

Chapter 2

Liquid Scintillation Counting as an Absolute Method

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INTRODUCTION

The liquid scintillation counter is well established as an analytical tool in physics, chemistry, biology and medicine (see for example Gibson and Lally, 1971).¹ The principle of the method for absolute counting is to dissolve a known weight of the isotope in the liquid scintillator and obtain an integral bias curve. Extrapolation of this bias curve to zero bias will give an activity which is less than the absolute activity because of statistical fluctuations which result in a significant probability that no output will be obtained from an event in the scintillator. This *zero probability* described by Gibson and Gale in 1968,² can be determined from the overall efficiency of the scintillator and the photomultiplier tube. This efficiency or *figure of merit* (Horrocks and Studier, 1961)³ is shown by the number of electrons produced at the input of the first stage (dynode 1) of the photomultiplier from the deposition of 1 keV of energy in the scintillator.

This chapter demonstrates the basis of the theory and includes methods of measuring the figure of merit, P , together with calculations of the modifying factors which cause losses in the scintillator and result in a reduction in the number of first stage electrons. The results of measurements for three isotopes will be given and a method of calculating the zero probability will be shown. The proposed use of a high gain photomultiplier is included.

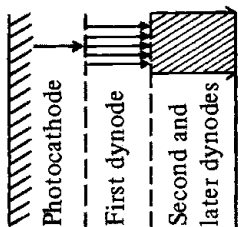
THEORETICAL METHOD

The essential processes in the liquid scintillation counter are shown in Table 1. The figure of merit is defined as:

$$P = \frac{n(E)}{E.F(E)} \quad (1)$$

where $n(E)$ is the average number of electrons at the first stage of the photomultiplier, E is the electron energy in the scintillator and $F(E)$ is the correction for energy losses due to high rates of energy deposition and losses into the walls of the scintillator cell. P is independent of the electron energy and defines the efficiency of the system. Thus if P is

Table 1. Schematic representation of a liquid scintillation counter with typical parameters at 5 keV.

System	Schematic	Process	EMI 9524S Gain	P.M. tube Quanta	RCA C31000D Gain	P.M. tube Quanta
Liquid Scintillator	β -ray (5 keV)	Energy (≈ 425 nm) ^a		1700		1700
	Solvent excitation	dE/dx losses	0.63	1050	0.63	1050
	Solute excitation	Quenching and light losses	0.01	10.5	0.01	10.5
	Light emission					
Photomultiplier		Conversion efficiency	0.13	1.4 ^b	0.30	3.15 ^c
		Stage gain	7.73	10.8	30.0	94.5
		Stage gain	2.12	23.0	3.16	300.0
		Overall gain	1.4×10^4	2×10^4	10^7	3×10^7
		Conversion to volts		100 μ V		4 mV
Electronics	Head amplifier	Gain	2×10^4	2 V	500	2 V
	Main amplifier					

^a Maximum emission of the scintillator
^b Zero probability, $\exp[-1.4] = 0.247$
^c Zero probability, $\exp[-3.15] = 0.044$

measured by one of the methods to be discussed, then n_i can be calculated for any energy E_i such that:

$$n_i = P.E_i.F(E_i) \quad (2)$$

The probability distribution of n_i at the first dynode is assumed to be a Poisson distribution of mean n_i .⁴ This Poisson distribution is modified by the photomultiplier to produce an output distribution which can be calculated exactly or be approximated by various functions, e.g. Gaussian, Gamma, etc.⁵

The zero probability for a single photomultiplier tube

The zero probability of a Poisson distribution is $\exp[-n_i]$. This probability is increased by the photomultiplier (see Appendix) such that at E_i :

$$Z_i = \exp[-n_i(1 - Z_s)] \quad (3)$$

where Z_s is the zero probability for a single electron input to the first dynode. Z_s is normally very small when the first stage is arranged to have a gain >5 ($Z_s < 0.01$) and Z_i approximates to $\exp[-n_i]$. Thus it is only necessary to determine Z_s accurately when the first stage gain is less than 5.

The precision of Z_i and hence the value of the absolute activity ($\propto(1 - Z_i)$) depends mainly upon the accuracy of n_i . Thus assuming $Z_s = 0$ in Eqn. (3) and differentiating:

$$\frac{dZ_i}{Z_i} = dn_i$$

or the relative precision of Z_i depends upon the absolute precision of n_i . For example, if $dn_i/n_i = 0.1$, then for an absolute activity, ϵ_i , $d\epsilon_i/\epsilon_i$ is as follows:

n_i	dn_i	Z_i	dZ_i	ϵ_i	$d\epsilon_i/\epsilon_i$
1	0.1	0.368	0.037	0.632	0.059
2	0.2	0.135	0.027	0.865	0.031
3	0.3	0.050	0.015	0.950	0.016
4	0.4	0.018	0.007	0.982	0.007
5	0.5	0.007	0.003	0.993	0.003
6	0.6	0.002	0.001	0.998	0.001

This shows that if the precision of n_i is only $\pm 10\%$ then at least six electrons must be produced at the first dynode to achieve a precision of 0.1% in the absolute activity. Fewer electrons or an improved precision would require a better measurement of n_i .

The total zero probability for a β -ray spectrum is obtained by dividing the spectrum into bands, calculating the probability for each band and summing to give the total probability (see Appendix).

Zero probability for two tubes in coincidence

In this case it is necessary to have an electron at the output to each tube. The prob-

ability of obtaining an output for a single tube is given by:

$$\epsilon_i = 1 - Z_i$$

where Z_i is given by Eqn. (3). If both the tubes have the same sensitivity then the probability of obtaining an output from both tubes is given by:

$$\epsilon_c = (1 - Z_i)(1 - Z_i)$$

and the zero probability is:

$$\begin{aligned} Z_c &= 2Z_i - Z_i^2 \\ &= 2.\exp[-n_i(1 - Z_s)] - \exp[-2n_i(1 - Z_s)] \end{aligned} \quad (4)$$

The total zero probability for β -ray spectra is obtained as before except that $[H_i \exp(-n_i)]^2 \neq H_i \exp(-2n_i)$ and the two terms in Eqn. (4) must be calculated separately.

The complete distribution

In absolute counting it is necessary to determine the shape of the bias curve near to zero bias in order to make the appropriate extrapolation. Gale and Gibson⁵ have shown that the differential bias curve can be approximated by the gamma function:

$$P(x) = Cx^\alpha \exp(-\beta x) \quad (5)$$

where α and β are constants dependent upon the electron energy and the gain of the system respectively. C is a constant for normalizing the spectrum such that:

$$\begin{aligned} C &= (1 - Z_i) \left[\int_0^\infty x^\alpha \exp(-\beta x) dx \right]^{-1} \\ &= (1 - Z_i) \frac{\beta^{\alpha+1}}{\alpha!} \end{aligned}$$

where:

$$\begin{aligned} \alpha! &= \Gamma(\alpha + 1) \\ &= \int_0^\infty x^\alpha \exp(-x) dx \quad (\alpha \geq -1) \end{aligned}$$

is the tabulated gamma function. The function $P(x)$ has a single peak at $x = \alpha/\beta$ and tends to a Gaussian distribution at large values of α . Z_i , the zero probability, is calculated from Eqn. (3) and α and β are calculated from the mean and variance of the theoretical distri-

tribution. Thus with stage gains m_1 and $m_2 = m_3 \dots = m_K$:

$$\begin{aligned} \text{Mean:} \quad \bar{r} &= n_i \cdot m_1 \cdot m_2^{K-1} \\ &= \frac{\alpha + 1}{\beta} (1 - Z_i) \end{aligned} \quad (6)$$

$$\begin{aligned} \text{Variance:} \quad \sigma^2 &= n_i \cdot m_1^2 \cdot m_2^{2(K-1)} \left[1 + \frac{m_2}{m_1(m_2 - 1)} \right] \\ &= \frac{\alpha + 1}{\beta^2} (1 - Z_i) [1 + Z_i(\alpha + 1)] \end{aligned} \quad (7)$$

The relative variance is σ^2/\bar{r}^2 and when Z_i is negligible (n_i large) then:

$$\begin{aligned} \frac{\sigma^2}{\bar{r}^2} &= \frac{1}{n_i} \left[1 + \frac{m_2}{m_1(m_2 - 1)} \right] \\ &= \frac{1}{\alpha + 1} \end{aligned} \quad (8)$$

In a practical system it may not be possible to determine the stage gains precisely enough to predict a value of α from Eqn. (8) and it is then necessary to obtain a numerical approximation by a method which will minimize the sum of the squares between the calculated and measured curves. This will only be necessary where the mean β -ray energy is small (<100 keV) and the precision required is of the order of $\pm 0.1\%$. Thus for a β -ray spectrum β is a constant which is approximately independent of energy, $(\alpha + 1)$ is proportional to n_i which is calculated from Eqn. (2) and Z_i is calculated from Eqn. (3).

The energy-dependent losses in the scintillator

The scintillation efficiency is assumed to be independent of the β -ray energy but this assumption requires corrections where the specific energy loss (dE/dx) is large (i.e. at low electron energies) and also where the range of the β -rays is of similar magnitude to the cell dimensions (large electron energies). Both these processes reduce the scintillation efficiency and their effect must be calculated in order to find n_i .

The effects of *ionization quenching* have been described by Birks.⁶ He showed that the specific light output (dL/dx) from any scintillator could be described by the simple formula for the quenching effect, i.e.

$$\frac{dL}{dx} = \frac{S dE/dx}{1 + kB \cdot dE/dx} \quad (9)$$

where S is the scintillation efficiency and kB is a constant. The total light output is obtained by numerical integration to give:

$$L = \int dL = S \int_0^E \frac{dE}{(1 + kB \cdot dE/dx)} = S \cdot E \cdot Q(E) \quad (10)$$

with $Q(E)$ equal to the value of the integral at E divided by E . dE/dx was calculated for the scintillator using the formula given by Nelms.⁷ Kolarov, Gallic and Vatin⁸ suggest that the specific light output will decrease more rapidly with increasing dE/dx but the evidence which they quote is for protons and heavy ions. The formula in Eqn. (9) should be adequate for electron interactions within the scintillator at energies in excess of a few keV. The value of kB is $9 \text{ mg cm}^{-2} \text{ MeV}^{-1}$ for a liquid scintillator⁶ and this value was used in the calculations. The error in kB will be less than $\pm 10\%$ and thus at 5 keV the error in $Q(E)$ will be less than $\pm 3\%$, and over a complete spectrum this error will be further reduced. If this produces too large an uncertainty in n_i and hence in ϵ_i (the absolute activity) then the scintillation efficiency can be checked by using a source of iron-55 to produce electrons of 5.9 keV.

At high energies Benjamin *et al.*⁹ produced a formula for the fraction of energy deposited within a cylinder of radius r and height h , i.e.

$$W(E) = 1 - 0.5 [1/r + 1/h] T(E) \quad (11)$$

where $T(E)$ is the electron range calculated from Nelms' formula.⁷ The value of $W(E)$ is stated to have a precision of $\pm 1\%$ (Benjamin *et al.*)⁹ but unless very small cells are used this effect is only important above 100 keV and will not affect the zero probability.

The total correction to the efficiency is thus:

$$F(E) = Q(E)W(E) \quad (12)$$

which should be accurate to $\pm 3\%$. Calculated values of $Q(E)$, $W(E)$ and $F(E)$ are given in Fig. 1.

MEASUREMENT OF THE FIGURE OF MERIT

The figure of merit, P , may be measured by one of four methods:

1. Comparison of the observed spectrum position with the single electron spectrum.
2. Comparison of the total spectrum shape (i.e. resolution) with the theoretical distribution.
3. Measurement of the zero probability.
4. Comparison between the output of the coincidence and single tube counting rates as described by Kolarov *et al.*⁸

The first three methods have been used in preliminary experiments but an assessment of the Kolarov method will be left until the publication of the second part of his paper.

Spectrum position

The output of the system can be expressed in terms of a single electron input to the first stage of the photomultiplier. This is obtained by using a low intensity light source (e.g. the phosphorescence of an empty cell which has been exposed to sunlight) to give an output distribution on a multi-channel analyser.

The output distribution from conversion electrons will have a peak at a position which is proportional to $E.F(E)$ and is quoted as the number of electrons, $n(E)$. Then P can be calculated using Eqn. (1). This method can be used without calculating the full output distribution but can be applied to a β -ray spectrum if computing facilities are available, e.g. Gale and Gibson.⁵ This may be necessary with conversion electrons if they are

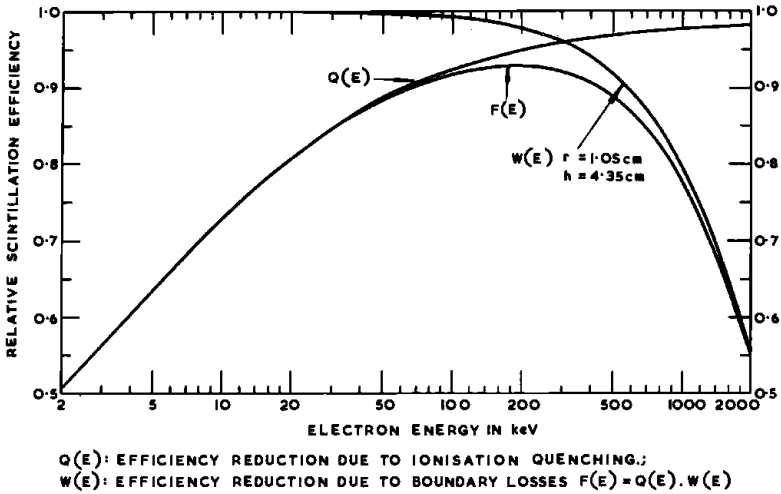


Fig. 1. Variation of scintillation efficiency with electron energy. (Reproduced from *J. Phys. E., Ser. 2*, 1, 99 (1968), with kind permission of the Institute of Physics).

produced from the K, L and M shells of the atom. This method should produce a value of n which is accurate to better than $\pm 5\%$ with conventional photomultiplier tubes, but this precision can be improved with high gain tubes. The precision of P and hence n at other values of E should be about $\pm 6\%$.

Spectrum shape and resolution

The peak from conversion electrons is practically a symmetrical distribution with a resolution R defined as the width w at half the maximum height divided by the peak position \bar{x} . This is related to the fractional variance such that:

$$R^2 = \frac{w^2}{\bar{x}^2} = \frac{\sigma^2}{\bar{r}^2} 8 \times \ln 2$$

and hence using Eqn. (8):

$$n = \frac{8 \times \ln 2}{R^2} \left[1 + \frac{m_2}{m_1(m_2 - 1)} \right]$$

This method is not as precise as the method of measuring the spectrum position since it is difficult to allow for conversion electrons of similar energies but it can be used as a check on the other method. Again it is more accurate to compare the total calculated distribution with the measured spectrum.

Zero probability

This is not really a distinct method of measuring the absolute activity but if the absolute activity is required for higher energy β -emitters e.g. carbon-14, then a low energy β -emitter such as tritium can be used to determine P . The precision with which the activity

of the tritium is required could be low. The value of n for carbon-14 is then calculated from the measured zero probability for the tritium [Eqn. (3)]. This method is not strictly absolute but it will give, for example, a precision of better than $\pm 0.1\%$ for carbon-14 from $\pm 5\%$ for tritium.

Kolarov method

This method (Kolarov *et al.*, 1970)⁸ is based upon three counts with a coincidence system:

- a) with tube 1,
- b) with tube 2, and
- c) with tubes 1 and 2 in coincidence.

The probability of an output for a single energy is, for the three cases:

- a) $C_1/\epsilon_0 = 1 - Z_1$
- b) $C_2/\epsilon_0 = 1 - Z_2$
- c) $C_c/\epsilon_0 = 1 - (Z_1 + Z_2) + Z_{12}$

where $Z_{12} \neq Z_1 Z_2$, from which Z_1 , Z_2 and ϵ_0 can be calculated if C_1 , C_2 and C_c are measured. A modification of the method to reduce the noise is discussed below (see p. 31).

PRELIMINARY EXPERIMENTAL MEASUREMENTS

These results have been presented previously² and hence will only be discussed very briefly to indicate how a precision of about $\pm 2\%$ can be obtained. Absolute standards were obtained from the Radiochemical Centre at Amersham (RCC) and from the National Bureau of Standards, USA (NBS). The results of a comparison between the liquid scintillation method and the certified activities are given in Table 2. A small correction has been applied to the results for carbon-14 and chlorine-36 to allow for the different method used to calculate the zero probability for a coincidence system.

Table 2. Comparison of the measured activity with RCC and NBS standards.

Isotope	$1 - Z$	Single tube system $P = 0.45$ electron keV^{-1}		Coincidence system $P = 0.36$ electron keV^{-1}		
		Measured activity d.p.s.	RCC standard d.p.s.	$1 - Z$	Measured activity d.p.s.	NBS standard d.p.s.
Tritium	0.629 ^a	3400 \pm 120	3480 \pm 70	0.430	1980 \pm 60	1930 \pm 19
Carbon-14	0.964	7.15 \pm 0.14	7.40 \pm 0.22	0.937	850 \pm 17	873 \pm 9
Chlorine-36	0.996	72.0 \pm 0.8	78.8 \pm 7.0	0.992	753 \pm 8	748 \pm 7

^a 1 ml of solution added: corrected for quenching, i.e. $P = 0.45 \times 0.82$

The single tube system had a very high noise level and it was therefore necessary to use 1 ml of aqueous solution in the tritium determination. This produced a significant quenching effect but Gibson and Gale¹⁰ have shown that quenching is equivalent to a simple gain change which is independent of energy. The *relative quenching factor*, g , is a constant which is less than or equal to unity and hence the figure of merit determined for an unquenched system is reduced from P to gP . The zero probability is then determined from Eqn. (3) by using gn instead of n .

These results were obtained with photomultipliers having a photocathode efficiency of about 13% at 425 nm for the single tube and about 20% for the coincidence systems. The latest efficiencies are in excess of 25% at this wavelength. This means that n will be increased and the precision will be improved (see Table 1). The use of the methods to be discussed below should also reduce the background from the single tube and hence improve the precision of the extrapolation.

PROPOSAL TO USE A HIGH GAIN PHOTOMULTIPLIER TUBE

Photomultiplier tubes with high quantum efficiency (30% at 425 nm) and high gain first dynodes (30 to 50) using gallium phosphide (RCA type C31000D) are now in use in various scintillation systems.⁸ They are expensive but could well prove to be very useful in the specific application of absolute counting. The high quantum efficiency means that the figure of merit for most liquid scintillators can be increased to $P \geq 1$ electron keV^{-1} for a single tube or $P \sim 0.5$ electron keV^{-1} for two tubes in coincidence. These values could be increased by using more efficient scintillators. However, if values of P of 1.0 and 0.5 electron keV^{-1} are assumed for single and coincidence systems respectively, then an assessment of this tube can be made.

Zero probabilities for single and coincidence systems

In absolute counting it may not be necessary to use the lowest possible background that is attainable with a coincidence system. The background counting rate for a single tube with an equivalent bias level of 1.5 electrons will be of the order of 10 c.p.s. Thus it is possible to compare a single tube counting two and more electrons with a coincidence system counting effectively all electrons. The ratio of the zero probabilities is given by:

$$\begin{aligned} \frac{Z(\text{single})}{Z(\text{coincidence})} &= \frac{\exp(-n)(1+n)}{2 \exp(-n/2) - \exp(-n)} \\ &= \frac{\exp(-n/2)(1+n)}{2 - \exp(-n/2)} \end{aligned}$$

This ratio is less than one for all values of $n > 0$ and thus as can be seen in Table 3 and Fig. 2, the single tube is always more efficient than the coincidence system.

Extrapolation of the integral bias curve

The shape of the differential bias curve for a conversion electron is calculated by using the gamma function described in Eqn. (5). The relative variance with a first stage gain of 30 and subsequent gains of 3.16 (overall gain $\sim 10^7$) will be $1.025/n$ and hence from Eqn. (8), $\alpha + 1 = n/1.025$ and $\beta = 1/1.025$ when $n \geq 5$. For $n < 5$, Z is significant and α and β can be calculated from Eqns. (6) and (8).

The complete β -ray spectrum is calculated for a series of discrete energy bands as described above. In theory the computed integral bias curve should agree with the measured bias curve but in practice it may be necessary to adjust α and β to obtain the best fit to the data. This can be done using a simple iterative or regression procedure.

Problems to be examined

The most difficult problems will be associated with the counting of tritium where the maximum efficiency for counting two and more electrons is 69% (Table 3). In this

Table 3. Comparison between the efficiency for a single tube counting two and more electrons and a coincidence system with half the figure of merit for each tube.

Isotope	Mean β energy (keV) E_a	Correction factor (Fig. 1) $F(E_a)$	Effective energy (keV) $E_a F(E_a)$	Single tube $P = 1.0$ electron keV^{-1}				Coincidence $P = 0.5$ electron keV^{-1}			
				Electron number n_a	Zero probability Z	Z + single elec. prob. $Z + 1e$	Efficiency	Electron number n_a	Zero probability Z	Efficiency	Zero Efficiency probability Z
Tritium	5.7	0.652	3.7	3.7	0.175	0.315	0.685	1.85	0.427	0.573	
Iron-55	5.9 ^b	0.463	2.7	2.7	0.067	0.248	0.752	1.35	0.451	0.549	
Radium-228	10.1	0.730	7.4	7.4	0.125	0.217	0.783	3.70	0.291	0.709	
Nickel-63	17.5	0.794	13.9	13.9	0.073	0.124	0.876	6.95	0.179	0.821	
Thulium-171	25.5	0.831	21.8	21.8	0.050	0.092	0.908	10.8	0.124	0.876	
Carbon-14	48.9	0.880	43.0	43.0	0.017	0.034	0.966	21.5	0.047	0.953	

^a $n_a = E_a F(E_a) P$, electrons

^b X-ray

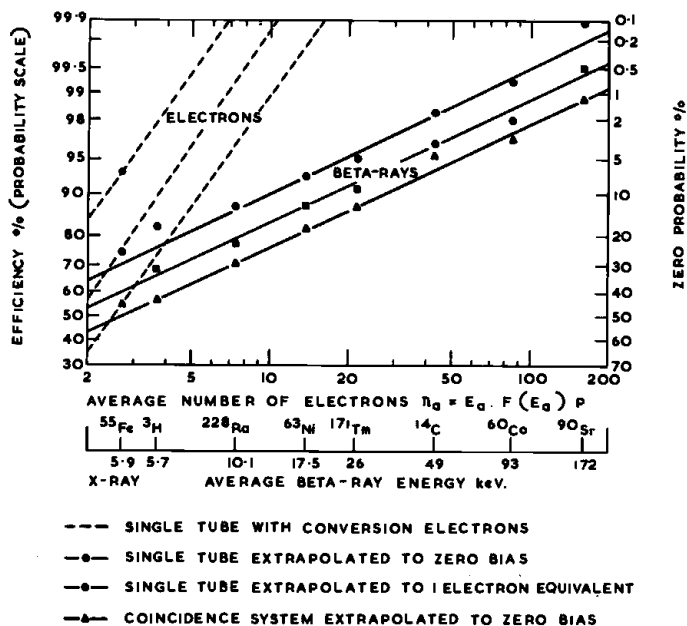


Fig. 2. Efficiency and zero probability for single and coincidence system at 1 electron keV^{-1} .

case it is most important to check the shape of the differential bias curve for tritium against a theoretical curve. This will demonstrate any variations in the system and give an indication as to how good a fit can be obtained with the gamma function. This can be repeated for other isotopes although the fit is less important for the smaller extrapolations.

The stability of the background, which is mainly due to photomultiplier noise in a single tube system, requires some study. The fluctuations can be reduced by cooling and the elimination of most single electron pulses should improve the background stability. Standard errors of ± 1 c.p.s. in the background mean that if 10^6 counts are required ($\pm 0.1\%$ standard error) then a source of output equivalent to 10^5 c.p.s. must be used to avoid an increased error in the count. The use of a second coincidence tube may well be necessary to avoid such high activities.

There is some evidence for gain reductions or fatiguing at high counting rates and this could well cause a drift in the bias curve during an experiment. The magnitude of this effect can be as high as 10% or higher for some photomultiplier tubes.¹¹

After-pulses are known to be a problem with most systems. These appear as an enhanced counting rate at low energies which is associated with the source and may be due to effects in the photomultiplier. These pulses reduce the precision of the extrapolation and should be eliminated if at all possible.

The shape of the β -ray spectrum near to zero β -ray energy is not well known for some isotopes and it is therefore important to confirm that the theoretical fit to the observed differential bias curve is correct.

Ionization quenching which was discussed on p. 27 is obviously important at low energies and the shape of the curve for light output [Eqn. (10)] requires confirmation

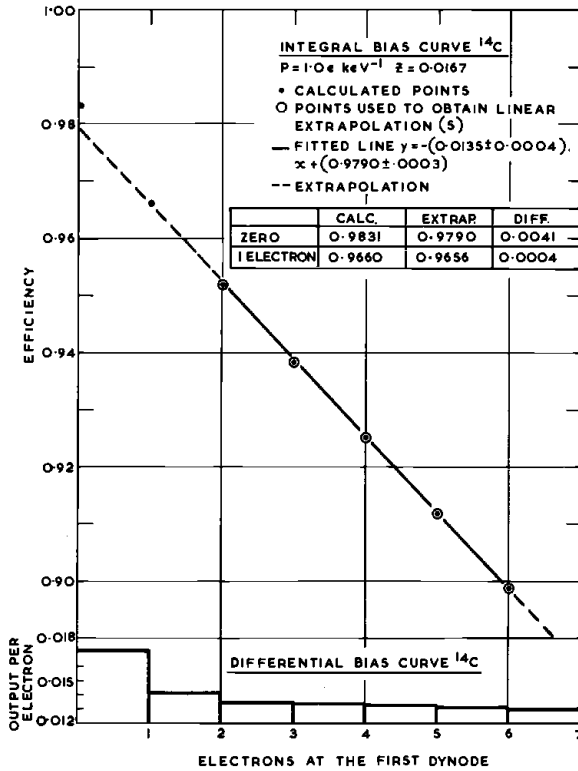


Fig. 3. A linear fit to the theoretical integral bias curve for carbon-14 from two to six electrons.

with the scintillator to be used. This could be examined by using β -excited X-ray sources placed within the scintillator since the establishment of the peak position is the essential requirement for this experiment.

Precision of the method

If a reasonable solution can be found to the points discussed above then the remaining problems are associated with:

1. the precise determination of Z , and
2. the extrapolation of the bias curve.

Z depends upon n , and with 1.85 electrons for tritium (Table 3) and a precision of $dn = \pm 0.10$ then, as was seen on p. 25, the final precision in the absolute activity will be $\pm 2\%$ (0.02). The value of dn could be reduced if an exact shape is determined for the light output curve. The extrapolation for tritium can be restricted to a limited part of the integral bias curve (< 3 electrons) or be fitted over a much wider range but it is unlikely that a precision of better than $\pm 2\%$ will be obtained. Much higher precision is to be expected at higher energies and above a mean energy of 20 keV the absolute activity can be calculated to better than $\pm 0.1\%$. The error in the extrapolation will then depend on the extent of the after-pulses but for carbon-14, with a mean energy of 48.9 keV, the extrapolation from a bias level of two electron equivalents is only 1% (see Fig. 3) and this should be measurable

to 0.1%. The overall error should be about $\pm 0.14\%$. Attainment of such precision will depend upon solution of the earlier problems.

CONCLUSIONS

It seems feasible that most isotopes which decay by β -ray emission can be counted absolutely in a liquid scintillation counter. A precision of $\pm 5\%$ is attainable for tritium (β mean 5.7 keV) and this could be improved to $\pm 2\%$ with careful investigation of various factors in the system. Errors of $\pm 2\%$ for carbon-14 and $\pm 1\%$ for chlorine-36 have been found but these measurements could well be improved to the 0.1% level if the efficiency of the system is carefully measured.

The problems requiring further investigation are:

1. the stability of the counter background
2. the effects of high counting rates on the gain of the system
3. elimination of after-pulses
4. the shape of the β -ray spectrum near to zero energy
5. the light output as a function of the energy of the incident electron.

Solution of these problems will ensure an accurate measurement of the figure of merit and hence give a precise value of the zero probability.

Fundamental improvements will only come with more efficient scintillators and photocathodes but a more detailed understanding of some of the problems of the liquid scintillator will probably make it very competitive with other forms of absolute standardization.

ACKNOWLEDGEMENT

The early experimental work and theoretical calculations were done with the active collaboration of Mr. H. J. Gale.

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APPENDIX

Calculation of the zero probability for a single photomultiplier tube

It is assumed that the input to the first dynode is Poisson distribution of mean n electrons. The photomultiplier tube consists of K stages with gains, $m_1, m_2, m_3 \dots m_K$.

If the stage gains are not all equal then it is necessary to calculate the zero probability for a single electron input backwards from the eleventh stage such that:

$$Z_s(K) = \exp(-m_K)$$

$$Z_s(K-1) = \exp[-m_{K-1}(1-Z_s(K))]$$

$$Z_s(K-2) = \exp[-m_{K-2}(1-Z_s(K-1))]$$

$$Z_s(1) = \exp[-m_1(1-Z_s(2))]$$

The zero probability at the input to the photocathode with an efficiency a is:

$$Z_s(0) = \exp[-a(1-Z_s(1))]$$

As an example let $a = 0.25$, $m_1 = 7$, m_2 to $m_9 = 2$, m_{10} to $m_{11} = 4$ and then:

Stage, K	m_K	$1 - Z_s(K+1)$	$Z_s(K)$
11	4.00	—	0.0183
10	4.00	0.9817	0.0196
9	2.00	0.9804	0.1406
8	2.00	0.8594	0.1796
7	2.00	0.8204	0.1938
6	2.00	0.8062	0.1996
5	2.00	0.8004	0.2020
4	2.00	0.7980	0.2030
3	2.00	0.7970	0.2032
2	2.00	0.7968	0.2032
1	7.00	0.7968	0.0038
0	0.25	0.9962	0.7795

The total zero probability for a complete β -ray spectrum is obtained by dividing the spectrum into bands, calculating the probability for each band and summing to give the total probability, i.e.

$$Z = \sum_i Z_i = \sum_i H_i \exp[-n(E_i)(1 - Z_s(1))]$$

where H_i is the fraction of the spectrum within band i and $\sum_i H_i = 1$.

DISCUSSION

J. B. Birks: Is the single-tube method superior to the coincidence method for absolute counting when allowance is made for the photomultiplier noise?

J. A. B. Gibson: Yes, provided the photocathode has a high conversion efficiency ($\sim 30\%$) and the single tube is specially selected for low noise. The exceptions are if the amount of available activity is low or the tube shows the effects of fatigue at high counting rates.

J. L. Spratt: I was struck by your comment that people want 0.1% accuracy. How many want, or even deserve, such a degree of accuracy?

J. A. B. Gibson: Probably relatively few. However, the International Bureau of Weights and Measures are interested in using liquid scintillation counters in place of other absolute counting methods if this is possible. For most uses i.e. for biological samples etc., certainly 1% and probably 5% is quite adequate.

B. E. Gordon: The method of Kolarov (*Intern. J. Appl. Radiation Isotopes* 21, 443 (1970)) was in fact described by Dr. V. P. Guinn in *Liquid Scintillation Counting* (ed. C. G. Bell and F. N. Hayes), 1958, p. 166, about 10 years ago and it became obvious that it was not accurate for tritium but appeared to be an adequate method to obtain the absolute activity of carbon-14 (perhaps $\pm 2\%$). I suspect that the problem for tritium still remains because of noise in counting samples of weak energy.

J. A. B. Gibson: Yes, I agree but the increased efficiency of photocathodes should improve the accuracy of tritium counting by this method.

The method as described by Guinn is indeed similar to Kolarov's method but contains a fallacy. Guinn states that the counting rates in channels 1 and 2 would be $A\epsilon_1$ and $A\epsilon_2$ with an absolute activity ϵ . He then says that the coincidence counting rate is $A\epsilon_1\epsilon_2$. This is only true for conversion electrons and is not true for a β -ray spectrum (see p. 26).