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# NEW POSSIBILITIES FOR $^{14}C$ MEASUREMENTS BY LIQUID SCINTILLATION COUNTING

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ABSTRACT. Results of intercomparison tests are presented on samples analyzed using gas and liquid scintillation techniques to study the capability of the LKB Quantulus to count an organic solution used for direct absorption of $CO_2$ and samples with low carbon content. Good agreement was obtained for small samples compared to standard sample size and for the direct absorption compared with the traditional techniques.

## INTRODUCTION

During the last decade, new technological contributions such as mini-gas counters and tandem accelerator mass spectrometers for microsamples have opened new horizons for the application of $^{14}C$ in different areas of research (Sayre *et al*, 1981; Polach *et al*, 1982; Otlet *et al,* 1983; Farwell *et al,* 1983; Donahue *et al,* 1983).

Furthermore, the technology related to $^{14}C$ counting by liquid scintillation counting has also been improved notably with the appearance of a new generation of liquid scintillation counters (LSC) (Kojola *et al,* 1985; Polach, 1987; Noakes & Valenta, 1989).

This paper presents data that has been gathered to study the capability of LSC, the Quantulus, to count organic solutions used for direct absorption of $CO_2$ and small samples using the benzene method.

## MATERIALS AND METHODS

Samples ranging from close to modern to ca 11,000 BP were used in this study. Most of the samples were run previously by gas counting as $CO_2$ and aliquots of the same sample gas were used for the tests by liquid scintillation counting.

A dilution line was used to add dead $CO_2$ to the carbon sample to complete the amount of $CO_2$ required for analyses (2.4g of carbon for benzene synthesis) or 2.21 of $CO_2$ at STP, that correspond to 1.2g of carbon for the absorption technique (Fig 1).

Samples ranging from 250–350mg of carbon were used to test the Quantulus for small samples using the benzene method. The organic cocktail used for the direct absorption of $CO_2$ was a mixture of 65% Carbosorb and 35% Permafluor (Canberra Packard). The basic equipment for the $CO_2$ absorption is presented in Figure 2. A detailed description of this method can be found in Qureshi *et al* (1989).

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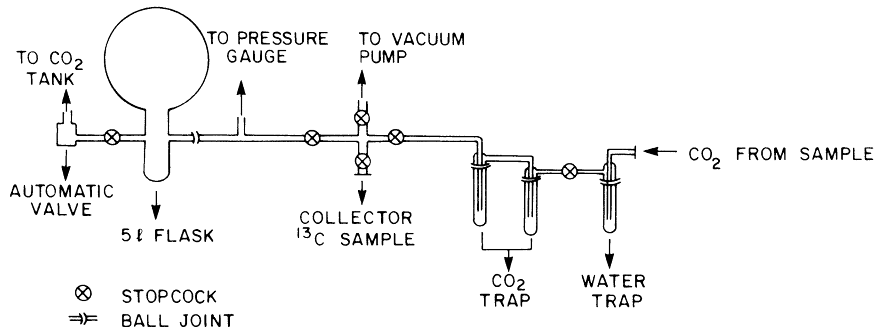


Fig 1. $CO_2$ dilution line

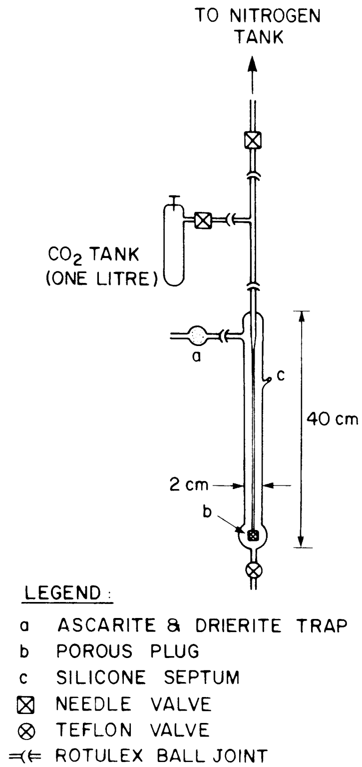


Fig 2. Preparation line for the absorption of $CO_2$ in an organic solution

The $^{14}C$ data is reported in years BP using 95%of the activity of oxalic acid in 1950 as a modern standard. ANU sucrose was also used as a secondary standard specifically for the direct absorption method.

## RESULTS AND DISCUSSION

The $^{14}C$ results for routine and small sample sizes are presented in Table 1. Good agreement is observed in the set of data generated by gas and LS counting. A general consensus about counting precision is that the gas counters are more precise than LS counters; however, with the appearance of the new low-level LS counters, their performance is similar to gas counters. This can also be seen in Table 1.

The data generated using small samples also agree well with data obtained analyzing routine size samples. The performance of the Quantulus for samples with different amounts of carbon is shown in Table 2. Samples with carbon content as low as 100mg can be counted with a detection limit of 22,600 yr for a counting time of 1000 min. It should be noted that these samples were counted in 22ml nylon vials. A better performance should be expected if the 3ml low background teflon vials available for the Quantulus are used.

TABLE 1

Intercomparison of $^{14}C$ results generated by LSC in the Quantulus, gas counting and AMS for standard and small-size samples

| Material* | Lab no. | Date | Sample size (g) |
|---|---|---|---|
| Wood | GSC**– 4155 | 2440± 50 | Ca 5 |
| | WAT† – 1592 | 2510± 70 | 2.0 –2.4 |
| | WAT – 1602 | 2340±150 | 0.25–0.35 |
| Organics | GSC – 4194 | 4410± 70 | Ca 3.5 |
| | WAT – 1594 | 4480± 80 | 2.0 –2.4 |
| | WAT – 1604 | 4190±170 | 0.25–0.35 |
| Shells | GSC – 4201 | 11,100± 90 | Ca 5 |
| | WAT – 1593 | 10,900±100 | 2.0 –2.4 |
| | WAT – 1609 | 11,100±400 | 0.25–0.35 |
| Wood | WAT – 1706 | 11,850±100 | 2.0 –2.4 |
| | WAT – 1919 | 11,700±400 | 0.25–0.35 |
| DOC, humics | TO‡ – 817 | 680± 60 | Ca 0.005 |
| | WAT – 1792 | 610±250 | 0.25–0.35 |

*The $CO_2$ that was prepared and counted previously in the GSC Laboratory by proportional gas counting was split for benzene synthesis

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TABLE 2

Quantulus performance for samples with different amounts of carbon, benzene and direct absorption techniques

| Vial | 1 Vol ml | 2 WTC mg | 3 B cpm | 4 E % | 5 FM Aon/$\sqrt{B}$ | Age limit (yr BP) Counting time 1 Kmin | 4 Kmin | Precision (%M) Counting time 1 Kmin | 4 Kmin |
|---|---|---|---|---|---|---|---|---|---|
| Nylon | 3 | 100 | 0.4 | 70 | 1.49 | 22,600 | 28,160 | 4.6 | 2.3 |
| 22ml benzene | | 200 | 0.4 | 70 | 2.97 | 28,140 | 33,700 | 3.3 | 1.6 |
| | | 400 | 0.4 | 70 | 5.96 | 33,730 | 39,300 | 2.3 | 1.2 |
| | | 800 | 0.4 | 70 | 11.92 | 39,300 | 44,870 | 1.6 | 0.8 |
| | | 1000 | 0.4 | 70 | 14.89 | 41,100 | 46,660 | 1.5 | 0.7 |
| | | 2430 | 0.4 | 70 | 36.20 | 48,200 | 53,800 | 0.9 | 0.5 |
| Glass | 20 | | | | | | | | |
| 22ml 65% Permafluor + 35% Carbosorb | | | | | | | | | |
| | | 460 | 1.4 | 60 | 3.19 | 28,700 | 34,300 | 2.3 | 1.2 |

1. Volume of sample
2. Weight of elemental carbon
3. Background cpm
4. Counting efficiency
5. $^{14}C$ dating "Factor of Merit" (Aon/$\sqrt{B}$), where Aon = 0.950 × ref std

Precision: defined as the minimum detectable percentile difference which can be distinguished from the Modern Reference Std at 1σ level. It is calculated using: 100 $\sqrt{(2/AoT)}$, where T is total counting time.

The intercomparison of $^{14}C$ results in samples run using the benzene method, gas counting and the $CO_2$ absorption technique (Table 3) show that the absorption technique has an acceptable accuracy when compared with traditional ones. The only difference is in the analytical error. It should be mentioned that the total counting time used for these samples was on the order of 1000 min. Longer counting times should lower the analytical errors of this method. The detection limit for 1000 min counting time is on the order of 29,000 yr. This technique is attractive because of the simplicity and low cost involved in the analysis (1/3 of the benzene synthesis price). This technique is in use routinely at Waterloo for hydrogeological investigations where high precision is not important, or in cases where fast output is necessary to program future sampling activities.

TABLE 3

Intercomparison of $^{14}C$ results in samples analyzed using benzene synthesis, gas counting and the $CO_2$ absorption technique

| Material | Lab no. | Date | Technique |
|---|---|---|---|
| Wood | WAT–1182 | 4050± 70 | Benzene |
| | WAT–1293 | 3900±350 | Carbosorb |
| Wood | WAT–1198 | 9870±140 | Benzene |
| | WAT–1294 | 10,650±620 | Carbosorb |
| Coral | WAT–1193 | 3780±120 | Benzene |
| | WAT–1330 | 3850±280 | Carbosorb |
| Coral | WAT–1192 | 6320±120 | Benzene |
| | WAT–1331 | 5910±350 | Carbosorb |
| Organics | GSC–4194 | 4410± 70 | $CO_2$ gas |
| | WAT–1471 | 4490±310 | Carbosorb |
| Wood | GSC–4352 | 5720± 70 | $CO_2$ gas |
| | WAT–1502 | 5820±370 | Carbosorb |
| Shells | GSC–4201 | 11,100± 90 | $CO_2$ gas |
| | WAT–1486 | 11,250±640 | Carbosorb |

## CONCLUSION

The Quantulus expands the possibilities of $^{14}C$ measurements by LS counting to samples as small as 100mg of carbon. It also makes possible the use of the direct $CO_2$ absorption technique in a wider age range than previously available, with an accuracy similar to the traditional techniques.

## ACKNOWLEDGMENTS

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