## CHAPTER 41

# The Optimization of Scintillation Counters Employing Burst Counting Circuitry

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## INTRODUCTION

Recognition of the versatility of liquid scintillation counters in environmental radioactivity, together with the advent of small gas proportional counters and the accelerator mass spectrometry technique (AMS) for small sample radiocarbon dating, has undoubtedly led to the development of a new generation of scintillation counters with much reduced background count rates and enhanced $E^2/B$ values. This consequently enables much lower detection limits. The two instruments most commonly employed in U.K. laboratories are the LKB-Pharmacia Quantulus and the Packard 2000CA/LL (and subsequent models). The Quantulus has much enhanced passive shielding in addition to an active coincidence guard counter; the counter contains a mineral oil based liquid scintillant enabling the detection of cosmic and environmental gamma radiations. Further features to optimize performance include a user-set pulse amplitude comparator and high purity Teflon/copper counting vials, the latter enabling a 30% reduction in background compared to glass vials.[1,2] The Packard 2000CA/LL does not require an active or enhanced passive shielding. Its ability to reduce background count rates via burst counting circuitry enables the characteristics of sample scintillation pulses to be differentiated from those of background pulses through pulse shape/duration analysis.[3] Most background pulses have a number of afterpulses in addition to the fast prompt pulse common to all events. Although true $\beta^-$ events, particularly at higher energies, may have a certain number of afterpulses, a good degree of discrimination is certainly achievable. The detector assembly incorporating the slow scintillating plastic, a feature of the Packard-2260XL, enhances this time resolved burst discrimination since its long decay constant increases the number of photons in the afterpulses of background radiation, therefore acting as a quasiactive guard.

One criticism of the Quantulus has been that a lack of uniformity in the

Teflon vial characteristics has meant characterizing each vial individually. This necessarily reduces the element of routineness obtainable from the more uniform glass vials, and hence caused their abandonment for $^{14}C$ dating at SURRC except with samples whose expected ages exceed 25,000 years. Here, the improvement in background can be critical in terms of age resolution. Nevertheless, for 2 mL (1.75 g) and 4 mL (3.5 g) geometries in 7 mL slimline glass vials, efficiencies of 65 and 67.6% and backgrounds of 0.44 and 0.70 cpm, respectively, are obtainable.

A criticism of the Packard 2000CA/LL has been that although background count rates are considerably reduced, there is also a considerable reduction in overall counting efficiency.[4] This implies that the burst counting circuit is not 100% effective and that a certain percentage of true $\beta^-$ events are being discriminated out, presumably because their prompt pulse widths are sufficiently broad or they have an uncharacteristically large number of afterpulses. A logical extension to this argument is that by sharpening these pulses, much of this loss in efficiency could be regained.

The results presented here are a résumé of a considerable data set built up while assessing counters employing burst counting circuitry.

## EXPERIMENTAL

This study can, in essence, be divided into three component stages. First, the influence of a range of scintillants, their concentrations, and their combinations were assessed to determine influences on counting efficiency. This was followed by an assessment of two modifications to the original system: (1) the detector assembly incorporating a slow scintillating plastic and (2) vial holders produced from the same material; studies were carried out on both $^3H$ and $^{14}C$. Finally, for any radiocarbon dating laboratory the ultimate test must be the production of accurate age measurements. Naturally, the sample counting is only one aspect of the entire dating process; however, recent studies indicate that it is particularly important in terms of overall accuracy.[5]

This third section can be subdivided as follows:

1. A sample of benzene, synthesized from the peat used in stage 3 of the recent International Collaborative Study, was re-vialed into two 7 mL slimline glass vials. This sample had previously been dated using an "old technology" Packard 4530, with butyl-PBD/bis-MSB as the scintillant, giving an age of 3360 ± 50 years BP. The mean result for the 28 laboratories who dated this material was 3388 BP.[6]
2. One aspect which arose from the international study and which caused some considerable concern was that the NERC Laboratory dated two duplicate samples of marine shell material, each separated into inner and outer fractions, thus yielding four age measurements. When using old technology counters, all four results were well within the overall spread, however, when using the burst counting circuit, one of the four was enriched relative to

modern. In this instance, butyl-PBD alone (13 mg $mL^{-1}$) was the scintillant employed. To determine whether this effect was specific to the scintillant, the sample was re-vialed into three separate vials with appropriate dilutions and additions of toluene and bis-MSB to exactly duplicate the scintillant used in the University of Glasgow Laboratory.

Throughout the optimization studies involving different scintillant combinations and concentrations, standard 20 mL low potassium glass vials were employed; 4.5 g of a $^{14}C$ benzene standard (178.5 ± 2.0 dpm/$g^{-1}$) were used throughout. The essential criteria for optimization were (1) constancy of efficiency with variation in scintillant concentration as measured in a 0 to 156 keV window and (2) constancy of quenching as determined by t-SIE value. t-SIE is the spectral index of the transformed Compton spectrum of the external standard. Values can in theory range between 0 and 1000; a value of 1000 indicating no quenching. The 2000CA/LL employs a 20 $\mu$Ci $^{133}Ba$ standard, the 2260XL an 8 $\mu$Ci $^{133}Ba$ standard.

The optimization studies on the burst counting circuit, slow scintillant detector assembly, and vial holders were carried out in 7 mL glass vials using 2 g of a high activity $^{14}C$ standard (2340 ± 8 dpm/$g^{-1}$ benzene) and 0.42 g of a butyl-PBD/bis-MSB (12 and 6 g/$L^{-1}$ respectively) scintillant combination dissolved in toluene. The same geometry was also adopted for all dating studies. For $^{3}H$ assessments, tritiated water (410 dpm/$g^{-1}$) was used throughout.

Dating of the benzene sample synthesized from peat was carried out in the 2000CA/LL using the burst counting circuit, in the 2260XL using the burst counting circuit, and finally with the addition of the vial holders to the 2260XL system. Dating of the shell-derived sample was carried out on the 2000CA/LL.

## RESULTS AND DISCUSSION

Table 1 indicates that with the burst counting circuit activated, open window counting efficiency decreases from 84.1 to 73.9% as the concentration of butyl-PBD increases from 2 to 14 mg/$g^{-1}$ benzene. In parallel, t-SIE values increase to a plateau value at 10 mg/$g^{-1}$ and above. With the burst circuit off, the same trend in t-SIE values is observed; however, efficiency remains constant between 4 to 20 mg/$g^{-1}$ at approximately 93.5%. These features are found to be common to virtually all scintillants and scintillant combinations. That is:

1. t-SIE value trends are virtually identical whether the burst counter is on or off.
2. Throughout virtually all the concentration ranges, efficiency is constant at approximately 93.5% with the burst counter off, but variable, tending to a plateau value with the burst counter on.

**Table 1. Effect to Butyl-PBD Concentration $^{14}C$ Spectral Stability and Counting Efficiency with and without the Burst Counter Circuit in Operation**

| Butyl-PBD (mg/g$^{-1}$ of $C_6H_6$) | Eff. (%) BC on[a] | t-SIE[b] BC on | Eff. (%) BC off | t-SIE BC off | Difference in % Eff. |
|---|---|---|---|---|---|
| 2 | 84.1 | 557 | 91.8 | 557 | 7.7 |
| 4 | 80.7 | 683 | 93.5 | 681 | 12.8 |
| 6 | 78.9 | 730 | 92.8 | 732 | 13.9 |
| 8 | 76.6 | 749 | 93.5 | 751 | 16.9 |
| 10 | 75.7 | 757 | 93.2 | 755 | 17.5 |
| 12 | 75.2 | 761 | 93.6 | 762 | 18.4 |
| 14 | 74.8 | 761 | 93.1 | 760 | 18.3 |
| 16 | 73.9 | 760 | 93.4 | 759 | 19.5 |
| 18 | 73.5 | 758 | 93.0 | 759 | 19.5 |
| 20 | 73.7 | 755 | 93.8 | 755 | 20.1 |

[a] BC = Burst counter.

[b] t-SIE = spectral index of hte transformed Compton spectrum of the external standard.

Table 2 represents the optima in efficiency for these plateau values using a range of scintillants and scintillant combinations. It should be noted that the highest efficiencies are always observed in the presence of bis-MSB, ie. bis-MSB alone, butyl-PBD/bis-MSB and PPO/bis-MSB, at about 89 to 90% compared with about 93.5% with the burst counter off. This suggests that bis-MSB differs in some respect from the other scintillants, a factor which undoubtedly merits further investigation in terms of the pulse shaping rather than the ultimate influence on efficiency.

Since the introduction of the Packard 2000CA/LL, several modifications have been introduced as previously described. Table 3 indicates the performance enhancements these can bring about. With the burst counting circuit off, i.e., used as a conventional liquid scintillation counter, optimum window efficiency is relatively poor (57.8%). This is due to the shape of the background spectrum. To maximize the $E^2/B$ parameter, the lower discriminator had to be set to 18 keV. With the burst counter on, although open window efficiency is slightly reduced, optimum window efficiency is greatly enhanced (65.0%). This is due to a lower discriminator setting of 12.5 keV, enabling

**Table 2. Optimum Concentrations of a Range of Scintillants/Scintillant Combinations for Achieving Maximum $^{14}C$ Efficiency with Stability of Quenching on the Packard 2000CA/LL**

| Scintillant (mg/g$^{-1}$ of $C_6H_6$) | Eff. (%) (Burst circuit on) | Eff. (%) (Burst circuit off) | Difference in % Eff. |
|---|---|---|---|
| Butyl-PBD (16) | 73.9 | 93.4 | 19.5 |
| PPO (5.6) | 83.6 | 93.5 | 9.9 |
| PPO (5.6) + POPOP (0.7) | 81.9 | 93.8 | 11.9 |
| PPO (5.6) + $Me_2$ POPOP (0.7) | 82.6 | 93.6 | 11.0 |
| PPO (5.6) + bis-MSB (2.7) | 89.6 | 93.7 | 4.1 |
| Butyl-PBD (12) + POPOP (0.7) | 78.7 | 93.2 | 14.5 |
| Butyl-PBD (12) + $Me_2$ POPOP (0.7) | 77.2 | 93.5 | 16.3 |
| Butyl-PBD (12) + bis-MSB (4.0) | 88.5 | 93.1 | 4.6 |
| Bis-MSB (5.3) | 88.5 | 93.0 | 4.5 |

**Table 3.** **Progressive Optimization for $^{14}C$ of the Packard Low-Level Counting System, Employing Burst Counting Circuitry (Packard 2000CA/LL) and Using (1) a Detector Assembly with a Slow Scintillating Plastic (Packard 2260XL) and (2) Vial Holders Made from the Same Material (Scintillant = Butyl-PBD/Bis-MSB in Toluene)**

| Counting Conditions | Open window % Eff. | Opt. window % Eff. | Opt. Window Background (cpm) | $E^2/B$ |
|---|---|---|---|---|
| 2000CA burst circuit off | 92.1 | 57.8 | 2.87 | 1166 |
| 2000CA burst circuit on | 88.1 | 65.0 | 1.31 | 3226 |
| 2000CA burst circuit on + vial holders | 87.5 | 66.0 | 0.85 | 5134 |
| 2260XL burst circuit on | 86.9 | 70.2 | 0.94 | 5269 |
| 2260XL burst circuit on + vial holders | 88.6 | 71.4 | 0.69 | 7383 |

$E^2/B$ to be maximized while excluding all $^3H$. A general feature of the modifications (slow scintillant detector assembly and vial holders) is that they enhance performance not only by an overall reduction in the background count rate, but by changing the background spectra shape and enabling reduced lower discriminator settings. $E^2/B$ is enhanced from 3226 (Packard 2000CA/LL burst counter on) to 7383 (Packard 2260XL plus vial holder). Similar trends are also observed for $^3H$ (Table 4). With a standard 20 mL glass vial, using 10 mL of tritiated water and 10 mL Picofluor LLT, $E^2/B$ is enhanced from 62 (2000CA/LL burst counter off) to 161 (2260XL). Similarly, with 3.5 mL tritiated water and 3.5 mL Picofluor LLT in a standard 7 mL slimline glass vial, $E^2/B$ is enhanced from 155 to 400. The holders do not appear to enhance performance beyond that of the 2260XL. With the data currently available it is not possible to determine whether the differences between the 2260XL, 2260XL plus vial holders, and 2000CA/LL plus vial

**Table 4.** **Progressive Optimisation for $^3H$ of the Packard Low-Level Counting System Employing Burst Counting Circuitry (Packard 2000CA/LL) and Using (1) a Detector Assembly with a Slow Scintillating Plastic (Packard 2260XL) and (2) Vial Holders Made from the Same Material**

| Counting Conditions | Open Window % Eff. | Opt. Window % Eff. | Opt. Window Background (cpm) | $E^2/B$ |
|---|---|---|---|---|
| (a) 10 mL $H_2O$ + 10 mL Picofluor LLT | | | | |
| 2000CA burst circuit off (glass vials) | 25.1 | 19.7 | 6.30 | 62 |
| 2000CA burst circuit on (glass vials) | 23.5 | 21.5 | 3.77 | 123 |
| 2260XL glass vials | 25.1 | 23.2 | 3.33 | 161 |
| 2000CA burst circuit on (plastic vials) | 22.6 | 18.5 | 1.93 | 178 |
| 260XL (plastic vials) | 24.3 | 21.3 | 2.12 | 215 |
| (b) 3.5 mL $H_2O$ + 3.5 mL Picofluor LLT | | | | |
| 2000CA burst circuit off | 26.9 | 19.7 | 2.51 | 155 |
| 2000CA burst circuit on | 25.5 | 22.6 | 2.06 | 248 |
| 2000CA burst circuit on + vial holders | 22.3 | 19.1 | 1.05 | 350 |
| 2260XL | 25.5 | 23.5 | 1.38 | 400 |
| 2260XL + vial holders | 23.7 | 22.0 | 1.32 | 367 |

**Table 5. $^{14}$C Age Determinations on Benzene Synthesized from Peat and Shell Material Used in the International Collaborative Study**

| | Counting conditions | Mean $^{14}$C Age |
|---|---|---|
| (a) | Peat sample | |
| | 2000CA/LL burst circuit on | 3410 ± 40 |
| | 2260XL | 3440 ± 60 |
| | 2260XL + vial holders | 3410 ± 70 |
| (b) | Shell sample | |
| | 2000CA\LL burst circuit on | 750 ± 70 |

holders are significant. Table 5 gives the age measurements made on the benzene synthesized from both the peat and shell samples. The peat results show excellent agreement with those of the international study regardless of the counting conditions employed. Results for the shell sample seem to confirm that the anomalous measurement on this sample is in some respect tied to the scintillant employed.

The mean age derived from the three replicate subsamples was calculated to be 750 ± 70, and considering the extra manipulations involved in re-vialing etc., this compares quite favorably with the mean result of 637 BP from 31 laboratories, and it is obviously significantly older than the previously derived modern age. It would appear that under certain circumstances a combination of vial plus contents and the butyl-PBD must enhance efficiency beyond the norm. The most obvious possibility would seem to be some impurity in the benzene, perhaps altering pulse shapes or variations in dissolved oxygen, which will influence the triplet state and reducing the delayed component.[2]

For $^{14}$C dating with the 2260XL, the counting time of the external standard was increased from 15 to 60 sec to reduce the greater variability in t-SIE observed. Determining a t-SIE value in the 2260XL requires an additional step. Along with the Compton spectrum produced by the vial-content interaction, there is also a spectrum produced by the interaction of the $\gamma$ radiations with the slow scintillating plastic in the detector assembly. The combination of these two spectra will not yield a true t-SIE value. To compensate for this, an additional spectrum must be measured, i.e., that of the external standard with an empty vial which, in effect, is brought about by interactions with the plastic. This second measurement subtracted from the first produces the "true" t-SIE value. A one minute counting time for the external standard plus sample reduces the variability in t-SIE to the same magnitude as found with the 2000CA/LL. Using the 2260XL with vial holders produces much greater variations in t-SIE which can not be overcome by increasing the external standard counting time, even to 4 min. To circumvent this problem, the following steps were taken. First, a uniform response of the vial holders has to be verified. This was carried out as follows.

1. Each vial holder was loaded with a vial containing 4.5 g of scintillation grade benzene and 0.95 g of butyl-PBD (12 g/L$^{-1}$) and bis-MSB (6 g/L$^{-1}$) in toluene.

Each vial was then counted for 5 × 100 min. The results were entirely consistent with a uniform background response.

2. A single high activity standard (2340 dpm/g$^{-1}$ benzene) was counted sequentially in each of the vial holders (3 × 25 min counts). The vial holders with the lowest and highest count rates then underwent further counting (4 × 50 min). At the end of this counting period, open and optimum window counting efficiencies were identical (87.4 and 71.0%, respectively). It appears that despite the variability in t-SIE values, between successive counts from a single vial holder and values from different vial holders, the background and efficiency responses are essentially constant within the 20 individuals tested.

Having established this constancy of response, a quench curve was constructed using 16 vials of 2 g high activity benzene standard quenched to differing degrees with acetone. This was carried out first without the vial holders and subsequently with them. A second degree polynomial regression analysis of the former yielded an $R^2$ value of 99.8%, the latter yielded a value of 79.9%. Finally, the count rate using the vial holders was regressed against the t-SIE values without the vial holders yielding a value of 99.6%. The same system was then employed to determine the degree of quenching in samples, backgrounds, and modern reference standards, i.e., a large number (50) of very short (0.1 min) sample counts, with 1 min counts of the external standard, were undertaken without the vial holders. The samples were then counted using the vial holders for a minimum of 2000 min via the quasisimultaneous batch counting method as would normally be adopted.[7]

## CONCLUSIONS

The results of these studies confirm that the burst counting circuit makes the efficiency of the Packard 2000CA/LL highly sensitive to scintillant concentration and type. Decreases of up to 20% in counting efficiency are observed compared to conventional counting. These can largely be overcome by careful manipulation of scintillant concentration and type. Best overall performance is always obtained in association with the secondary scintillant bis-MSB. Efficiencies approaching 90% are routinely observed, i.e., within approximately 4% of conventional levels. It is proposed that bis-MSB sharpens pulse widths thereby bringing many more true $\beta^-$ events within the cut-off threshold of the burst counter. In some instances it has been observed that efficiency increases as the degree of quenching increases which is completely contrary to normal theory. This obviously reflects the complexity of the pulse shape analyses and must represent a complex balance of sufficient scintillant, self absorption, and the energy transfer process.

The use of the detector assembly incorporating both the slow scintillating plastic (2260XL) and the slow scintillating plastic vial holders enable significant enhancements in performance for $^{14}$C. The burst counter and plastic detector assembly both enhance $^3$H performance, although it is questionable whether the vial holders with the plastic detector assembly represents any further enhancement. With standard 20 mL plastic vials containing 10 mL tritiated water + 10 mL Picofluor LLT a limit of detection of 1.4 Bq/L is achievable for a 500 min count.

In terms of actual $^{14}C$ age measurements, the limited results so far indicate that accuracy is possible with burst counting circuitry and subsequent modifications to this system using butyl-PBD/bis-MSB as the scintillant. Many more measurements, however, are required to confirm this, particularly when the use of vial holders and the associated modifications of normal $^{14}C$ dating practices are envisaged. The use of butyl-PBD alone as a scintillant for $^{14}C$ dating obviously has associated problems, and until these can be identified and eliminated, its use should not be recommended.

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