TEFLON VIALS FOR LIQUID SCINTILLATION COUNTING OF CARBON-14 SAMPLES

by

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Abstract

The design of Teflon counting vials for use in liquid scintillation counting of ^{14}C samples is discussed. When compared with the more commonly used glass vials, Teflon vials give a slight increase in the ^{14}C detection efficiency (E) and a significant reduction in the background count rate (B) resulting in an increase of about 30% in the Figure of Merit (E^2/B).

This increase in performance, when applied to radiocarbon dating, is equivalent to extending the maximum determinable age of a sample by about 2,000 years.

Introduction

Teflon vials of 20 ml capacity give a much higher Figure of Merit ($Efficiency^2/Background$; E^2/B) for tritium counting than commercially available counting vials (1,2). As the use of vial material with a high Figure of Merit is particularly important in low level counting, Teflon vials have been designed, tested and applied to radiocarbon dating, using commercially available liquid scintillation spectrometers.

Carbon-14 Counting

The results of an investigation of ^{14}C counting efficiency of various commercially available 20 ml counting vials and of a 20 ml Teflon vial are shown in Table I. In this study, ^{14}C labelled hexadecane was used and count rates were measured in a Packard 3375 Liquid Scintillation Spectrometer operating at +8°C. Discriminator settings corresponding to a ^{14}C efficiency of about 87% were selected, and remained set for the duration of the experiments. Optimal E^2/B counting ratios were obtained by adjustment of the amplifier gain.

TABLE I

COMPARISON OF ^{14}C COUNTING EFFICIENCY AND E^2/B OF COMMERCIALLY AVAILABLE AND TEFLON COUNTING VIALS

Vial(*)	Efficiency (E) %	Background (B) counts min^{-1}	Figure of Merit (E^2/B)
Low ^{40}K glass	86.3 ± .2	28.7 ± .1	260
Quartz	87.1 ± .2	28.1 ± .1	270
Polyethylene	87.5 ± .2	27.1 ± .1	280
Nylon	87.7 ± .2	25.5 ± .1	300
Teflon	88.0 ± .2	22.5 ± .1	340

*) Each vial contained 1.4×10^{-2} µCi of n-Hexadecane-1-^{14}C and .08 g PPO in 18 ml of O-Xylene (L.R. grade). O-Xylene with the same concentration of PPO was used for the background determinations.

The differences in E^2/B between low ^{40}K Glass, Quartz and Polythene vials are not very significant. Polythene vials (even the high density grade used for this experiment) absorb aromatic hydrocarbons and distort on prolonged use and hence are not suitable for low-level counting experiments. Only the Nylon and Teflon vials show a significant increase in the Figure of Merit which is due to increased ^{14}C counting efficiency and a significant decrease in background. Further tests on Teflon, which had the largest Figure of Merit, showed that it is not permeable to hydrocarbons, and that vials can be re-used if thoroughly washed in benzene and dried under vacuum at +50°C for at least 2 hours. Under these conditions, no memory effect (solvent retention and contamination of subsequent sample) has been observed when alternating ^{14}C labelled and background samples, a factor of particular importance to high precision low-level counting such as radiocarbon dating.

Radiocarbon dating

The organic sample, whose radiocarbon age is to be determined by the liquid scintillation counting method, is generally first converted to carbon dioxide which is further synthesised to acetylene (3,4). The acetylene is then catalytically trimerized to benzene (5). The ^{14}C activity of the sample benzene is then related to the ^{14}C activity of a modern reference standard. The benzene for the sample and standard is prepared following the same synthesis procedures, and both activities are measured on the same equipment, using the same settings and the same counting vials for which the background has been predetermined. For reasons of sample size available for dating, ease of handling of synthesis procedures and taking into consideration the required precision of the ^{14}C age determinations, most workers using the liquid scintillation counting technique have chosen to work with 3 g to 5 g equivalents of elemental carbon, that is 3.7 ml to 6.2 ml of benzene. For this purpose a modified 5 ml volume glass vial is the most efficient (6,7,8).

Design of Teflon vials

Two Teflon vials (Fig 1, A and B) both of 5 ml capacity have been designed and their performances evaluated.

Both are equally suitable for radiocarbon age determinations. Teflon (DuPont PTPF rod SG 2.1-2.3) was used in their manufacture, particular care being taken to obtain a uniform side wall thickness of 0.95 ± 0.05 mm. The width of both designs (27.5 mm) conforms to standard 20 ml glass vial; the height of design A has been adjusted to place the sample in the centre of photomultiplier tube axis. However as this was not found to contribute to a greater detection efficiency, the overall height of design B is that of a 20 ml standard glass vial and the sample volume is placed at the bottom of the vial to allow the maximum thickness of aluminium shielding cap. Both vials have the same ^{14}C detection efficiency and background in fully (top) shielded liquid scintillation counters.

In Design A (Fig 1), a 20 ml glass counting vial plastic screw cap lined with cork and tin foil was used to seal the vial. The Teflon vial is mounted on an aluminium base by a small lug. It is particularly suitable for bottom loading and top shielded refrigerated liquid scintillation counting systems. At +8°C the solvent loss through the screw cap seal is in the order of 2 mg of benzene per week. For this loss, if so desired, an appropriate count rate correction can be made.

Design B (Fig 1) was developed specifically for ambient temperature top loading counting systems. The Teflon vial, on a thickened base, is sealed by a Viton 'O' ring which is held in an aluminium screw cap, which also acts as additional shielding. The solvent loss at +18°C is about 0.5 mg of benzene per week.

Performance of Teflon vials

A study comparing the efficiency of 5 ml low ^{40}K glass and the Teflon vials described above indicates that the 5 ml Teflon vials have distinct advantages.

A significant reduction in background (10 to 40%) resulted from the use of Teflon vials for all instruments tested (Table II), due to elimination of ^{40}K induced count rate, reduction of Cerenkov radiation and due to the light scattering properties of Teflon which probably bring about a reduction of the cross talk between the opposed photomultiplier tubes.

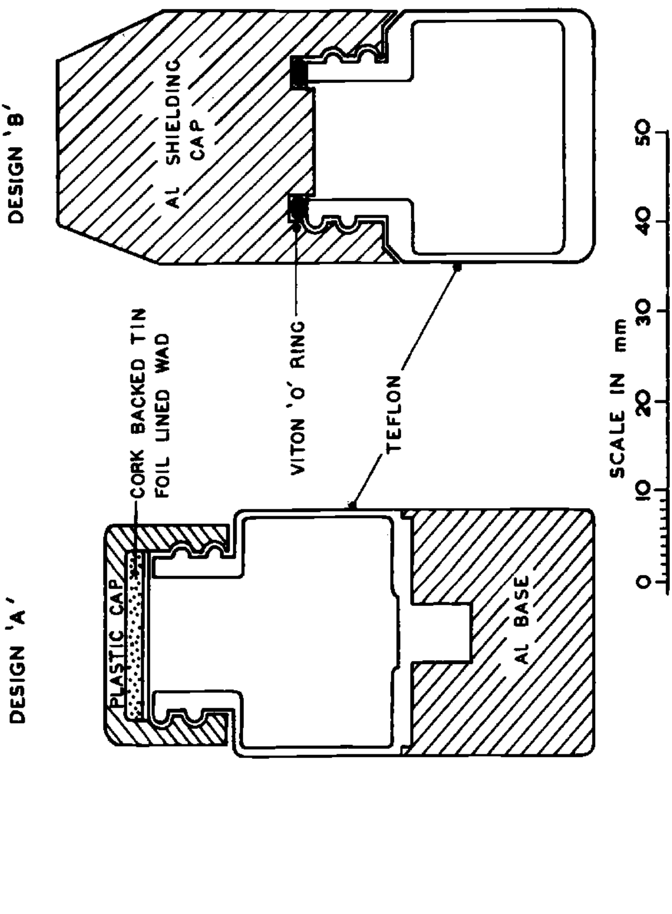

FIGURE I TEFLON VIALS

TABLE II

COMPARISON OF ^{14}C COUNTING EFFICIENCY, F, E^2/B OF SPECIAL DESIGN 5 ml LOW ^{40}K GLASS AND TEFLON VIALS

INSTRUMENT	Sample (a) grams Benzene	5 ml GLASS VIAL					5 ml TEFLON VIAL						COMMENT ON L.S. SYSTEM
		No (b) counts min^{-1}	B (c) counts min^{-1}	F (d)	% E(e)	E^2/B	No counts min^{-1}	B counts min^{-1}	F	% E	E^2/B	VIAL DESIGN	
PACKARD 3375	4.395	49.38	14.8	12.8	90.0	540	47.88	9.5	15.5	87.3	800	'A'	counter set-up for high ^{14}C efficiency and operating at 8^oC.
PACKARD 3375	4.395	30.98	4.4	14.8	56.5	730	32.44	3.4	17.6	59.1	1030	'A'	counter set-up for max. E^2/B at minimum photomultiplier EHT setting.
AAEC COUNTER (f)	4.395	29.72	3.3	16.4	54.2	890	32.77	2.0	23.2	59.7	1780	'A'	counter optimised for max. E^2/B and operating at 8^oC.
PICKER NUCLEAR LIQUEMAT 220	3.516	30.41	4.8	13.9	69.3	1000	31.07	3.9	15.7	70.8	1290	'A'	Ambient temperature operation (11)
BECKMAN LS-200	3.516	31.95	7.6	11.6	72.8	700	-	-	-	-	-	'B'	Ambient temperature operation
BECKMAN LS-200	3.516	30.77	5.5	13.1	70.1	890	32.66	5.1	14.5	74.4	1090	'B'	6 mm mask on photomultipliers
BECKMAN LS-200	4.395	Theoretical values only to demonstrate merit of full vial counting					40.83	5.1	18.1	74.4	1090	'B'	Not Tested

(a) 4.395g benzene = 5 ml benzene with scintillant PPO added in dry form.
3.516g benzene = 4 ml benzene with scintillant PPO and POPOP dissolved in 1 ml. toluene which is added to sample to make volume to 5 ml.

(b) No = 95% of observed count rate of NBS Oxalic acid contemporary standard in counts min^{-1}. (corrected to the year 1950 and $\delta^{13}C = -19^o/oo$ PBD).

(c) B = Background count rate in counts min^{-1} for 5 ml A.R. benzene plus scintillant or for 4 ml benzene plus 1 ml toluene containing scintillants.

(d) F = Radiocarbon dating system figure of merit $F = No/(B)^{\frac{1}{2}}$

(e) % E = Percent efficiency calculated using the data that 95% of the N.B.S. oxalic acid is equivalent to 13.53 ± 0.07 disintegration min^{-1} g^{-1} carbon (corrected to the year 1950 and $\delta^{13}C = -19^o/oo$ PBD). (9)

(f) Australian Atomic Energy Commission counter designed for ^{14}C low level counting (10).

Between 0.5 and 2 background counts min^{-1} (depending on the ^{14}C window width setting) can be directly attributed to external and cosmic radiation. All top loading instruments such as the Beckman, Packard and Picker will therefore benefit from the additional shielding being placed above the counting vial. Thus the aluminium cap of Teflon vial design 'B' (Fig 1) reduces the background count rate by about 0.5 counts min^{-1} for a 5 ml vial in top loading liquid scintillation spectrometers.

A further improvement is suggested for Radiocarbon Dating Laboratories. As the use of a 5 ml vial is established, it is more efficient to use all the available vial volume for sample counting and weigh in the required amount of dry scintillant. This replaces the previous commonly used method suggested by Tamers (7) where the scintillant is dissolved in 1 ml of toluene, which is added to 4 ml of sample benzene.

Procedures used to increase Figure of Merit of Commercial Counters

Extensive tests were carried out using two types of liquid scintillation counting systems:

(a) Packard 3375 which has a linear amplifier

and (b) Beckman LS-200 which has a logarithmic amplifier.

Both counters were operated with the lower discriminator set to cut off most of the tritium spectrum (at about 18 keV) which resulted in a loss of not more than 20% of the ^{14}C count and with the upper discriminator set at about 145 keV, towards the end of the ^{14}C spectrum, which gives a further loss of ^{14}C count of not more than 5%. Optimal count rates and balance point operation (8,12) were then achieved by adjusting the amplifier gain settings.

In the Packard 3375, it was found that the E^2/B can be increased by decreasing the photomultiplier high voltage to its minimum setting, resetting the discriminators, and compensating for the loss in gain in the photomultiplier tubes by increasing the amplification. This operation significantly reduces the background, reduces the ^{14}C counting efficiency by about 40% but increases the E^2/B by about 30%. (See Table II).

In the Beckman LS-200, it was found that cross-talk between the photomultiplier tubes is the main contributing factor to the background which remained constant (for equivalent discriminator settings) at various EHT settings. This cross-talk is believed to originate in the periphery of the photomultiplier tubes, and a 6 mm copper shim mask was fixed onto the outside edge, of each photomultiplier. This resulted in a reduction in ^{14}C background by about 30%, a slight reduction in ^{14}C counting efficiency and an increase in the E^2/B of about 25%. (See Table II).

Significance of Standard and Background Count Rates to Radiocarbon Dating

One of the most important factors in radiocarbon dating is the detection of count rates marginally above background from the background count rate. The maximum age that can be determined is governed by the minimum sample count rate that can be distinguished statistically from the mean background count rate.

Callow (13) proposed the 4 sigma detection criterion, and Polach (8) suggested the use of the 3 sigma detection criterion* for counting systems giving stable (statistically reproducible) background determinations.

The age of the sample is calculated from

$$\text{Age (in years)} = \frac{T_{\frac{1}{2}}}{\ln 2} \ln \left({}^{No}/{}_{N_s}\right)$$

$$= 8033 \ln \left({}^{No}/{}_{N_s}\right) \qquad \ldots (1)$$

where $T_{\frac{1}{2}}$ = the half life of ^{14}C = 5568 years

No = Modern References Standard corrected net count rate in counts min^{-1}

N_s = net sample count rate in counts min^{-1}

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* The difference in net sample count rate (N_s) and background count rate (B) is not detectable if it is less than three times the square root of the combined squares of the standard deviations of the sample $\sigma^2(N_s)$, and background $\sigma^2(B)$ that is $N_s - B < 3\left[\sigma^2(N_s) + \sigma^2(B)\right]^{\frac{1}{2}}$.

If the maximum age corresponds to the lowest detectable sample count rate based on 3 σ criterion and using the same approach as Jansen (14) then

$$N_s \text{ minimum} = 3\left[\sigma^2(N_s) + \sigma^2(B)\right]^{\frac{1}{2}} \quad . \qquad \ldots (2)$$

For count rates close to background, where $N_s \approx B$, equation (2) approximates to

$$N_s \text{ minimum} = 3\ \left[2\ B/t\right]^{\frac{1}{2}} \qquad \ldots (3)$$

where t = the counting time in minutes and B = background count rate in counts min^{-1}.

The maximum measurable age (A max) can therefore be expressed as

$$A \max = 8033\ \left[No/N_s \text{ minimum}\right] \qquad \ldots (4)$$

$$= 8033\ \ln\ (t/_{18})^{\frac{1}{2}} + 8033\ \ln\ \left[No/(B)^{\frac{1}{2}}\right] \ . \qquad \ldots (5)$$

The first term in equation (5) is a constant for a given counting time, t minutes, and is independent of the counting system. It depends on the detection criterion (in this case taken to be 3 σ). The second term depends on counting efficiency, background and activity of the modern standard.

We introduce here a new concept which we call the Radiocarbon Dating System Figure of Merit, F ($F = No/(B)^{\frac{1}{2}}$), which defines the limitation of the counting system for determination of radiocarbon age. When the value of F is substituted into the second term of equation (5) it gives the number of years which can be added to (or subtracted from) the counting time dependent but counter independent first term.

If 4000 minutes is a reasonable maximum counting time, and substituting for t in the first term of equation (5) then

$$\left.\begin{array}{l} A\ max\ (t = 1000\ min) \simeq 16{,}100 \\ A\ max\ (t = 2000\ min) \simeq 18{,}900 \\ A\ max\ (t = 3000\ min) \simeq 20{,}550 \\ A\ max\ (t = 4000\ min) \simeq 21{,}700 \end{array}\right\} + 8033\ \ln[No/(B)^{\frac{1}{2}}] .$$

Substitution of F values from Table II gives the theoretical maximum ages of an assumed 4000 minute counting period as listed in Table III.

TABLE III

MAXIMUM ^{14}C AGES, BASED ON A 4000 MIN COUNTING PERIOD FOR GLASS AND TEFLON COUNTING VIALS

System	Maximum theoretical ^{14}C age	
	5 ml glass vial	5 ml Teflon vial
BECKMAN (Lowest F)	42,400	43,200
AAEC (Highest F)	44,200	47,000

The increase in the Maximum Age Limit of 800 and 2,800 years is due to the improved performance of counting systems when Teflon vials are used.

Conclusion

The significant increase in Figure of Merit of Teflon vials used for ^{14}C counting as indicated in Table I and II makes the use of these vials particularly desirable for low level counting and offers an opportunity for existing liquid scintillation Radiocarbon Dating Laboratories to improve their performance without costly or time consuming modifications.

For commercial liquid scintillation spectrometers it is suggested that Vial Design 'B' be used because of its aluminium shielding cap. While more expensive shielding studies are indicated, they were beyond the scope of this paper.

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