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SMALL SAMPLE ^{14}C DATING BY LIQUID SCINTILLATION SPECTROMETRY

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ABSTRACT. Small sample ^{14}C dating is tested using conventional as well as high-resolution low-level liquid scintillation (LS) spectrometers. Contrasted are the results obtained dating ~25, 125 and 250mg of elemental carbon in standard size counting vials (3mL) and 0.3mL teflon and quartz vials. It is demonstrated that the improved performance of the 0.3mL counting vials enables just adequate resolution of 25mg and very good resolution of 100mg carbon samples both at *Modern* and *Old* age limits when the determination is made in a high-resolution low-level LS spectrometer.

INTRODUCTION

There is a real need to extend the use of existing nuclear counter technology (and their handling expertise) to small sample radiocarbon dating. The changing demands of research programs relating to environmental sciences as well as the more traditional applications to archaeology and geology make such a study pertinent.

Small sample ^{14}C radiometry has peaked with the advent of miniature gas proportional counters enabling resolution of signal from as little as 5mg of elemental carbon (Otlet, Huxtable & Sanderson, 1986).

Liquid scintillation (LS) spectrometry deals routinely with 2.4 to 6g of carbon in the traditionally 3 or 7mL counting vials. By diluting the sample during its gas or liquid preparation stages as little as 125mg of carbon can be counted, albeit with reduced effectiveness (Polach, 1987a, b).

This paper deals with the ^{14}C performance of a newly developed 0.3mL teflon LS counting vial (Wallac Oy) and tests its effectiveness in conventional as well as high-resolution low-level LS spectrometers (Kojola *et al*, 1984). The result for a 0.3mL quartz vial in a conventional LS counter (Devine & Haas, 1987) is also given.

METHOD AND RESULTS

Labeled benzene with ^{14}C activity of ~200% *Modern* (*M*) (*ie,* twice the activity of 0.95 Oxalic 1 acid (No)) and analytical reagent grade benzene, as background (B), were used in various LS counters and counting vials. An aliquot of the 200% *M* was weighed out on an analytical balance to 3 decimal places and diluted (as required) with background benzene to fill the test vials. Butyl-PBD scintillant was added as a dry powder to the benzene sample to give a concentration of 15g/L. The observed count rate (cpm) for the 200% *M* standard and background were determined in 3000-minute counting intervals. Calculated, for each filling, dilution, and vial sizes were: the derived 0.95 Oxalic 1 reference standard (No) net cpm, background (B) cpm, *factor of Merit* (No/SQRT(B)), *Old* age limit, and error at limit and at *Modern* in years BP. Calculations adhere to the Stuiver and Polach (1977) recommendations: age BP definition, excluding delta ^{13}C corrections but

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including dilution errors and the 2 sigma detection criterion based on a 3000-minute counting interval for the sample, standard, and background. This enables direct comparison of all results, which are given in Table 1.

The conventional LS counters are represented by the LKB-Wallac 1215 at the Radiocarbon Dating Research Laboratories of the Australian National University (ANU), Canberra, the Intertechnique LS20 and the LKB-Wallac 1215 'Kangaroo' at the Southern Methodist University (SMU), Dallas. SMU results (item 3, Table 1) are based on a 3mL teflon vial and item 4 on a 0.3mL quartz vial (Devine & Haas, 1987). These results will be compared to the teflon vials, 0.3 and 3mL, in similar age and technology LS counters at ANU (items 5 and 6). As the *factor of Merit* value of 1.5 and 1.7 indicates there is no practical difference in resolution of the ^{14}C signal between the quartz 0.3mL at SMU and the teflon 3mL with a diluted sample at ANU. However, the new teflon 0.3mL vial (item 6) gives significantly better resolution both in terms of error *Modern* and *Old* age limit. This is due to its high efficiency and low background.

The high resolution low-level LS spectrometer used is the LKB-Wallac 1220 Quantulus™ which today is acknowledged as the best LS counter for ^{14}C dating (Polach *et al,* 1987). The Quantulus™ is located in a surface laboratory at ANU which, due to its 1.5m of ordinary concrete shielding, maintains a high but constant environmental radiation flux. Compared are the performance of the 0.3 and 3mL teflon vials within the same counter (items 1 and 2, Table 1). The 0.03mL sample volume (~25mg carbon) diluted up to 3mL (item 1) yields senseless values both at *Modern* and *Old* age limits. However, the same sample size in a 0.3mL teflon vial (item 2)

TABLE 1

Small sample ^{14}C dating results diluted and undiluted in 3 and 0.3mL vials

Lab code	Vial size mL	Sample* mL	Eff %	B cpm	No** cpm	*fM* No/√B	Age Limit† (yr BP)	Error at *Modern*
1. ANU‡	3.0	0.3	76.8	0.21	2.53	5.5	37290	137
		0.15	76.8	0.21	1.26	2.8	31710	235
		0.03	76.8	0.21	0.25	0.6	18580	1020
2. ANU§	0.3	0.3	80.8	0.05	2.66	11.9	43230	130
		0.15	80.8	0.05	1.33	5.9	37660	185
		0.03	80.8	0.05	0.27	1.2	24690	530
3. SMU¶	3.0	0.3	76.2	1.81	2.51	1.9	28720	175
4. SMU#	0.3	0.3	71.4	1.99	2.35	1.7	27840	225
5. ANU@	3.0	0.3	76.5	3.02	2.52	1.5	26730	195
6. ANU°	0.3	0.3	82.9	1.00	2.73	2.7	31750	165

* Sample vol always made up, by dilution, to equal the vial size
** Derived net cpm for ^{14}C reference standard, 0.95 oxalic (No)
† With an error of ±4415 y
‡ Teflon/copper vial in LKB-Wallac Quantulus™
§ Teflon vial in special holder in LKB-Wallac Quantulus™
¶ LKB-Wallac 1215 'Kangaroo'
# Quartz vial in special holder in Intertechnique LS20
@Teflon/copper vial in LKB-Wallac 1215
° Teflon vial in special holder in LKB-Wallac 1215

yields much improved results the application of which is nevertheless limited due to the large determination error involved. The practical and generally accepted *Modern* error limit in an archaeologic and geochronologic context, in our view, is ±200 yr *M*. On the other hand, the *factor of Merit*—hence, the *OLD* age limit—is significantly extended by the usage of the 0.3mL teflon vial (item 2). The superior results obtained by the 0.3mL vials (teflon and quartz) prove their merit for practical applications to radiocarbon dating.

CONCLUSIONS

The old technology LS counters can effectively resolve 250mg carbon ^{14}C samples (0.3mL benzene) with acceptable but variable precision at the *Modern* and *Old* age limits. The new technology high resolution low-level LS spectrometers enable 150mg sample dating, with an error of ±200 yr *M*, using dilution techniques and down to ~25mg sample 'age evaluations' using the newly developed 0.3mL teflon vial. However, at extreme dilutions, the error of ±530 yr is not acceptable for routine dating. The practical limit, using the Quantulus™ and the 0.3mL teflon vial technology at ANU, would be 100mg sample carbon with an error of 2.5% *Modern* (±200 yr) and an *Old* age limit, 25,000 BP, in 3000-min counting times. The observed difference in the results of the 0.3mL teflon and quartz vials in old technology LS counters is probably dominated by the variation in the residual background of the counters, hence, is counter rather than vial related. Quartz, therefore, offers an attractive alternative to teflon for small vial design and 0.3mL benzene LS ^{14}C counting. ^{14}C age resolution by the Quantulus™ LS spectrometer of 25mg of elemental carbon in 3000 minutes is enabled by the excellent performance (high efficiency and relatively low background) of the new 0.3mL teflon vial and will open, in the view of the authors, a specialized and useful field of very small sample radiometry.

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