ASSESSMENT OF NEW FEATURES ON A COMMERCIAL LIQUID SCINTILLATION SPECTROMETER FOR RADIOCARBON DATING

G. T. COOK and ROBERT ANDERSON

Scottish Universities Research and Reactor Centre, East Kilbride, Glasgow G75 0QU, Scotland

ABSTRACT. The current generation of Packard Instrument Company liquid scintillation spectrometers incorporates burst counting circuitry (BCC) to differentiate true β events from unquenchable background. The discrimination is made on the number of afterpulses following the prompt pulse. The 2550TR has two new features, a variable timing "delay before burst" and a variable coincidence gate. We examined these features for counting performance, particularly in radiocarbon dating. Using a cocktail that we developed for ^{14}C dating (2.8 mg butyl-PBD and 3.0 mg bis-MSB per gram of benzene) on an instrument with non-variable BCC, we could not enhance the optimum E^2/B by varying the "delay-before-burst" feature on the 2550TR. We increased counting efficiency, but at the expense of a small increase in background. On the other hand, using a fluor concentration of 15 mg butyl-PBD per gram benzene (such as what might be used in the LKB Wallac Quantulus, and which previously gave a poor efficiency response with BCC), we significantly increased the optimum E^2/B by increasing the delay before burst. We estimate that, at a delay setting of 300 nsec, we can achieve values similar to those obtained using our optimized cocktail. We found, as might be expected, that varying the coincidence gate between 10 and 18 nsec had no significant effect on E^2/B.

INTRODUCTION

In liquid scintillation (LS) spectrometry, the concept of measuring pulse shapes, as opposed to simply measuring pulse amplitudes, is not new. Horrocks (1970) and Thorngate, McDowell and Christian (1974) used this analytical technique two decades ago to separate different types of radiation using a number of experimental devices; however, its use as a background reduction feature is much more recent (Valenta 1986; van Cauter 1986). The current generation of Packard Instrument Company spectrometers uses a technique termed burst-counting circuitry (BCC) to differentiate unquenchable background events from true beta events. BCC is based on the fact that true β background events tend to have more afterpulses following the prompt pulse. This has led to the development of low-background instruments, which differ only in their analog circuitry from standard models; also they require neither an anticoincidence guard and its associated circuitry nor enhanced passive shielding. For ^{14}C dating researchers, an initial problem related to BCC was that, despite significantly reduced background, efficiency was adversely affected (Polach *et al.* 1988). We believe the problem is that many workers prefer to use a primary fluor only and at relatively high concentrations. The fluor can be weighed accurately into the counting vials as a solid; this limits the volume to that of sample only, with no requirement for a liquid cocktail, hence, minimizing background. However, we have found a way to accurately add two fluors to a vial in small quantities, without increasing the volume (Anderson & Cook 1991). The problem with using a primary fluor only is that PPO and, in particular, butyl-PBD give relatively low counting efficiencies; this indicates that a relatively large number of true β events are misidentified as background events and are rejected (Cook *et al.* 1990). Our work has demonstrated that most of the efficiency may be regained by the addition of the secondary fluor, bis-MSB. Its mode of action does not seem to be the traditional one of a wavelength shifter, because 1) neither POPOP nor dimethyl POPOP have the same effect, and 2) a much higher concentration than normal is required (higher than that of the primary fluor for optimum response). Thus, the bis-MSB either sharpens prompt pulses or, more likely, suppresses afterpulses. Using the 2000CA/LL and 2260XL spectrometers, we have demonstrated that a cocktail consisting of 3 mg of bis-MSB and 2.8 mg of butyl-PBD per gram of benzene gives both relatively high efficiency and resistance to quenching

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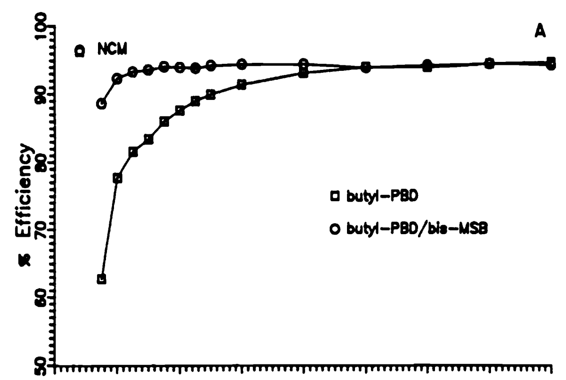

Fig. 1A. Open-window (0–156 keV) efficiencies at a range of burst delay settings for both butyl-PBD and butyl-PBD/bis-MSB (15 g benzene)

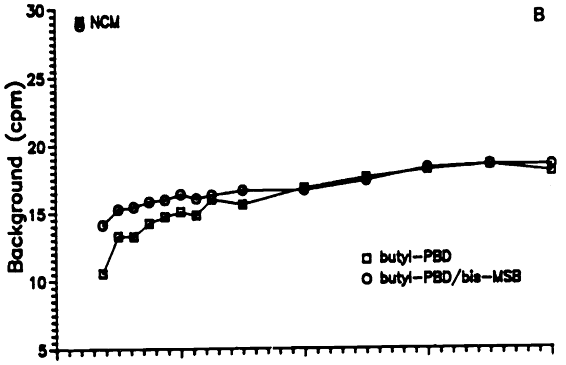

Fig. 1B. Open-window (0–156 keV) backgrounds at a range of burst delay settings for both butyl-PBD and butyl-PBD/bis-MSB (15 g benzene)

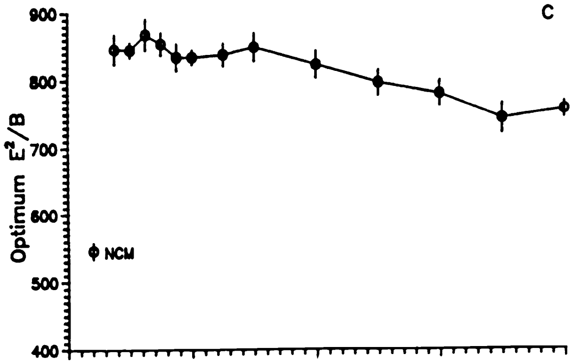

Fig. 1C. Effect of increasing delay before burst on optimum E^2/B using butyl-PBD/bis-MSB (15 g benzene)

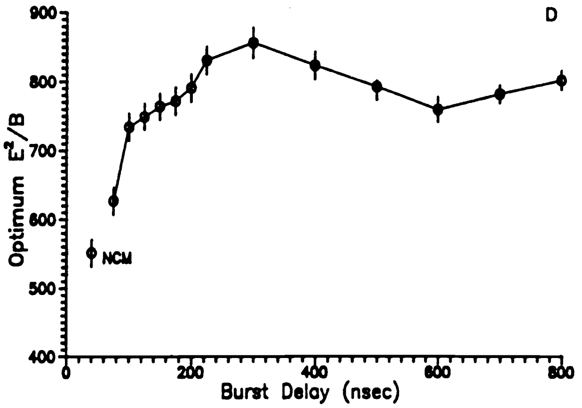

Fig. 1D. Effect of increasing delay before burst on optimum E^2/B using butyl-PBD cocktail (15 g benzene)

TABLE 1. Effect of Varying the Coincidence Gate on Background, Efficiency and Optimum E^2/B Using the 2550TR

Gate	% Efficiency (0–156 keV)	Background (cpm) ± 2σ (0–156 keV)	E^2/B ± 2σ
A. butyl-PBD/bis-MSB at a burst delay of 125 nsec			
10	92.9	15.33 ± 0.50	846 ± 42
12	93.1	16.01 ± 0.50	829 ± 40
14	93.0	15.34 ± 0.50	852 ± 42
16	93.1	14.94 ± 0.48	881 ± 44
18	93.2	15.52 ± 0.50	903 ± 44
B. butyl-PBD alone at a burst delay of 300 nsec			
10	89.8	15.46 ± 0.50	792 ± 40
12	89.9	14.87 ± 0.48	842 ± 42
14	90.0	15.21 ± 0.50	845 ± 42
16	89.9	15.72 ± 0.50	786 ± 38
18	90.2	15.78 ± 0.50	763 ± 38

(Anderson & Cook 1991). Efficiency is generally in the range of 89–90% for a 0–156 keV window, but with more than a twofold decrease in background. This brings about a considerable increase in E^2/B.

The normal burst-counting circuit has a 75 nsec delay between the initiation of a coincident event and measurement of the burst of afterpulsing. The 2550TR allows this delay to vary from this value to a maximum of 800 nsec. The purpose of this study was to assess the effect of varying this delay before burst on 1) the cocktail formulation that we fully optimized for use on instruments with BCC, *i.e.*, 2.8 mg of butyl-PBD and 3.0 mg of bis-MSB per gram benzene, and 2) a cocktail that previously gave a relatively low efficiency response, *i.e.*, 15 mg of butyl-PBD per gram benzene, that might be used in other instruments, such as the LKB Wallac Quantulus.

It is also possible to vary the coincidence gate on the 2550TR; we studied the effect of this on the limits of detection for the above-mentioned cocktails.

METHODS

We counted vials containing 15 g of ^{14}C-labeled benzene (4850 dpm) and either 1) 2.8 mg of butyl-PBD and 3.0 mg of bis-MSB per gram benzene or 2) 15 mg of butyl-PBD per gram benzene to an error limit of 0.2% (1 σ) at a range of delay-before-burst settings from 75 to 800 nsec. In parallel, we also counted vials containing 15 g of scintillation-grade benzene and similar concentrations of fluors for at least 250 min, but typically up to 1000 min at the same delay-before-burst settings. Figure 1A shows the efficiency results and Figure 1B, background. Using "in-house" software, we calculated optimum E^2/B values for the two cocktails, presented in Figures 1C and 1D. Having established optimum burst delay settings for both cocktails, we recounted the vials at these delays over a range of coincidence gate settings from 10 to 18 nsec; these results are given in Table 1. Finally, we compared three instruments (Packard 2250CA/LL, Packard 2260XL and Packard 2550TR) using the two cocktails described above, but with 4 g benzene in 7-ml glass vials; these results are presented in Table 2.

TABLE 2. Comparison of Packard 2250CA, 2260XL and 2550TR for ^{14}C Dating Using Two Cocktails

Model	BCC	Burst delay	% Eff. (0–156 keV)	Opt. % Eff.	Opt. bkgd. (cpm)	Opt. E^2/B ± 2σ
A. butyl-PBD/bis-MSB (2.8 and 3.0 mg g^{-1})						
2250CA	Off	N/A	96.1	66.4	4.15	1063 ± 74
2250CA	On	Normal	91.3	67.2	1.81	2499 ± 108
2260XL	Off	N/A	95.1	79.2	14.10	445 ± 16
2260XL	On	Normal	91.0	76.7	1.50	3907 ± 316
2550TR	Off	N/A	96.2	66.4	4.02	1097 ± 50
2550TR	On	Normal	89.5	68.0	1.74	2655 ± 128
2550TR	On	125 nsec	93.9	71.7	2.05	2502 ± 112
B. butyl-PBD (15 mg g^{-1})						
2250CA	Off	N/A	96.3	65.8	3.75	1154 ± 42
2250CA	On	Normal	72.9	53.8	1.34	2159 ± 108
2260XL	Off	N/A	93.2	78.5	13.35	461 ± 18
2260XL	On	Normal	10.1	4.3	0.11	164 ± 44
2550TR	Off	N/A	97.1	66.4	3.50	1259 ± 60
2550TR	On	Normal	63.0	45.3	1.17	1760 ± 72
2550TR	On	300 nsec	92.1	68.2	1.95	2381 ± 108

RESULTS AND DISCUSSION

Figure 1A illustrates that, with the BCC option disabled, both cocktails give an open-window counting efficiency of ~96%. However, under normal BCC conditions (*i.e.*, 75 nsec delay), counting efficiency for the 15 mg butyl-PBD cocktail falls to ~63%, whereas, in contrast, the loss in efficiency for the butyl-PBD/bis-MSB cocktail is much smaller (open-window efficiency = 89%). By increasing the delay before burst beyond 75 nsec, efficiency for both cocktails increases. For butyl-PBD, counting efficiency increases initially from 75 to 100 nsec (63–78%). Similarly, for the butyl-PBD/bis-MSB cocktail, the increase in efficiency between 75 and 100 nsec is the most rapid. For both cocktails, the efficiency plateau is at about 94%; however, this requires a burst delay of about 500 nsec for the butyl-PBD cocktail and a delay of about 125–150 nsec for the butyl-PBD/bis-MSB combination. In parallel with these observations, Figure 1B indicates that background increases as the burst delay is increased. Again, the major effect appears to be between 75 and 100 nsec. Background count rates from the butyl-PBD cocktail are consistently lower until ~400 nsec.

No increase in the burst delay significantly enhances the E^2/B factor for the butyl-PBD/bis-MSB cocktail (Fig. 1C). The values remain generally constant, gradually decreasing above a setting of about 400 nsec. The trend for the butyl-PBD cocktail is quite different, with a systematic increase from 75 to 300 nsec, corresponding to an E^2/B increase from 627 to 856 (Fig. 1D). Varying the coincidence gate had no significant effect on E^2/B (Table 1). From the results of the 4-g benzene geometry in Table 2, the following may be observed for butyl-PBD/bis-MSB:

1. For the 2250CA, BCC decreases open-window efficiency by <5%; however, the E^2/B factor more than doubles as a result of the twofold reduction in background.
2. Similarly for the 2260XL, ~5% efficiency is lost with BCC. Without BCC, background is very high, and we do not recommend its use in this mode. When we use BCC, the E^2/B factor is ~8 times greater than when BCC is disabled. It is also ~1.5 times greater than that of the 2250CA, indicating its superiority for ^{14}C dating.

3. For the 2550TR, efficiency decreases ~7% when BCC is enabled, but by increasing the burst delay to 125 nsec, it decreases ~2%. The E^2/B for the increased delay setting is not significantly different from the 75 nsec setting. Both settings double E^2/B relative to the BCC-disabled condition.

For butyl-PBD alone:

1. Efficiency decreases by >20% in the 2250CA when BCC is enabled, although E^2/B approximately doubles.
2. Efficiency decreases by >80% in the 2260XL when BCC is enabled. This must be due to an increase in the burst component brought about by the quasi-active plastic guard used as an additional background reduction feature. Because of high background with disabled BCC and very low efficiency with enabled BCC, we do not recommend using butyl-PBD alone in the 2260XL. We even tried simulating the 2260XL using the 2550TR with vial holders made from the same plastic as the guard, and then increasing the delay to determine whether we could regain the efficiency. Our maximum absolute efficiency was 77% at an 800-nsec delay.
3. More than 30% efficiency is lost in the 2550TR with BCC enabled; however, this loss can be reduced to 3% by increasing the burst delay to a setting of 300 nsec. At this setting, E^2/B is significantly increased compared with the normal 75-nsec setting; however, it is not significantly different from the butyl-PBD/bis-MSB cocktail used in the 2550TR at a 125-nsec delay, or in the 2250 with butyl-PBD/bis-MSB and the BCC option enabled.

CONCLUSIONS

These results demonstrate that a variable burst delay feature makes the 2550TR much more flexible than previous models, because efficiency is now much less cocktail-dependent. This is an important consideration in ^{14}C dating because 1) many researchers are unwilling to change fluor concentrations due to the considerable effort involved; 2) some may wish to carry out intralaboratory comparisons between instruments, which, depending on the cocktail employed, may not have been possible previously; and 3) it now becomes much easier to weigh fluors in solid form. The results also tend to confirm that bis-MSB acts as an afterpulse suppressor rather than a prompt-pulse sharpener. Nevertheless, the 2260XL remains the superior instrument for ^{14}C dating if a butyl-PBD/bis-MSB cocktail is employed, because it appears unlikely that a delay-before-burst feature will enhance the performance of the butyl-PBD cocktail sufficiently.

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