

COMMENTS ON ASPECTS OF ABSOLUTE ACTIVITY MEASUREMENTS

OBTAINED BY LIQUID SCINTILLATION COUNTING

G. C. LOWENTHAL

Australian Atomic Energy Commission  
Research Establishment  
Lucas Heights. N.S.W. 2232.

These comments are concerned principally with reported work on pure  $\beta$  emitters especially those with end point energies below about 200 keV. The overwhelming majority of radioactivity measurements of these  $\beta$  emitters are made by means of liquid scintillation counting but this technique has not been very successful for determining absolute activities, the more accurate results being obtained by gas proportional counting. Two of the reasons for the relatively less accurate performance of liquid scintillation counters are considered in more detail: the problems created by the marked rise in pulse rates at low pulse heights and the relative inefficiency with which scintillations due to low energy electrons are converted into detectable signals. Accurate results have been realised by extrapolating plots of countrates taken as function of discriminator levels but only for  $\beta$  emitters with end point energies above about 200 keV. Besides, extrapolation procedures are as yet unsupported by accepted models of the liquid scintillation detection process. However, more recently introduced methods are making it possible to count the activities even of  $^{14}\text{C}$  and  $^3\text{H}$  with accuracies comparable to those attained in internal gas proportional counters, i.e. about  $\pm 1$  per cent.

## 1. INTRODUCTION

The activity  $A$  of a radionuclide is expressed as  $A = \Delta N / \Delta t$  where  $\Delta N$  is the number of nuclear transformations in the sample which occur within the time interval  $\Delta t$ . Radioactivity measurements are described as absolute if every nuclear transformation is accounted for. It is then a necessary though not a sufficient requirement for absolute counting that overall counting efficiencies in a given apparatus are known for each sample and that differences between a measured countrate and the rate, which would be obtained if the overall counting efficiency were 100 per cent, can be determined uniquely and with the necessary degree of accuracy.

To limit the scope of this discussion only pure  $\beta$  emitters will be considered. Actually, the bulk of liquid scintillation counting (LS counting) is in any case made with pure  $\beta$  emitters namely  $^{14}\text{C}$  and  $^3\text{H}$  which between them account for the overwhelming majority of LS measurements. Their number has been estimated as well in excess of 10 million per year. Beta spectra extend to zero energy so that source self-absorption effects are perennial problems with  $\beta$  measurements. When radionuclides are dissolved in a scintillator solution, source self-absorption is negligibly small because neither carrier nor other inactive materials, in practice mainly organic materials, prevent the interaction of emitted electrons with the scintillant.

However, there are other problems which users of LS counting techniques must face (1,2). These include the following:

- (i) the various quenching effects and changes in these effects as functions of time and of many other variables;
- (ii) problems connected with keeping radionuclides in solution and generally with maintaining the homogeneity of solutions;
- (iii) problems due to the marked rise in the pulse rate at low pulse heights; and

## LIQUID SCINTILLATION COUNTING

- (iv) the relative inefficiency with which scintillations caused by low energy electrons (roughly  $E < 10$  keV) are converted into detectable signals.

Problems which affect other counting techniques as much as LS counting will be disregarded.

The extent to which the difficulties listed under (i) to (iv) affect LS counting results depends strongly on the physical and chemical characteristics of a radionuclide but very much less strongly on whether the aim is a true disintegration rate or only a relative countrate. For the purpose of this brief review, attention can be focussed only on points (iii) and (iv) which are in fact of somewhat greater relevance for absolute than for non-absolute counting (2).

### 2. EXTRAPOLATION METHODS

When LS counting is employed for absolute measurements one often plots countrates as functions of discriminator settings resulting in a linear plot which is extrapolated to obtain the countrate at zero bias which is accepted as the disintegration rate of the source (3). In what follows this procedure will be called the linear extrapolation method (Figure 1).

Largely for reasons stated in (iii) and (iv) above LS counting requires the imposition of a relatively high energy threshold generally well above 1 keV (it is 10 keV in Figure 1). This leads necessarily to the exclusion of the low energy end of the  $\beta$  spectrum and so requires some form of extrapolation procedure or an equivalent to close the resulting gap. The loss in counting efficiencies which must be allowed for is clearly the greater the lower the end point energy of the  $\beta$  spectrum. For example a 2 keV threshold will cause a loss of around 20 per cent of  $^3\text{H}$  betas but only around 2 per cent of  $^{14}\text{C}$  betas (Figure 2).

An important function of the imposed thresholds is to exclude small pulses which are not part of a measurable background but which do not correspond with disintegrations either. Most of the small pulses are due to

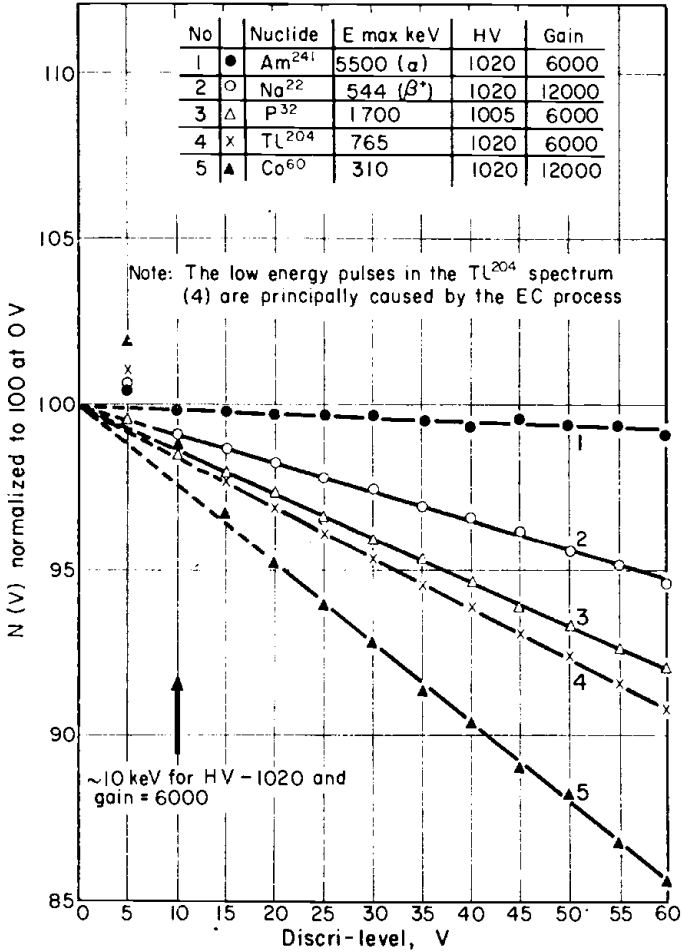


Figure 1 Examples of integral spectra for a number of radionuclides (from Ref. 3, Figure 3).

## LIQUID SCINTILLATION COUNTING

chemiluminescence and to after pulsing (1,2), effects which can be expected to be the higher, the higher the end point energy of the  $\beta$  spectrum. However, they are also potentially serious sources of error when counting low energy events.

When the linear extrapolation method is used it is often assumed that it is only these spurious counts easily seen at low bias settings (Figure 1) which cause the plotted points to be above a straight line defined by results obtained at the higher bias settings, but this is an arbitrary assumption (2,4). A linear plot is in itself no proof of a correct trace of disintegration events. Many  $\beta$  spectra including those of  $^3\text{H}$  and  $^{14}\text{C}$  are markedly non-linear in the region approaching zero electron energies (Figure 2) so that a linear extrapolation could be expected only if it could be shown on general grounds that the pulse height distribution remains a horizontal line down to zero energies. This has not been done so far.

As a rule it is possible to adjust the gain of a system to obtain a reasonably close to linear plot for extrapolation to zero bias (Figure 3). However, even if the shape of the pulse spectrum is actually horizontal or very nearly so this could be due to compensating errors (see below), bearing in mind that a horizontal pulse spectrum is not predicted by any established model. The validity of extrapolations is in doubt not only for linear but equally for exponential extrapolations which have been used for  $^3\text{H}$  activity measurements (2,5).

Notwithstanding this, extensive experiments have shown that provided the end point energies of the  $\beta$  spectra exceed about 200 keV and that one takes account of known sources of errors, including those listed earlier, the results of activity measurements made with the linear extrapolation method agree with results obtained by established absolute methods, i.e.  $4\pi$  gas flow proportional counting, and the uncertainties in these results are also of the same order, generally 1 to 2.5 per cent for a 99 per cent confidence interval (c.i. 99) (3).

It is still necessary to refer to the use of LS detectors with  $4\pi$   $\beta$ - $\gamma$  coincidence counting, a method

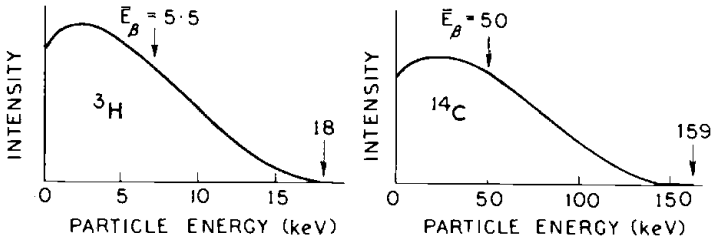


Figure 2 Computed  $\beta$  spectra for  $^3\text{H}$  and  $^{14}\text{C}$ .

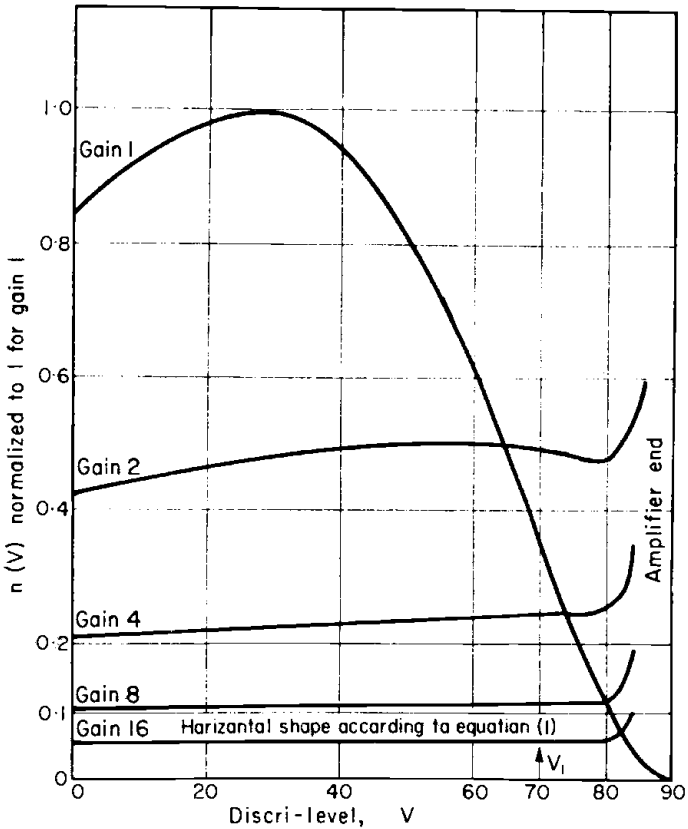


Figure 3 Differential pulse height spectra obtained with a LS counter at different amplifications (from Ref. 3 Figure 2).

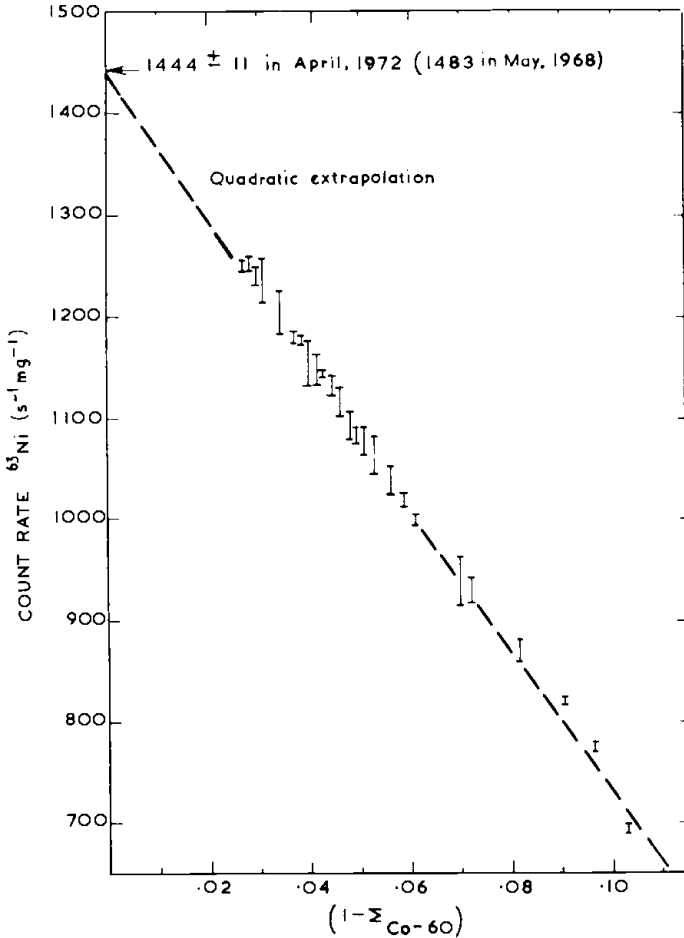
## LIQUID SCINTILLATION COUNTING

applicable e.g. to  $^{60}\text{Co}$  where  $\beta$  decay is followed virtually instantaneously by  $\gamma$  emissions. With this method the overall counting efficiencies of  $\beta$ - $\gamma$  emitters can be unambiguously measured and it is this fact which established  $4\pi$   $\beta$ - $\gamma$  coincidence counting, wherever it can be properly applied, as the most accurate procedure for absolute activity measurements (6). Since  $4\pi$  detection is achieved with LS counting as well as with gas counting the LS method can be and has been used for  $4\pi$   $\beta$ - $\gamma$  coincidence counting.

Moreover, and this is the relevant point for the present purpose, it has been possible to use  $\beta$ - $\gamma$  coincidence counting as an aid for measuring the activities of pure  $\beta$  emitters. The procedure is known as the efficiency tracing method (6). A  $\beta$ - $\gamma$  and a pure  $\beta$  emitter, e.g.  $^{60}\text{Co}$  ( $E_{\beta\text{max}} = 310$  keV) and  $^{63}\text{Ni}$  ( $E_{\beta\text{max}} = 67$  keV) are mixed homogeneously and in known proportions. Sources are prepared from this mixture which differ in their counting efficiencies and these sources are counted to obtain their total  $\beta$  countrates ( $^{60}\text{Co} + ^{63}\text{Ni}$ ) as function of the measured counting efficiencies for the betas of  $^{60}\text{Co}$ . The data is plotted (Figure 4) and the plot is extrapolated to 100% counting efficiency for  $^{60}\text{Co}$ . The plot is a quadratic and not a linear function and this was predicted by theory based on simplifying assumptions (7) and so still subject to significant residual uncertainties.

The pure  $\beta$  activity,  $^{63}\text{Ni}$  in this example, can be calculated from the corresponding total countrate value since the  $^{60}\text{Co}$  activity in the source is known. Non-linear extrapolations of plots of results of efficiency tracing measurements yield far more reliable pure  $\beta$  activity measurements than do estimates of counting efficiencies when only  $4\pi\beta$  counting is used.

Unfortunately, the use of LS counting in  $\beta$ - $\gamma$  coincidence measurements has never so far been really successful. To obtain acceptable results it has been necessary to introduce arbitrary assumptions and the accuracies were always below the levels attainable with  $4\pi$  gas counting of thin sources (8-10). However, there are many cases when solutions of radionuclides contain too high a solute concentration for making adequately thin sources and it is in these cases that LS counting can be the



**Figure 4** Plot of efficiency tracing measurements in a  $4\pi$  (proportional gas flow)  $\beta$ - $\gamma$  coincidence apparatus where  $^{60}\text{Co}$  was employed for the efficiency tracing of  $^{63}\text{Ni}$ . The  $^{63}\text{Ni}$  countrate marked along the ordinate was obtained by subtracting in each case the known  $^{60}\text{Co}$  contribution from the measured  $4\pi\beta$  countrate.

## LIQUID SCINTILLATION COUNTING

relatively more accurate technique but the emphasis is on the term relative.

### 3. THE PROBLEM OF ZERO RESPONSE PROBABILITY

When LS counting is used to measure the activities of  $\beta$  emitters with end point energies around 150 keV or less the production of spurious pulses is much reduced. It is the non-detection of scintillations (point iv above) also described as the zero response probability, which is then likely to be the dominant factor in causing uncertainties in the results (1,2,4).

The relative inefficiency of conversions of weak light pulses into detectable signals is reflected in the poor energy resolution of LS detectors. The resolution shown in Figure 5 is fairly typical for contemporary general purpose counters equipped with PM tubes with bialkali cathodes. It is seen that to discriminate against the 25.5 keV Ag K edge the level must be set to correspond not to just above this energy but to at least 36 keV. Thus, poor energy resolution introduces uncertainties into the setting of discriminator thresholds and so also into the results of activity measurements which involve extrapolations where one of the variables is a function of the discriminator setting.

A substantial improvement in the performance of LS counters was made possible some 5 years ago with the introduction of photomultipliers (e.g. RCA type 8850) whose first dynode is coated with gallium phosphide which gives this dynode a 5 to 6 times greater amplification factor than it has in other tubes with bialkali cathodes. The detection efficiency for  $^3\text{H}$  which had already risen from 20% in 1960 to 60% in the late sixties (1) became 80 to 82% when using just a single tube and close to 90% when using two tubes operated in the pulse summation mode. This detection efficiency corresponds to an effective average cut-off energy close to 0.7 keV.

With this and other recently developed instrumentation the activity of  $^3\text{H}$  can now be measured with an estimated accuracy close to 2.5% (c.i. 99) and the activity of  $^{14}\text{C}$  to within 1.0% (11). However, the equipment used to achieve these accuracies is costly and the required

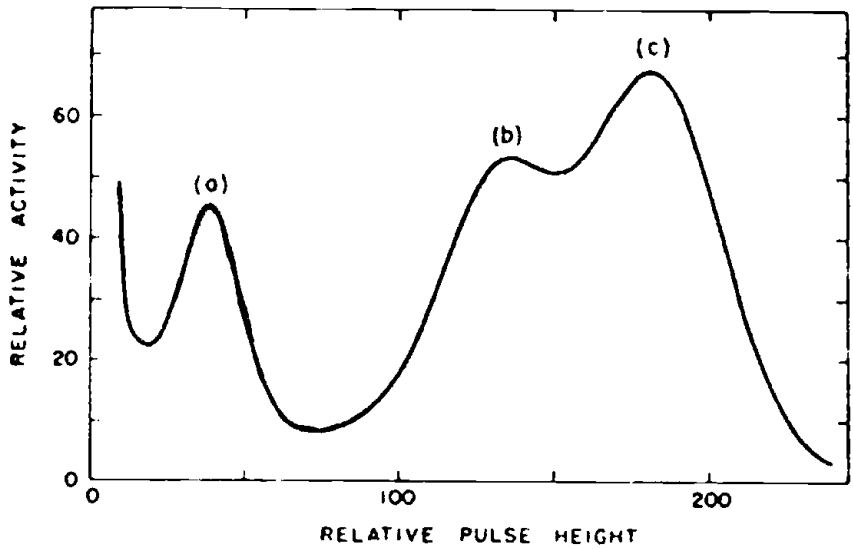


Figure 5 LS pulse height spectrum for  $^{109}\text{Cd}$ . The peaks represent the 25.5 keV Ag K edge (a), and the 65.9 keV and 88 keV conversion electrons (b,c). The resolution (FWHM) at 25.5 keV is about 60 per cent (from Ref. 2, Figure 11).

## LIQUID SCINTILLATION COUNTING

standard of measurement expertise very high. The same applies to a different method first reported in 1966 (4) where pulses due to radionuclide decays are compared with light pulses whose intensity is modulated by an analogue device incorporating the shape of the relevant  $\beta$  spectrum as calculated from  $\beta$  decay theory. Here the accuracy achievable for activity measurements of  $^{14}\text{C}$  and  $^{35}\text{S}$  ( $E_{\beta\text{max}}$  equals 159 keV and 167 keV respectively) is estimated to be close to 2.0% (c.i. 99) (12).

### 4. PROBLEMS WITH USING CERTIFIED STANDARDS

For the time being it cannot be expected that similar accuracies can be reached outside very well equipped standard laboratories. As a rule LS counting systems are calibrated with samples whose disintegration rate has been certified by a standard laboratory. To what extent the accuracy of the measurement of users approaches the certified accuracy of the activity of the standard depends principally on the awareness of users of the many possible sources of uncertainty (13). It would be rare that a known source of error would not be properly dealt with. What could be far more frequent is that sources of error which, given the present state of knowledge could have been known, are disregarded. If one looks at the expense and expertise brought into play by groups of specialists to achieve, say, an accuracy within  $\pm 2\%$  (c.i. 99) for a  $^{14}\text{C}$  activity measurement one is a little surprised and perhaps more than a little sceptical when reading reports where similarly high accuracies are claimed with a very much more modest input in resources including relevant experience. The fact that independent verifications of results are rarely if ever practical outside standards laboratories explains at least in part why it is easy to make unrealistic estimates of accuracies.

### 5. COMPARATIVE PERFORMANCE OF SYSTEMS USED FOR ABSOLUTE COUNTING

Before making such comparisons it is necessary to define the area of interest. The principal concern continues to be with pure  $\beta$  emitters having end point energies below 200 keV. There are two groups of radionuclides in this category; those with properties which

permit thin solid sources to be made and those where that cannot be done (6).

When thin solid sources can be made, e.g. for  $^{35}\text{S}$  ( $E_{\beta\text{max}} = 167 \text{ keV}$ ) and  $^{63}\text{Ni}$  ( $E_{\beta\text{max}} = 67 \text{ keV}$ )  $4\pi$  gas flow proportional counting yields more accurate absolute counting results than LS counting (1). To give a very brief explanation: proportional counting in gaseous detecting media yields a much more sharply defined response when counting low energy events, say  $E < 3 \text{ keV}$ , than does LS counting. Reasons why LS counting faces difficulties in that energy region were summarised earlier. A few data about the performance of proportional counters will be given below.

Absolute activity determinations of pure  $\beta$  emitters have to be made by extrapolation procedures no matter which counting method is used. They are therefore subject to additional uncertainties which one seeks to minimise by extending the measurements to the highest counting efficiencies (see e.g. Figure 4) which include the largest fraction of low energy events. So far these procedures have been more successful for proportional than for LS counting and this is an important reason why results obtained in LS counters are invariably verified with reference to results obtained in  $4\pi$  proportional counters, assuming this can be done and not the other way around (3, 8,12).

That nevertheless LS counting has its strongly established position is due largely to the many situations where  $4\pi$  proportional counting of solid sources simply can not be used because it is completely impractical to make solid sources of an acceptable quality. The outstanding example is  $^3\text{H}$  but there are many others. Here the LS counter has a virtual monopoly on measurements and, as was pointed out earlier, it has been used successfully also for absolute activity determinations (11,12).

So far the standards of activity for  $^3\text{H}$  and  $^{14}\text{C}$  are still those established by internal proportional gas counting. Difficulties with source making are avoided by introducing the radionuclides as components of the counting gas, e.g. as tritiated methane. The accuracies which have been attained are within 1.0% (c.i. 99) (14,15).

## LIQUID SCINTILLATION COUNTING

Internal gas counting is cumbersome for normal use and could never compete with LS counting whenever the latter method can be used. Absolute internal gas counting is, if anything, more costly in effort and equipment than are the absolute LS methods referred to earlier. However, one or two comments on the performance of the internal gas proportional counter may help to illustrate why conditions in gaseous media are more favourable for counting low energy events than conditions in liquid scintillants.

Assuming optimum conditions, i.e. skilled use of equipment incorporating PM tubes similar to the RCA type 8850, one can obtain threshold settings of around 0.7 keV and it is possible to resolve photon or electron energies down to about 2 keV (2). On the other hand the cut-off energy for internal gas proportional counting is within 0.05 keV, i.e. over ten times lower than what can be achieved in LS counters and the energy resolution is also proportionally higher (14).

It is apparent therefore that LS counting has not yet bridged the gap separating it from gas proportional counting as regards the response to low energy events. Nevertheless there are other aspects to the accuracy of counting apart from the response at the lowest energies and it is likely that, taking everything into consideration, the activities of  $^3\text{H}$  and  $^{14}\text{C}$  can now be measured by means of LS counting with about the same low uncertainty attained so far with internal proportional gas counters.

### 6. REFERENCES

1. R. Vaninbroukx and I. Stanef, "Present Status in the Field of Liquid Scintillation Counting", Proc. 1972 Int. Summer School on Radionuclide Metrology, Herceg Novi, Yugoslavia; Nucl. Instrum. Methods (to be published).
2. Houtermans, "Probability of Non-Detection in Liquid Scintillation Counting", Proc. 1972 Int. Summer School on Radionuclide Metrology, *ibid*; See also in same publication A. Williams, "After Pulses in Liquid Scintillation Counters".
3. R. Vaninbroukx and A. Spornol, Int. J. Appl. Rad. Isotopes, 16, 289 (1965).

G. C. LOWENTHAL

4. J. Bryant, D.G. Jones and A. McNair, I.A.E.A. Symp., STI/PUB/139, SM 79-28, Vienna (1967).
5. K.F. Flynn, L.E. Glendinin and V. Prodi, Organic Scintillators and Liquid Scintillation Counting, p. 687, (D.L. Horrocks, Ed.) Academic Press (1971).
6. A.P. Baerg, Metrologia, 2, 23 (1966) and 3, 105 (1967)
7. A. Williams and I.W. Goodier, I.A.E.A. Symp., STI/PUB/139, SM 79-30, Vienna (1967).
8. J. Steyn and F.J.W. Hahne, Proc. Nat. Conference Nucl. Energy, p. 30, Pretoria, South Africa (1963).
9. G. Erdtmann and G. Herrmann, Int. J. Appl. Rad. Isotopes, 16, 301 (1965).
10. J. Steyn, I.A.E.A. Symp., STI/PUB/139, SM 79-16, Vienna (1967).
11. V. Kolarov, Y. LeGallic and R. Vatin, Int. J. Appl. Rad. Isotopes, 21, 443 (1970).
12. D.G. Jones and A. McNair, "Radioactivity Calibration Standards", NBS Special Publication No. 331, p. 37, National Bureau of Standards, Washington D.C. (1970).
13. G.C. Lowenthal, Atomic Energy in Australia (to be published).
14. A. Spagnol and B. Denecke, Int. J. Appl. Rad. Isotopes 15, 241 (1964).
15. W.B. Mann, R.W. Medlock and O. Yura, Int. J. Appl. Rad. Isotopes, 15, 351 (1964).