

OPTIMIZATION OF LIQUID SCINTILLATION COUNTING CONDITIONS WITH TWO KINDS OF VIALS AND DETECTOR SHIELDS FOR LOW-ACTIVITY RADIOCARBON MEASUREMENTS

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ABSTRACT. Low-level radiocarbon measurements were made using two liquid scintillation (LS) counters, both with passive lead shields of approximately the same dimensions. The first one had a conventional background reduction with low-activity lead and "high-low" coincidence bias selection, and the second one had a spectrum analysis background reduction based on the different three-dimensional pulse-height signal of background and beta pulses.

The performance of commercial teflon-copper and glass vials were compared with both LS counters. Optimum counting conditions for the two detectors studied were also established. From results obtained, quality parameters and characteristics of quench curves were studied. Performances of each counter in the working conditions established were also compared.

INTRODUCTION

Liquid scintillation (LS) counting of low-level ^{14}C activity ensures the lowest detection limits as well as high-precision measurement. In our laboratory, we have tested two counters which have different background reduction design concepts. An LKB 1217 Rackbeta Kangaroo with a conventional passive low-activity lead shield surrounding the counting chamber, "high-low" coincidence bias selection, and the optimum use of teflon-copper (TC) vials for background reduction (Polach *et al*, 1983b; Calf & Polach, 1974; Kuc & Rozanski, 1978; Polach *et al*, 1983a; Rauret, Mestres & Garcia, 1988). The other counter tested is a Packard TriCarb 2000 CA/LL with spectrum analysis which recognizes the different three-dimensional pulse-height distribution of background pulses and ^{14}C beta pulses, thus reducing the background counts at the expense of efficiency (Operation manual TriCarb 2000/LL). This paper compares the performance of the two LS counters for low-level ^{14}C measurements under optimum conditions.

Quality parameters and characteristics of quench curves were also studied. One of the quality parameters calculated was the oldest attainable age that corresponds to the lowest measurable activity determined according to a defined criterion. The sample count rate was considered greater than background when the difference between both was larger than twice the standard deviation of the background (Stuiver & Polach, 1977). The determination of ^{14}C activity by LS counting of pure benzene has the advantage of working under constant quench conditions. In practice, however, we realized that even under these conditions the spectral end-point of ^{14}C is not constant but presents some small variations (Rauret, Mestres & Garcia, 1988), so that each counting vial must be individually calibrated based on external standard ratio determinations of counting efficiency.

EXPERIMENTAL

We used two counters, an LKB-Wallac Rackbeta 1217 Kangaroo and a Packard TriCarb 2000 CA/LL. The characteristics of the first counter are: high voltage stabilization circuit, "high-low" coincidence bias selection, linear amplification and logarithmic 256 channel spectra (1–2800 keV range) display, four independent channels with variable windows for data accumulation, automatic external standardization with a Ra-226 source, and refrigeration (10°C).

The characteristics of the second counter are: linear amplification, MCA of 4096 channels (1–2000 keV range) a variable range background discriminator based on the three-dimensional spectrum analyses SPECTRALYZER™, three independent regions with variable limits for data accumulation, external standard source of Ba-133, spectrum storage possibility and refrigeration.

Two kinds of vials were used: teflon-copper (TC) 7ml (LKB-Wallac), modified (Rauret, Mestres & Garcia, 1988) and the standard low-potassium-content borosilicate 20ml glass vials (Packard).

We also used analytical reagents grade (AR), benzene and toluene (Carlo Erba, RPE) and ¹⁴C-labeled toluene (Packard). We prepared active toluene in benzene solutions of 2428.2 dpm/ml (A) and 3697.7 dpm/gr (B) from the previous solution. As quencher, solutions of CCl₄ in benzene: 0.5, 1.0, 2.0 and 4.0% (v/v) were used. The four scintillators used were: commercial cocktail Instagel, butyl-PBD (2.5% w/v and 5% w/v in benzene), PPO (0.4% w/v) in toluene and a mixture PPO (0.4% w/v) dimethyl-POPOP (0.01% w/v) in toluene (all Packard).

The standard procedure employed 3ml of total counting solution obtained with 2.4ml sample benzene and 0.6ml of scintillator solution. In all cases, including commercial cocktail Instagel, we maintained the same 4:1 ratio between sample benzene and scintillator solutions. To carry out performance comparison of glass and teflon vials, we used solutions with PPO-dimethyl-POPOP as scintillator and 3ml of total counting volume for the LKB counter and butylPBD and 4ml for the Packard counter. The blank was solutions with the same composition and conditions as the samples.

In the quenching efficiency correlation study, the standards were prepared as follows: for the LKB counter, 3.0ml of A solution, 0.4ml of butyl-PBD (5%), variable volumes of CCl₄ benzene solution and inactive benzene up to a total volume of 4.0ml were added to each TC vial. Twelve activity standard solutions with increasing CCl₄ concentrations from 0 to 0.40% (v/v) were obtained. For the Packard counter, 1.0ml of B solution was weighted in the glass vial previously tared; then the same procedures as before were followed.

With the LKB counter, the spectra were plotted manually 10 channels at a time. Overall counting time for the standard ¹⁴C was 6 hr and for the background 12–20 hr. With the Packard, the spectra were obtained with the low-level correction option and with a counting time of 2–4 hr for the standard ¹⁴C and 6–12 hr for the background.

For the study of the correlation between quenching and efficiency, the two sets of activity standards were counted for 10 periods of 10 min each, in

the corresponding counters. The quenching parameter was provided by the external standard. For the LKB counter, an external standard channel ratio was used; the external standard window partition used is that which furnishes the maximum variation of the parameter between the less-quenched and the more-quenched solutions. The t-SIE parameter was used in the Packard counter.

RESULTS AND DISCUSSION

The following results were obtained from the integration of experimentally obtained spectra. In each case, the integration thresholds chosen as the optimum window were those which gave the best figure of merit.

Performance of Glass and Teflon Vials

The characteristics of TC and low-potassium borosilicate glass vials were compared in both counters. From the results obtained for background and efficiency, the figure of merit for each case was calculated. Table 1

TABLE 1
Background, efficiency and figure of merit of glass and teflon vials

	B(cpm)	LKB E(%)	FM	B(cpm)	PACKARD E(%)	FM
<i>Type of vial</i>						
Glass	2.36	33.8	483	1.92	69.8	2538
Teflon-copper	1.41	59.9	2548	3.38	61.8	1130
<i>Scintillator</i>						
Instagel	1.54	66.7	2890	0.64	52.1	4216
Butyl-PBD	1.78	72.5	2950	0.73	52.4	3760
PPO	1.43	59.3	2460	0.89	54.9	3403
PPO+dimethyl- POPOP	1.33	54.6	2240	0.88	55.3	1726
<i>Volume</i>						
3ml	1.78	72.5	2950	0.73	52.4	3760
5ml	2.47	73.7	2202	0.87	52.6	3168
7ml	3.39	73.8	1609	1.21	51.3	2165

shows the results. For the LKB counter, the figure of merit is much higher for TC vials than for glass because of the higher background count rate at low energies in the glass vials due to Cerenkov radiation. Figure 1 shows the spectra of the background for the glass and TC vials. For the Packard counter, on the contrary, the glass vials yield a much higher figure of merit than the one obtained with TC.

Scintillator Effect

Once the best class of vial for each counter was chosen, the effect of different scintillators on performance was tested. Table 1 shows results relating to efficiency (E) and background (B) and figure of merit for each counter and four scintillators.

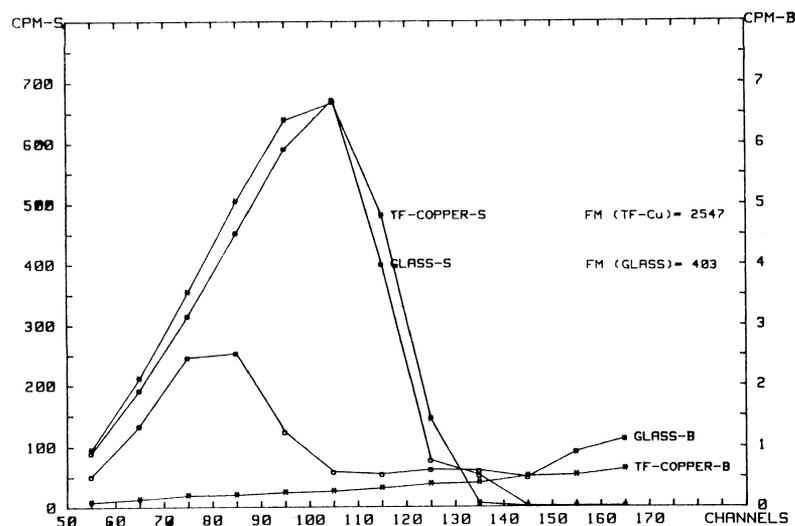


Fig 1. Radiocarbon (S) and background (B) spectra for glass and teflon vials

Based on the figure of merit, it can be concluded that for the LKB, as described earlier (Rauret, Mestres & Garcia, 1988), butyl-PBD is the best scintillator, followed by Instagel, PPO and PPO + dimethyl-POPOP. These results agree with those found by Polach *et al* (1983). On the other hand, for Packard, the best scintillator is Instagel and the descending order of figure of merit is: Instagel > butyl-PBD > PPO > PPO + dimethyl-POPOP. Although the ^{14}C beta particle to photon energy transfer is better using butyl-PBD as scintillator, the shape of the ^{14}C spectrum in this counter shifted for Instagel to lower energy values, allowing us to work with a window for which the background is smaller for Instagel than for butyl-PBD with a similar efficiency. Under these conditions, the figure of merit for Instagel is better.

Volume Effect

In order to compare the volume effect, we chose butyl-PBD as scintillator for both counters.

It has been established previously (Rauret, Mestres & Garcia, 1988) that, for the LKB counter, background increases linearly with volume whereas efficiency remains approximately constant with volume, so that the figure of merit increases when volume decreases. Similar behavior has been observed with the Packard counter. The values of efficiency (E), background (B) and figure of merit for both counters are also given in Table 1.

Considering that loss of sensitivity occurs with small volumes of solution, we propose to standardize on a total volume of 4.0ml (3.2ml sample + 0.8ml scintillator solution).

Quench Correlation Curves

If TC vials are used in the LKB counter, the quenching parameter ranges from 474 to 534. For glass vials with the Packard counter, this range is narrower, ranging from 769 to 813. This has compelled us to study the correlation between efficiency and quenching for each counter in order to

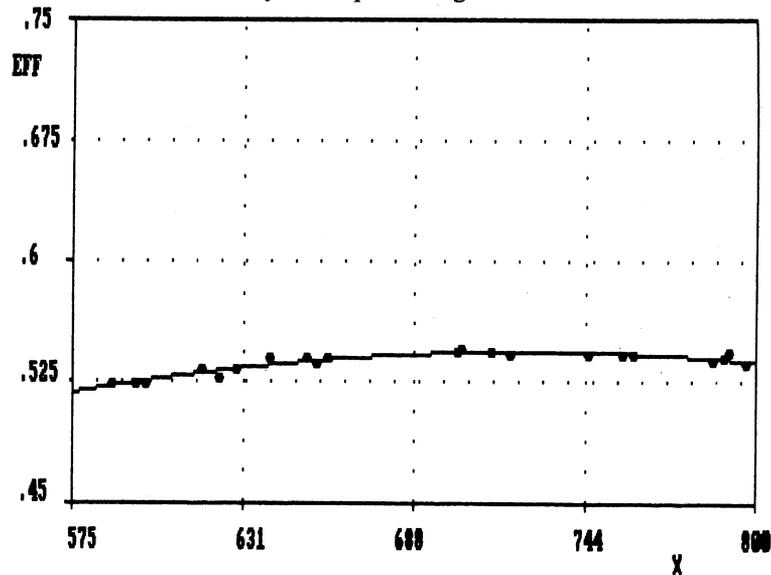


Fig 2. Quenching correlation curve for the Packard counter

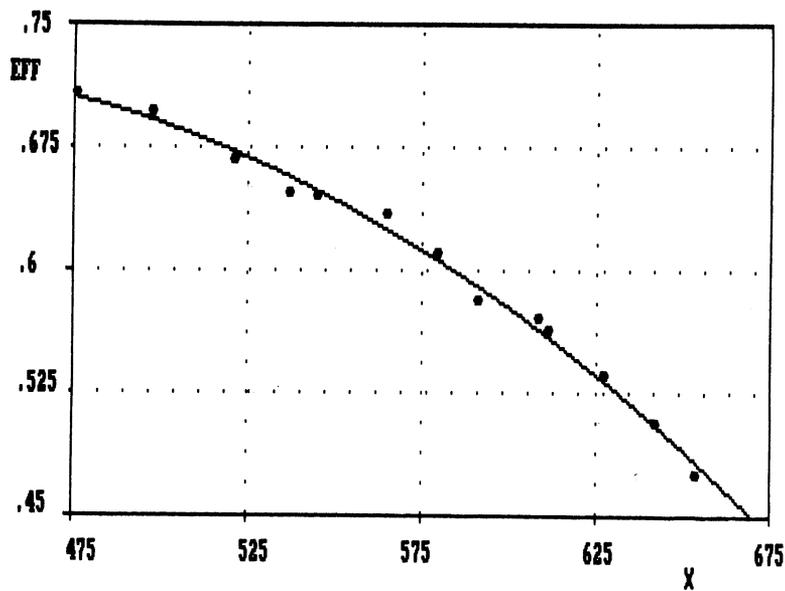


Fig 3. Quenching correlation curve for the LKB counter

correct the small variations of efficiency in the working window. Figures 2 and 3 show the quenching correlation curves obtained for each counter. Efficiency drops quickly when the quenching increases for the LKB counter and it remains nearly constant in the quenching range studied for the Packard counter. In both cases, the working window used was that which gives the best figure of merit corrected for the possible interference of tritium. With the LKB counter, the possibility of using a window, the efficiency of which was not sensitive to small variations of quench, was rejected because of the drop of figure of merit obtained in these conditions, which was considered less advantageous for these kinds of measurements.

Optimum Working Conditions for Both Counters

From the results obtained in the previous sections, we have established the optimum working conditions for LKB and Packard counters to measure low-level activity ^{14}C samples. Table 2 gives these conditions.

TABLE 2
Optimum working conditions for the counters studied

Counter	Vial	Scintillator	Volume	B(cpm)	E(%)	FM
LKB	Teflon-copper	Butyl-PBD	3ml	1.78	72.5	2950
PACKARD	Glass	Instagel	3ml	0.64	52.1	4216

Oldest Attainable Age

Let us assume that the smallest measurable activity is

$$A_m = \frac{2S(B)}{a \times E}$$

where a is the weight of benzene measured and E is the efficiency of counting. Then, the greatest attainable age is given by:

$$t_m = \frac{5568}{\ln 2} \ln \frac{A_{ON}}{2S(B)} aE$$

According to this equation, the oldest attainable age may be calculated in two ways: with the theoretical standard deviation corresponding to background counting, and with the experimental standard deviation of the background. The oldest attainable ages for each counter in optimum working conditions with theoretical and experimental background standard deviations are nearly the same value for the LKB counter, 44,300 yr, and for the Packard counter, 45,000 yr, for theoretical (Poisson) and 41,100 for experimental. The experimental standard deviation gives, with the Packard counter, smaller values because the experimental standard deviation of the background is higher than the theoretical.

CONCLUSIONS

For measurements of low ^{14}C levels, both counters perform well. Nevertheless, it is necessary to optimize conditions to attain lower detection limits. The main differences observed under optimal conditions are related to the vial and the scintillator. If we compare the performances of each counter with optimal conditions, we can conclude that the LKB has a more stable background but its efficiency is more dependent on the degree of quenching. Contrasting behavior is observed for the Packard counter.

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