THE EFFECT OF SHIFT OF TOTAL ABSORPTION PEAKS ON THE ACCURACY OF DETERMINATION IN NON-DESTRUCTIVE ACTIVATION ANALYSIS (THE CASE OF COVELL'S DIGITAL METHOD)

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The shift of a total absorption peak in the gamma spectrum of the sample relative to a corresponding peak in the gamma spectrum of the standard is considered to be an inevitable fact. The effect on the value of the systematic error has been discussed with reference to the case in which Covell's method is applied.

Suggestions have been made as regards the way of determining the channel zero, the number of channels to be covered in calculations and the position of the peak in a pulse height analyser.

1. *Introduction*

A comparison of the total absorption peaks (in sample and standard spectra) is the last step of the procedure in non-destructive activation analysis. As multi-channel analysers are commonly used now, the method developed by Covell [1, 2] is very often applied in evaluating the areas of total absorption peaks. They are represented by a quantity N defined as

$$N = \sum_{i=-n}^{+n} a_i - \left(n + \frac{1}{2}\right) (a_n + a_n) \tag{1}$$

where a_i is the number of counts in channel i, n is the number of channels covered in calculations, to the left and rght from channel zero.

As it is quick and simple, Covell's method is very convenient in laboratory practice. It assumes, however, a straight line character of the background counter in the registered total absorption peak region, a condition which is rarely fulfilled in complex gamma spectra. Thus, when applying this method, there is the hazard that the results obtained are laden with a systematic error. The effect of the shape of background on the systematic error has been discussed elsewhere [3].

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In practice, the instability of the spectrometer is often the reason why the sample and standard peaks are shifted one to another. This effect may also result in a considerable systematic error. Its importance depends on the shift itself, but also on whether the channel zero is the same for both (sample and standard) peaks or not; two different channels of maximum counts being selected in the latter case.

The results of investigation on the effect of shift of peaks on the accuracy of determination are presented below. The causes of the shift of peaks and methods of eliminating it make a separate problem.

2. *Theoretical*

It is well known that the counts registered in channels of a correctly operating pulse height analyser lay out a Gaussian curve [4, 5]. More exactly, not the counts themselves but their expected values. If the statistics of counting is "good" the points practically lie on a Gaussian curve. An example is given in Fig. 1 in which the points are the counts of the total absorption peak and the full line is the theoretical Caussian curve which has been fitted to them.

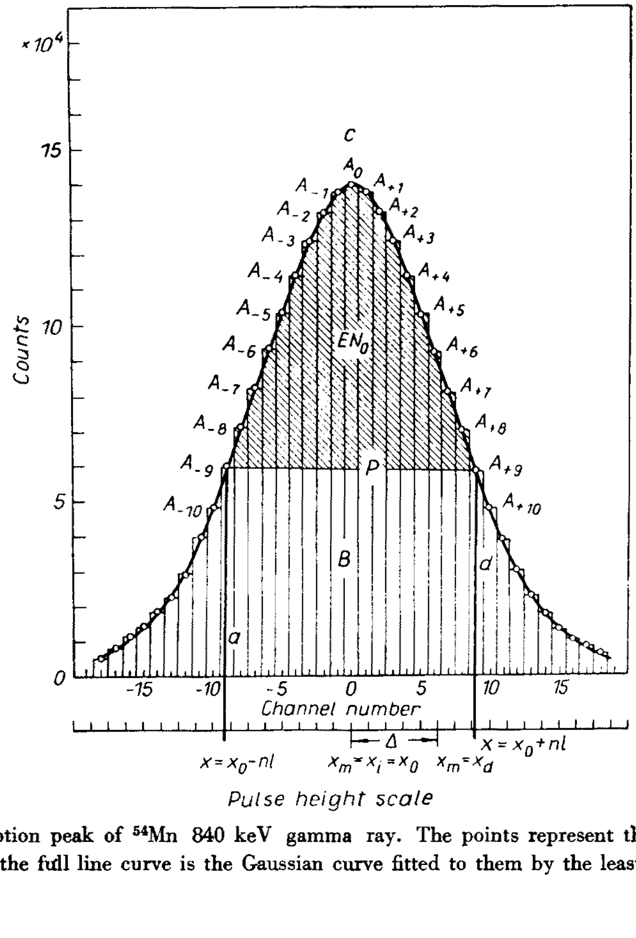

Fig. 1. Total absorption peak of ^{54}Mn 840 keV gamma ray. The points represent the counts registered in channels, and the full line curve is the Gaussian curve fitted to them by the least squares method

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Let A_i be the expected value of the count a_i in channel i ($A_i = Ea_i$). Then, for any value of A, one has the relation

$$A = A_t \frac{1}{\sqrt{2\pi}\,\sigma_m} \exp\left(-[x-x_m)^2/2\sigma_m^2\right] \tag{2}$$

$$\sigma_m^2 = \varrho_m^2/8 \ln 2$$

where A_t is the total expected number of counts in the peak, registered during a time t; x_m is the position of the peak maximum, in pulse height (voltage) scale; σ_m and ϱ_m are the standard deviation and the half-width, respectively, for a peak maximum situated at x_m.

Let us suppose that, as a result of a shift of the peak, the position of its maximum, x_m, has changed by a value Δ. (In practice this may mean a shift of the peak in the sample spectrum with respect to the corresponding peak in the standard spectrum). If x_i is the initial position of the peak maximum (for instance, that in the standard spectrum) and x_d is its shifted position (*i. e.* the position of the peak maximum in the sample spectrum) then $\Delta = x_d - x_i$. The peak in a new position x_d is described by another Gaussian curve (different from that which described the peak in position x_i). The value of the standard deviation σ_m — Eq. (2) — is also changed. Since the resolution r for a given energy does not depend upon the position of the peak, hence $r = \varrho/x_m =$ constant and

$$\varrho_d = \varrho_i \frac{x_d}{x_i} = \varrho_i \left(1 + r \frac{\Delta}{\varrho_i}\right). \tag{3}$$

Let us consider two cases

1° Channel zero in Covell's formula is the same in the sample and standard spectra — although a shift is found. To simplify the problem let us assume temporarily that the position of the middle of channel zero coincides with the initial position of the peak x_i, *i. e.* $x_0 = x_i$ (see Fig. 1).

With these assumption the expected value of N from Eq. (1), for this case refered to as N_1, can be evaluated in the following manner (Fig. 1):

$$EN_1 \approx P - B$$

where

$$P \triangleq A_t \frac{1}{\sqrt{2\pi}\sigma_a} \int\limits_{x_i - nl}^{x_i + nl} e^{-\frac{(x-x_d)^2}{2\sigma_d^2}} dx$$

$$B = \frac{1}{2} \cdot 2nl \left[A_t \frac{1}{\sqrt{2\pi}\,\sigma_d} e^{-\frac{(x_i+nl-x_d)^2}{2\sigma_d^2}} + A_t \frac{1}{\sqrt{2\pi}\,\sigma_d} e^{-\frac{(x_i-nl-x_d)^2}{2\sigma_d^2}} \right]$$

Putting

$$\Phi(x) = \frac{1}{\sqrt{2\pi}} \int\limits_0^x e^{-\frac{1}{2}t^2} dt$$

$$F(x) = \frac{1}{\sqrt{2\pi}} e^{-\frac{1}{2}x^2}$$

and making use of Eq. (3) we can express EN_1 in a form suitable for calculations

$$EN_1 \triangleq A_t \left\{[\Phi(u)-\Phi(v)]-2.354\,\frac{nl}{1+r\Delta}\,[F(u)+F(v)]\right\} \tag{4}$$

where

$$u = 2.354\,\frac{\Delta+nl}{1+r\Delta}, \quad v = 2.354\,\frac{\Delta-nl}{1+r\Delta}.$$

The shift and the width of channel l are expressed in ϱ_i-units. The evaluation of EN_1 using relation (4) is more accurate when the width l of the channel is narrower (see Appendix A).

2° In this case we make the position of the middle of channel zero coincide with the peak maxima, *i.e.* $x_0 = x_i$ for the standard and $x_0 = x_d$ for the sample. It happens, of course, that in actual spectrometric measurements $x_0 \neq x_m$, but the accepted assumption does not effect the general character of the present considerations. This problem will be discussed below in more detail.

Let N_2 be the value of N for this case. Putting x_d instead of x_i, the expected value EN_2 can be evaluated in the same way as before:

$$EN_2 \triangleq 2A_t\left[\Phi\left(2.354\,\frac{nl}{1+r\Delta}\right)-2.354\,\frac{nl}{1+r\Delta}\,F\left(2.354\,\frac{nl}{1+r\Delta}\right)\right]. \tag{5}$$

If $\Delta = 0(x_d = x_i)$ then we should have $EN_1 = EN_2 = EN_0$ (N_0 is the value of N for $\Delta = 0$). This is true since as can be seen from Eqs (4) and (5),

$$\Phi(-x) = -\Phi(x) \text{ and } F(x) = F(-x).$$

For EN_0 one has

$$EN_0 \triangleq 2A_t\,[\Phi(2.354\,nl)-2.354\,nl\,F(2.354\,nl)].$$

3. *Discussion*

Equations (4) and (5) contain information on the effect of the shift of the peak Δ and the number of channels upon the accuracy (systematic error) of the value of N calculated from digital data of a multi-channel pulse height analyser.Both EN_1 and EN_2 have been normalized against EN_0 (unshifted peak). A comparison of two corresponding peaks which are shifted relative to each other lades the determination with a systematic error. Its importance depends on the manner of selecting channel zero, on the number n of channels used and on the width l of the channel; it does not depend on the value of A_t (intensity of radiation).

Fig. 2 presents the ration EN_1/EN_0, calculated according to Eq. (4), for several value of nl (expressed in ϱ_i-units). It can be seen that a comparison of two peaks shifted relatively to each other by Δ involves a considerable systematic error if the same channel zero is taken for both sample and standard spectra (case 1°). It is more important when the number of channels n (for l = const) is smaller. It should be noted that the axis of coordinates is not

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an axis of symetry for the curves shown in Fig. 2, as the expression (4) is not an even function with respect to Δ. For negative shifts the ratio EN_1/EN_0 is closer to unity than for the symmetrical positive shifts.

The results obtained in the case 2°, (the channel zero always at the peak maximum) are far more accurate than those which are obtained in the case 1°. Fig. 3 presents the ratios EN_1/EN_0 and EN_2/EN_0 (full line curve) as a function of the shift for the two extreme cases:

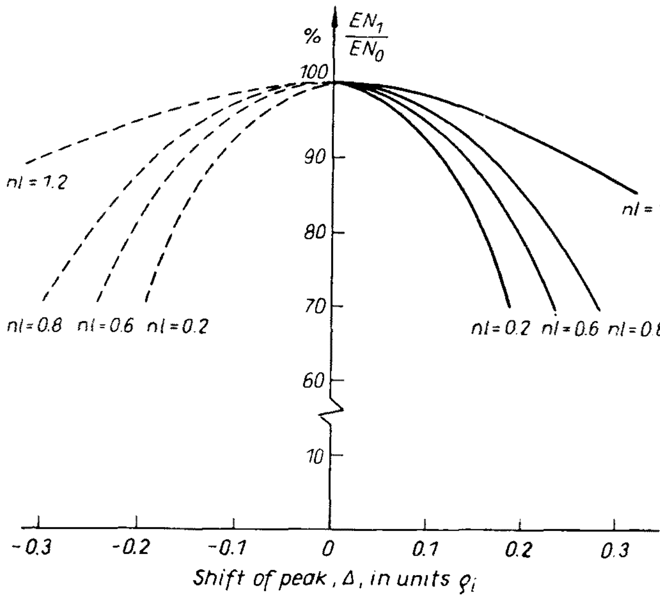

Fig. 2. The effect of the value Δ on the accuracy of values of total absorption peak areas calculated by digital method according to case 1° (*i.e.* the same channel zero for the sample and the standard). Explanation of the symbol in the text

$nl = 0.17\ \varrho_i$ ($n = 2$ channels) and $nl = 0.87\ \varrho_i$ ($N = 10$ channels). It can be seen that these ratios differ by almost one order of magnitude. The ratio EN_2/EN_0 for any shift Δ is closer to unity when the product nl is bigger.

A practical conclusion can be drawn from the discussion given above: the channel zero should be selected in the way described in the case 2°. The number of channels taken into account should be the highest possible.

One has to remember that, as has been mentioned above, in the actual spectrometric measurements the peak maximum rarely coincides with the middle of the maximum count channel. On the other hand, the observed shifts of the corresponding sample and standard peaks generally do not exceed 0.1 the half-width, *i. e.* 1 to 2 channels. Figure 4 presents five typical configurations of counts in the proximity of the peak maximum (*ca* 5×10^4 counts). They have been selected from a big series of measurements. It can be seen that the points corresponding to the maximum count can be 0.5 channel away from the peak maximum (*a* and *e* in Fig. 4). If Covell's method is used for comparing two of the five peaks presented

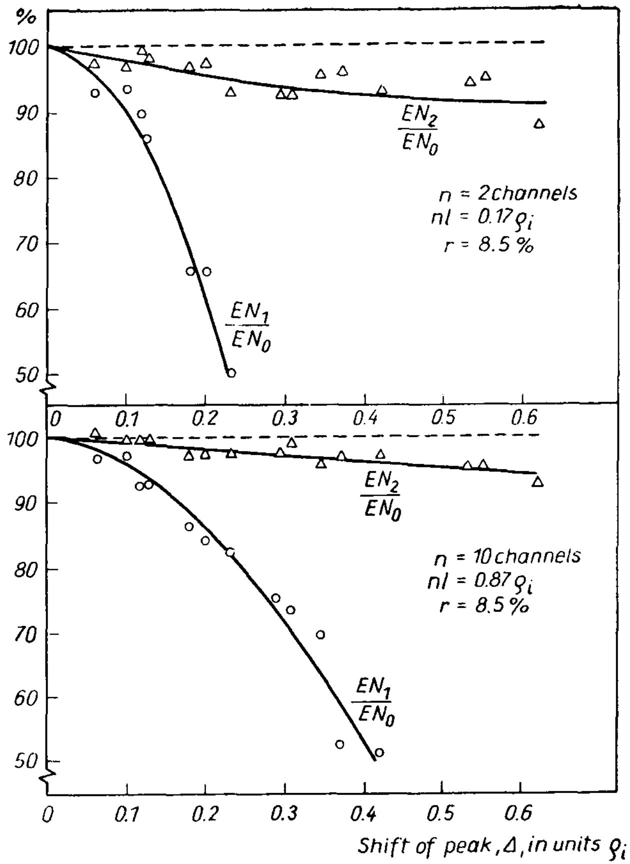

Fig. 3

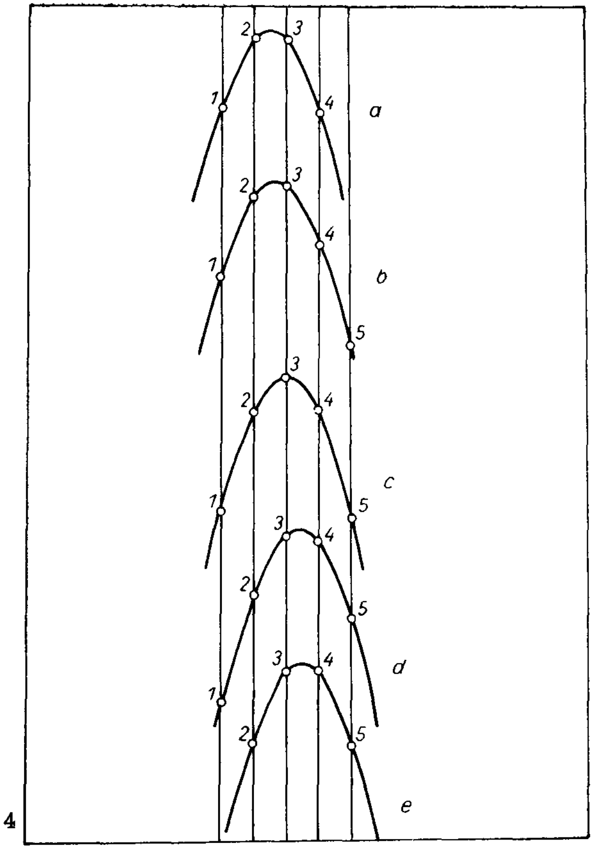

Fig. 4

Fig. 3. Comparison of the accuracy (systematic error) for the two ways of choosing channel zero in Covell's method. Points represent results of the blank experiments

Fig. 4. The typical cases of configuration of points (counts in channels) in proximity of the gamma-ray total absorption peak maximum. These examples have been chosen from a large series of ^{54}Mn 840 keV gamma-ray measurements. If the peak c is considered to be in position zero the shifts of peaks, a, b, d and e are $\Delta_a = 0.5$, $\Delta_b = -0.2$, $\Delta_d = +0.3$ and $\Delta_e = +0.5$

in Fig. 4 and the channel 3 is considered to be zero for both of them, the result is laden with an error described in the case *1°* (Fig. 2). Its value is highest for the pair of peaks *a* and *c*: 0.5 channel. For the pair of peaks *a* and *e* the error is due exclusively to the asymmetry of the curves shown in Fig. 2, although the shift is as high as 1 channel.

It may seem that a reduction of the channel width (by displacing the peaks to the right) would improve the accuracy. This is not true: at a very low l value (the peak spread out over many channels) an error, sometimes serious, due to statistical fluctuation of counts can be made in selecting the peak maximum from the printer. On the other hand, at high l-values the shift can be considerable, as for instance for the pair a—c in Fig. 4. A series of mesurements proved that the most advantageous conditions are when $\varrho = 8$ to 12 channels.

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4. *Conclusions*

1° The channel with maximum counts should be taken for the channel zero.

2° If Covell's formula is used, as many channels as possible should be taken into account.

3° The peaks on which the determination is based should be situated in a position so as to have a half-width of $\varrho = 8$ to 12 channels.

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APPENDIX A

The evaluation of the accuracy of an approximation of the value EN_0 on the basis of the difference P—B (Fig. 1)

The expected EN of the number N (Covell's formula) has been replaced in the theoretical considerations by the difference of two areas, P—B. As the integral P stands for the sum of correspodning rectangles, this difference is only approximately equal to EN.

An evaluation of the accuracy of such an approximation is given below (for the case represented in Fig. 1, *i. e.* for $\Delta=0$ which does not affect the general character of the consideration):

According to Eq. (4) the area P in Fig. 1 is

$$P = 2A_t\Phi(2.354\, nl). \tag{A1}$$

The expected value of the number of counts in channel i is given by Eq. (2). A simple transformation lets us express A_i as

$$A_i = A_t\,\frac{2.354}{\varrho}\,F(2.354il). \tag{A2}$$

Hence, the area S_i of the i-th rectangle is

$$\begin{aligned} S_i &= A_i l \cdot \varrho \\ &= A_t\, 2.354\, l\, F(2.354\, il). \end{aligned} \tag{A3}$$

The integral P from (A_1) corresponds to the sum

$$I = \sum_{i=-n}^{+n} S_i - S_n. \tag{A4}$$

The ratio $r = \frac{I-P}{P}$ is an index of accuracy of the approximation $I \triangleq P$ and, indirectly, of the approximation $EN_0 = P-B$.

From (A1), (A3) and (A4) it follows that

$$r = \frac{2.354\, l\{\sum_{i=-n}^{n} F(2.354il) - F(2.354nl)\} - \Phi(2.354nl)}{\Phi(2.354nl)}. \tag{A5}$$

It can be shown (on the basis of the definition of the definite integral) that $r \to 0$ if $l \to \infty$. That is why the most important deviation of I-values from P takes place at high values of l.

TABLE I

The ratio r as a function of n for $l = 0.2$

n	2	3	4	5	6	7	8	9	10
r%	−1.20	−0.74	−0.32	−0.05	+0.10	+0.16	+0.17	+0.18	+0.18

Nevertheless, as can be seen from Table 1, even for $l = 0.2$ (*i. e.* $\varrho = 5$ channels) the accuracy of the approximation I through P is satisfying.

REFERENCES

[1] D. F. Covell, *Analyt. Chem.*, **31**, 1785 (1959).
[2] F. Adams, J. Hoste, *Non-Destructive Activation Analysis*, *Atomic Energy Review*, **4**, 113 (1966).
[3] S. Sterliński, *Analyt. Chem.*, in press.
[4] S. Sterliński, *Nukleonika* (Poland) **8**, 709 (1963).
[5] R. L. Heath, *CU (PNPL)*-227.

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