PERFORMANCE AND DESIGN OF 0.3-ML TO 10-ML SYNTHETIC SILICA LIQUID SCINTILLATION VIALS FOR LOW-LEVEL ^{14}C DETERMINATION

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ABSTRACT. I evaluate the detection of ^{14}C at natural or below natural abundances in synthetic silica vials of 0.3-ml, 3-ml and 10-ml volumes, and demonstrate the merit of multisize vials for ^{14}C dating by liquid scintillation (LS) spectrometry, using butyl-PBD in benzene analyzed in a Quantulus spectrometer. I describe performance limits, design and other details for the 0.3-, 3- and 10-ml volumes. For multi-user and multiproject ^{14}C dating, as practiced in most laboratories, the 3-ml silica vial serves best. Nevertheless, 0.3-ml minivials provide accurate results with adequate precision for many applications, for samples containing 120–240 mg of carbon. I recommend the 10-ml vial for high-precision work at better than ± 0.5% modern carbon (pMC).

INTRODUCTION

Significant progress has been made in technique and instrumentation over three decades of ^{14}C dating by liquid scintillation counting (LSC) of benzene. Modern trends aim at increasing both the precision of the method, and also its accuracy, as demonstrated by the proliferation of international intercomparison studies (*e.g.*, Aitchison *et al.* 1990; Rozanski *et al.* 1992).

The sample vial influences both precision and accuracy. The precision is affected by the level of self-induced radiation that a vial contributes to the observed background count rate. Accuracy is affected by the level of chemical resistance the vial has to both benzene and dissolved scintillators. Polach *et al.* (1983) describe the characteristics of an ideal vial as having a high photon transmission efficiency, a low self-induced radiation component and no memory. They recognized the great merit of borosilicate glass and fused quartz because of their non-reactive nature, but considered glass less than ideal because of its high background levels, and quartz because of its expense and the difficulties in manufacturing vials to precise specifications. They introduced low-background copper/Teflon vials, which could be machined to very close tolerances and which did not exhibit memory effects with re-use. Subsequent research has verified the excellent counting performance of Teflon in terms of ^{14}C detection efficiency and background, but some researchers have experienced difficulties associated with physical properties of the vials (*e.g.*, Devine & Haas 1987; Kalin & Long 1989; Hogg *et al.* 1991). The latter demonstrated the superior physical properties and high counting performance of cylindrical synthetic silica vials in counters using true anticoincidence detection and extensive passive shielding (as in the Wallac Quantulus). Hogg and Noakes (1992) described further refinements to the silica vial, with a new design based upon the standard 7-ml counting vial.

Here, I present modifications to the standard 3-ml vial described in Hogg and Noakes (1992), and introduce two new synthetic silica vials for ^{14}C dating: minivials of 0.3-ml capacity and larger vials of 10-ml capacity.

DESIGN AND SPECIFICATIONS OF VIALS, STOPPERS AND HOLDERS

Waikato Standard 3-ml Counting Vial

Hogg and Noakes (1992) describe the Waikato 3-ml synthetic silica LS vial and Delrin holder (Fig. 1). It consists of a flat-bottomed cylindrical cell (16 mm OD, height = 40 mm) composed of synthetic silica. The standard 3-ml counting vial and 0.3-ml minivial are both sealed by a stainless

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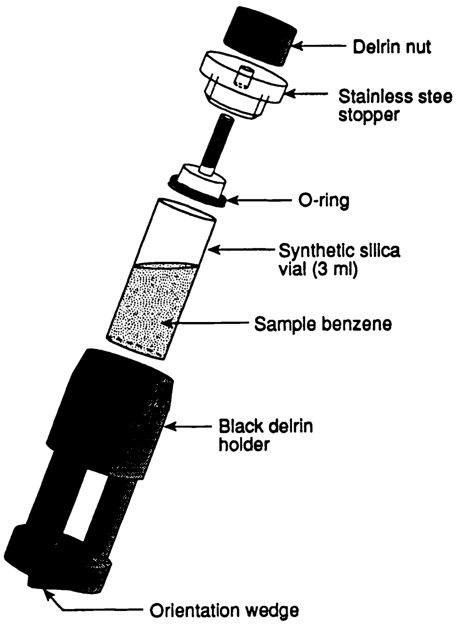

Fig. 1. Schematic diagram of the Waikato 3-ml synthetic silica vial, including Delrin holder and stainless steel stopper

steel (SS) stopper utilizing a Viton O-ring, which expands against the internal walls of the cylinder as the stopper is tightened. The cylindrical vial also requires a black acetyl (Delrin) holder or adapter to center it in the counting chamber and minimize crosstalk between the photomultiplier tubes (PMT). We adopted the design suggested by Butterfield and Polach (1983, Fig. 1C). The base of the holder incorporates a V-shaped orientation wedge, which allows a reproducible optical alignment of the vial. The lift mechanism of the LS counter must be modified to allow location of the orientation wedge to maintain a reproducible optical geometry when vials are cycled.

Benzene loss at room temperature (*ca.* 20°C) from the Waikato standard vial was measured over a 15-week period at 0.14 mg per day. Measurement of benzene loss from the Waikato vials undertaken by the Queen's University of Belfast Laboratory recorded a similar loss of 0.12 mg per day. By lapping (polishing) the stainless steel stopper, the Belfast lab reduced benzene loss more than five-fold, reducing it to 0.02 mg per day at ambient temperatures (McCormac, personal communication 1992). Although evaporative loss in a cooled counting environment is significantly lower than the values given above, it can be important where samples are counted over long periods of time (*e.g.*, standards counted over many weeks). This technique of lapping the stoppers has now been adopted for the Waikato vials.

Figure 2 shows the chemical susceptibility of various O-rings to benzene. The O-rings were immersed in benzene for 15 days, and changes in OD and weight recorded. O-rings composed of black chemraz are the most suitable, being virtually unaffected by immersion in benzene, but they are very expensive (~$35.00 US each). Other O-rings from different manufacturers are presently being tested.

Waikato 0.3-ml Minivial

Small-sample LS spectrometry is now practiced in many laboratories for samples not requiring the higher precision obtainable by accelerator mass spectrometry (AMS). Hogg (1992) recommended minivials for undersized samples, avoiding potential errors associated with high gas dilution effects,

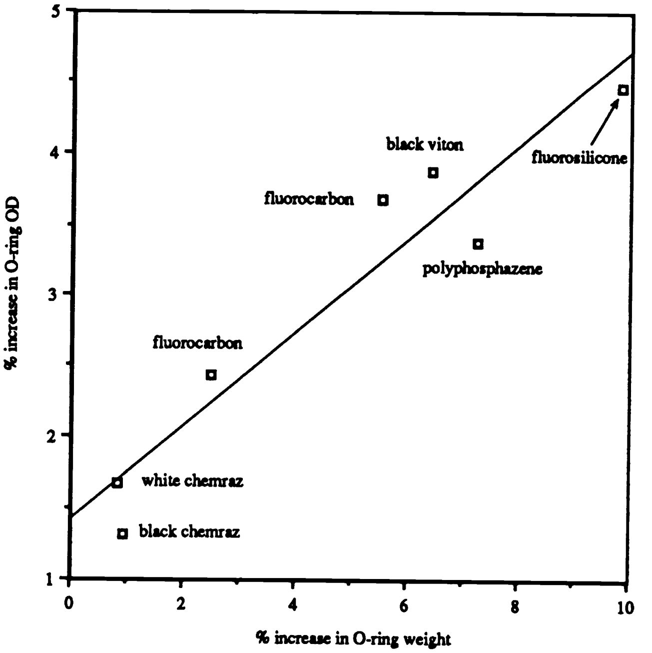

Fig. 2. Chemical susceptibility of O-rings of various compositions to benzene. All O-rings shown except black Viton, are manufactured by Greene, Tweed & Co., Kulpsville, Pennsylvania USA.

such as vacuum line memory or dilution gas activity. Polach *et al.* (1988) and Kaihola, Kojola and Heinonen (1992) described experimental 0.3-ml copper/Teflon vials (Wallac), with a theoretical sample-size limitation of 100 mg C. Clear square quartz minivials have been used successfully and are available commercially (*e.g.*, Devine & Haas 1987). However, both of the vials described above are susceptible to benzene loss.

The Waikato 0.3-ml minivial (Fig. 3), as in the Waikato standard 3-ml vial, has an SS stopper, synthetic silica cylindrical cell and Delrin holder. The cylindrical cell has an OD of 8 mm, height of 33 mm and capacity of ~0.4 ml. Because of the narrow cell diameter, benzene loss is <0.02 mg

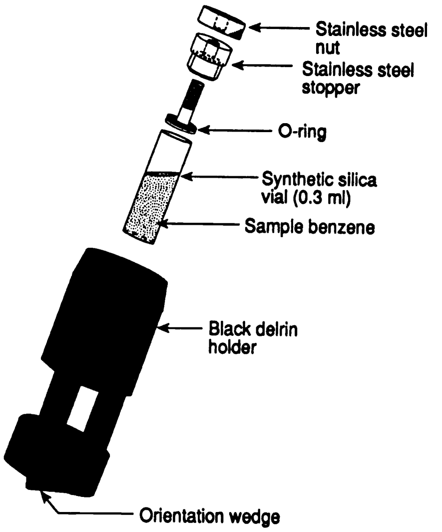

Fig. 3. Schematic diagram of the Waikato 0.3-ml synthetic silica minivial, including Delrin holder and stainless steel stopper

per day, and the SS stopper does not require lapping. A size-005 black Viton O-ring is used. The Delrin holder has similar external dimensions to the 3-ml vial holder, but has a thicker base and sides.

Waikato 10-ml Vial

As a result of the lower background and higher counting efficiency of modern LS spectrometers, ^{14}C dates have become more precise. Standard errors have been further reduced by counting larger samples, usually within either 20-ml low-K glass vials, or 15-ml Wallac copper/Teflon vials. The Waikato 10-ml vial was designed for high-precision applications, providing a vial that combines good physical properties with good counting characteristics.

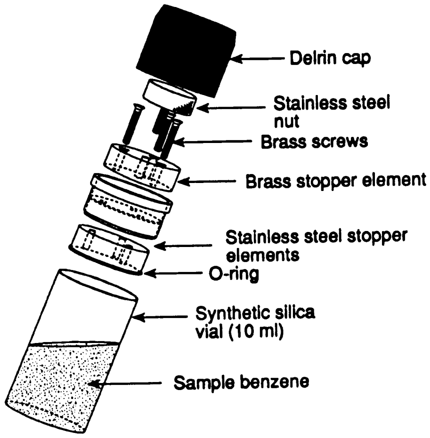

Fig. 4. Schematic diagram of the Waikato 10-ml synthetic silica vial, including stopper and Delrin cap

The vial (Fig. 4) is based upon the standard 20-ml LS counting vial, and consists of a flat-bottomed synthetic silica cylindrical cell, 50 mm high and 28 mm in OD, with an SS and brass stopper and Delrin cap. The stopper uses a size-018 O-ring, composed of black chemraz rather than black Viton, because of the larger volumes of benzene exposed to the O-ring. The 10-ml vial stopper does not have the same design as the 0.3- or 3-ml stoppers, because of the much larger vial internal diameter (ID) (*cf.* ID of 6 mm, 14 mm and 25 mm for the 0.3-, 3-and 10-ml vials, respectively). A brass stopper element is housed within an upper SS element and is screwed firmly to a lower SS element. The SS nut is threaded through the brass element and tightens against the upper SS element. When tightened, the lower SS element is drawn up, thereby compressing the O-ring. The entire stopper assembly is shielded from the PMTs by a Delrin cap.

RESULTS AND DISCUSSION

Table 1 summarizes typical counting performance (*i.e.*, count rate of the modern ^{14}C reference standard (N_0), and background (B)) for selected synthetic silica and Teflon in 0.3-ml minivials, 3-ml standard vials and 10-ml vials in the Wallac Quantulus. The data in Table 1 derive from a wide window (generally 100–550 keV) from typical background and modern count rates in several identical counters. It does not indicate the maximum performance data for either Teflon or silica. The scintillator used for both silica and Teflon is butyl-PBD, at a concentration of 15 g liter^{-1}. High coincidence bias is selected for all measurements. Figures 5, 6 and 7 summarize results for the silica vials. In Figure 5, the modern dating standard count rate (N_0) is plotted against factor of merit (fM) for various sample sizes. Additional data are provided for 0.35 g, 0.75 g and 4.5 g benzene (all in synthetic silica vials). In Figure 6, the magnitude of the standard error (1 σ) is

TABLE 1. Performance Data for Silica and Teflon Vials for 0.3-, 3- and 10-ml Vials in a Wallac Quantulus Spectrometer

Vial type	Vial holder	Vial* vol. (ml)	B** (cpm)	N_0† (cpm)	^{14}C efficiency (%)	fM‡	FM§	tmax¶ (yr)	tmin# (yr)
Teflon‖	Delrin	0.3	0.04	2.71	82.3	13.2	161,210	44,600	127
Silica	Delrin	0.3	0.04	2.47	74.8	12.5	143,350	44,100	133
Teflon	None	3	0.29	27.97	84.8	51.7	24,530	55,500	39
Silica	Delrin	3	0.25	25.66	77.8	51.4	24,290	55,500	41
Teflon	None	10	0.85	103.22	82.5	112.0	8000	61,700	20
Silica	None	10	1.03	108.09	86.4	106.7	7260	61,300	20

*Benzene weights used, for 0.3 ml = 0.2637 g; 3 ml = 2.637 g; 10 ml = 10.0 g
**B = background
†N_0 = derived net cpm for ^{14}C reference standard, 0.95 oxalic acid
‡fM = factor of merit (N_0/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
‖Wallac experimental vial, supported by a Delrin holder with aluminized reflectors having no orientation wedge

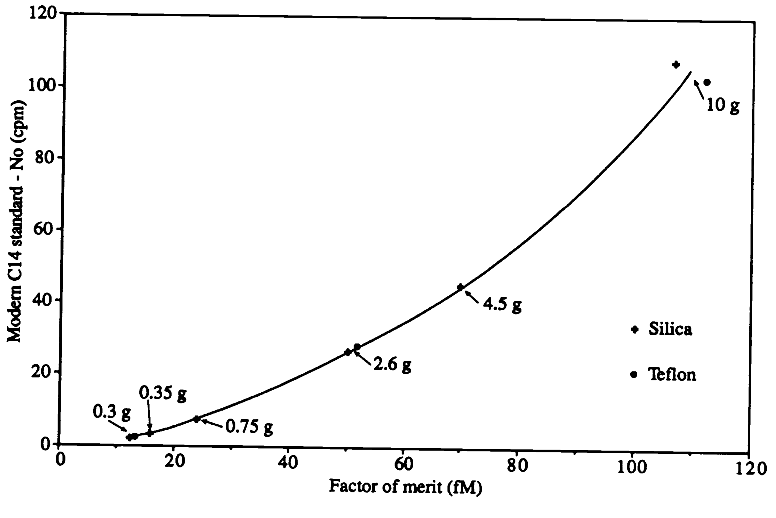

Fig. 5. Summary of the performance data for silica and Teflon vials containing varying amounts of benzene. The higher the value of N_0 or fM, the higher the precision of a date.

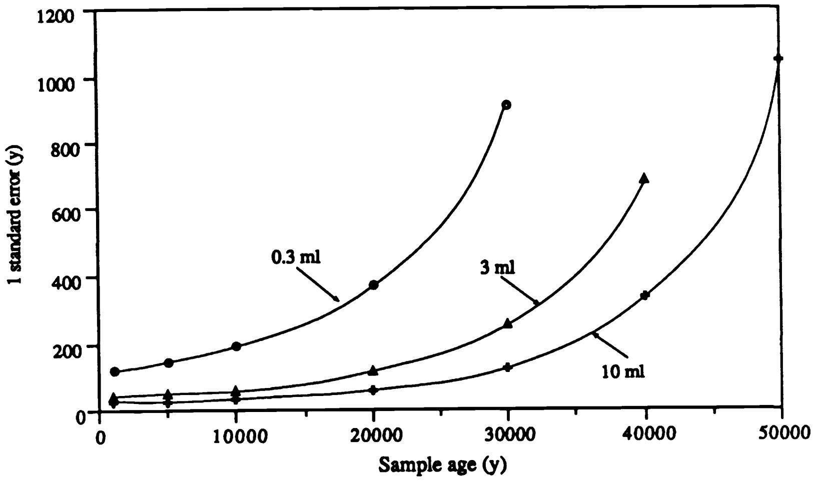

Fig. 6. The standard error (± 1 σ) for various ages for each of the three vials

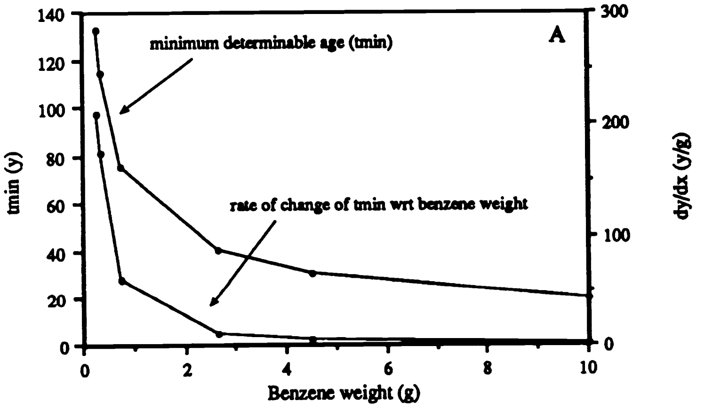

Fig. 7A. Relation between tmin and benzene weight, and rate of change of tmin

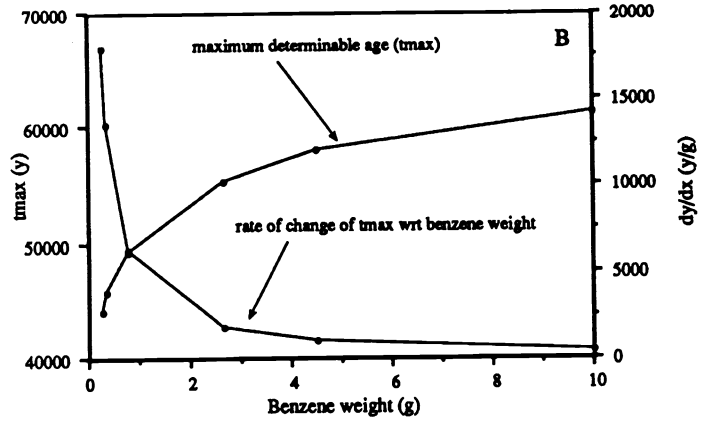

Fig. 7B. Relation between tmax and benzene weight, and rate of change of tmax calculated for various ages for each of the three vials. In Figure 7, tmax and tmin, and the rates of change of these parameters are plotted against benzene weight.

CONCLUSION

The fM and tmax and tmin columns in Table 1 and Figure 5 demonstrate that Teflon and silica vials have equal merit for ^{14}C dating for all three Waikato LS vials. Figure 5 also confirms the fact that counting performance (precision) improves as sample size (sample benzene weight) increases.

When the 0.3-ml and 10-ml data are compared in Table 1, it is apparent that the ~38-fold increase in sample size increases tmax by only *ca.* 17 ka, and reduces tmin only ~6-fold. However, standard errors as high as ± 130 yr at modern ages are unacceptable, and errors as low as ± 20 yr at modern are unnecessary for most ^{14}C determinations. The plots of tmax and tmin against sample size (Fig. 7A, B) show a very rapid improvement in these parameters for low benzene weights, with a much reduced change as the weights become larger. The rates of change of these plots show the 3-ml volume (~2.6 g benzene) represent an optimum point on the curves, where an increase in sample size has a rapidly reducing influence on the precision of a date. The 3-ml volume is characterized by a tmax of *ca.* 55 ka and a tmin of *ca.* 40 yr. These performance limits are acceptable for most samples submitted to laboratories involved in multi-user and multi-project ^{14}C dating.

Although minivial standard errors may be too high for most studies of very young material (*e.g.*, <1000 yr), Figure 6 shows standard errors to be <200 yr at 10 ka and <400 yr at 20 ka. As Hogg (1992) demonstrated, 0.3-ml minivials can provide accurate results with acceptable precision for many applications, for samples containing as little as 120 mg of carbon. For unusually high-precision work at better than ± 0.5% pMC, or for very old samples, I recommend the 10-ml vial. Standard errors of *ca.* 20 yr can be achieved for young samples (Table 1, Fig. 6), and higher precision is also achievable for very old samples (*e.g.*, 1040 yr at 50 ka).

The synthetic silica 0.3-ml minivials and 3-ml standard vials, complete with stoppers and holders, were manufactured at the University of Waikato in New Zealand, and will become available commercially.

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