CHAPTER 11

Application of High Purity Synthetic Quartz Vials to Liquid Scintillation Low-Level ^{14}C Counting of Benzene

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ABSTRACT

High purity synthetic quartz is evaluated for low-level ^{14}C detection through liquid scintillation (LS) counting of benzene. A simple cylinder-cell vial design is presented, which incorporates a Teflon® stopper and Delrin shield. The counting characteristics (counting efficiency and background) of the quartz vials are compared to the Wallac Teflon and low-K glass vials, in new technology LS spectrometers (Pharmacia-Wallac, Quantulus, at ANU and Waikato, and the Packard 1050 CA/LL, modified at UGA). The effect of the vial counting characteristics upon maximum and minimum detectable ^{14}C age and the magnitude of the counting error, for both low and high count rate samples, is examined. Synthetic quartz is shown to have counting characteristics superior to low-K glass and is equal to Teflon vials for most applications. Further, quartz does not require the extensive cleaning procedures necessary for Teflon.*

INTRODUCTION

The application of commercially available liquid scintillation (LS) counters for radiocarbon (^{14}C) dating has evolved over the last decade from the utilization of general purpose instruments, to new technology low-level LS spectrometers. The old technology counters, even with extensive in-house modifications, yield at best, between 60 to 75% ^{14}C counting efficiency, characterized by a high background, which at best is >10% of the ^{14}C Modern reference signal (Polach et al., 1983). Two modern low-level LS spectrometers, such as the modified Packard 1050 CA/LL and Pharmacia-Wallac, Quantulus, use electronic optimization (e.g., pulse shape, duration and ratio analyses), and Quantulus uses active and enhanced passive shield, to generally further reduce the background. The performance of these LS spectrometers in relation to ^{14}C dating has been described.[1,2] The best performance is at >80% ^{14}C efficiency characterised by an ultralow background at 0.8% of the ^{14}C reference signal.

*Teflon is a Registered Trademark of E. I. DuPont de Nemours.

Such improved performance gives higher precision, extended detectable age limit, or significantly smaller sample ^{14}C LS radiometry.[3] The critical application to low-level ^{14}C spectrometry not only requires evaluation of LS counter performances, but it necessitates consideration of errors and assurances[4] and counter unrelated parameters such as counting vial design, materials, benzene purity, and scintillant performance.

This paper deals with different counting vial materials and their significance to low-level ^{14}C detection characteristics and performance.

COUNTING VIALS

A great variety of counting vial materials are available and were applied to ^{14}C isotope detection in benzene. Glass, quartz, Teflon, and Delrin were found suitable, albeit different in performance characteristics. Polyethylene (PE) and high density PE were not suitable due to their permeability of benzene. Shapes and volumes of vials include special purpose large volume cylinders (50 to 100 mL), square or cylindrical mini-vials within special holders (0.3 to 3 mL), and those based on the standard 20 mL LS counting vial design. High precision ^{14}C low count rate determinations require calibration of each vial independently for efficiency and background; therefore, it is general practice to reuse the same set of vials over many years.

The glass and quartz vials have excellent physical counting properties. Their ^{14}C signal and background detection efficiency remains constant over many years, and memory effects are nil with only minimal washing between samples. Quartz vials give inherently lower backgrounds than K-free glass counting vials.

Teflon and Delrin have excellent counting properties (high efficiency and inherently low backgrounds) but many researchers experience difficulties in their usage due to deformation over a period of time. Memory effects require rigorous cleaning procedures between samples, and alter efficiency over time (Figure 1).

EXPERIMENTAL PROCEDURES AND VIAL DESIGN

Using available LS spectrometers, the authors tested vials of various designs and materials in their laboratories. The University of Georgia, Packard counter, used low-K glass vials in all their measurements. The Australian National University and the University of Waikato used Wallac counters with Wallac Teflon and quartz vials of various origins and sample sizes.

The Teflon vials were used as supplied by their manufacturer (Wallac Oy).[5] One has a wall thickness of 0.9 mm the other of 1.1 mm. This affects their performance (cf. Table 1).

The synthetic quartz vials were manufactured using material from three differ-

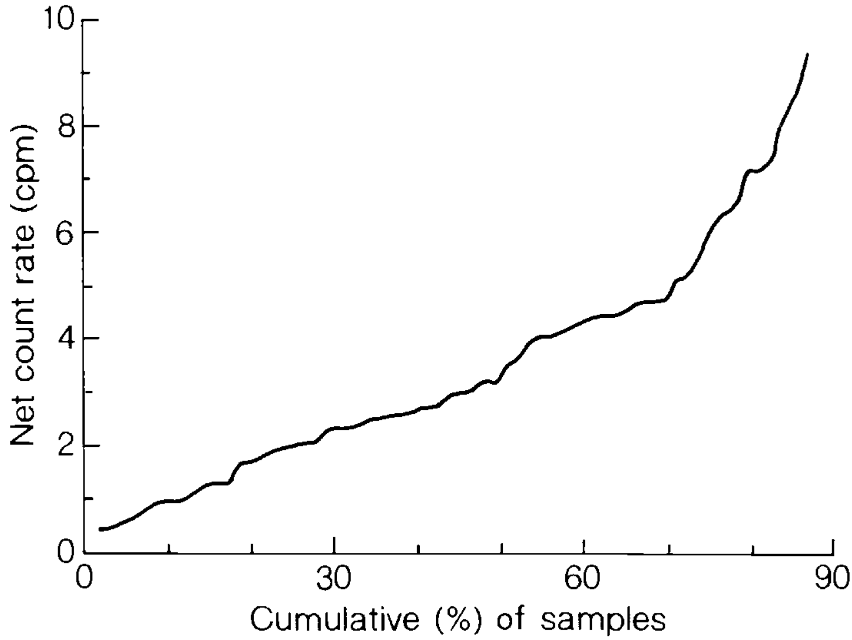

Figure 1. Time series plot of SQPE (external standard endpoint) values for Teflon vials compared to low-K glass vials. Changes in endpoint in Teflon with time correspond to a related change in count rate of the modern reference standard, from 24.2 to 23.7 ± 0.1 CPM, while the background remained the same (within statistical limits). Such changes in performance must be allowed for in high resolution ^{14}C counting.

ent sources: (1) Thermal Syndicate, UK (TS silica), (2) Mikro-Glasstechnik, Germany (MG silica), and (3) GM Associates, USA (GM silica).

The silica vial consists of a flat bottomed cylindrical cell, 34 mm high and 25 mm in diam, sealed by a Teflon stopper containing a Viton 'O'ring (Figure 2). The Teflon stopper contains a partially threaded central opening which is sealed, after the stopper is inserted, by a close fitting tapered stainless steel pin.

Table 1. Counting Characteristics of Teflon, Silica and Low-K vials of 3 mL and 5 mL Benzene Samples at ANU and Waikato, Wallac Quantulus Counters

VIAL	VOL[a]	B[b]	N_0[c]	E[d]	fM[e]	FM[f]	tMAX[g]	tMIN[h]
0.9mm Teflon	3	0.29	27.6	83.7	51.3	24,200	55,400	39
1.1mm Teflon	3	0.24	24.3	73.5	49.5	22,500	55,100	42
MG silica	3	0.32	27.5	83.3	48.6	21,700	55,000	40
TS silica	3	0.43	28.0	84.8	42.7	16,700	54,000	39
GM silica	3	0.36	27.5	83.3	45.8	19,300	54,500	40
Low-K	3	0.50	22.8	69.2	32.2	9,600	51,700	44
0.9mm Teflon	5	0.45	47.5	84.4	70.8	15,800	58,000	30
MG silica	5	0.58	47.7	84.7	62.7	12,400	57,000	30

Note: [a–i]see Table 2.

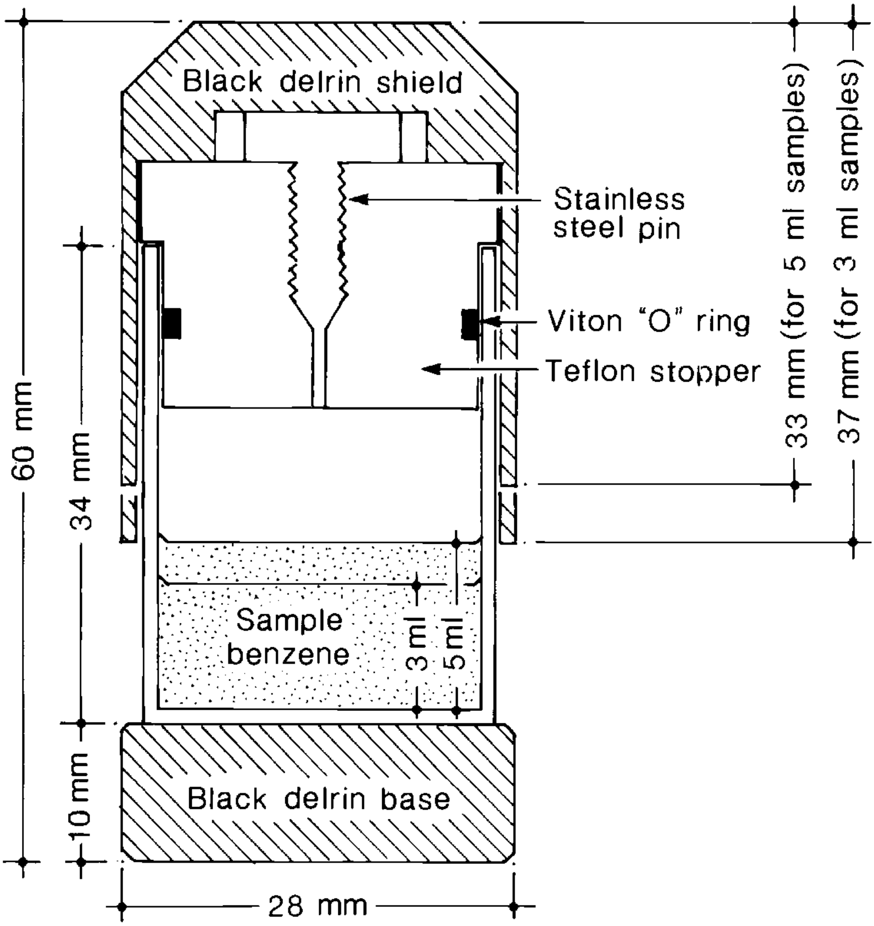

Figure 2. Cross section of the experimental silica counting vial. A Teflon stopper with a single O-ring is shown. Later experiments gave a significant reduction in vapor loss when a double O-ring was used. The Delrin masks are made in two lengths, one to reach the 5 mL and the other the 3 mL sample meniscus.

The opening prevents the sample from becoming pressurized when the stopper is inserted. A black Delrin base, 10 mm high and 28 mm diam centers the vial along the optical axis of the photomultiplier tubes. A black Delrin shield is fitted over the vial, up to the meniscus of the sample benzene, to reduce optical cross talk. The practical counting volume range is 3 mL to 5 mL of benzene.

The ANU and Waikato experiments with quartz and Teflon used 15 g/L concentrations of Butyl PBD as scintillant, while UGA used 6 g/L PPO with 0.2 g/L secondary pulse length shifter POPOP in benzene.

In all cases the counters were set up to give optimal ^{14}C detection performance, e.g., highest obtainable ^{14}C reference sample signal to background ratio.

Table 2. Counting Characteristics of Low-K vial of 3 mL and 5 mL Benzene Samples at UGA Packard Counter

VIAL	VOL[a]	B[b]	N_0[c]	E[d]	fM[e]	FM[f]	tMAX[g]	tMIN[h]
Low-K[i] (1050)	3	0.46	21.08	63.09	31.0	8653	51,400	45
	5	0.75	35.17	64.74	41.0	5588	52,400	35

[a]Volume of benzene (3 mL = 2.637g; 5 mL = 4.5g).
[b]B = background, cpm.
[c]N_0 = 95% Oxalic Acid Modern reference standard, cpm.
[d]E = % counting efficiency.
[e]fM = factor of Merit, $N_0/\sqrt{B}$.
[f]FM = Figure of Merit, E^2/B.
[g]Age limit, tMAX—3000 min for B, N_0, and S (2 SD detection criterion, reference 7, p 96), years.
[h]Minimum age, tMIN—3000 min for B, N_0, and S (1 SD detection criterion, Reference 7, p 97), years.
[i]7 mL low ^{40}K borosilicate glass vial with Teflon cap liner. Counted using Packard 1050 modified with scintillating plastic detector guard.

As two important sources of sample ^{14}C count rate variations are known, their effect on performance was tested:

1. Handling the counting vials, exposing them to light, stirring the counting cocktail, or allowing an electrostatic discharge can cause spurious counts at the beginning of the counting cycle.[6] Both Teflon and MG silica were tested for this effect in the Wallac counters. Vials were: (1) rubbed by a Nylon cloth to induce an electrostatic charge, (2) agitated for 30 minutes, (3) exposed for 30 minutes to fluorescent light 15 cm distance, and (4) irradiated by gamma and beta particles from an external high energy and countrate source. A sample of ca., 150% Modern (ANU-Sucrose ^{14}C standard) was counted for 5 min intervals for 30 minutes (6 repeats). All tests were negative. No induced count rate variation could be detected.
2. Loss of sample benzene during prolonged low-level counting times (1 to 3 days) will also cause variation in the observed count rate with time. The evaporative loss in the Teflon vials were nil per day at room temperature. The evaporative loss of the experimental silica vials (Figure 1) was 0.7 mg/d. To minimize this a double 'O'ring stopper was later tested and achieved 0.1 mg/d losses.

Results

The ^{14}C low-level counting characteristics of Teflon, silica, and low-K glass in the Wallac counters are presented in Table 1. Similar data for the low-K glass vial from UGA using the Packard counter is presented in Table 2. The performance of the vials with 3 mL and 5 mL of sample benzene in the various counters is characterized, by their background (B) and net ^{14}C countrate (N_0), at 95% of the Oxalic Acid International Reference Standard. To assist evaluation of data, the radiocarbon dating "factor of Merit" (fM = $N^o/\sqrt{B}$), the conventional "Figure of Merit" (FM = E^2/B), and the oldest (tMAX)[7] and youngest (tMIN)[7] detectable ^{14}C age were included. In the Wallac counters the best performance was obtained with Teflon at 5 mL followed by the MG silica.

DISCUSSION AND CONCLUSIONS

The background and modern reference sample count rates determine the ^{14}C dating performance of both the counter and counting vial: the magnitude of the counting error limits the minimum and maximum determinable ages as well as the minimum countable sample size. Sample size is another variable which affects ^{14}C age resolution.

While counted benzene volumes are usually fixed (in our study to 3 mL or 5 mL), the sample component within the benzene varies in practice. Indeed, all radiometric laboratories dilute the sample, CO_2 or C_6H_6, with gas or benzene containing no ^{14}C. A case study of sample sizes dated at the University of Waikato is given in Figure 3 (count rates are plotted against age). The full size (undiluted) samples must lie on the solid line. The vast majority are diluted and lie below the line. In Figure 4, the samples shown in Figure 3 are expressed as a cumulative plot of sample % for a given count rate (Figure 4). The plot indicates that the count rate rather than sample age is therefore, in practical terms, the limiting variable in ^{14}C age determinations.

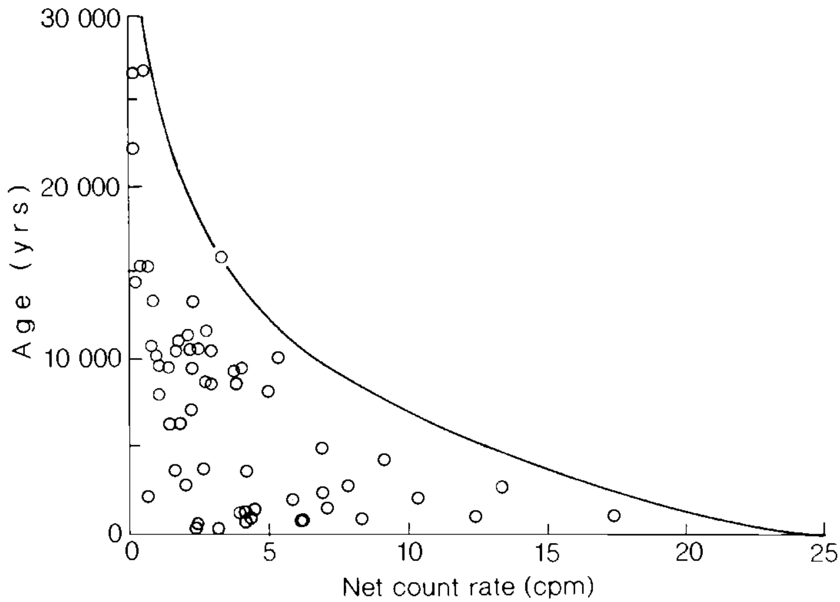

Figure 3. Scatter plot of routine ^{14}C age determination samples counted in the Wallac Quantulus at Waikato over a 12 months period. The solid line gives age and count rate limits for undiluted 3 mL samples. Most samples were diluted with ^{14}C free material to make up the required counting volume.

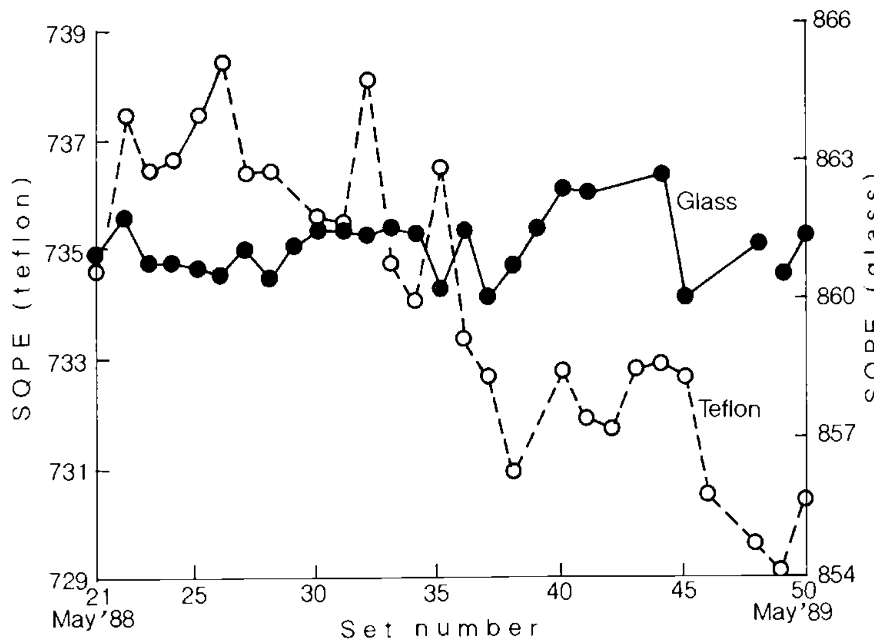

Figure 4. Cumulative % of samples shown on Figure 3, plotted against the net sample count rate. The plot demonstrates that in routine ^{14}C dating the majority of samples have significantly lower count rates than the modern reference standard, primarily due to the high degree of sample dilution rather than age. High resolution, close to the limit of detection is therefore an important factor in routine ^{14}C dating applications.

To assess the merit of vials, we have taken the 3 mL data (Table 1) for the Quantulus and related each type of counting vial tested to the best vial (0.9 mm thick Teflon). The difference in calculated counting error (1 Standard Deviation, SD), expressed in years, with respect to the net sample count rate is the merit of vials (Figures 5A and 5B).

We can conclude the following:

- The majority of samples ^{14}C dated at ANU and Waikato give low count rates, predominantly due to sample size, rather than the age of material submitted for dating. Whenever this is the case, high resolution ^{14}C counting at the lowest attainable background and highest efficiency is very desirable.
- When dealing with low count rates samples (old or highly diluted, where ^{14}C signal approaches noise), a reduction in counting efficiency (E) is tolerable only if accompanied by a compensating reduction in background (B). For example, a reduction of ~84 to 74% E and almost proportional reduction in B only marginally affects tMAX (e.g., 0.9 and 1.1 Teflon, 3 mL, Table 1) and slightly increases the counting error by 15 years at 30 K years (Figure 5A). A reduction of ~84 to 69% E without compensating reduction in B has a significant effect on tMAX (e.g., 0.9 Teflon and low-K, 3 mL, Table 1) and significant increase in the counting error by 90 years at 30 K years (Figure 5A).
- When dealing with high count rate samples (signal approaches reference stan-

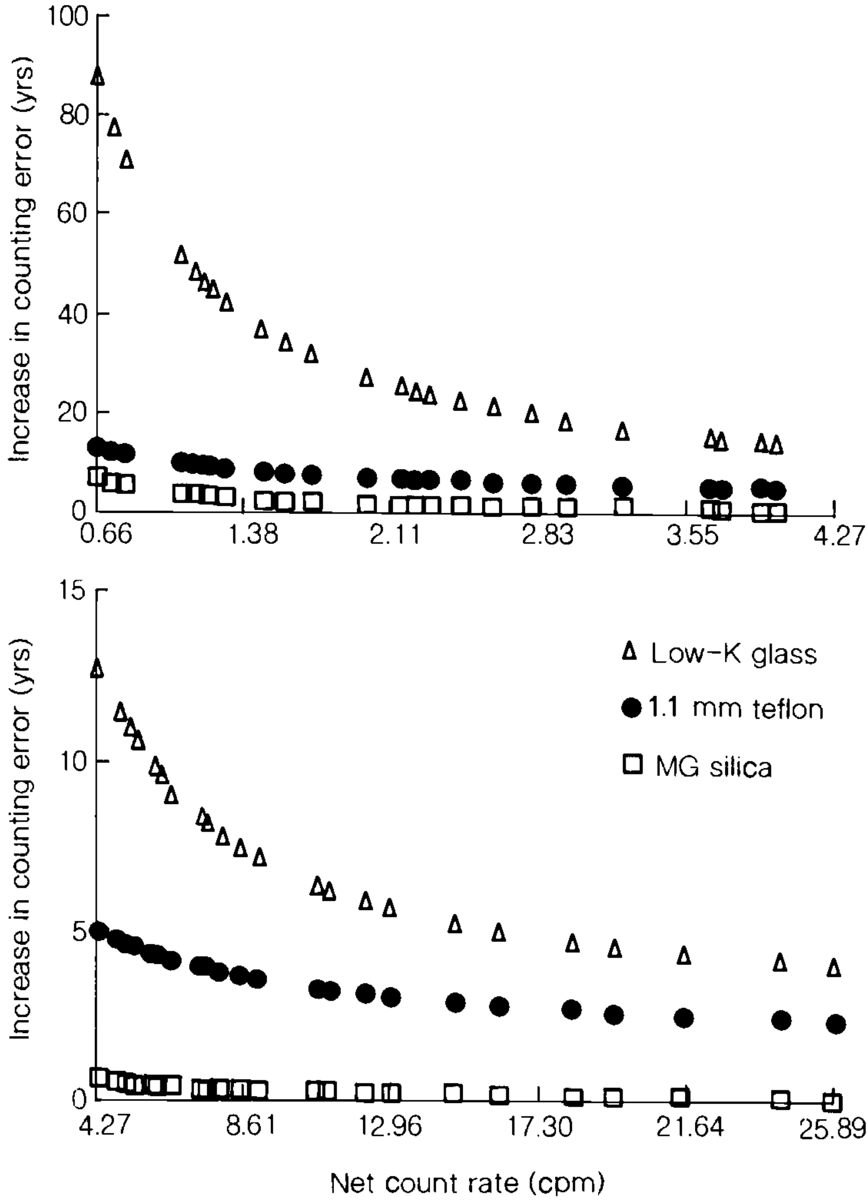

Figure 5. The difference in the standard deviation (SD) between the best performing vial (0.9 mm wall Teflon) and 3 other vials is given as "increase in counting error years." It is plotted against net count rate (CPM). Figure 5A covers the age range equivalent to 30 to 15 K years for undiluted sample. Figure 5B covers the age range equivalent to 15 K years to 500 years for undiluted samples. All counting times were fixed at 3000 minutes.

dard count rate) an increase in B is tolerable if % E becomes higher (e.g., 0.9 Teflon, B = 0.29 cpm, and TS silica, B = 0.43 cpm, both give the same tMIN, Table 1). However, should the E be significantly decreased and or B significantly increased (e.g., low-K, Table 1 and Figure 5) the tMIN, tMAX, and error deteriorate significantly.

- The performance of the MG silica is closely related to that of the 0.9 Teflon in the Wallac counters. The tMAX and tMIN are not significantly different nor is there a significant difference in the error of determination at the low and high end of count rates (Figure 5).
- Silica varies in performance both in terms of efficiency and background. When suitable material selection is made, and the high resolution and ultralow background characteristics of the Quantalus are used to the utmost, silica will be an effective substitute for Teflon.
- The low-K glass vials in both the Quantulus and Packard counters have similar counting performances (Table 1 and 2). It is hoped the improved silica vial counting characteristics exhibited by the Quantulus measurements can also improve the counting capability for the Packard counters.
- Since the silica vial configuration, as shown in Figure 2, could not be accommodated in the Packard 1050 under optimum 7 mL vial configuration, measurements will be delayed until suitable vials can be fabricated.

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