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EVALUATION OF HIGH-PURITY SYNTHETIC SILICA VIALS IN ACTIVE AND PASSIVE VIAL HOLDERS FOR LIQUID SCINTILLATION COUNTING OF BENZENE

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ABSTRACT. We evaluate high-purity synthetic silica vials in both delrin and active plastic holders (Pico adapters™) for ^{14}C dating, using liquid scintillation counting of benzene. We have designed synthetic silica vials in the form of simple cylinder-cells based on the standard 7-ml vial. We have also designed a delrin holder for supporting 7-ml silica or glass vials. We compare the counting efficiency and background of the silica vials with Teflon, plastic and low-K glass vials for both delrin holders and Pico adapters in the 1220 Quantulus and Packard Tri-Carb 2660 XL, fitted with a plastic detector guard. In the 1220 Quantulus, synthetic silica vials in Pico adapters have the highest figure of merit (FM), closely followed by silica in delrin holders and Teflon. In the Packard Tri-Carb 2660 XL, plastic vials in Pico adapters give the highest FM.

INTRODUCTION

The development of commercially available low-level spectrometers during the late 1980s has enabled significant advancements in ^{14}C dating by liquid scintillation counting (LSC) of benzene. Only two commercial spectrometers, the Packard Tri-Carb® 2050 and succeeding instruments, and the Pharmacia Wallac 1220 Quantulus, have achieved true low-level performance. Cook, Harkness and Anderson (1989) report a maximum background-to-^{14}C-reference-signal ratio, for 3 ml of benzene, of 4% for the Packard Tri-Carb 2250 (at 65.5% efficiency), and Polach *et al.* (1988a), in a comparison of low-level spectrometers, measured the Quantulus performance in a normal counting environment[1] at >80% ^{14}C counting efficiency with a background of 0.8% of the ^{14}C reference signal, also for 3 ml of benzene.

Such improved capabilities result in higher precision, extension of the detectable age limit and the capability of handling significantly smaller samples (*e.g.*, Polach *et al.* 1988b). The success of LS spectrometry in ^{14}C dating depends not only on achieving maximum counter performance, but also on benzene purity, and on the counting environment, which includes the design and composition of both vials and holders.

We examine here a variety of vial and vial holder designs and compositions, and consider their significance for low-level ^{14}C spectrometry. The motivation for such a study stems from our desire to satisfy the 'total optimization' concept, as outlined by Polach *et al.* (1984), in which all known parameters affecting accuracy, including counting vials, are fully optimized for routine dating.

EXPERIMENTAL PROCEDURES

A number of different vials and vial holders were tested in a Pharmacia Wallac 1220 Quantulus at the University of Waikato, and in a Packard Tri-Carb 2660 XL analyzer at the Center for Applied Isotope Studies at the University of Georgia.

[1]This excludes the data from Polach *et al.* (1988a) for the Pharmacia Wallac low-level laboratory, in which backgrounds are reduced by massive shielding to 0.7% of the ^{14}C reference signal (at 70% efficiency), for 3 ml benzene.

Counting Vials

Commercially available LS vials used for benzene counting are commonly composed of either Teflon, quartz or low-K glass (*e.g.*, Polach *et al.* 1983; Haas 1979; Devine & Haas 1987; Noakes & Valenta 1989). Polyethylene and polypropylene vials are very useful for non-aromatic solvents, but their permeability makes them unsuitable for repeatable long-term benzene use. In a comparison of different vial types, Hogg *et al.* (1991) concluded that, for spectrometers using true anti-coincidence detection and extensive passive shielding (as in the Quantulus), Teflon or synthetic silica vials produced the highest performance in terms of ^{14}C detection efficiency and background. The authors also noted that synthetic silica had superior physical properties to Teflon. They examined synthetic silica from a variety of sources, and identified silica produced in Germany (Mikro-Glastechnik) as having the most suitable counting characteristics of those tested.

We have designed a new synthetic silica vial[2], in two sizes to contain either 3 or 5 ml benzene. The design is based upon the standard 7-ml LSC vial. It is a flat-bottomed cylindrical cell 16 mm in outside diameter (OD), with heights of 40 mm (for 3-ml samples) and 50 mm (for 5-ml samples) (Fig. 1). Other vials examined in this study for purpose of comparison, include vials made from plastic, Teflon-copper (Wallac), and low-K borosilicate glass (Packard).

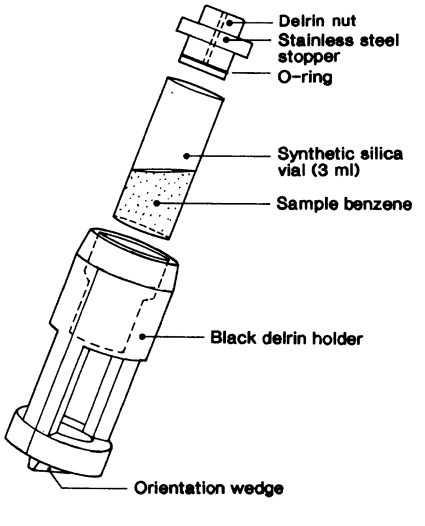

Fig. 1. Schematic diagram of the Waikato 3-ml synthetic silica vial, including delrin holder and stainless steel stopper

Vial Stoppers

We have designed a new vial stopper that reduces benzene loss to <0.1 mg per week without compression of the sample during insertion (Fig. 2). The stainless steel stopper has three parts. A lower stainless steel plate is connected to an upper delrin nut by a threaded rod. The central stainless steel portion has a 45° angle at the base, which expands the O-ring against the vial walls as the delrin nut is tightened. Evaporative loss measurements from the major vials studied (silica, using stainless steel stoppers), Teflon (tufbond disks) and low-K glass (using Teflon liners)) showed that all vials lost <0.1 mg per week at 12°C.

[2]Silica also from Mikro-Glastechnik

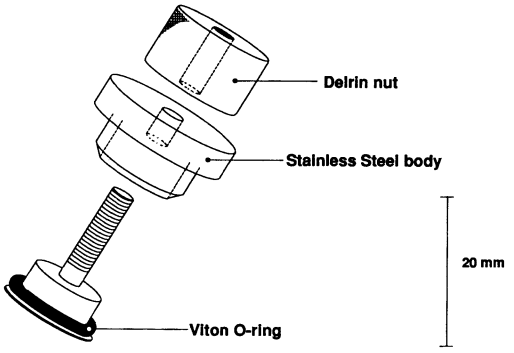

Fig. 2. Schematic diagram of the Waikato stainless steel stopper

Vial Holders

The practical advantage of the standard 7-ml vial design over its 20-ml counterpart is less benzene loss during sample loading. However, its significant disadvantage is that it requires a holder or adapter to center the vial in the counting chamber and to minimize cross-talk between the photomultiplier tubes (PMTs). While the Packard Tri-Carb analyzers do not require special holders for routine use of 7-ml vials, the Quantulus is designed for vials with the standard 20-ml vial OD of *ca.* 27 mm, and therefore, vial adapters are necessary with narrower diameter vials.

We tested two vial adapters. We made the Packard Tri-Carb measurements either without any adapter, or using the active plastic holders (Pico adapters™) described in Noakes and Valenta (1989). The active vial holder is a 27-mm OD cylinder that envelopes the 7-ml vial. It is composed of a blend of both primary and secondary scintillators that amplify the spectral characteristics of background radiation events, thereby enhancing their detection and elimination. Measurements in the Wallac Quantulus used either the Pico adapters described above, or a specially designed passive holder constructed from black delrin (Fig. 1). We considered delrin most suitable because it has inherently low radiation characteristics with excellent machining properties and low light reflectance. The holder is a cylinder (28 mm OD) with opposed cut-away sides to provide a light path between the vial and PMTs (Fig. 1). A machined wedge (*ca.* 16 mm long and 5 mm deep) extending from the base of the holder prevents holder rotation and consequent alteration of the counting efficiency. A narrow, V-shaped groove machined into the elevator shaft of the Quantulus mates with the wedge and aligns the holder as it is lifted into the counting chamber. The groove in the piston head allows orientation of the holders, while retaining the ability to use vials with flat bases. The modification to the piston head can be carried out by a precision engineering machine shop without disturbing the piston alignment. The delrin holders are constructed in two sizes, to suit both 3 and 5-ml vials.

Results

Table 1 gives the counting performance (*i.e.*, count rate of the modern ^{14}C reference standard [N_o], and background [B]) of Teflon, synthetic silica and low-K borosilicate glass vials in either Pico adapters or delrin holders in the Wallac Quantulus, for 3 and 5 ml benzene. Table 2 shows the results for similar measurements on synthetic silica, low-K borosilicate glass and plastic vials with and without the Pico adapters, for the Packard Tri-Carb 2660 XL. Other parameters, provided to assist in evaluating the results, include the factor of merit (fM), the figure of merit (FM), and the oldest (tmax) and youngest (tmin) detectable ages.

TABLE 1. Performance data for various vials and vial holders at the University of Waikato radiocarbon laboratory, using the Pharmacia Wallac Quantulus spectrometer

Vial type	Vial holder	Vial* vol (ml)	Optimized PAC or PSA setting	Background (cpm)	N_o** (cpm)	^{14}C efficiency (%)	fM†	FM‡	tmax§ (yr)	tmin‖ (yr)
Teflon	None	3	Not optimized	0.29	27.97	84.8	51.7	24,530	55,500	39
Silica	Pico	3	PSA = 10	0.20	26.21	79.5	58.6	31,560	56,500	41
Silica	Delrin	3	PAC = 180	0.25	25.66	77.8	51.4	24,300	55,500	41
Glass	Pico	3	PSA = 10	0.45	26.08	79.1	39.1	14,050	53,300	41
Glass	Delrin	3	PAC = 180	0.57	27.89	84.6	37.0	12,610	52,800	39
Teflon	None	5	Not optimized	0.42	47.31	84.0	73.0	16,820	58,300	30
Silica	Pico	5	PSA = 20	0.31	47.12	83.7	84.6	22,600	59,500	30
Silica	Delrin	5	PAC = 180	0.38	46.89	83.3	76.1	18,250	58,600	30
Glass	Pico	5	PSA = 10	0.87	47.21	83.9	50.6	8090	55,300	30
Glass	Delrin	5	PAC = 180	1.10	44.96	79.9	42.8	5780	54,000	31

*Benzene weights used, for 3 ml = 2.637 g; for 5 ml = 4.5 g

**N_o = derived net cpm for ^{14}C reference standard, 0.95 oxalic acid

†fM = factor of merit ($N_o/\sqrt{B}$)

‡FM = figure of merit (E^2/B)

§tmax = maximum determinable age (using 3000-min count time, and 2 σ criterion)

‖tmin = minimum determinable age (using 3000-min count time, and 1 σ criterion)

TABLE 2. Performance data for various vials and vial holders at the Center for Applied Isotope Studies at the University of Georgia, using the Packard Tri-Carb 2660 XL spectrometer

Vial type	Vial holder	Vial* vol (ml)	Optimized E^2/B energy region (KeV)	Background (cpm)	N_o** (cpm)	^{14}C efficiency (%)	fM†	FM‡	tmax§ (yr)	tmin‖ (yr)
Silica	Pico	3	10–72	0.50	19.66	59.6	27.8	7100	50,500	47
Silica	None	3	11–80	0.70	19.61	59.4	23.4	5040	49,100	47
Glass	Pico	3	16–79	0.40	19.22	58.2	30.4	8480	51,200	47
Glass	None	3	14–90	0.80	18.65	56.5	20.9	3990	48,200	48
Plastic	Pico	3	12–94	0.40	20.36	61.7	32.2	9510	51,700	46
Plastic	None	3	11–81	0.30	20.02	60.7	36.6	12,260	52,700	46
Silica	Pico	5	9–65	0.90	34.42	61.1	36.3	4150	52,700	35
Silica	None	5	5–57	1.40	36.70	65.2	31.0	3030	51,400	34
Glass	Pico	5	8–54	0.60	32.54	57.8	42.0	5560	53,800	36
Glass	None	5	13–100	0.90	32.34	57.4	34.1	3660	52,200	37
Plastic	Pico	5	10–81	0.50	33.92	60.2	48.0	7250	54,900	36
Plastic	None	5	12–94	0.60	34.05	60.5	44.0	6090	54,200	36

*Benzene weights used, for 3 ml = 2.637 g; for 5 ml = 4.5 g

**N_o = derived net cpm for ^{14}C reference standard, 0.95 oxalic acid

†fM = factor of merit ($N_o/\sqrt{B}$)

‡FM = figure of merit (E^2/B)

§tmax = maximum determinable age (using 3000 min count time, and 2 σ criterion)

‖tmin = minimum determinable age (using 3000 min count time, and 1 σ criterion)

Results for the Wallac Quantulus

We used different scintillator types and concentrations with different holders. For Teflon vials and vials supported by the delrin holder (both silica and glass), we used butyl-PBD (15 g/l). The Pico adapters have a higher maximum absorption wave length (Noakes & Valenta 1989), and require a secondary wave shifter. The secondary scintillator was bis-MSB, at a concentration of 1.0 g/l (after Cook, Harkness & Anderson 1989).

We obtained optimum counting conditions experimentally for each type of vial and holder, by varying pulse-amplitude comparator (PAC) levels and pulse-shape analysis (PSA) levels. We also measured the performance of the Pico adapters with and without operation of the Quantulus electronic guard. We selected Hi coincidence bias for all measurements.

We conclude the following from the Quantulus data shown in Table 1:

- Synthetic silica vials in Pico adapters demonstrated the highest performance of all the vials tested. Using the PSA capabilities of the Quantulus, we obtained a FM of 31,560 from a wide spectrum (79.5% efficiency) for 3 ml benzene. The effectiveness of the Pico adapter is significantly reduced if either the Quantulus active guard is inoperative (B rises to 0.78 cpm), or if lower purity low-K borosilicate vials are used (FM falls to a low 14,050). The Pico adapters have the significant advantage of not requiring the Quantulus piston head modifications necessary for the delrin holders, but have the disadvantage of requiring the poorly soluble secondary scintillator bis-MSB.
- Synthetic silica vials in delrin holders and Wallac Teflon-copper vials both provide an alternative to the Pico adapter, as all three have high FMs (ranging from 24,300 to 31,560 for 3 ml benzene). Teflon-copper vials are commercially available, they have very good sealing characteristics, but some users have experienced difficulties associated with the physical properties of the vials (*e.g.*, Devine & Haas 1987; Kalin & Long 1989; Hogg *et al.* 1991). Silica vials (and delrin holders) of the type described here are also available commercially and have good sealing characteristics, but require piston-head modifications. However, once the modifications are complete, other vial holders (*e.g.*, for minivials) can also be used. Further, as the silica vial does not rotate within the holder, an alignment mark allows fixed orientation of the vial with respect to the PMTs. This counteracts the objection to cylindrical vials made in other studies, where uneven wall thicknesses have resulted in variations in sample count rates of up to 1% (Haas 1979). Although the silica vials clearly satisfy the 'total optimization' concept, the improvement in counting performance is significant only for lower activity samples (*i.e*, for older or undersized material).
- Average ^{14}C efficiencies are slightly higher for 5-ml than for 3-ml samples (Table 1). Background levels are also higher, because of the difference in benzene weights. The amount of increase from 3- to 5-ml background levels depends on vial type, with Teflon and silica increasing by 45–55%, and glass showing a significantly larger increase of 93%.

Results for the Packard Tri-Carb 2660 XL

The Packard system was refrigerated and all samples were temperature-equilibrated and dark-adapted prior to counting. The Packard Tri-Carb 2660 XL contains an active scintillating plastic detector guard installed between the PMTs. The scintillator cocktail consisted of PPO (6 g liter^{-1}) and POPOP (0.2 g liter^{-1}). We determined an optimized energy region for each vial and holder combination. From the Packard data (Table 2) we conclude:

- For highest performance, the Packard system requires the Pico adapter, which significantly reduces background levels, increasing the FM for the various vials from 19% (for 5 ml benzene in plastic) to 112% (for 3 ml benzene in glass). Plastic vials (FM = 12,260 for 3 ml benzene), yielded the best results and low-K borosilicate glass (FM = 8480 for 3 ml benzene) next best.
- Synthetic silica contains far less natural radioactivity than low-K borosilicate glass. This appears to inhibit the ability of the Pico adapter to recognize background events.
- Detection efficiency increases very slightly from 3 to 5 ml benzene. Background depends on vial type and benzene weight. The different vial types have different energy distributions in the optimized region of interest, thus affecting the background count rate.

CONCLUSIONS

Figure 3 summarizes the performance data for the various vials, holders and spectrometers. In the Wallac Quantulus, synthetic silica vials in Pico adapters yield the highest performance. The delrin holder performs almost as well as the Pico adapter, and has the added advantage of reproducing the vial alignment. Teflon vials have counting characteristics similar to synthetic silica, but have less desirable physical properties. Plastic vials give the best counting performance in the Packard Tri-Carb spectrometer, but low-K borosilicate glass vials are more suitable for ^{14}C dating. Synthetic silica vials do not perform well in the Packard counting system. The Pico adapter significantly increased the performance of all vials measured in the Packard Tri-Carb 2660 XL.

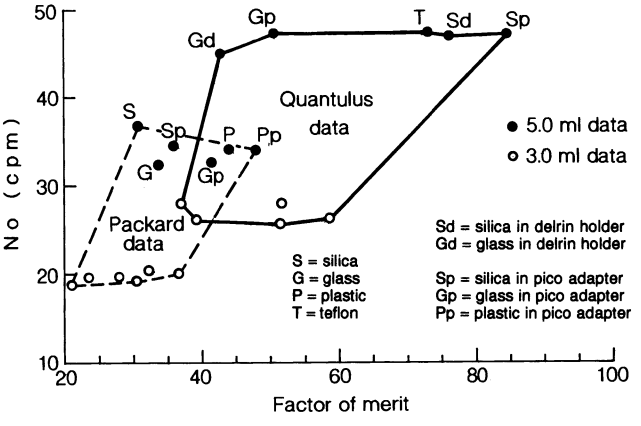

Fig. 3. Summary of the performance data for the various vials, adapters and spectrometers. The merit of a vial or holder for ^{14}C dating is based upon both N_0 (the count rate of the modern ^{14}C reference standard) and the factor of merit. The higher the value of N_0 or factor of merit, the better the vial or holder.

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