1}{M}\left(1^i I_i^j - 1^j\right) \cdot N^i = 0^j, \tag{30}$$

The mean square error, $\overline{(E^j)^2}$ is

$$\overline{(E^j)^2} = \left(1^i \frac{1}{M} f_i * (q^j)^2 [j \neq i] + \frac{1}{M} f^j * \left(q^j - 1^j\right)^2\right) \cdot N^i$$

$$= \frac{N^i}{M}\left(1^i f_i * (q^j)^2 - 1^j\right), \tag{31}$$

since $f^j * q^j = 1$ (32)

and $f^j * 1 = 1$. (33)

Using $\hat{c} = \frac{1}{M} 1^i f_i$ (the 'average spectrum') (34)

so that $\overline{(E^j)^2} = N^i\left(\hat{c} * q^{j^2} - \frac{1}{M}\right)$ (35)

the 'unit error' in estimating the jth component is

$$\tilde{E}^j = \sqrt{\overline{(E^j)^2}/N^i}. \tag{36}$$

Eq. (29) is based on the a priori assumption that all components are equally likely. The definition (34) is based on this. If there should be any basis for assuming otherwise, $\hat{c}$ as defined in (34) may be replaced by

$$\hat{c} = W^i f_i, \qquad W^i 1_i = 1. \tag{37}$$

Where the incrementing method used here is used, c^i is not known. If it is known we could use it in (35) which

would become

$$\tilde{E}^j = \sqrt{c' * (q^j)^2 - \frac{1}{M}} \qquad \text{or} \qquad \sqrt{c' * (q^j)^2 - W^j}\,. \tag{38}$$

The optimum form of q^j must be such as to minimise the errors as defined by eq. (36). We denote the variable part of this expression by C_j, so that

$$C^j = \hat{c} * (q^j)^2.$$

$$\tilde{E}^j = \sqrt{C^j - 1/M} \qquad \text{or} \qquad \sqrt{C^j - W^j}\,. \tag{39}$$

The calculus of variations may now be used to minimise C^j. Reverting here to the full integral notation q^j is subject to the restriction

$$\int q^j f_i \mathrm{d}x = I_i^j. \tag{40}$$

b is an arbitrary function and B a differential constant, giving the variation Bb on q^j and the resulting variation in C^j is

$$\delta C^j = 2B \int \hat{c} q^j b \mathrm{d}x + B^2 \int \hat{c} b^2 \mathrm{d}x.$$

Eliminating the term in B^2, since B is small,

$$\delta C^j = 2B \int \hat{c} q^j b \mathrm{d}x.$$

The restrictions (40) mean that b must satisfy

$$\int b f_i \mathrm{d}x = 0_i. \tag{41}$$

Putting $q^j = \hat{p}^j / \hat{c}$ (42)

then, for minimum error (ie. $\delta C^j = 0^j$), we have

$$\int \hat{p}^j b \mathrm{d}x = 0^j. \tag{43}$$

From (41) and (43) it follows that $\hat{p}_j$ is any linear combination of the f_i; which particular combination is determined by (40). So, defining $\hat{p}_j$ as the a priori relative probabilities

$$\hat{p}_j = \frac{1}{M} f_j / \hat{c}, \text{ or as in (37), } W_j f_j / \hat{c} \tag{44}$$

then $g_j = \hat{p}_j$ in (19) will give orthogonalised incrementing functions for which the unit error given by (39) will be a minimum. The relative probabilites have the additional property that

$$\hat{p}_j 1^j = 1, \tag{45}$$

which leads to

$$Q = q_j 1^j = 1, \tag{46}$$

which means that every count acquired leads to a set of increments which add to exactly 1. Thus the sum of the estimates is exactly equal to the actual number of counts, i.e.

$$N = N' 1_i = N'.$$

Eqs. (44) and (19) together constitute a solution to the task set out in section 1. A step by step procedure for executing this procedure is set out in fig. 1., together with an extension of the method which allows the q_j to be reduced to binary functions giving maximum data compression.

A simpler measure of the accuracy of the method is given by the sum of the mean square errors

$$E^2 = 1^j E_j^2 = \hat{c} * q^2 - 1, \qquad q^2 = q_j q^j. \tag{47}$$

Substituting (18) and (44) into (47) and using the definition (11), this expression simplifies to

$$E^2 = W_i Q_i' - 1, \tag{48}$$

in which $W_i Q_i'$ means the average value of the diagonal elements in the correction matrix – the inverse of the projection matrix, $g^i * f_j$.

For the case where there are only two components, f_1 and f_2, this expression may be evaluated as follows:

$$E^2 = \tfrac{1}{2} A / (1 - A)$$

with $A = \int f_1(x) f_2(x) / \tfrac{1}{2}[f_1(x) + f_2(x)] \cdot \mathrm{d}x$

for the following special cases, this leads to:

Non overlapping spectra,

$[f_1(x) f_2(x) = 0]$: $\quad A = 0,\ E^2 = 0$:

Identical spectra,

$[f_1(x) = f_2(x)]$: $\quad A = 1,\ E^2 = \infty$:

Gaussians separated by 1 fwhm:

$A = 0.345,\ E^2 = 0.263,\ E_1 = 0.363.$

For more than two components, if the spectra f_i are not linearly independent, then $|P| = 0$ and $Q_i' \to \infty$. A could be called the spectrum overlap.

Fig. 2 shows the variation of the unit error $\tilde{E}$ with more familiar parameters. The unit error is approximately linearly dependent on co-resolution (mean fwhm/peak separation) [8,13] but depends on the spectrum shape, measured by the peak/total ratio (proportion of spectrum lying within the fwhm, 0.5 for an exponential or a typical pulse height spectrum, 0.75 for a Gaussian, 1 for a rectangular distribution).

If the approximate composition is known in advance, or using the estimated composition itself, improved estimation of the error is possible by using a weighted average of the fwhm.

The trade-off between detector resolution and detection efficiency may be measured using fig. 2.

Note that the estimates and errors considered here relate to spectrum population, not isotope activity, for which the proportional error is always $1/\sqrt{N'}$, additive

in quadrature to the unit error calculated here. $\tilde{E}$ originates from statistical variation in energy, not rate of decay.

Appendix III

Significance of the estimate

The hypothesis that the composite c' contains only members of the ensemble of library spectra, f_i may not be true; foreign components may be present or the detector may be affected by voltage drift. Alternatively, the statistical variations, d'_j, may be sufficiently large to reduce the reliability of the estimate. These factors are detectable to the extent that they contribute towards a lack-of-fit between the "constructed" spectrum, c, and the actual composite, c'. Measurement of this lack-of-fit will show whether the unit error, $\tilde{E}_j$ is based on significant hypotheses. This cannot be an a priori measure like $\tilde{E}_j$, which is known in advance of the acquisition of c', but must be generated in the same way as the estimates N^j. χ^2 measurement of the lack-of-fit provides one possible avenue, but a method which can be carried out by the incrementing technique is preferred.

The lack-of-fit is

$$d' = c' - c \tag{49}$$

$$d' * 1 = 0, \tag{50}$$

$$\text{where } c' = f'_i N'' \quad \text{and} \quad c = f_i N^i. \tag{51}$$

Defining a fitting measure, s

$$s = S' g_i - 1, \tag{52}$$

in which the set of coefficients, S^i, must be such that

$$s * f^j = 0^j \text{ (orthogonality)}. \tag{53}$$

The incrementing tables g_i are arbitrary but for detecting the presence of foreign spectra $g_i = f^i$ is optimal, and for detecting drift in detector gain etc. $g_i = f_i^{(1)}$ is optimal.

Substituting (52) into (53), using (4), and defining

$$F_i^j = g_i * f^j, \tag{54}$$

$$\text{then } S' F'_i = 1^j, \qquad \text{that is } S^i = 1^j \left(F_i^j\right)^{-1}. \tag{55}$$

Considering the projection of s, $F' = s * c'$ using $c' = f_i N^i + d'$ and noting (53), then

$$F' = s * d'. \tag{56}$$

Or, using (26), (51) and (53), this reduces to

$$F' = s * d'_i N''. \tag{57}$$

From here the expected value of F', $\bar{F}$, and the expected square value of F', $\overline{F^2}$, can be calculated:

$$\bar{F} = s * \bar{d}'_i N'' = 0,$$

$$\overline{F^2} = s^2 * \left(d'_i d'^j\right) N'' N'_j.$$

Since variations in the separate components of the spectra are uncorrelated and there is Poisson statistics (ie. mean square deviations = mean frequency) in each channel, this becomes

$$\overline{F^2} = s^2 * f_i N'^2_i. \tag{58}$$

N'^2 is not known in advance of acquisition, but $\overline{F^2}$ can be calculated for a range of compositions, and the appropriate value selected for comparison, using the estimated composition.

$$\text{Putting } \dot{N}_i = N'/M \text{ for } N'_i \tag{59}$$

and using the definitions (34) and (37) and

$$\tilde{F} = \sqrt{\overline{F^2}/N'} \tag{60}$$

$$(58) \text{ becomes } \tilde{F} = s^2 * \hat{c}. \tag{61}$$

F' will be normally distributed with the standard deviation, $\tilde{F}$. If F' deviates significantly from zero, then this will indicate that the estimates N^i are invalid. F' does not give a means of improving the estimates however. Foreign spectra exist which will not be detected by F' and drift in detector gain will have null effect at some composition, c, so more than one significance measure may be necessary to ensure that the estimates have been made under valid conditions. Where feasible such significance measures are computed in real time as additional projections. The presence of background radiation may be dealt with by reducing the library spectra by background subtraction, and including the background spectrum, f_0, in the ensemble, so that the incrementing tables, q_i, are orthogonal to f_0 [1]. The incrementing table q_0 corresponding to the background, and the projection N_0, being an estimate of the background count, need not however be computed.

Appendix IV

Comparison with other methods of separation [6,7]

(A) Least Squares fitting of composite spectrum by composite of library spectra [3,12]: this method begins from the requirement that

$$d' * d' = \text{minimum, } i.e.\ \partial/\partial N^k (d' * d') = 0_k \tag{62}$$

from which follows,

$$f^j * \left(f_k N^k - c'\right) = 0^j, \tag{63}$$

$$\text{i.e. } N^k = \left(f^j * f_k\right)^{-1} f^j * c', \tag{64}$$

which is eq. (17) with f^j for g^j. This is not the optimal choice, but the methods described above can be applied to this method. Eq. (46) does not apply.

(B). χ^2 method of fitting composite spectra: Here, the value of the composite spectrum is usually used to weight the contribution of each channel to the fitting

measure. Following a similar argument to (62), (63), (64) above, it can be shown that this method is equivalent to using

$$g^j = \frac{1}{M} f^j / c', \tag{65}$$

which differs from (44) only by using c' instead of $\hat{c}$. In fact χ^2 tests should use the a priori frequency for the weight in each channel so (44) represents a true χ^2 method. The traditional use of c' in χ^2 curve fitting is erroneous and leads to systematic errors especially for low count numbers [11]. Since c' is not available before acquisition, the above erroneous form of χ^2 cannot be used for real-time analysis. The identity between the method derived here as optimal for estimation of intensities and the well-established χ^2 method lends weight to the results obtained above.

The use of χ^2 rather than least squares (method A) in curve fitting leads to equal contribution to the sum-of-squares by each count. Each channel has it's contribution normalised by the standard deviation of its contribution. This leaves out of account physical rather than statistical arguments, that channels having a high frequency are less affected by noise, unrelated to the source, and should therefore carry greater weight, as in case (A) above.

(C). Least squares (or χ^2) fitting of first derivatives of intensity curves [4,5]: Since

$$\int f^{(1)^2}(x)\mathrm{d}x = -\int f^{(2)}(x) f(x)\mathrm{d}x$$

provided $f^{(1)}(x) \to 0$ as $x \to \pm\infty$, we have here

$$g^j = f^{(2)^j}. \tag{66}$$

This method will lead to greater emphasis being placed on the peaks, for which the same comments apply as above, which essentially relate to whether or not the library spectra do represent the component spectra.

(D). Window method: Here $g^j = 1$ or 0, according to which of the relative probabilites, p^j is the greatest. The resulting estimate of the composition must be corrected by multiplication by the correction matrix Q'_j.

Pre-multiplication of the binary functions, g^j, by Q'_j, as in eq. (18) leads to a 'real-time' method similar to the one described above. We could describe the method derived above as a 'relative' window method, since each count is divided between the various N^j in proportion to the values of $\hat{p}^j$, rather than being allocated entirely to one or the other.

The window method has the great advantage that it uses only binary integers, with consequent saving of memory-space, and provided the correction matrix, computed to full accuracy, is applied to the output, the accuracy of the window method is only marginally less than that obtained by using exact values of $\hat{p}^j$. A technique has been described above for adapting the above 'relative probability' method to binary integer incrementation, achieving optimum data-compression.

Appendix V

A summary of symbols used in the appendices is given below

- B, b differential constant, arbitrary variation on g_j;
- c' actual composite spectrum. c composite of library spectra approximating c'. $\hat{c}$, a priori composite;
- C_j variable part of errors in estimating intensities;
- d_j deviation of actual components of spectra from ideal form;
- d' deviation of actual composite from form 'constructed' from library spectra.
- D'^j_k deviation of transformation matrix from its ideal, unit matrix, form;
- E'^j error in estimating intensity N'^j (mean = $\bar{E}^j$, standard value = $\tilde{E}^j$);
- E square root of sum of mean square errors, E'^j;
- f^j pure library spectra; f'^j actual component spectra;
- F'_j matrix of product integrals of pure library spectra;
- F' projection of significance function, (standard value, $\tilde{F}$);
- g^j arbitrary incrementing function (also referred to as 'tables') (optimal form is relative probabilities $\hat{p}_j$);
- I'_k Unit matrix. I'^j_k matrix transforming actual composition into estimated composition;
- N' actual number of counts. N, sum of estimated intensities;
- N'^j actual intensities of components. N^j, estimated intensities;
- P'^j projections of g^j;
- P'^j_j actual projection matrix. P^j_j, projections of $g^{j'}$ with pure library spectra f_j;
- $\hat{p}_j$ a priori relative probabilities;
- q_j orthogonalised incrementing functions (tables). Q (constant) sum of q_j;
- Q'^j_j correction matrix transforming projections (estimates) into actual composition. Q'_j ideal form of Q'^j_j;
- s incrementing function for significance measure;
- S' coefficient of f_j in s;
- W_j a priori composition of spectra;
- x energy;
- i, j, k ($= 1$ to M) indices indicating one of the M component spectra.

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