

A RADIOCARBON DATING PROTOCOL FOR USE WITH PACKARD SCINTILLATION COUNTERS EMPLOYING BURST-COUNTING CIRCUITRY

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ABSTRACT. Considerable research has been carried out in this laboratory on the use of Packard scintillation counters employing burst-counting circuitry. The nature of the pulse-shape discrimination circuit has led to redefining our sample vialing philosophy and scintillation cocktail optimization. Results presented here demonstrate: 1) the enhancements in efficiency that are achievable using a two-component cocktail compared with the use of a primary fluor only; 2) the development of a cocktail in which efficiency and quenching are relatively unaffected by moderate variations in fluor concentrations and ratio; 3) the rationale behind the use of screw-cap vials rather than sealable ampules; 4) the advantage of nickel/chromium-plated brass caps over standard plastic caps.

INTRODUCTION

The new generation of Packard liquid scintillation counters (LSC) employs a feature, termed burst-counting circuitry, that differentiates background events from true β^- events by pulse-shape/duration analysis (Valenta 1986). Most background prompt pulse events are accompanied by a number of after-pulses of much smaller amplitude. In contrast, prompt pulses of true β^- events (particularly the soft β^- s) induce few or no after-pulses. This difference is the basis of the background reduction feature (van Cauter 1986; Noakes, de Filippis & Valenta 1988). Prior to the laboratory's purchase of the first model of this new generation of counters (Packard 2000CA/LL), all ^{14}C measurements were carried out using sealable ampules and a scintillation cocktail comprising butyl-PBD and bis-MSB dissolved in toluene. However, since the trend amongst practitioners of the dating method seemed to be toward using a primary fluor only (as the early requirement of a wave length shifter had now long disappeared with the advent of modern photomultiplier tubes) and Polach *et al.* (1983) had demonstrated the superior resistance to quenching of butyl-PBD alone, we decided to follow this recommendation and use only butyl-PBD as the fluor in this instrument. This had the added advantage that, at the recommended concentration ($15 \text{ mg}\cdot\text{ml}^{-1}$), it could be weighed with adequate accuracy. Consequently, this would reduce overall volume and, hopefully, background. Almost simultaneously, Polach *et al.* (1988) demonstrated that although the 2000CA/LL significantly reduced the background count rate, efficiency decreased. The logical deduction from these results was that a proportion of true β^- events was being rejected because of prompt pulse widths or numbers of after-pulses exceeding cut-off thresholds. We were also concerned with the use of sealable ampules. The sealing process, using a glass-blowing torch, could conceivably influence the oxygen and/or nitrogen pressures in the ampules, which in turn, could influence pulse shapes and thereby efficiency.

Two factors required detailed investigation: 1) scintillant optimization; 2) selection of a suitable counting vial. The results presented here summarize research carried out in our laboratory to develop a ^{14}C dating protocol for use with this type of counter using burst-counting circuitry (low-level counting mode).

METHODOLOGY AND RESULTS

Scintillation Cocktail Optimization

Figure 1 shows the influence on counting efficiency as the butyl-PBD concentration ranged from

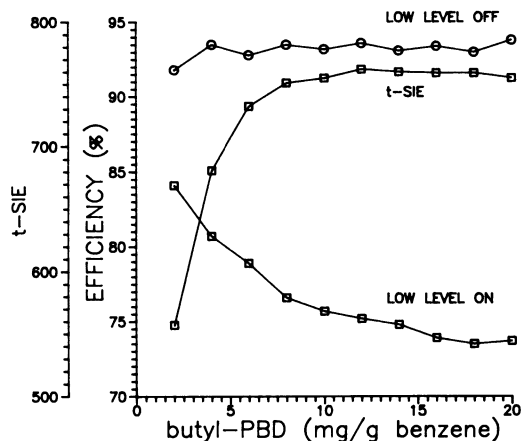


Fig. 1. Influence on efficiency and t-SIE of increasing the butyl-PBD concentration from 2–20 mg·g⁻¹ benzene

2–20 mg·g⁻¹ of benzene: 1) with the low-level option enabled, efficiency generally decreases as the concentration of the fluor increases; 2) with the low-level mode disabled, the fluor has much less effect on efficiency. Only at the lowest concentration is efficiency significantly influenced. It is also worth noting that at the lowest concentration, efficiency is at a maximum with the low-level mode enabled and at a minimum when disabled; 3) with the low-level mode enabled, efficiency decreases as the t-SIE (transformed spectral index of the external standard) parameter, which is a measure of quenching, increases (*i.e.*, indicating a decrease in quenching). This anomalous response of the t-SIE parameter probably indicates the complexity of the balance of sufficient scintillant, self-absorption and energy transfer to scintillants capable of sharpening pulse widths and suppressing after-pulsing. It obviously enforces the requirement for a scintillation cocktail that stabilizes t-SIE within reasonable limits. Similar results (not presented here) were obtained for PPO, although the magnitude of the differences and rate of reduction in efficiency with increasing PPO concentration are not as substantial.

Figure 2 indicates the effects of secondary fluors added to a fixed concentration of butyl-PBD (12 mg·g⁻¹ of benzene). The addition of POPOP and di-methyl POPOP marginally improve the effi-

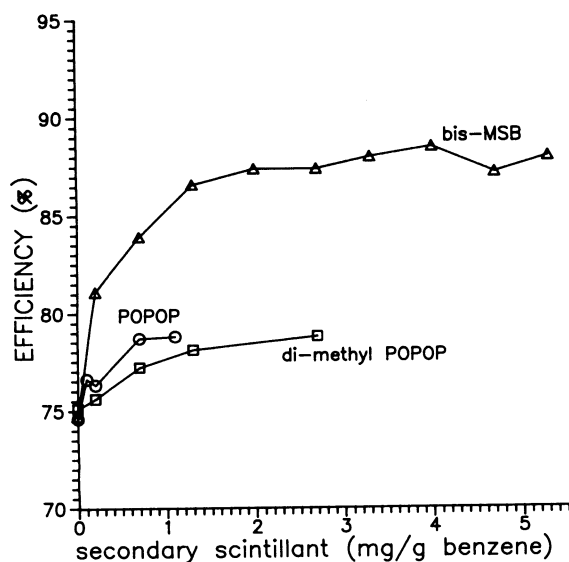


Fig. 2. Influence on efficiency of the addition of secondary scintillants to a fixed concentration of butyl-PBD (12 mg·g⁻¹ benzene)

ciency, and bis-MSB very significantly enhances it. Other results with PPO, again not presented here, indicate that neither POPOP nor di-methyl POPOP enhance efficiency, indeed the trend is towards a slight decrease. Bis-MSB, however, again substantially increases efficiency. We propose that bis-MSB enhances efficiency by sharpening pulse widths and/or suppressing after-pulsing. Thus, it would appear from these results that a combination of butyl-PBD/bis-MSB or PPO/bis-MSB should produce optimum counting efficiency. The latter was not considered because of its poorer chemical stability (Polach, personal communication). Figure 3A indicates the stability of efficiency from a range of butyl-PBD and bis-MSB concentration ranges ($0.5\text{--}19.6\text{ mg}\cdot\text{g}^{-1}$ and $0.5\text{--}5.0\text{ mg}\cdot\text{g}^{-1}$, respectively). Figure 3B demonstrates the stability of the t-SIE parameter for these same concentration ranges. In terms of t-SIE, the results demonstrate that: 1) at low butyl-PBD concentrations ($0.5\text{--}2\text{ mg}\cdot\text{g}^{-1}$), t-SIE increases to a more-or-less stable plateau value as the concentration of bis-MSB increases, the gradient becoming less steep as the butyl-PBD concentration is increased from $0.5\text{--}2\text{ mg}\cdot\text{g}^{-1}$; 2) at $3\text{ mg}\cdot\text{g}^{-1}$ of butyl-PBD, t-SIE is stable across the entire bis-MSB concentration range; 3) at higher butyl-PBD concentrations ($6\text{--}19.6\text{ mg}\cdot\text{g}^{-1}$), t-SIE decreases almost continuously; 4) the t-SIE values tend towards convergence as the bis-MSB concentration increases. From a consideration of stability of t-SIE, these results suggest an optimum of $3\text{ mg}\cdot\text{g}^{-1}$ of butyl-PBD, and bis-MSB in the range $2\text{--}5\text{ mg}\cdot\text{g}^{-1}$. From a consideration of efficiency, the range $2\text{--}4\text{ mg}\cdot\text{g}^{-1}$ bis-MSB shows stable efficiency for the $3\text{ mg}\cdot\text{g}^{-1}$ butyl-PBD concentration. These results indicate that a fluor combination of 3 mg of butyl-PBD and 3 mg of bis-MSB per gram of sample benzene gives optimum stability of both efficiency and t-SIE. This combination, together with others, including $1:3$ and $2:3\text{ mg}\cdot\text{g}^{-1}$ butyl-PBD/bis-MSB, were tested for their resistance to quenching. The $3:3$ proved to be most resistant. Table 1A indicates the stability of both t-SIE and efficiency as the butyl-PBD is varied around the $3\text{ mg}\cdot\text{g}^{-1}$ value. The results suggest that, for full optimization, the butyl-PBD concentration should be reduced to $2.8\text{ mg}\cdot\text{g}^{-1}$. Table 1B indicates the excellent stability of both efficiency and t-SIE that is achievable even when both components are varied but the ratio is kept constant. Thus, from these results, we deduce that the combination of fluors that gives the best resistance to quenching together with sta-

TABLE 1. Effects on efficiency and quenching (t-SIE) of variations in butyl-PBD and bis-MSB around approximate optimum concentrations. Low-level option enabled in Packard 2000CA/LL.

	Butyl-PBD ($\text{mg}\cdot\text{g}^{-1}\text{ C}_6\text{H}_6$)	Bis-MSB ($\text{mg}\cdot\text{g}^{-1}\text{ C}_6\text{H}_6$)	% Efficiency ($0\text{--}156\text{ keV}$)	t-SIE
A.	2.6	3.0	88.9	635
	2.8	3.0	88.8	634
	3.0	3.0	88.8	639
	3.2	3.0	88.6	641
	3.4	3.0	88.7	645
B.	2.51	2.69	88.9	623
	2.66	2.84	88.8	623
	2.73	2.92	88.8	625
	2.80*	3.00	88.8	626
	2.87	3.08	88.9	625
	2.94	3.16	88.8	626
	3.09	3.31	88.7	629

*Selected as absolute optimum combination

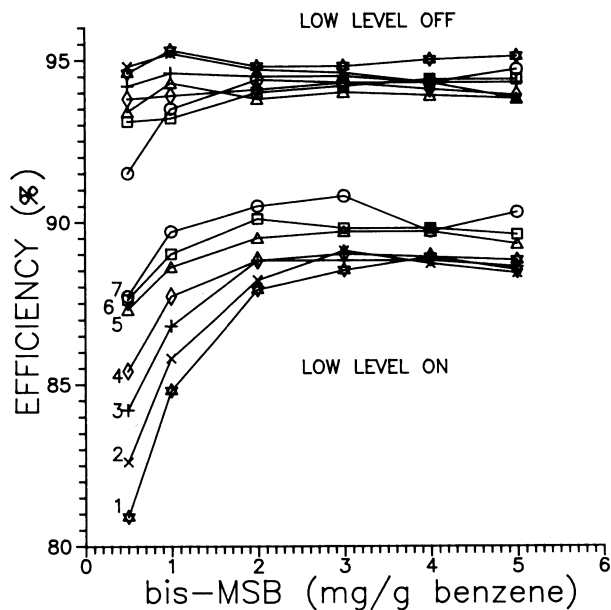


Fig. 3A. Optimization of efficiency using a range of butyl-PBD ($0.5\text{--}19.6\text{ mg}\cdot\text{g}^{-1}$ benzene) and bis-MSB ($0.5\text{--}5.0\text{ mg}\cdot\text{g}^{-1}$ benzene) concentrations. 1 = 19.6; 2 = 13.1; 3 = 6.0; 4 = 3.0; 5 = 2.0; 6 = 1; 7 = 0.5 mg of butyl-PBD per gram benzene. Same symbols apply for low level on and off.

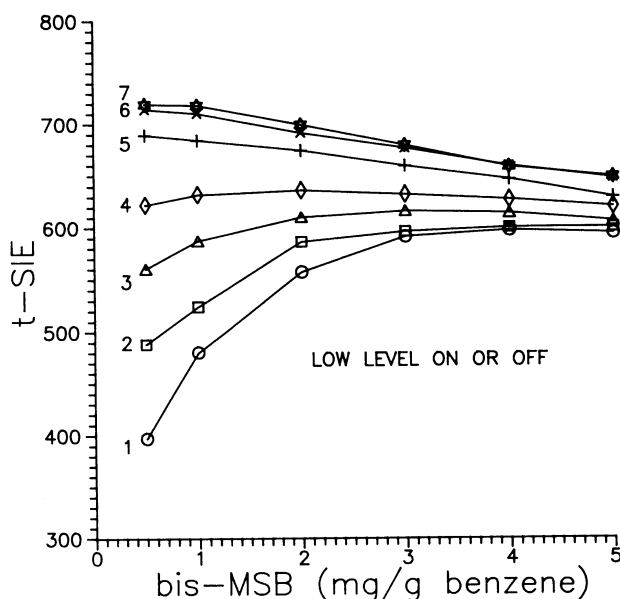


Fig. 3B. Stability of t-SIE using the same ranges of scintillants as Figure 3A. 1 = 19.6; 2 = 13.1; 3 = 6.0; 4 = 3.0; 5 = 2.0; 6 = 1; 7 = 0.5 mg of butyl-PBD per gram benzene.

bility of performance is $2.8\text{ mg}\cdot\text{g}^{-1}$ of butyl-PBD and $3\text{ mg}\cdot\text{g}^{-1}$ of bis-MSB.

Vial Selection

The basic choices of vial type are: 1) 20-ml low-potassium borosilicate glass with screw-caps; 2) 7-ml low-potassium borosilicate glass with screw-caps; 3) 20-ml borosilicate sealable ampules; 4) 7-ml borosilicate sealable ampules; 5) Teflon vials as used in the Quantulus. Table 2 confirms our concern about using sealable ampules. With the low level on, purging the samples with oxygen

brings about no change in efficiency within an open window, but a considerable reduction of efficiency occurs within the optimum window due to quenching of the spectrum. Conversely, purging with nitrogen decreases efficiency, since the triplet state will not then be quenched. This will have the effect of producing tailed pulses, in some cases, indistinguishable from background events. With the low level off, oxygen decreases efficiency in both the open and optimum windows; nitrogen has no effect. In terms of background count rates, with the low level on, nitrogen purging tends to reduce background count rates; oxygen has the opposite influence. With the low level off, oxygen enhances the background slightly; nitrogen has no effect. The apparent constant efficiency within an open window due to oxygen purging with the low level enabled is probably a balance of loss of efficiency by quenching and a regaining of the 4–5% efficiency that is lost when the low level is enabled (*ca.* 90% efficiency low level on, *cf.* *ca.* 95% low level off). The effects of purging may be further confirmed by examining the t-SIE values. Predictably, nitrogen increases the t-SIE while oxygen decreases it. We propose that these effects prohibit the use of sealable ampules, since the sealing process may influence the oxygen and/or nitrogen pressures in the ampules, and hence, lead to variations in counting efficiency and background. We have observed occasional increases in SIE values above the norm in cases of difficult-to-seal ampules counted in Packard 4530 and 460 C instruments. This suggests a loss of oxygen from the ampules.

TABLE 2. Background count rates and efficiencies from oxygen and nitrogen purged vials using the Packard 2250CA

Purging	% Efficiency		Background (cpm)		t-SIE
	(0–156 keV)	(11–90 keV)	(0–156 keV)	(11–90 keV)	
<i>A. Low level on</i>					
None	89.7	71.6	6.50	2.19	595
Nitrogen	84.0	66.7	5.90	1.80	676
Oxygen	89.9	60.5	7.57	2.71	328
<i>B. Low level off</i>					
None	94.5	75.5	18.05	6.21	596
Nitrogen	94.5	75.2	17.93	6.18	675
Oxygen	91.5	61.9	19.18	6.74	329

The disadvantages of screw-cap vials are: 1) the samples are prone to evaporative losses, particularly from the 20-ml vials; 2) the standard plastic caps are hygroscopic, which makes accurate estimates of weight losses very difficult. Table 3 shows typical background count rates and efficiencies from 20-ml and 7-ml screw-cap vials for 2-gram and 4-gram geometries (using the optimum fluor concentrations) counted in both the Packard 2250CA and 2260XL. We noted that: 1) for the 4-g geometry, efficiencies are essentially comparable in both the 7- and 20-ml vials. For the 2-g geometry, there is some indication of an increase in efficiency in the 7-ml vial over the 20-ml; 2) in the 2250CA, there are no significant differences in background count rates (within the counting window) for comparable geometries but different vial sizes; 3) in the 2260XL, background count rates from the 7-ml vials are significantly reduced, compared to the corresponding geometries in 20-ml vials. G. W. Pearson (personal communication) uses a cap constructed from nickel/chromium-plated brass to overcome the hygroscopy problem in the 20-ml vials. A three-component seal consisting of teflon, silicon rubber and indium foil minimizes evaporative losses. We have constructed an almost identical cap for use with Packard 7-ml vials, but using a two-com-

TABLE 3. Efficiencies and backgrounds for 2-g and 4-g geometries for 7-ml and 20-ml vials. Counted using the Packard 2250CA and 2260XL with the low-level options enabled.

Vial	% Efficiency		Background (cpm)	
	(0–156 keV)*	(11–90 keV)	(0–156 keV)	(11–90 keV)**
<i>A. 2250CA (4-g geometry)</i>				
7 ml	89.6	71.6	6.45	2.13
20 ml	89.4	71.2	6.61	2.14
<i>B. 2250CA (2-g geometry)</i>				
7 ml	89.6	71.7	5.23	1.34
20 ml	89.1	70.1	5.56	1.41
<i>C. 2260XL (4-g geometry)</i>				
7 ml	89.4	71.2	3.74	1.44
20 ml	89.0	70.5	4.29	1.56
<i>D. 2260XL (2-g geometry)</i>				
7 ml	89.3	71.2	2.49	0.81
20 ml	88.5	68.9	3.19	0.95

*Counted to 0.1% precision

**Typical background error range 0.02–0.03 cpm

ponent seal consisting of 1.5-mm silicon rubber and 0.25-mm indium foil. More recently, we replaced the indium/silicon rubber seal with the standard foil seal used in conjunction with the plastic caps. Table 4 displays the cumulative average weight change for batches of 25 vials, with standard plastic caps and foil liners, with Ni/Cr plated brass caps and standard foil liners and with brass caps and indium/silicon rubber liners. The results indicate that the brass caps are completely stable with no uptake of moisture at 65–75% relative humidity. After 24 h, there is absolutely no change in total vial weight. This is followed by an extremely small weight loss over the following four weeks, on average resulting in a weight loss of about 0.5 mg/week for the indium/silicon rubber seals and 0.25 mg/week for the standard foil seals. Therefore, the indium/silicon rubber seal, which is relatively expensive, seems to offer no advantage. On the other hand, the plastic caps are rather unstable. Weight increases over the first 24 h by *ca.* 1–2 mg, this trend continues, apparently approaching an equilibrium after 3–4 weeks. This means that it is impossible to assess accurately benzene losses from these vials. The closest estimate we could come to was again 0.5 mg/week. However, this involved several manipulations with possible sources of error. Thus, we recommend brass caps and standard foil seals for minimization of vapor losses and stability to moisture uptake.

TABLE 4. Cumulative average weight change (mg) for 7-ml vials (2 g benzene), kept in 2250CA at 14°C. Relative humidity *ca.* 65–75%.

Cap type	1 day	1 week	2 weeks	3 weeks	4 weeks
1. Plastic cap/foil liners	+1.44	+7.56	+14.36	+17.16	+17.32
2. Ni/Cr-plated brass cap/foil liner	0.00	0.00	0.00	-0.32	-1.00
3. Ni/Cr-plated brass cap/indium and silicon rubber liner	0.00	0.00	-0.88	-2.12	-2.00

Finally, we compared the background count rates and efficiencies from 20-ml screw-cap vials with

those from 15-ml Teflon vials (Table 5). The results indicate that, in an open window (0–156 keV), efficiencies are within error. However, the background for Teflon vials is significantly higher. In a counting window optimized for the glass vials, the efficiency for the Teflon vials was slightly greater. However, the background was a factor of 2 greater (3.56 cpm *cf.* 1.68). We conclude that, because all of our counting geometries are less than 7-ml volume, standard 7-ml screw-cap vials should be used, but with Ni/Cr plated brass caps and foil liners.

TABLE 5. Comparison of efficiencies and background count rates between 15-ml Teflon vials and 20-ml glass vials in Packard 2260XL with the low-level option enabled (4.5 g geometry and optimum fluor concentrations/ratios). LL option on.

Vial type	% Efficiency (0–156 keV)	Background (cpm)	% Efficiency (8.5–75 keV)	Background (cpm)
Glass	89.9	5.40	72.0	1.68
Teflon	89.6	8.55	73.1	3.56

Vial Preparation

Because 1) the recommended concentrations of fluors are low, and 2) two components are to be added to a single vial, this poses problems for accurate dispensing. This is further compounded by the fact that the bis-MSB is of limited solubility, which makes the task of achieving the optimum concentration impossible without adding it in a large volume of scintillation-grade benzene. Table 3 makes it obvious that increasing the volume will significantly increase the background count rate. To overcome this, we have devised a method whereby the fluors are weighed out in bulk at the appropriate ratio and dissolved in benzene. Sufficient solution is then weighed into a number of vials to give the required concentration for the particular sample geometry being employed. The benzene can then be removed by freeze drying. We have devised a primitive freeze drier consisting of a large vacuum desiccator to hold the vials, a cold finger surrounded by liquid nitrogen to remove the benzene vapor and a small vacuum pump to create the vacuum. The cocktail should be frozen in the vials prior to benzene removal; otherwise, the benzene boils. Once the benzene removal is underway, application of a limited amount of heat to the desiccator speeds up the process. This technique consistently gives total removal with no loss of fluors, which are almost totally confined to the bottom of the vials. A further advantage of this technique is that, prior to freeze-drying, the vials can be counted for an appropriate length of time to screen them for uniformity of response, *i.e.*, variations in t-SIE and background count rate.

CONCLUSIONS

As a result of our extensive research on the use of this type of LS spectrometer, we recommend that a combination of butyl-PBD and bis-MSB be employed as the scintillation cocktail. The respective concentrations required for optimum stability are 2.8 and 3.0 mg·g⁻¹ of sample benzene. Screw-cap vials should be used in preference to sealable glass ampules or Teflon vials, and if counting geometries do not exceed 7 ml, we would recommend the smaller vial size. We prefer to use nickel and chromium-plated brass caps, as they are non-hygroscopic and allow accurate evaporative weight loss measurements. Standard foil liners minimize evaporative losses.

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