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## SCINTILLATION COCKTAIL OPTIMIZATION FOR $^{14}\text{C}$ DATING USING THE PACKARD 2000CA/LL AND 2260XL

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**ABSTRACT.** In terms of both quenching and, in particular, counting efficiency, scintillation counters employing burst counting circuitry are sensitive to changes in scintillant concentration. Our research demonstrates that there are plateau regions where neither parameter is significantly influenced by moderate changes in a cocktail containing butyl - PBD and bis - MSB. One of these, consisting of butyl - PBD  $2.8\text{mg}\cdot\text{g}^{-1}$  and bis - MSB  $3\text{mg}\cdot\text{g}^{-1}$  of benzene is recommended for these counters, as it enables open window counting efficiencies of ca 90% while exhibiting optimal resistance to quenching. A method for accurate dispensing of such small weights is also described.

### INTRODUCTION

An almost inevitable consequence of the much improved performance of the modern generation of 'low level' liquid scintillation counters for  $^{14}\text{C}$  dating is a growing complexity in design and operation. The addition of multi-channel analyzer capability and the power of microcomputers have made time-consuming tasks, such as counting window optimization, possible in a time-scale of hours/days rather than weeks. However, to achieve truly optimum performance, the researcher needs a significant level of understanding of the current technology. In the LKB Quantulus, for example, which uses pulse amplitude comparison (PAC), an optimum balance of reduction in background and decrease in efficiency is essential. Also, pulse shape analysis (PSA) may be used to advantage with low potassium glass vials. In this case, a variation in scintillant composition, *ie*, the addition of bis - MSB, is required to optimize this response (Kaiholo 1989). The Packard 2000 series of liquid scintillation counters employs burst counting circuitry to differentiate background events from true  $\beta^-$  events by comparing their pulse shape characteristics (Valenta 1986). Most background prompt pulse events are accompanied by a number of randomly spaced after-pulses of much smaller energy, *ie*, amplitudes similar to single photo-electrons. In contrast, a pulse produced by sample decay consists of a prompt pulse followed by very few or no trailing pulses. Thus, we take advantage of this difference in afterpulse characteristics to reduce background count rates (Noakes, de Filippis & Valenta 1988).

The complexity of these counters lies not in the balance of user variable PAC and PSA settings but rather in the type and concentration of scintillants required, not only to maximize performance but also to ensure stability of response. For example, Polach *et al* (1988) demonstrated that when using butyl - PBD as the scintillant, efficiency was markedly reduced compared to counters with 'conventional' circuitry. In contrast, Cook, Harkness and Anderson (1989) were able to regain much of this loss in efficiency by the addition of the secondary scintillant bis - MSB. This enhancement in efficiency was probably due to a sharpening of pulse widths/loss in afterpulsing rather than to its traditional use as a wavelength shifter, since the effect was not observed to any marked extent with other secondary scintillants such as POPOP and dimethyl POPOP.

In addition to this influence of scintillant type, we also observed that measurable changes in efficiency accompanied changes in scintillant concentration. In contrast, with the burst counting circuit disabled, we observed a much more stable efficiency response. Cook *et al* (1989) also observed occasional anomalously high efficiencies when using butyl - PBD alone as scintillant. This effect could be eliminated by the addition of bis - MSB.

A further complicating factor is decreased efficiency with an apparent reduction in the degree of quenching as measured by the transformed spectral index of the external standard (t-SIE) (Cook, Harkness & Anderson 1989). From these observations, it is apparent that complete optimization of the scintillant is necessary to establish a balance of high and yet constant efficiency uninfluenced by moderate variations in the concentration of either the primary or secondary scintillant and where the degree of quenching is similarly unaffected. In this way, small variations in the weighing/dispensing of the scintillant will have a negligible influence on response.

During previous studies (Cook, Harkness & Anderson 1989; Cook *et al* 1989, 1990), we directed some effort towards optimizing the butyl - PBD/bis - MSB combination, but complete optimization was not attained. We rejected using bis - MSB alone because, despite enabling comparable efficiencies to the above combination, it was much less tolerant to the addition of a quenching agent (Cook *et al* 1990). We did not consider the combination of PPO/bis - MSB because of the poorer chemical stability of PPO (Polach, pers commun). Primarily, the object of this study was to assess a wide range of butyl - PBD/bis - MSB combinations, to determine one or several where variations in either component will have no influence on response, thus producing the definitive cocktail for  $^{14}\text{C}$  dating. Second, because a two-component scintillation cocktail is required and, in light of the results from this study indicating that the required weight of each component is relatively low, we felt that accurate weighing of such small amounts was extremely difficult and time-consuming. We also had a problem dissolving the cocktail in scintillation-grade benzene since it was difficult to dissolve sufficient bis - MSB in benzene to maintain the required concentration when added to the sample benzene. Under normal circumstances, secondary scintillants are used at much lower concentrations than primary (Birks 1975). In any event, the addition of a large volume of cocktail would only serve to increase the background count rate, which we hoped could be avoided. We discuss below a method of dispensing the butyl - PBD/bis - MSB cocktail in benzene followed by evaporation of the solvent.

## EXPERIMENTAL

We assessed seven concentrations of butyl - PBD (0.5, 1.0, 2.0, 3.0, 6.0, 13.1 and 19.6mg.g<sup>-1</sup> benzene), each with six associated concentrations of bis - MSB (0.5, 1.0, 2.0, 3.0, 4.0 and 5.0mg.g<sup>-1</sup> benzene), yielding 42 different combinations (4 replicate vials per combination) in both the Packard 2000CA/LL and 2260XL liquid scintillation counters, with and without the low-level mode (burst counting circuitry) enabled. Each vial underwent a total of 4 x 5 minute counts per counting condition. The counting geometry consisted of 2g of  $^{14}\text{C}$  benzene (4860 ± 30 dpm.g<sup>-1</sup>) to determine efficiency with appropriate backgrounds produced from scintillation-grade benzene. All work was carried out in Packard 7ml low potassium glass vials. To avoid the errors which could be incurred in weighing such small quantities of scintillants into each vial, each combination of scintillants +  $^{14}\text{C}$  benzene was made in bulk and approximate 2g aliquots accurately weighed into each vial. On the basis of these studies, we selected optimum combinations and assessed their resistance to quenching by acetone. On determining the combination that was most resistant to quenching, we assessed a much closer range of butyl - PBD concentrations around this central combination in an identical manner.

TABLE 1  
Assessment of the optimum butyl-PBD/bis-MSB scintillation cocktail for the Packard 2000CA/LL

butyl-PBD (mg.g <sup>-1</sup> benzene)	bis-MSB (mg.g <sup>-1</sup> benzene)	t-SIE (LLCM)*	t-SIE (NCM)**	% Eff (LLCM)	% Eff (NCM)	Difference in % eff
0.5	0.5	397	397	88.0	91.7	3.7
0.5	1.0	480	479	89.9	93.4	3.5
0.5	2.0	557	554	90.6	94.5	3.9
0.5	3.0	591	588	90.0	94.8	4.8
0.5	4.0	597	594	89.2	94.2	5.0
0.5	5.0	594	591	89.4	94.6	5.2
1.0	0.5	488	485	88.3	93.4	5.1
1.0	1.0	524	524	88.8	93.1	4.3
1.0	2.0	586	585	89.9	93.8	3.9
1.0	3.0	596	595	89.8	93.8	4.0
1.0	4.0	600	599	89.7	94.2	4.5
1.0	5.0	600	600	89.4	94.2	4.8
2.0	0.5	560	559	87.5	93.6	6.1
2.0	1.0	587	584	89.0	93.7	4.7
2.0	2.0	610	610	89.0	94.0	5.0
2.0	3.0	616	615	89.2	93.9	4.7
2.0	4.0	614	612	89.3	93.8	4.5
2.0	5.0	606	605	88.5	94.0	5.5
3.0	0.5	622	620	86.1	94.1	8.0
3.0	1.0	632	632	87.7	94.0	6.3
3.0	2.0	636	635	88.9	93.9	5.0
3.0	3.0	632	632	88.8	94.1	5.3
3.0	4.0	627	627	88.8	93.7	4.9
3.0	5.0	620	620	88.5	94.0	5.5
6.0	0.5	689	685	84.4	94.5	10.1
6.0	1.0	684	682	86.3	94.4	8.1
6.0	2.0	674	669	88.4	94.1	5.7
6.0	3.0	659	654	88.7	94.6	5.9
6.0	4.0	646	642	88.2	94.3	6.1
6.0	5.0	629	626	88.2	93.8	5.6
13.1	0.5	714	708	83.0	94.8	11.8
13.1	1.0	710	706	85.6	94.8	9.2
13.1	2.0	691	686	87.8	94.6	6.8
13.1	3.0	676	672	88.7	94.9	6.2
13.1	4.0	659	652	88.1	94.2	6.1
13.1	5.0	647	640	87.9	93.9	6.0
19.6	0.5	719	712	81.4	94.9	13.5
19.6	1.0	718	711	84.9	95.2	10.3
19.6	2.0	699	692	87.1	94.7	7.6
19.6	3.0	679	674	87.9	94.6	6.7
19.6	4.0	658	654	88.3	94.8	6.5
19.6	5.0	648	642	88.4	94.9	6.5

\*Low-level count mode (burst counting circuit enabled)

\*\*Normal count mode

TABLE 2  
Assessment of the optimum butyl-PBD/bis-MSB scintillation cocktail for the Packard 2260XL

butyl-PBD (mg.g <sup>-1</sup> benzene)	bis-MSB (mg.g <sup>-1</sup> benzene)	t-SIE (LLCM)	t-SIE (NCM)	% Eff (LLCM)	% Eff (NCM)	Difference in % eff
0.5	0.5	408	403	87.7	91.5	3.8
0.5	1.0	487	489	89.7	93.5	3.8
0.5	2.0	570	570	90.5	94.4	3.9
0.5	3.0	602	604	90.8	94.3	3.5
0.5	4.0	611	609	89.7	94.3	4.6
0.5	5.0	610	613	90.3	94.7	4.4
1.0	0.5	487	494	87.6	93.1	5.5
1.0	1.0	530	529	89.0	93.2	4.2
1.0	2.0	598	598	90.1	94.0	3.9
1.0	3.0	612	611	89.8	94.2	4.4
1.0	4.0	613	620	89.8	94.4	4.6
1.0	5.0	609	608	89.6	94.4	4.8
2.0	0.5	565	566	87.3	93.4	6.1
2.0	1.0	597	600	88.6	94.3	5.7
2.0	2.0	623	620	89.5	93.8	4.3
2.0	3.0	636	632	89.7	94.0	4.3
2.0	4.0	632	629	89.7	93.9	4.2
2.0	5.0	624	617	89.3	93.8	4.5
3.0	0.5	635	631	85.4	93.8	8.4
3.0	1.0	652	646	87.7	93.9	6.2
3.0	2.0	655	648	88.8	94.1	5.3
3.0	3.0	652	647	89.0	94.3	5.3
3.0	4.0	648	643	88.9	94.1	5.2
3.0	5.0	635	632	88.5	93.9	5.4
6.0	0.5	701	698	84.2	94.2	10.0
6.0	1.0	697	701	86.8	94.6	7.8
6.0	2.0	689	685	88.8	94.5	5.7
6.0	3.0	680	671	88.8	94.5	5.7
6.0	4.0	666	666	88.8	94.3	5.5
6.0	5.0	645	641	88.6	94.3	5.7
13.1	0.5	722	725	82.6	94.8	12.2
13.1	1.0	726	729	85.8	95.2	9.4
13.1	2.0	704	707	88.2	94.7	6.5
13.1	3.0	688	695	89.1	94.6	5.5
13.1	4.0	681	681	88.7	94.3	5.6
13.1	5.0	660	658	88.4	93.8	5.4
19.6	0.5	726	725	80.9	94.6	13.7
19.6	1.0	736	731	84.8	95.3	10.5
19.6	2.0	709	711	87.9	94.8	6.9
19.6	3.0	691	693	88.5	94.8	6.3
19.6	4.0	671	672	88.9	95.0	6.1
19.6	5.0	662	661	88.8	95.1	6.3

Finally, to assess the effects of varying both fluors simultaneously, we dissolved butyl - PBD/bis - MSB, at the optimum ratio, in benzene and added varying weights to a range of vials. We devised this such that when the solvent was removed by the freeze-drying technique described here, the middle concentration of fluors in the range would correspond to the correct concentration for optimum performance when 2g  $^{14}\text{C}$  benzene was added. We then assessed quenching and counting efficiency.

## RESULTS AND DISCUSSION

The results in Tables 1 and 2 indicate the following:

With the low-level count mode on:

1. For fixed concentrations of butyl - PBD, efficiency tends to increase to a plateau value followed in some instances by a marginal decrease as the concentration of bis - MSB increases.
2. Conversely, in general terms, for fixed levels of bis - MSB, efficiency decreases as the level of butyl - PBD increases. This trend is less dramatic at the higher bis - MSB concentrations (3-5  $\text{mg.g}^{-1}$  of benzene).
3. At low butyl - PBD concentrations (0.5 - 2 $\text{mg.g}^{-1}$  of benzene), t-SIE increases to a plateau value as the concentration of bis - MSB increases. At an intermediate concentration (3 $\text{mg.g}^{-1}$ ), there is a minimal change in t-SIE throughout the entire bis - MSB concentration range. At high butyl - PBD concentrations (6 - 19.6 $\text{mg.g}^{-1}$ ), t-SIE decreases continuously as the concentration of bis - MSB increases.

On the basis of the results, we selected three combinations which we felt represented the most stable counting conditions as reflected by constancy of both t-SIE and counting efficiency. These were:

1. 1mg of butyl - PBD and 3mg of bis - MSB per gram of benzene
2. 2mg of butyl - PBD and 3mg of bis - MSB per gram of benzene
3. 3mg of butyl - PBD and 3mg of bis - MSB per gram of benzene.

Experiments on quenching were carried out solely on the 2000CA/LL. Initial work on resistance to quenching indicated little difference between these; however, more detailed studies and plots of t-SIE vs amount of quenching agent prove that the third of these 'optima' is the most resistant to quenching (Fig 1). Although the open window counting efficiency for this combination is marginally lower than the others, when optimum windows are derived for unquenched samples, all combinations yield  $E^2/B$  values of ca 4000. Further work was conducted solely on the combination of 3mg butyl - PBD and 3mg bis - MSB per gram of benzene. Table 3 presents the results of a closer examination of varying the butyl - PBD concentration. These indicate that efficiency is perhaps more sensitive to variations in butyl - PBD than bis - MSB (see Table 1). However, there is an area of constancy of efficiency and quenching between 2.6 and 3.0 $\text{mg.g}^{-1}$ . The cocktail was modified from 3.0 and 3.0 $\text{mg.g}^{-1}$  of butyl - PBD and bis - MSB to 2.8 and 3.0 $\text{mg.g}^{-1}$ , respectively.

To overcome the difficulties involved in weighing such small quantities of fluors, we developed a technique of preparing the scintillants in bulk and dissolving them in benzene: 3g of bis - MSB and 2.8g of butyl - PBD are accurately weighed and dissolved in benzene, the total weight being made up to 1 kg. Sufficient cocktail can then be accurately dispensed/weighed in order to yield the optimum concentrations of scintillants. The benzene is then removed in a primitive freeze drier consisting of a large vacuum desiccator to hold the vials, a cold finger surrounded by liquid nitrogen to freeze out the benzene vapor and a small rotary pump to create a vacuum. The cocktail must be frozen in the vial prior to commencement of benzene removal.

This technique consistently gives total benzene removal with no loss of fluors, these being confined almost totally to the bottom of the vials. It also has an additional advantage that the vials can be screened for variations in t-SIE and, if required, in background prior to freeze drying. This enables the selection of vials of uniform specification, which is currently being investigated. When varying weights of this cocktail in benzene were added to a series of vials and the benzene removed leaving only the fluors, the results (Table 4) indicate that quite substantial changes in fluor concentrations (constant butyl - PBD/bis - MSB ratio) could be made without significantly influencing efficiency or quenching. Butyl - PBD was varied from 2.51 to 3.09mg.g<sup>-1</sup> of benzene with corresponding variations in bis - MSB (2.69 to 3.31mg.g<sup>-1</sup> benzene).

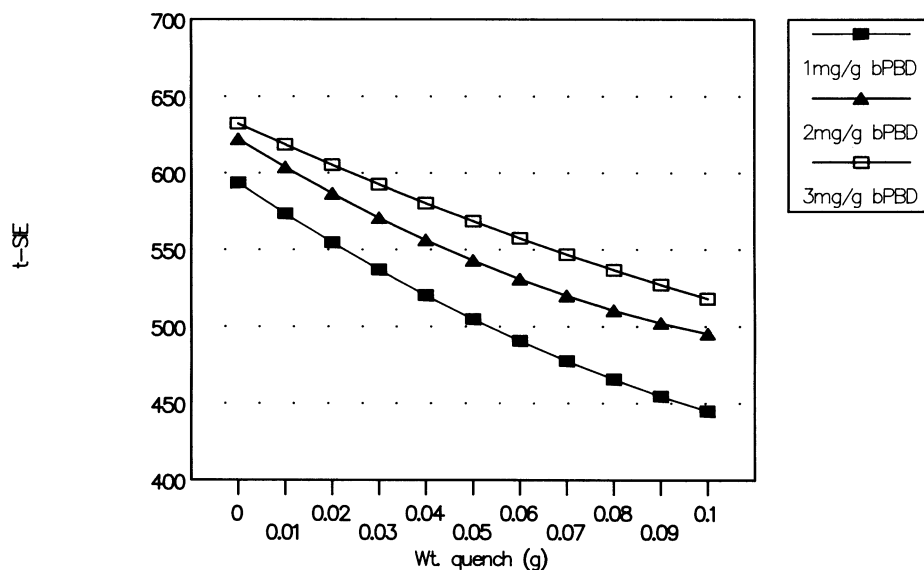


Fig 1. Plot of t-SIE vs weight of quenching agent added (5% acetone in benzene), bis - MSB fixed at 3 mg.g<sup>-1</sup> benzene, butyl - PBD = 1, 2 or 3mg.g<sup>-1</sup>

TABLE 3  
Influence of varying the butyl - PBD concentration around the 3mg.g<sup>-1</sup> benzene on counting efficiency and t-SIE; bis - MSB constant at 3mg.g<sup>-1</sup> benzene

butyl-PBD (mg.g <sup>-1</sup> benzene)	bis-MSB (mg.g <sup>-1</sup> benzene)	t-SIE LLCM	t-SIE NCM	% Eff LLCM	% Eff NCM	Difference in % eff
<i>A. 2000CA/LL</i>						
2.6	3.0	635	635	88.9	94.3	5.4
2.8	3.0	635	634	88.8	94.3	5.5
3.0	3.0	639	637	88.8	94.3	5.5
3.2	3.0	641	641	88.6	94.4	5.8
3.4	3.0	646	645	88.7	94.3	5.6
<i>B. 2260XL</i>						
2.6	3.0	646	657	89.3	94.2	4.9
2.8	3.0	645	655	89.3	94.2	4.9
3.0	3.0	656	660	89.3	94.3	5.0
3.2	3.0	658	664	89.1	94.2	5.1
3.4	3.0	665	672	88.9	94.2	5.3

TABLE 4

Influence on efficiency and quenching of varying the concentration of butyl - PBD and bis - MSB but while maintaining the same ratio as for the optimum (butyl - PBD/bis - MSB 2.8/3.0mg.g<sup>-1</sup> benzene) All measurements made with burst circuit enabled on 2000CA/LL

butyl-PBD (mg.g <sup>-1</sup> benzene)	bis-MSB (mg.g <sup>-1</sup> benzene)	Optimum window % eff 15-81keV	Open window % eff 0-156keV	Mean t-SIE
2.51	2.69	62.5	88.9	623
2.66	2.84	62.4	88.8	623
2.73	2.92	62.4	88.8	625
2.80*	3.00*	62.5	88.8	626
2.87	3.08	62.5	88.9	625
2.94	3.16	62.4	88.8	626
3.09	3.31	62.4	88.7	629

\*Optimum concentrations of fluors per gram benzene

#### CONCLUSIONS

The results of this study indicate that, although counting efficiency and the degree of quenching in general vary with changes in scintillant concentration, there are plateau regions where these parameters are unaffected by moderate variations in scintillant. On the basis of 1) the spectral shape from samples that are, in relative terms, unquenched, and 2) the resistance to quenching, one of these (butyl - PBD, 2.8mg.g<sup>-1</sup> benzene and bis - MSB, 3.0mg.g<sup>-1</sup> benzene) was selected for detailed study. Such a combination enables open-window counting efficiencies of ca 90% in both the Packard 2000CA/LL and 2260XL whereas variations in either the bis - MSB concentration (2.0 - 4.0mg.g<sup>-1</sup> benzene) or the butyl - PBD (2.6 - 3.0mg.g<sup>-1</sup> benzene) have no effect on efficiency and a negligible influence on quenching. Similarly, both fluor concentrations can be varied simultaneously while maintaining the ratio of the optimum concentrations (2.8/3.0), *ie*, from 2.51 and 2.69mg.g<sup>-1</sup> of butyl - PBD and bis - MSB, respectively, to 3.09 and 3.31mg.g<sup>-1</sup> of butyl - PBD and bis - MSB, without significant effects on these parameters. Thus, we recommend that a scintillation cocktail consisting of 2.8mg of butyl - PBD and 3.0mg of bis - MSB per gram of sample benzene should be used with Packard 2000 series counters. Beckman or LKB counters may be much different. Obviously, the ultimate assessment of these instruments for radiocarbon dating must be in their ability to produce accurate age determinations. The above cocktail is now routinely used in this laboratory, and results of an on-going intercomparison with 'old technology' scintillation counters are showing excellent agreement.

#### REFERENCES

- Birks, JB 1975 *In solutes and solvents for liquid scintillation counting*. Koch-Light Publication.
- Cook, GT, Anderson, R, Harkness, DD and Naysmith, P (ms) 1989 The optimisation of scintillation counters employing burst counting circuitry. Paper presented at Internatl conf on new trends in liquid scintillation counting and organic scintillators, 2-5 Oct, 1989, Gatlinburg, Tennessee.
- Cook, GT, Harkness, DD and Anderson, R 1989 Performance of the Packard 2000CA/LL and 2250CA/XL liquid scintillation counters for <sup>14</sup>C dating. *In* Long, A and Kra, RS, eds, Internatl <sup>14</sup>C conf, 13th, Proc. *Radiocarbon* 31(3): 352-358.
- Cook, GT, Naysmith, P, Anderson, R and Harkness, DD 1990 Performance optimisation of the Packard 2000CA/LL liquid scintillation counter for <sup>14</sup>C dating. *Nuclear Geophysics* 4(2): 241-245.
- Kaiholala, L (ms) 1989 Liquid scintillation counting performance using glass vials in the Wallac 1220 Quantulus™. Paper presented at Internatl conf on new trends in liquid scintillation counting and organic scintillators, 2-5 Oct, 1989, Gatlinburg, Tennessee.
- Noakes, JE, De Filippis, SJ and Valenta, RJ 1988 Low background liquid scintillation counting using an active sample holder and pulse discrimination electronics. *In Internatl seminar for liquid scintillation analysis*. Tokyo, Packard Japan KK: 5-42.
- Polach, H, Calf, G, Harkness, DD, Hogg, A, Kaiholala, L and Robertson, S 1988 Performance of new technology liquid scintillation counters for <sup>14</sup>C dating. *Nuclear Geophysics* 2(2): 75-79.
- Valenta, RJ 1986, Patent. *Reduced background scintillation counting*. US Patent No. 4, 651, 006.