

Performance of Small Quartz Vials in a Low-Level, High Resolution Liquid Scintillation Spectrometer

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ABSTRACT

To meet an increased demand for the radiocarbon dating of small samples via liquid scintillation counting, Haas¹ introduced a technique which employed square, optically flat, quartz vials, with optimal UV transmission characteristics, as counting solution containers. Benzene samples as small as 0.3 mL (240 mg carbon) were dated using these vials. With proper installation and handling, these vials were shown to provide excellent long-term stability and precision.

We now report results on small quartz vials used in a modern low-level LS counter, the LKB-Wallac 1220 Quantulus, in the underground counting laboratory at the University of Arizona. Counting solutions comprise sample benzene diluted by the addition of "dead" benzene to a counting volume of 0.3 mL, with approximately 0.95 weight % butyl-PBD scintillant. A low-background copper vial holder was designed to accommodate the vials; constant orientation and alignment during loading is maintained by the heavy weight of the holder. Samples and standards are counted for 1200 min (60 × 20 min count periods). Background cpm, based on running average, is 0.0454 ± 0.006 cpm at a counter efficiency of 67.4%. Figure of merit $E^2/B = 100,130$; signal/noise (net modern standard B cpm/background cpm) = 53.5. Maximum determinable age, based on the Stuiver and Polach² criterion, is 39,200 years before present. These performance characteristics compare favorably with data presented for 0.3 mL Teflon vials³ and 3.0 mL glass vials.⁴

INTRODUCTION

In the past decade there has been an effort to push the limits of nuclear counting techniques. The introduction of improved liquid scintillation (LS) instruments⁵⁻¹¹ has reduced background noise dramatically. This decrease in noise enables the user to measure smaller samples with improved accuracy.

Small sample ¹⁴C dating techniques use miniature gas proportional counting systems to measurement as little as 5 mg of carbon.¹²⁻¹⁵ Haas¹ introduced the use of 0.3 mL quartz spectrophotometric vials for ¹⁴C LS counting. Devine¹⁶ reported a figure of merit value of 2477 when using these vials in an Intertech-

nique LS20 counter. The comparison of 0.3 ml quartz and teflon vials in various counters³ shows that small sample counting has benefited greatly from developments in LS technology.

This chapter presents the results of small sample (0.3 mL of benzene) counting using quartz spectrophotometric vials in an LKB-Wallac 1220 Quantulus LS counter at the University of Arizona, Radiocarbon Dating Lab.

METHODS

Two quartz spectrophotometric vials of 1 mm path length, like those used by Haas,¹ were used (Figure 1). A special vial holder was manufactured from low-background, low-oxygen copper (Figure 2) such that the maximum area of sample can be seen by the photomultiplier tubes, and the vial holder blocks photomultiplier crosstalk in the rest of the sample chamber. The diameter and height of this vial holder is identical to that of a 20 mL glass LS vial.

Benzene samples are synthesized from Oxalic Acid I (OXI) primary standard and from Mississippian limestone background material. Spectrophotometric benzene is also used as background. Samples to be dated, yielding

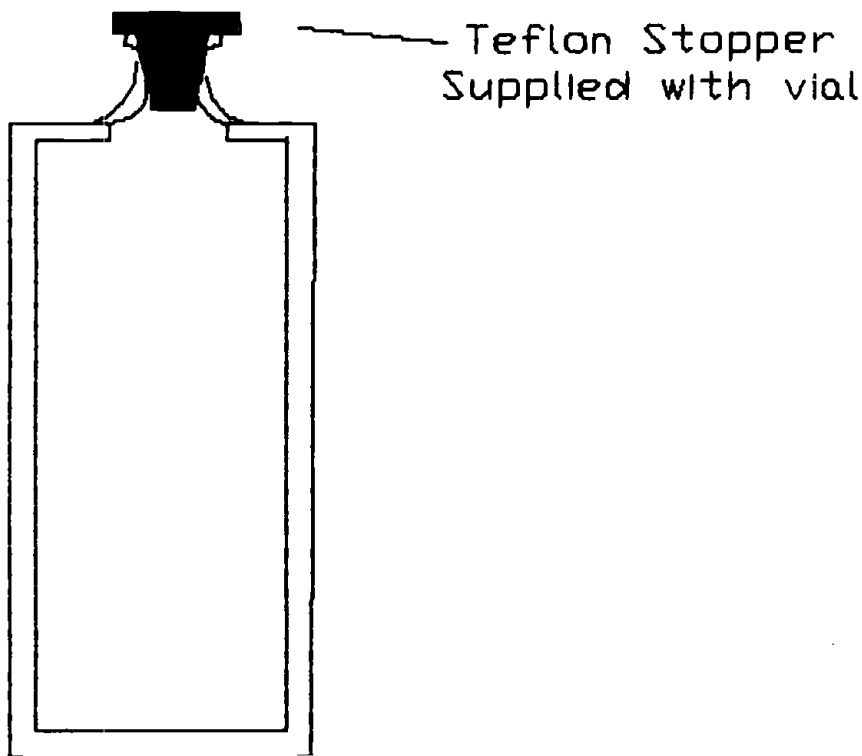


Figure 1. One millimeter pathlength quartz spectrophotometric vial.

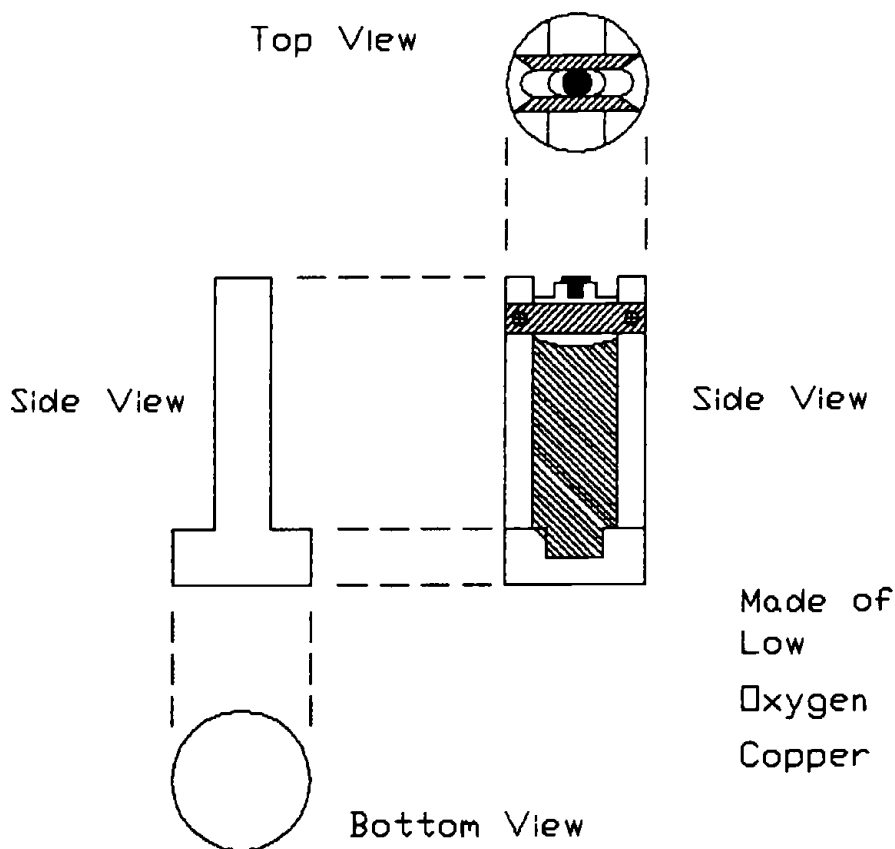
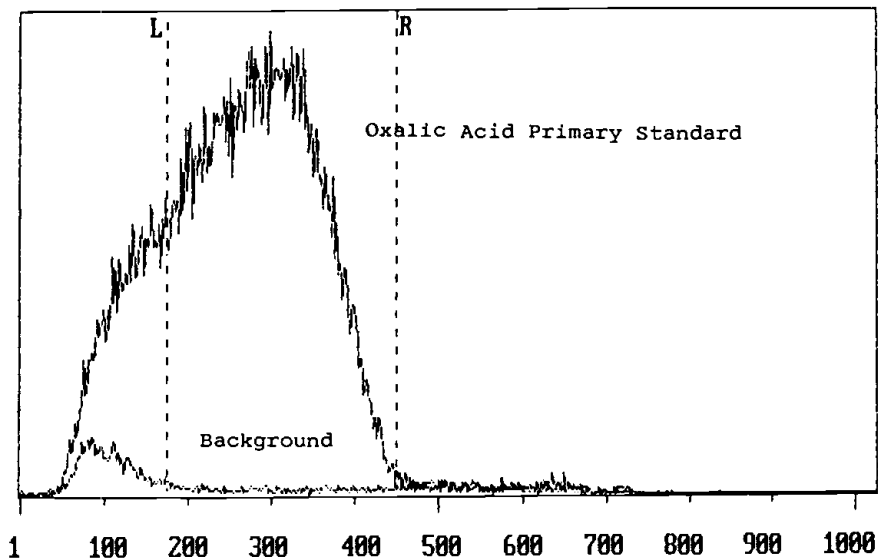


Figure 2. Low-background, low-oxygen copper vial holder.

benzene and weighing between 80 and 350 mg, are diluted to 350 mg carbon as benzene. Butyl-PBD, 0.95 wt-percent, is added to the benzene. The sample is introduced into the quartz vial via syringe, weighed, and placed into the LS counter, counted 60×20 min intervals, weighed after counting, and removed from the vial with a syringe. The quartz vials are flushed with spectrophotometric benzene repeatedly, then dried.

Time series data on OXI and background are compiled and averaged for age calculations.² Laboratory quality assurance—quality control (QA/QC) samples of well known age are analyzed as unknowns and used to check the validity of the time series data.

The energy spectrum of a synthesized OXI ^{14}C benzene and background (BKG) benzene samples for the LKB-Wallac 1220 Quantulus are shown in Figure 3. The energy windows for this study were set to maximize efficiency while avoiding the low energy background peak.



Channels 175 - 450 Efficiency = 61.22 %

Figure 3. Spectrum output from LKB-Wallac 1220 Quantulus of OXI primary ^{14}C standard and background benzene.

RESULTS AND DISCUSSION

Efficiency of photon measurement is related to the alignment of the quartz vial in the LS counter. The faces of the vial must be parallel to the faces of the photomultiplier tube. The vial holder was placed in the sample tray so that the optimal alignment occurs when the elevator lifts the sample into the chamber. The degree of rotation of the copper vial holder during elevator operation was determined by raising and lowering the vial holder. Some misalignment was found over 60 repeat events, but the weight of the copper vial holder produces no noticeable misalignment for one loading event. Therefore, no special alignment mechanism was manufactured, rather, samples are loaded into the chamber, and 60×20 min repeat counts are taken without unloading the sample vial.

Performance characteristics of the 0.3 mL quartz vials in the LKB-Wallac 1220 Quantulus counter (Table 1) compare favorably to those of the 0.3 mL Teflon vials,³ and to 3 mL glass vials.⁴ The difference in efficiency between the 0.3 mL Teflon vials and the 0.3 mL quartz vials is due to the exclusion of the low-energy end of the energy spectrum for this study. This area of low-energy background noise seen in the spectrum (Figure 3) is instrument dependent. A second LKB-Wallac 1220 Quantulus, which is next to this instrument, does not have this noise peak.⁴ Differences in photomultiplier tube composition most

Table 1. Small Sample ¹⁴C Results in 0.3 mL Quartz Vials, 0.3 mL Teflon Vials³ and 3.0 mL Glass Vials⁴

	0.3 mL Quartz Vial	0.3 mL Teflon Vial	3.0 mL Glass Vials
¹⁴ C efficiency (E)	67.4%	80.8%	74.0%
Average background (B)	0.04537 CPM	0.05	0.49
Average modern ^a signal (N ₀)	2.5286 CPM	2.66	27.5
Figure of merit E ² /B	100,130	130,570	11,090
Factor of merit (fM) N ₀ /B	11.9	11.9	39.1
S/N (modern/background)	53.46	53.2	55.7
Maximum determinable age	39,200 ^b	43,230 ^c	53,400
Error modern sample (yrs)	140	130	50

^aModern signal = 0.95 Oxalic Acid I primary standard.

^bSample Counted 1200 minutes.

^cSample Counted 3000 minutes.

likely leads to this variation among instruments (P. Makinen personal communication).

The distribution of measured events in each 20 min time period for OXI (Figure 4) and BKG (Figure 5) fit a Poisson distribution.

This technique was used for samples containing between 80 and 350 mg of carbon. The statistical uncertainty for samples less than 125 mg is usually

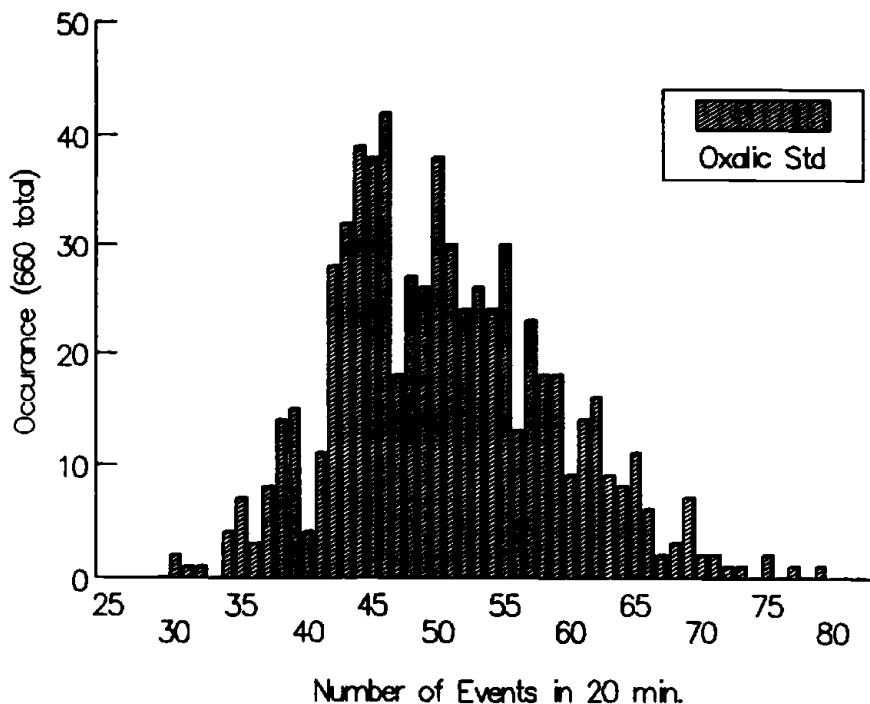


Figure 4. Distribution of the number of events measured during each 20 min time interval for OXI primary standard.

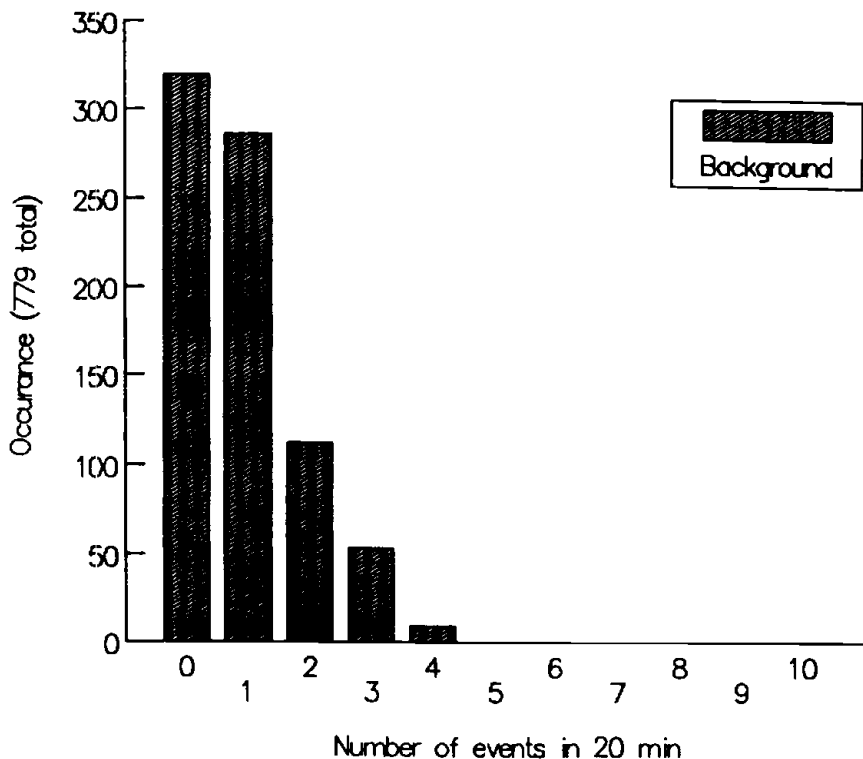


Figure 5. Distribution of the number of events measured during each 20 min time interval for BKG samples.

unacceptable (> 500 years), but for certain applications this information may be useful.

The results of three analyses of our in-lab QA/QC program, using the small quartz vials, is presented with the 1988 to 1989 results of the same sample for 3.0 mL vials from three different counters (Figure 6). These three samples were less than 350 mg carbon, thus they were diluted before measurement. At one standard deviation, the error bars overlap with the known age range of this sample.

The performance of small sample counting with the quartz vials makes LS counting an option for those who need radiocarbon dates on small samples but do not have access to, or funds for, AMS determinations. The disadvantage of small sample counting, compared to our routine determinations,⁴ is the loss of some accuracy and a reduction of the age limit which we can attain.

Techniques of low-level counting, including small sample techniques, need not be limited to ^{14}C dating. Application of low-level counting to environmental testing and biomedical research would allow a decrease in dosimetry while maintaining a high signal to noise ratio. This could reduce costs of materials and may ease some of the problems of radioactive waste disposal.

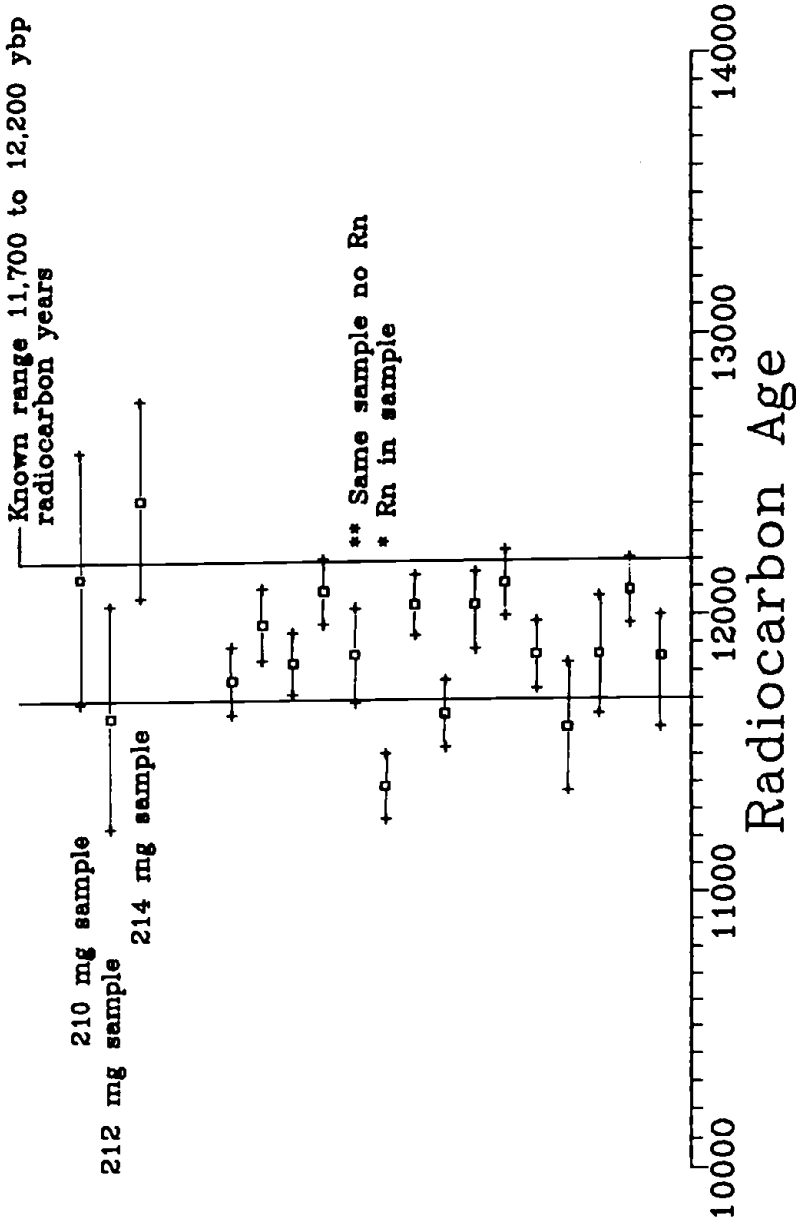


Figure 6. Small sample QA/QC results with the July 1988 to June 1989 QA/QC results of the Arizona Radiocarbon Laboratory.

CONCLUSION

The advent of new LS technology has allowed our lab to decrease the minimum sample size for ^{14}C dating to less than 300 mg of carbon. Special alignment mechanisms are not required to keep the vial in the optimal position, provided the vial is loaded only once into the chamber. The performance of the 0.3 mL quartz vials compares favorably with that of 0.3 mL Teflon vials and 3.0 mL glass vials. Signal and background events fit a Poisson distribution. Samples as small as 80 mg have been measured, but they lose accuracy. QA/QC samples determined with this method are within an acceptable range. Applications beyond ^{14}C dating of milligram size samples should be explored using techniques for small sample LS determinations.

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