ASSESSMENT OF 0.3-ML MINIVIALS FOR RADIOCARBON DATING BY LIQUID SCINTILLATION COUNTING OF BENZENE

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ABSTRACT. I have made an evaluation of 0.3-ml minivials for ^{14}C dating of small samples by liquid scintillation counting of benzene. A calibrated wood standard was diluted by varying amounts of ancient CO_2, with synthesized benzene counted in both conventional 3.0-ml vials and 0.3-ml minivials in a 1220 Quantulus. The accuracy and precision of results are compared for samples ranging in weight from 50 to 240 mg of carbon. I examined two significant potential problems associated with handling small samples, namely, memory effects within the vacuum system, and signal within the dilution gas. Although accurate radiocarbon dates can be obtained using either standard vials or minivials, minivials are more suitable for dating small samples because they are less influenced by these sources of error.

INTRODUCTION

The best modern low-level liquid scintillation (LS) spectrometers have ^{14}C counting efficiencies exceeding 80%, and ultra-low backgrounds as little as 0.8% of the ^{14}C reference signal (*e.g.*, Polach *et al*. 1988a; Hogg *et al*. 1991). The potential for small-sample radiocarbon dating using LS spectroscopy is one application of these reduced background levels (*e.g.*, Polach *et al*. 1988b).

The LS method generally utilizes 2.4–6 g C in 3.0- or 7.0-ml counting vials (Polach *et al*. 1988b). In small-sample dating, where less carbon is available, many laboratories have traditionally diluted samples with either ancient CO_2 or benzene. More recently, however, minivials of 0.3-ml volume have been developed (Devine & Haas 1987; Polach *et al*. 1988b), with superior counting characteristics for sample sizes <240 mg C. Although published modern and background count rates have enabled calculation of the precision to be expected from minivials (*e.g.*, Polach *et al*. 1988b), no attempt has been made to determine their accuracy. Such an attempt should proceed beyond vial parameters alone, to embrace total laboratory procedures.

I show here tests on 0.3-ml minivials, by analyzing the accuracy and precision of dates obtained from a calibrated wood standard, varying in size from 50 to 240 mg C, in both 0.3-ml minivials and traditional 3.0-ml counting vials, and also highlight two potential sources of error in handling very small samples.

EXPERIMENTAL

I used a calibrated wood standard (Glasgow wood – 2185 BP), supplied by the Glasgow University intercalibration project in this study (Aitchison *et al*. 1990). The absolute date of the sample was determined by the Belfast dendrochronological laboratory at 241–260 BC (Scott *et al*. 1990). This corresponds to a radiocarbon age of 2220–2160 cal BP, using the calibration data of Pearson *et al*. (1986). A nominal ^{14}C age of 2185 BP is shown in Figures 1 and 2.

I made measurements in a Wallac 1220 Quantulus spectrometer, using Wallac 3.0-ml teflon-copper vials and experimental 0.3-ml teflon minivials, also made by Wallac (Polach *et al*. 1988b). ^{14}C ages are calculated for three sample weights (50, 120 and 240 mg C) in each vial, with undersized samples diluted with ancient CO_2. The dilution gas is high-purity CO_2 stripped from natural gas, derived from the Kapuni Gas Field in New Zealand.
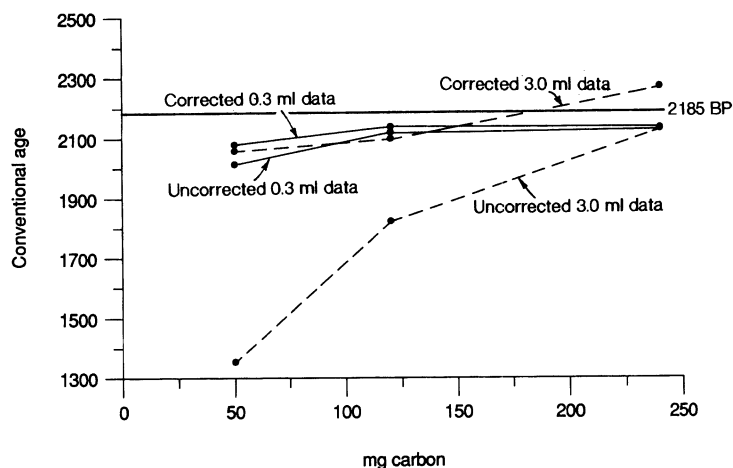
Fig. 1. Initial and corrected ^{14}C ages of the Glasgow wood standard for 50, 120, and 240 mg C in 3.0- and 0.3-ml vials. The horizontal line represents the nominal age for the standard (2185 BP).
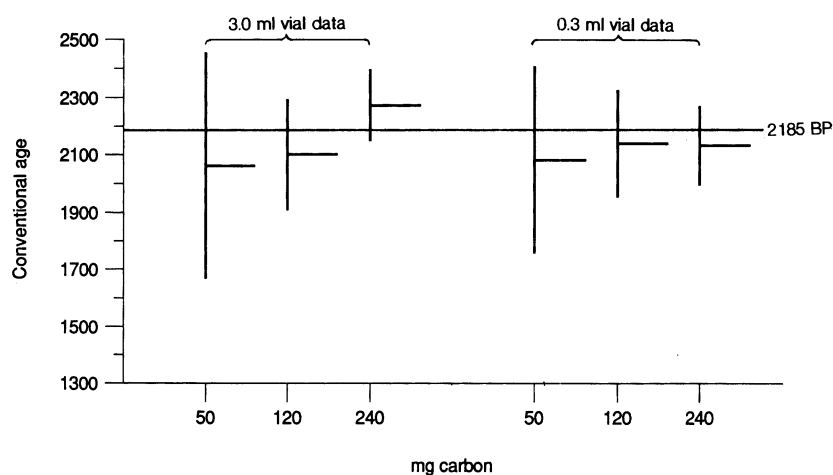

Fig. 2. Corrected conventional ages of the Glasgow wood standard (2185 BP – horizontal line) for 50, 120, and 240 mg C in both 3.0- and 0.3-ml vials. The error bars denote 1 σ errors.

The 3.0-ml vials were standardized for 3.0 ml of benzene (2.637 g benzene), using analytical-grade reagent benzene[1] and the modern secondary reference standard, ANU sucrose (Currie & Polach 1980). Similarly, the 0.3-ml vials were standardized for 0.3 ml of benzene (0.2637 g benzene) with the same standard materials. All samples were analyzed for 3000 min, with standard errors based upon 3000-min background and reference counting times.

The vacuum lines required for the conversion of CO_2 to benzene were prepared for low-activity measurements by processing a train of ancient samples in a specific order designed to eliminate, largely, memory effects from previous samples. The order of analysis was: ancient swamp kauri,

[1]In this paper, analytical-grade reagent (AR) benzene, used directly in the counting vials to establish background levels, is distinguished from synthesized (syn) benzene, which is generated in the laboratory by combusting AR benzene.

synthesized benzene 1, synthesized benzene 2, a background oxalic acid standard containing no ^{14}C, marble and lastly, dilution gas.

RESULTS AND DISCUSSION

Table 1 shows ^{14}C age determinations for 50, 120 and 240 mg C for both 3.0- and 0.3-ml vials. The initial results obtained for the 3.0-ml vials showed ages up to two standard deviations too young.

TABLE 1. Conventional ages of the Glasgow calibrated wood sample (2185 BP) for various sample sizes in traditional 3.0- and 0.3-ml minivials. All measurements based upon 3000-min counting times for both sample and standards.

1 Vial size (ml)	2 Percent dilution gas	3 Sample size (mg C)	4 Initial uncorrected age (yr BP)	5* Background corrected age (yr BP)	6** Dilution gas corrected age (yr BP)	7 Final corrected age (yr BP)
3.0	90	240	2135 ± 117	2177 ± 118	2229 ± 121	2272 ± 122
	95	120	1824 ± 175	1907 ± 179	2015 ± 186	2100 ± 189
	98	50	1354 ± 333	1559 ± 347	1841 ± 375	2060 ± 390
0.3	0	240	2131 ± 131	2133 ± 131	2131 ± 134	2133 ± 134
	50	120	2121 ± 172	2128 ± 174	2132 ± 182	2139 ± 183
	80	50	2014 ± 276	2035 ± 282	2060 ± 316	2081 ± 322

*Background correction based upon syn benzene activity of $4.12 \times 10^{-3} \pm 8.62 \times 10^{-4}$ cpm
**Dilution-gas correction based upon dilution-gas activity of $9.70 \times 10^{-3} \pm 2.46 \times 10^{-3}$ cpm

Sources of Error

Initial uncorrected ^{14}C ages (for the 3.0-ml vials in particular, Table 1, Column 4), show errors that clearly increase with the degree of dilution. Two factors are responsible for this – memory effects in the vacuum system and a small signal in the dilution gas.

Memory Effects. Memory effects in the vacuum systems provide a potential source of error. This was quantified by combusting AR benzene in a gas bubbler, and converting the CO_2 back to benzene in the normal manner. The measured activity for the syn benzene is *ca.* 0.04 pMC (Table 1, *). This effect artificially elevates sample activity, and the error is magnified in proportion to the degree of dilution. The initial ages for memory effect are shown in Table 1, Column 5 ("Background corrected age").

Dilution Gas. Analysis of the Kapuni dilution CO_2 revealed a significant source of activity, amounting to *ca.* 0.1 pMC (Table 1, **), possibly the result of contamination from modern CO_2 during separation. This activity also artificially elevates sample activity. The effect of this error is seen in Table 1, Column 6, which shows initial ages corrected for the dilution gas activity ("Dilution gas corrected age").

When the proportion of dilution gas in any sample exceeds *ca.* 90%, the sources of error described above result in a significant underestimation of age. Although 0.3-ml minivials are subject to the same sources of error as their 3.0-ml counterparts, the lower proportion of dilution gas (*e.g.,* 50% for 120 mg C in 0.3-ml minivials, *cf.* 95% for 3.0-ml vials) results in substantially lower errors.

Comparative Accuracy of 3.0- and 0.3-ml Vials

^{14}C ages corrected for both background and dilution gas effects are given in Table 1, Column 7 ("Final corrected age"), and compared with the "initial age" in Figure 1. Corrected conventional ages, including their standard errors, for both vials are presented in Figure 2.

All corrected results lie within 1 σ of the nominal age, thus validating the use of both standard 3.0-ml vials and minivials. However, the background memory and dilution-gas effects are far less significant in the minivials. If the contributions of these types of error to sample activities are not precisely known, or are variable (as may be the case with background memory effects), accurate dates are more likely to be achievable for small samples, using minivials.

Comparative Precision of 3.0- and 0.3-ml Vials

The magnitude of the standard errors for the Glasgow wood shows little variation between the two sets of measurements (Table 1 & Fig. 2). However, higher precision is achieved in the minivials with older samples, particularly when sample weights are <240 mg C (*e.g.*, for a sample containing 120 mg C, use of the minivials would result in a 15% lowering of 1 σ errors at 5 ka, and a 44% reduction at 20 ka).

Sample size limits of 100 mg C have been set for routine dating at the Australian National University (ANU) by Polach *et al.* (1988b). This produces an error of ± 200 yr at Modern, and an old age limit of 25 ka for 3000-min counting times. Standard errors for the three sample weights used in this study are plotted against sample age in Figure 3A, and are expressed as a percentage of the sample age in Figure 3B. The graph shows an optimum range, which will vary, depending upon application, for which minivials are most useful. Data for 50 mg C suggested limited application for routine dating purposes.

Small-sample LS spectrometry cannot seriously challenge accelerator mass spectrometry (AMS) dating in terms of precision for samples <240 mg C, but it can provide a cost-effective alternative for studies not requiring maximum precision (*cf.* the 240 mg C minivial sample error of ± 134 *vs. ca.* ± 70 for AMS (data from Scott *et al.* 1990) and *ca.* ± 40 for 2400 mg C (*i.e.*, 3 ml benzene) by a Quantulus spectrometer using 3000-min counting times).
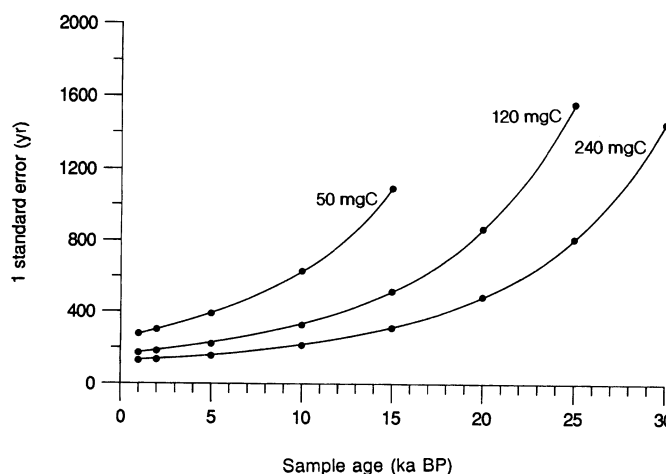

Fig. 3A. Plot of standard error against sample age for 0.3-ml vials
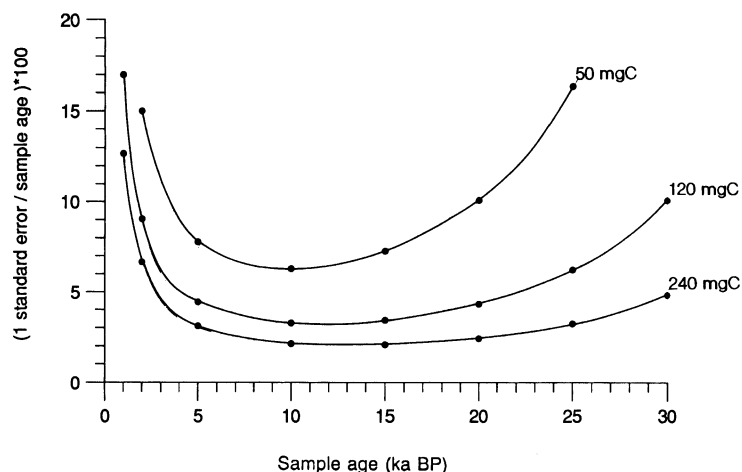
Fig. 3B. Standard error expressed as a percentage of sample age, *vs.* age for 0.3-ml vials

CONCLUSIONS

Although accurate radiocarbon dates can be obtained using either standard or minivials, minivials are more suitable for dating small samples because they are less influenced by background memory and dilution gas activity. Where small sample sizes require a high level of gas dilution (*i.e.*, where the proportion of dilution gas exceeds 90%), significant underestimation of age can be expected. As a result of this study, I recommend the use of minivials for very small-sample radiometry, as they eliminate the need for high dilution, and provide more accurate results without the necessity of applying extensive correction factors.

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