

THEORETICAL EXPRESSIONS FOR THE COUNTING EFFICIENCY AND PULSE  
HEIGHT DISTRIBUTION OBTAINED FOR A BETA-EMITTING ISOTOPE BY A  
LIQUID SCINTILLATION COUNTER

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ABSTRACT

A probabilistic description of the liquid scintillation process is used in order to derive formulae which express the counting efficiency of a liquid scintillation counter and the pulse height distribution obtained by it as a function of the photon yield of the scintillation liquid. This photon yield is described by an energy-dependent function containing only two unknown parameters "a" and "b". Parameter "a" varies with the amount of chemical quenching in the cocktail while "b" is dependent on the nature of the solvent. The expressions also include the coincidence resolving time, but because of the complicated nature of the time-dependency of the prompt and delayed fluorescence yield, exact expressions can only be derived for coincidence resolving times that are long enough to incorporate most of the photons from both the prompt and delayed emissions.

A theoretical quench curve is made up of counting efficiency plotted as a function of the mean number of photoelectrons produced in one disintegration. This curve is then compared with the experimental data for a series of sealed quenched standards measured with a multi-channel analyser. The theoretical curve is valid only for chemically quenched, homogeneous samples.

INTRODUCTION

Liquid scintillation counting using a commercial instrument for routine measurements is not an absolute technique as the counting efficiency can be determined only by comparing the quench level of the unknown samples with a set of calibration standards. A method that is widely used is to make up a calibration curve using samples of more or

less known activity with different levels of quenching. The quench level is measured by determining either the channels ratio of the isotope pulse height distribution, as originally proposed by Baillie<sup>1</sup>, or the mean pulse height<sup>2 3</sup>. For low activity samples, the Compton-photons from an external  $\gamma$ -radiating isotope placed beside the sample, may be measured.

During the last decades a few "absolute" methods have been proposed. These have been based on theoretical expressions for the counting efficiency but they have not met with great success. Horrocks and Studier<sup>4</sup> as early as 1961 proposed a method based on the ratio between coincidence and total counts, although not using the correct theoretical expressions for these two counting efficiencies. Kolarov et al.<sup>5</sup> have developed this method by introducing the correct theoretical expressions. The coincidence counting efficiency,  $\epsilon_c$ , and the total counting efficiency of either of the two photomultipliers alone,  $\epsilon_j$ , were given by the expressions

$$\epsilon_c = \int_0^E S(E) (1 - e^{-a_1 \cdot L(E,b)}) (1 - e^{-a_2 \cdot L(E,b)}) dE \quad (1a)$$

$$\epsilon_j = \int_0^E S(E) (1 - e^{-a_j \cdot L(E,b)}) dE \quad (j=1,2) \quad (1b)$$

where  $S(E)$  is the normalized  $\beta$ -distribution according to Fermi<sup>6</sup>, and  $E_m$  is the maximum energy of the electron. The constants  $a_j$  are products of the scintillation efficiency, which depends on the quench level, and the probabilities that a photon will liberate a photoelectron in either of the two photomultipliers. The "ionization quenching" function  $L(E,b)$  can be considered as a function giving the energy finally available for excitation of solvent molecules to singlet states (prompt or delayed). The available energy equals the electron energy  $E$  only if  $b = 0$ . The function originally given by Birks<sup>7</sup> has been widely used:

$$L(E,b) = \int_0^E \frac{dE'}{1 + b(dE'/dx)} \quad (2)$$

where  $b$  is a constant depending only on the solvent and  $dE/dx$  is the stopping power of the solvent. An excellent review<sup>8</sup> of stopping power

has recently been published.

The method of absolute counting was reviewed in 1971 by Gibson<sup>9</sup> and since then not very much has happened. All the methods introduced until now depend on knowledge of the constant  $b$ , and experimental determination of the quench variables  $a_j$  by using, for example, the coincidence/total method. There are at least four expressions for  $L(E,b)$  proposed in current literature<sup>7 10 12</sup> but no comprehensive measurements of the constant  $b$  for different scintillation solutions. Some method should exist to determine  $b$  for each of the four  $L(E,b)$  functions, and to determine which of the functions is the most accurate one.

We have undertaken a thorough theoretical study into the factors influencing the pulse height distribution and counting efficiency in order to develop a method to determine the constant  $b$  in liquid scintillation solutions for different  $L(E,b)$ -functions. This method also gives some indication of which function is the most accurate one.

#### THEORETICAL BACKGROUND

Assuming that the scintillation process is governed by Poisson statistics and that the mean number of photons produced in a scintillation is given by  $a' \cdot L(E,b)$ , where  $a'$  is the scintillation efficiency, an expression for the photon distribution can be written as follows

$$P(n|a',b) = \int_0^E S(E) \frac{e^{-a' \cdot L(E,b)} [a' \cdot L(E,b)]^n}{n!} dE \quad (3)$$

This expression gives the probability that  $n$  photons will be emitted from one decay. In the following derivations the abbreviations  $L$  for  $L(E,b)$  and  $S$  for  $S(E)$  are used.

The detector chamber consists of three parts: photomultiplier no. 1 ( $pm_1$ ), photomultiplier no. 2 ( $pm_2$ ) and a "hole". The probability that a photon will produce a photoelectron in  $pm_1$  or  $pm_2$  is  $p_1$  and  $p_2$  respectively. These are generally spatial functions which depend on the point  $\underline{r}$  in the solution where the photon originates and on phototube quantum efficiencies. For simplicity, let the symbols  $\underline{p}_1$  and  $\underline{p}_2$  denote

these spatial functions. Every photon that does not cause any photoelectron is trapped in the "hole". The probability for this is  $1 - (\underline{p}_1 + \underline{p}_2) = 1 - \underline{p}$ . In this case, the probability of having  $k_1$  photoelectrons at  $pm_1$  and  $k_2$  at  $pm_2$  when  $n$  photons are emitted is given by the trinomial theorem as:

$$P(k_1, k_2 | n, \underline{p}_1, \underline{p}_2) = \frac{n!}{k_1! k_2! (n - k_1 - k_2)!} \underline{p}_1^{k_1} \underline{p}_2^{k_2} (1 - \underline{p}_1 - \underline{p}_2)^{n - k_1 - k_2} \quad (4)$$

where  $k_1 + k_2 = k < n$ . The probability that a pulse consisting of  $k_1$  and  $k_2$  photoelectrons will be detected by the coincidence analyser is denoted by  $P(k_1, k_2 | t_c)$ , where  $t_c$  is the coincidence resolving time. The expression for this probability reads:

$$P(k_1, k_2 | t_c) = 1 - \int_0^{\infty} [\phi(t) k_1 \phi(t)^{k_1 - 1} \phi(t + t_c)^{k_2} + k_2 \phi(t)^{k_2 - 1} \phi(t + t_c)^{k_1}] dt \quad (5)$$

where  $\phi(E)$  is the normalized fluorescence decay function containing both the prompt and delayed components, <sup>13</sup> and  $\phi(t)$  is defined by:

$$\phi(t) = 1 - \int_0^t \phi(u) du \quad (6)$$

As both  $\phi(t)$  and eq. (5) are fairly complicated functions and  $\phi(t)$  also depends on the quench level, it is advantageous to use such long coincidence resolving times that  $P(k_1, k_2 | t_c) \approx 1$ . In that case the following theoretical treatment is simplified.

If the pulses from both photomultipliers are summed and the integration time is long enough to include all photons from one decay, then the registered pulse height is equal to  $k = k_1 + k_2$ . The probability to have a total of  $k$  photons is generally given by:

$$P(k | n, \underline{p}_1, \underline{p}_2) = \sum_{\substack{k_1 = k_0 - 1 \\ k_2 = k - k_1}}^{k-1} P(k_1, k_2 | n, \underline{p}_1, \underline{p}_2) \cdot P(k_1, k_2 | t_c) \quad (7)$$

where  $k_0 = 2$  for the coincidence distribution and  $k_0 = 1$  for the total

distribution. If  $P(k_1, k_2 | t_c) = 1$  and  $k_0 = 2$ , then this sum can be simplified to:

$$P(k | n, p_1, p_2) = \binom{n}{k} (1-p)^{n-k} (p_1^k - p_2^k - p^k) \quad (8)$$

The probability of having  $n$  photons was given by equation (3), hence, the total probability for  $k$  photoelectrons is given by:

$$\begin{aligned} P(k | a', b, p_1, p_2) &= \sum_{n=k}^{\infty} P(n | a', b) \cdot P(k | n, p_1, p_2) = \\ &= (p_1^k - p_1^k - p_2^k) \frac{1}{k!} \int_0^E S e^{-a'L} \sum_{n=k}^{\infty} \frac{(a'L)^n (1-p)^{n-k}}{(n-k)!} dE = \\ &= (p_1^k - p_1^k - p_2^k) \frac{1}{k!} \int_0^E S e^{-pa'L} (a'L)^k dE \end{aligned} \quad (9)$$

This equation is valid for a point  $\underline{r}$  in the solution. For a solution with volume  $V$ , eq. (9) must be integrated

$$P(k | a', b, V) = \int_V P(k | a', b, p_1, p_2) d\underline{r} \quad (10)$$

For further treatment it is convenient to use the approximation that  $p_1 = p_2 = p/2$ , which means that  $p_1$  and  $p_2$  are equal and independent of volume. This approximation is valid providing that the sample solution is clear and uncoloured.

The counting efficiency, according to definition, is:

$$\epsilon(a', b, V) = \sum_{k=k_0}^{\infty} P(k | a', b, V) = \int_V \sum_{k=k_0}^{\infty} P(k | a', b, p_1, p_2) d\underline{r} \quad (11)$$

where  $k_0 = 1$  for the total efficiency of both tubes together ( $\epsilon_t$ ), and  $k_0 = 2$  for the coincidence efficiency ( $\epsilon_c$ ). If equation (9) is used, then  $\epsilon_c$  can be written as:

$$\begin{aligned} \epsilon_c(a', b, p_1, p_2) &= \int_0^E S e^{-pa'L} \sum_{k=2}^{\infty} (p_1^k - p_1^k - p_2^k) \frac{1}{k!} (a'L)^k dE = \\ &= \int_0^E S (1 - e^{-p_1 a'L}) (1 - e^{-p_2 a'L}) dE \end{aligned} \quad (12)$$

which is the efficiency for a point  $\underline{r}$ . This equation is quite similar to the well-known equation (1a). The overall efficiency for the whole volume is computed by integrating this expression as in eq.(10), but if the approximation  $\underline{p}_1 = \underline{p}_2 = p/2$  is introduced, eq. (12) yields:

$$\epsilon_c(a,b) = \int_0^E S(E) (1 - e^{-(a/2) \cdot L(E,b)})^2 dE \quad (13)$$

where  $a = a' \cdot p$ . Similarly, the total efficiency  $\epsilon_t$  for two phototubes is given by (compare eq. (1b)):

$$\epsilon_t(a,b) = \int_0^E S(E) (1 - e^{-a \cdot L(E,b)}) dE \quad (14)$$

The mean pulse height or the first moment of the pulse height distribution is defined as

$$f(a',b,V) = \frac{1}{\epsilon(a',b,V)} \int_V \sum_{k=k_0}^{\infty} k \cdot P(k|a',b,\underline{p}_1, \underline{p}_2) d\underline{r} \quad (15)$$

where  $k_0=1$  for the moment of the total distribution,  $f_t$ , and  $k_0=2$  for the moment of the coincidence distribution,  $f_c$ . If equation (9) is inserted,  $f_c$  takes the form:

$$\begin{aligned} f_c(a',b,\underline{p}_1,\underline{p}_2) &= \frac{1}{\epsilon_c} \int_0^E S(E) e^{-\underline{p}a'L} \sum_{k=2}^{\infty} \frac{k}{k!} [(a'L)^k (\underline{p}^k - \underline{p}_1^k - \underline{p}_2^k)] dE \\ &= \frac{a'}{\epsilon_c} \int_0^E S(E) L (\underline{p} - \underline{p}_1 e^{-\underline{p}_2 a'L} - \underline{p}_2 e^{-\underline{p}_1 a'L}) dE \end{aligned} \quad (16)$$

This equation is valid for a point  $\underline{r}$  in the solution. If we again assume that  $\underline{p}_1 = \underline{p}_2 = p/2$ , eq. (16) yields

$$f_c(a,b) = \frac{a}{\epsilon_c(a,b)} \int_0^E S(E) L(E,b) (1 - e^{-(a/2) \cdot L(E,b)}) dE \quad (17)$$

In a similar way we can derive an expression for  $f_t(a,b)$ :

$$f_t(a,b) = \frac{a}{\epsilon_t(a,b)} \int_0^E S(E) L(E,b) dE \quad (18)$$

In this work we will use the coincidence/total ratio  $R = \epsilon_c/\epsilon_t$  and  $f_c$  as experimental functions to which the theoretical function  $R = R(f_c)$  will be fitted, thus giving a value for  $b$ .

## EXPERIMENTAL

The pulse rates and pulse height distributions were measured using two EMI phototubes (type 9829QB) connected through pre-amplifiers to a pulse shaping integrating amplifier (Spectral Amplifier Model 2021, Canberra Industries Inc., USA). The output from this unit was connected to an analog-to-digital converter (Model 8075, Canberra Industries Inc., USA). A coincidence analysing circuit with variable resolving time delivered a coincidence pulse to the converter. The output of the converter was connected to a multichannel storage memory (Canberra MCA, Series 88, Canberra Industries Inc., USA). The integration time in the amplifier was  $\approx 0.5 \mu s$  and the coincidence resolving time  $0.4 \mu s$ , which proved to be long enough to record all coincidence pulses containing only two to three photons.

The set of 18 standards was made up of glass vials with 10 ml of a commercial scintillation solution (Lipoluma<sup>R</sup>, Lumac B.V., Netherlands), with xylene as solvent, but unknown fluors. The radioactive substance was standard reference material from the National Bureau of Standards, USA. Only tritium (<sup>3</sup>H-toluene, SRM No. 4947) with an estimated accuracy of  $\pm 1.0\%$  was used. The estimated accuracy of the final standards was  $\pm 1.5\%$ . The quenching agent was carbontetrachloride (CCl<sub>4</sub>). The efficiency of the standards was between 6.7 - 67%.

The ratio  $R$  was determined by measuring the pulse rates,  $C$ , with the coincidence gate on ( $C_c$ ) and off ( $C_t$ ). Photomultiplier noise was measured separately and subtracted from the total counts. The mean pulse height, in channel numbers,  $\langle h_c \rangle$ , and in photoelectron units,  $f_c$ , was determined by using a multichannel pulse height analyser. If  $N(h)$  denotes the number of coincidence counts in channel  $h$  (of pulse height

h), then the experimental first moment, in photoelectron units, is given by:

$$f_c = \frac{1}{\alpha} \frac{\sum_{h=1}^{h_{\max}} h \cdot N(h)}{\sum_{h=1}^{h_{\max}} N(h)} = \frac{1}{\alpha} \langle h_c \rangle \quad (19)$$

where  $\alpha$  is a proportionality constant which gives the relationship between  $k$  and  $h$ ;  $h = \alpha \cdot k$ . This constant was determined by recording the pulse height distribution for coincidence pulses containing only two photoelectrons. The photon sources investigated were a low intensity light emitting diode, a chemiluminescence solution and a heavily quenched  $H^3$  scintillation solution. If the mean pulse height  $\langle h_c \rangle$  of these sources equals two photoelectrons, then  $\alpha = \langle h_c \rangle / 2$ . The summation in eq. (19) did not extend over all the channels used because high level background pulses cause considerable error in  $f_c$ . The value of  $h_{\max}$  was calculated theoretically by the use of equation (9) to correspond to 99.9% of all pulses.

## RESULTS AND DISCUSSION

Three functions for the available energy  $L(E,b)$  were tested by fitting theoretical curves to the data. Apart from the function (2) given by Birks<sup>7</sup>, two other functions were tried:

$$L(E,b) = \int_0^E e^{-b(dE'/dx)} dE' \quad (\text{"Voltz"}) \quad (20)$$

and

$$L(E,b) = \frac{1}{2b} \int_0^E \frac{\ln[1 + 2b(dE'/dx)]}{(dE'/dx)} dE' \quad (\text{Wright}) \quad (21)$$

Function (20) is a simplified version of the one given by Voltz et al.<sup>11</sup> and function (21) was suggested by Wright<sup>12</sup>. The function suggested by Chou<sup>10</sup> was not tried as it is merely an extension of Birks' equation (2) introducing a second unknown constant.

All computations were made on a HP-85 desk computer and the

integrations were performed using a 24 point Gauss-Legendre method.

In order to investigate the  $L(E,b)$  functions a theoretical fit was first made to the experimental data plotted as  $R$  versus  $f_c$ . The goodness of the fit, expressed in terms of the percentage mean squared relative error  $\langle \delta_R \rangle$ , is shown in Figure 1 as a function of  $b$ , for the three  $L(E,b)$  functions.

$\langle \delta_R \rangle$  is given by the expression:

$$\langle \delta_R \rangle = 100 \% \sqrt{\frac{1}{w} \sum_{i=1}^w \left[ \frac{R(f_c(i)) - R(i)}{R(i)} \right]^2} \quad (22)$$

where  $R(f_c(i))$  and  $R(i)$  are the theoretical and experimental coincidence/total ratios for sample  $i$ . The optimum  $b$  values given in Table 1 are drawn from figure 1.

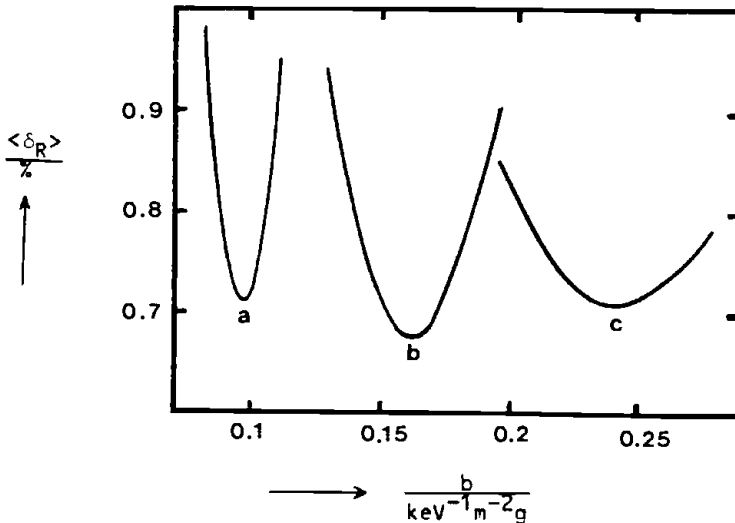


Figure 1. The mean squared relative error of the fit  $R = R(f_c)$  to experimental points for three  $L(E,b)$  functions: curve a = "Voltz", curve b = Birks and curve c = Wright.

As a second test, the variable  $a$ , which varies with the quench level, was determined from experimental values for  $f_c$ , using equation (17) and optimum  $b$  values. Finally the efficiency  $\epsilon_c$  was calculated

using eq. (13) and compared to experimental values. The correlation between calculated and observed efficiencies is illustrated in table 1 by the correlation coefficient  $r$ , and the mean relative error, defined according to:

$$\langle \Delta \epsilon / \epsilon \rangle = 100 \% \frac{1}{w} \sum_{i=1}^w [\epsilon(a(i)) - \epsilon(i)] / \epsilon(i) \quad (23)$$

L(E,b)	$\frac{b}{\text{keV}^{-1} \text{m}^{-2} \text{g}}$	$\frac{\langle \Delta \epsilon / \epsilon \rangle}{\%}$	r
"Voltz", eq. (20)	0.097	-2.409	0.99797
Birks, eq. (2)	0.162	-0.158	0.99997
Wright, eq. (21)	0.240	+0.486	0.99989

TABLE 1. Optimum  $b$  values, the correlation coefficient and the mean relative error of the fit to experimental counting efficiencies for the three L(E,b) functions.

From the data in Table 1 it can be seen that the best fit was achieved by using Birks' function. The optimum  $b$  value, however, does not correspond to the range of values (0.07 - 0.11 keV<sup>-1</sup>m<sup>2</sup>g) discussed by Birks.<sup>14</sup> The approximation that  $p_1 = p_2 = p/2$  may cause a small error in  $b$ , probably of the order of  $\pm 2\%$ .

The incomplete "Voltz" function used here did not reproduce the correct counting efficiencies, but the complete function given by Voltz et al.,<sup>11</sup> containing two more adjustable parameters, probably could be fitted to the experimental data as equally well as Birks' function. The equation by Wright is almost as good as that by Birks. The constant  $b$ , having quite different values, does not have the same physical meaning in these two equations.

In order to show the accuracy of equation (9) with  $p_1 = p_2 = p/2$  this equation has been fitted to an experimental pulse height distribution, as shown in Figure 2, using Birks function with  $b = 0.16$  keV<sup>-1</sup>m<sup>2</sup>g. Two common misunderstandings should now be corrected. Firstly, the pulse height distribution as shown in Figure 2 does not

have its characteristic form due to the  $\beta$ -distribution  $S(E)$ , but only to the coincidence condition; the total spectrum containing also single photon pulses looks nothing like this. Secondly, at the low energy end, the pulse height scale is not linearly proportional to the electron energy.<sup>15</sup>

## CONCLUSION

Three different functions for the "available energy" or "ionization quenching" function  $L(E,b)$  in liquid scintillation solutions have been investigated using a combination of the previously known<sup>4</sup> coincidence/total method and a new method based on theoretical expressions for the pulse height distribution. The function given by Birks<sup>7</sup> was found to be most accurate.

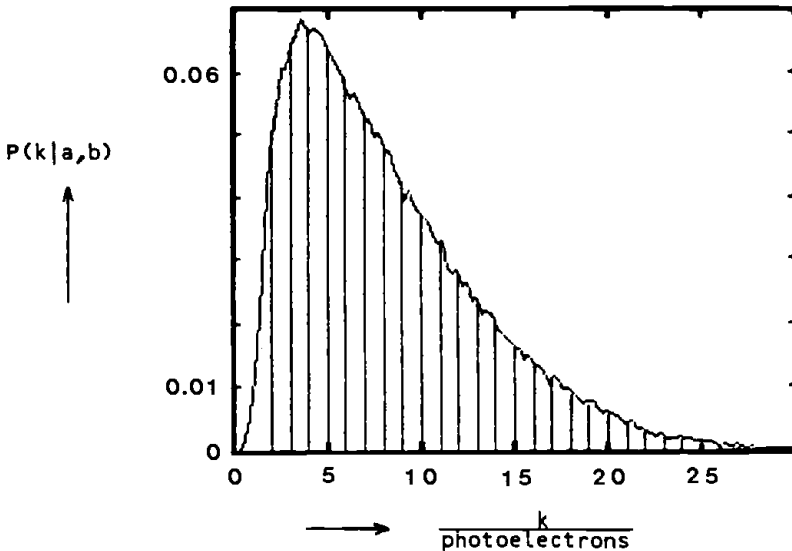


Figure 2. Theoretical pulse height distribution (vertical lines) and experimental distribution (whole line,  $\epsilon_c = 66.3\%$ ) scaled to fit the  $P(k|a,b)$  values of eq. (9).

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