

LARGE-VOLUME LIQUID SCINTILLATION COUNTING OF CARBON-14

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ABSTRACT. Efforts have been undertaken to further improve the relatively simple technique of low-level liquid scintillation counting of ^{14}C . Two different approaches have been made. By synthesizing more benzene for ^{14}C measurement than usual (with up to 19.5g of carbon) an experimental detection limit of about 0.1 percent modern has been achieved (97.5% confidence level, 1000 min). Absorption of CO_2 with up to 5.3g of carbon in 160ml of an absorbent-scintillation solution and counting in a special measuring chamber resulted in an experimental detection limit of about 1 percent modern, with the sample preparation taking only 1 hour. The detection limits achieved by the two techniques correspond to ^{14}C ages of about 55,000 and 35,000 years BP, respectively.

INTRODUCTION

In competition with large and costly accelerators, less expensive conventional techniques of ^{14}C low-level measurement are expected to remain in use in the future if sufficient carbon is available for analysis. Attempts to further improve the relatively simple method of liquid scintillation counting of ^{14}C appear rewarding.

The ^{14}C content c of a sample is given by

$$c = \frac{n_1 - n_0}{n_{1,\text{st}} - n_0} \times 100 \% \text{ modern} \quad (1)$$

where n_1 represents the gross count rate of the sample, n_0 the blank count rate and $(n_{1,\text{st}} - n_0)$ the net count rate of the ^{14}C standard (100 % modern), *ie*, 95 percent of the count rate of the NBS oxalic acid referred to the year 1950. For a confidence level $P = 95$ percent (two-sided problem) or 97.5 percent (one-sided problem) the relative 1.96-fold standard deviation of c is

$$\frac{\sigma'(c)}{c} = \sqrt{\left(\frac{\sigma'(n_1)}{n_1 - n_0}\right)^2 + \left(\frac{n_1 - n_{1,\text{st}}}{(n_{1,\text{st}} - n_0)(n_1 - n_0)} \sigma'(n_0)\right)^2 + \left(\frac{\sigma'(n_{1,\text{st}})}{n_{1,\text{st}} - n_0}\right)^2} \quad (2)$$

where $\sigma'(n_1)$, $\sigma'(n_0)$ and $\sigma'(n_{1,\text{st}})$ are the 1.96-fold standard deviations of n_1 , n_0 and $n_{1,\text{st}}$, respectively. In the following, σ' is referred to as the two-fold standard deviation. The detection limit is defined as the smallest concentration c_{min} for which $\sigma'(c_{\text{min}}) = c_{\text{min}}$ with $P = 97.5$ percent. With this, one obtains

$$c_{\text{min}} \approx \frac{1}{n_{\text{st}}} \sqrt{\sigma'(n_1)^2 + \sigma'(n_0)^2} \approx \frac{1.96}{13.56 \eta x} \sqrt{\frac{2n_0}{\tau}} \quad (3)$$

where $n_{\text{st}} = n_{1,\text{st}} - n_0 = 13.56 \eta x$

η = counting efficiency

x = amount of carbon [g]

τ = counting time for sample, blank and ^{14}C standard [min]

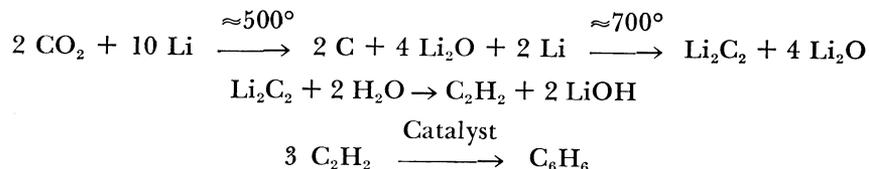
and if $\sigma'(n_1) \approx \sigma'(n_0) \approx 1.96 \sqrt{n_0/\tau}$.

Consequently, a decrease of $\sigma'(c)/c$ and c_{\min} might be obtained through an extension of the counting time τ , a lowering of the blank count rate n_0 , and an increase of the ^{14}C standard count rate n_{st} . However, for routine measurements, the counting time per sample is usually limited to the order of about 1000 min. The blank count rate can be reduced to a certain degree, in a simple manner, if the liquid scintillation counter can be placed in a sub-surface laboratory or in a room shielded with low-activity heavy concrete. The effect of an additional anticoincidence shielding will be discussed in the section on CO_2 absorption.

Since the counting efficiency cannot be increased substantially, attempts were made to lower $\sigma'(c)/c$ through the measurement of more carbon than is usual. This can be achieved by synthesizing more benzene than is commonly done or by absorbing larger than usual amounts of CO_2 in suitable scintillation solutions.

Benzene synthesis technique

Synthesis of benzene from CO_2 obtained through combustion or acid treatment of carbon-bearing samples and subsequent liquid scintillation counting is, besides gas counting, a widely used conventional method of low-level ^{14}C analysis (eg, Burleigh, Hewson, and Matthews, 1977). The synthesis follows the well-known reaction path:



A preparation line with two 1.9L reaction vessels is shown in figure 1, which is suitable for the preparation of two benzene samples per day with volumes of up to 8ml.

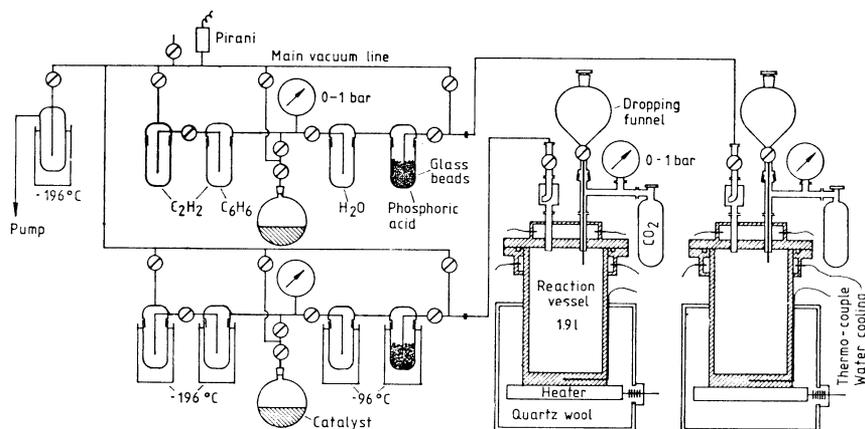


Fig 1. Preparation line for two samples of benzene per day, with volumes up to 8ml each.

Another line for the synthesis of 10 to 24ml of benzene has an additional freezing trap for water and a flask for the determination of the acetylene yield. To produce 24ml of benzene containing 19.5g of carbon, ≥ 1.7 moles of CO_2 are reacted in a stainless-steel reaction vessel (8L volume) with at least 65g of metallic lithium (≥ 10 percent excess) to form Li_2C_2 . After cooling of the reaction vessel to room temperature, acetylene is generated with 4L of "dead" water and catalytically transformed to benzene using 200 to 250g of KC-Perlkator D1 (Kalichemie AG, Hannover; comparable to type Durabead 1, Mobil Oil Corp, New York). Overall yields reach up to 94 percent.

Lithium (Metallgesellschaft AG, Frankfurt/Main) is used in the form of bars and stored under argon or vacuum. Before use, the bars are cleansed of traces of oil by rinsing in hexane. The catalyst is heated in air in a muffle furnace for at least 2 hours at 500°C . It is filled hot into a pyrex reaction flask and evacuated on the preparation line. Acetylene is admitted after the catalyst has cooled to less than 50°C .

Permafluor I scintillator (Packard Co) is added to the synthesized benzene in a ratio of 1:24 and liquid scintillation counting of ^{14}C is done in commercial nylon vials (Nuclear Chicago) at temperatures of 6° to 8°C . Each sample is counted at least 10 times for 100 min for about two to four weeks.

Characteristic data for benzene samples synthesized from tank CO_2 ¹ and fermentation CO_2 (normalized to the ^{14}C standard (100 percent modern)) are summarized in table 1. Different volumes of benzene were synthesized and, for each volume, several samples were prepared and counted in nylon vials (with different liquid scintillation counters of the type Mark II (Searle Co)). Besides the standard deviation due to counting statistics (σ_{cs}), the experimental standard deviation (σ_{exp}) which additionally includes variations due to sample preparation, counting geometry etc, is given in the table for a typical background and standard sample. The conventionally calculated values of σ_{exp} were multiplied by a factor t ($P = 95\%$), derived from Student's t distribution, to compensate in the case of small numbers of samples, for the decrease of the confidence limit, which is valid for the standard deviation in the case of great numbers of samples. With these values of σ' ($\sigma' = t \sigma_{\text{exp}}$), the mean values of $n_{1,\text{st}}$ and n_0 , and under the simplifying assumption² that $\sigma'(n_1) = 1.96 \sqrt{n_1/\tau}$, the relative two-fold standard deviation $\sigma'(c)/c$ is shown as a function of c in figure 2, calculated from equation 2 for a counting time of 1000 min for n_0 , $n_{1,\text{st}}$ and n_1 .

The counting efficiencies are close to 70 percent and are rather independent of the volume of benzene and vial type (data obtained on teflon vials are not reported in table 1). Blank count rates for samples in vials with 24ml and 2ml of benzene are about 5cpm and 2cpm, respectively. It may be noted that window settings different for small and large ben-

¹ These samples can be considered to be free of ^{14}C because background count rates were identical with those obtained from reagent-grade benzene.

² This leads to a somewhat lower detection limit than is given in table 1.

TABLE I

	Liquid scintillation counting										Gas counting	
	Benzene synthesis Nylon vials (25.5ml)					CO ₂ absorption PE vials (24ml)					Methane synthesis 2.6L counter	
Amount of carbon	[g]	1.6	3.2	6.4	8.1	19.5	0.7	3.0	5.3	2.6	3.9	
Volume of benzene	[ml]	2.0	4.0	8.0	10.0	24.0						
Volume of absorbent	[ml]			0.32	0.40	1.00	10	40	80			
Volume of scintillator	[ml]			1000	4000	2000	1000	1000	1000			
Measuring time	[min]											
Count rate in ¹⁴ C window:												
Blank, n ₀	[cpm]	2.18	2.64	2.80	3.06	5.16	12.83	24.2	22.42	2.85	2.95	
±σ(n ₀) _{cs}	[cpm]	0.05	0.05	0.05	0.03	0.05	0.11	0.16	0.14			
±σ(n ₀) _{exp}	[cpm]	0.11 (10)	0.07 (19)	0.06 (6)	0.05 (6)	0.07 (10)	0.17 (4)	0.24 (8)	0.20 (10)			
±t σ(n ₀) _{exp}	[cpm]	0.25	0.15	0.15	0.13	0.16	0.54	0.57	0.45			
Standard, n _{1, st}	[cpm]	17.45	34.24	64.9	77.30	194.73	20.77	54.55	72.95	26	39	
±σ(n _{1, st}) _{cs}	[cpm]	0.14	0.19	0.25	0.14	0.31	0.14	0.23	0.27			
±σ(n _{1, st}) _{exp}	[cpm]	0.25 (6)	0.21 (11)	0.43 (4)	0.35 (5)	0.55 (6)	0.14 (6)	0.25 (8)	0.34 (10)			
±t σ(n _{1, st}) _{exp}	[cpm]	0.64	0.47	1.37	0.97	1.41	0.36	0.59	0.77			
Counting efficiency	[%]	70	73	72	68	72	88	75	70	66	68	
Detection limit:												
C _{m.in, cs}	[% modern]	0.9	0.5	0.2	0.21	0.11	3.9	1.5	0.8	0.7	0.4	
C _{m.in, exp}	[% modern]	2.4	0.6	0.4	0.28	0.12	10	2.7	1.3			

Characteristic data of various measuring set-ups for low-level counting of ¹⁴C, placed in a room with 75cm thick walls of heavy concrete. The benzene samples were measured in two different liquid scintillation counters (type Mark II, Searle Co), the CO₂-absorption sample containing 0.7g C in a liquid scintillation counter of the type BF 5000 (Berthold, Wildbad), and the CO₂-absorption samples containing 3.0 and 5.3g C in a special measuring chamber connected to a BF 2240 electronic unit (Berthold, Wildbad).

n_{1, st} = gross count rate, normalized to a 100% modern ¹⁴C standard

σ_{cs} = standard deviation due to counting statistics (P = 68.3%)

σ_{exp} = experimental standard deviation calculated as usual from measurements on equal samples, the number of samples indicated in parentheses (P = 68.3%)

t = factor derived from Student's t distribution for P = 95%

C_{m.in, cs} = detection limit (P = 97.5%) due to counting statistics, applying a counting time of 1000min for each sample, blank and standard

C_{m.in, exp} = experimental detection limit (P = 97.5%) calculated from equation (3), assuming σ'(n₁) = σ'(n₀) = t σ(n₀)_{exp}.

zene samples, turned out to be optimum for ^{14}C counting. The lowest experimental detection limit is obtained for 24ml benzene samples, being close to 0.1 percent modern ($P = 97.5\%$, $\tau = 1000$ min) which corresponds to a ^{14}C age of about 55,000 years BP. For comparison, table 1 contains typical data for a 2.6L ^{14}C gas counter filled with synthesized methane. Table 1 and figure 2 show that, under our counting conditions, $\sigma'(c)/c$ and c_{\min} are nearly identical for gas counting and liquid scintillation counting of a sample containing about 3.2g of carbon. For much larger amounts of carbon than can be introduced in our gas counter, liquid scintillation counting becomes superior (however, see Geyh, 1972).

Sample vials: Using teflon vials manufactured by us, detection limits could be lowered only by 10 to 20 percent in comparison to those obtained with nylon vials. In addition, results were sensitive to variations in wall thickness of different teflon vials. Also, nylon vials that are commercially available are not always uniform and differences in blank count rates can only be reduced if vials are preselected for use, eg, on the basis

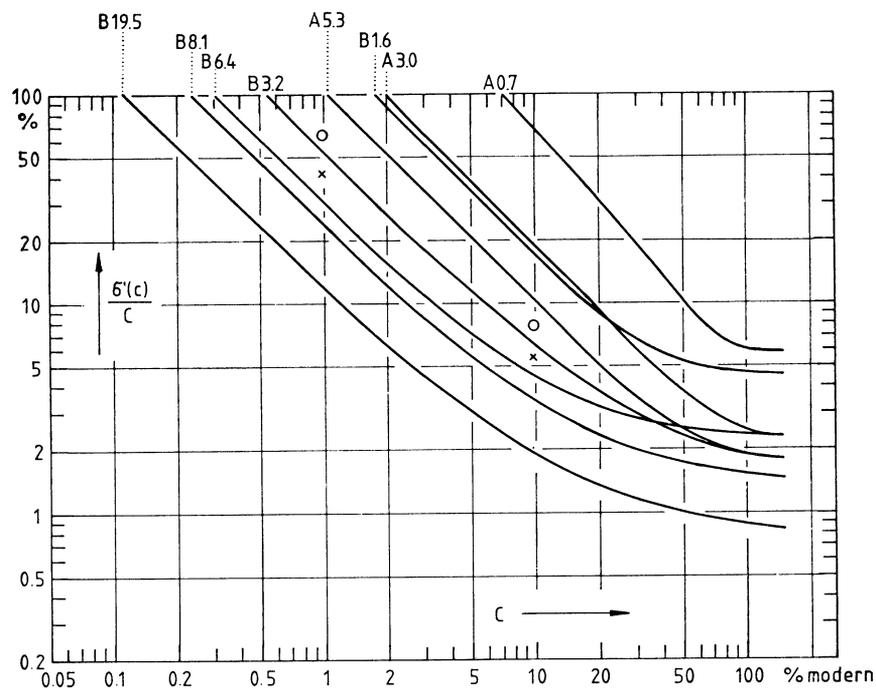


Fig 2. Relative two-fold experimental standard deviation $\sigma'(c)/c$ as a function of ^{14}C concentration c for liquid scintillation counting subsequent to benzene synthesis (B) and CO_2 absorption (A). The numbers behind A and B represent the amount of carbon (grams) measured.

The curves have been calculated from equation (2) with the values taken from table 1 and related to a measuring time of 1000min each for a sample, a ^{14}C standard and a blank.

For comparison, data for methane gas counting are indicated by "O" (2.6g C) and "x" (3.9g C).

The detection limit corresponds approximately to $\sigma'(c)/c = 100\%$.

of their weight. As can be seen from table 1, the test measurement on background samples with 2ml of benzene in 25.5ml nylon vials gave relatively large experimental standard deviations, which, perhaps, could be reduced with special vials of smaller volumes.

Radon: Contrary to general experience with small benzene samples, counting of freshly prepared 24ml benzene samples gave, in few cases, up to 5cpm in the energy range above the ^{14}C spectrum. This is due to the presence of ^{222}Rn , which at least partly, can originate from the catalyst. About 20 percent of the "overflow" count rate appears in the ^{14}C window. Such samples must be stored for several weeks as is frequently done for gas counting.

Long-time measurements: The application of Pearson's chi-square test to the measurement results suggests a total counting time of 1000min to be, in most cases, meaningful for blanks, whilst a shorter time could be appropriate for ^{14}C standards or samples with similar activity. In order to obtain information on the long-time stability under the most favored conditions, a blank of 10ml reagent-grade benzene was counted in a fixed position for 24,000 min. No significance difference between σ_{c} and σ_{exp} was observed. However, the practically meaningful measuring times seem to be essentially shorter. This is suggested by the result of applying the chi-square test to 2000 min counts of 10 synthesized blanks containing 24ml of benzene, and to 4000 min counts of 6 synthesized blanks containing 10ml of benzene. Following these and other experiences, we conclude that, for the limitation of the meaningful counting time, instrumental instabilities are less significant than reproducibility of sample preparation (depending, among other things, on the purity of the lithium), stability of the sample, variations in vial characteristics and difficult to recognize radon contents. However, the final determination of meaningful counting times requires further study, one reason being that these investigations are exceedingly time-consuming.

CO₂ absorption method

A significant simplification of sample preparation is possible if several grams of carbon are available and a somewhat lower precision and higher detection limit are sufficient than can be achieved on benzene samples. This might be the case, for example, with many hydrogeologic investigations.

A known preparation technique for liquid scintillation counting of ^{14}C -labelled compounds consists in binding combustion CO_2 by amines. The thus formed carbamates are mixed with a scintillator in commercial 24ml vials (eg, Rapkin and Reich, 1972). In order to obtain, on this basis, 160ml of a scintillation solution with up to 5.3g of sample carbon, a simple preparation line was constructed (fig 3). Following flushing with N_2 , a CO_2 absorbing solution (Luma-Sorb I, Lumac, or Carbosorb, Packard Co) and scintillator (Carbo-Luma, Lumac, or Permafluor V, Packard Co) are filled into the apparatus and mixed in a ratio of 1:1. The CO_2 generated from the sample as usual, is bubbled through the

solution and more than 99 percent is absorbed. Total preparation time is approximately one hour and analytical costs are about US \$3 per sample.

Liquid scintillation counter for large samples

For measurement of large samples of low-energy beta emitters, a special measuring chamber was constructed and connected to a conventional liquid scintillation counter. Following extensive tests, the construction shown in figure 4, with a sample volume of 160ml, was found optimum for ^{14}C measurements in several grams of carbon as well as for the determination of ^3H in water samples. Sample containers are made from cylindrical quartz tubing with end-windows of Herasil I (Heraeus, Hanau) and have an outside reflective coating of titanium dioxide (see also L'Orange, 1969). Shielding against radioactive environmental radiation is provided by layers of Pb, Hg, Cd and Cu with a total thickness of 11cm.

For counting, the sample container is positioned in the opened measuring chamber, the high-voltage at the photo-tubes being shut off. Following the closure of a shielding segment, light-tight shutters between sample and photo-tubes are lifted, the photo-tubes moved towards the sample container, and the high voltage is switched on. The samples are measured at a temperature of about 6-8°C for a few 100 to about 1000 min.

As can be seen from table 1 and figure 2, the experimental detection limit is 1 percent modern ($P = 97.5\%$, $\tau = 1000\text{min}$) for a sample con-

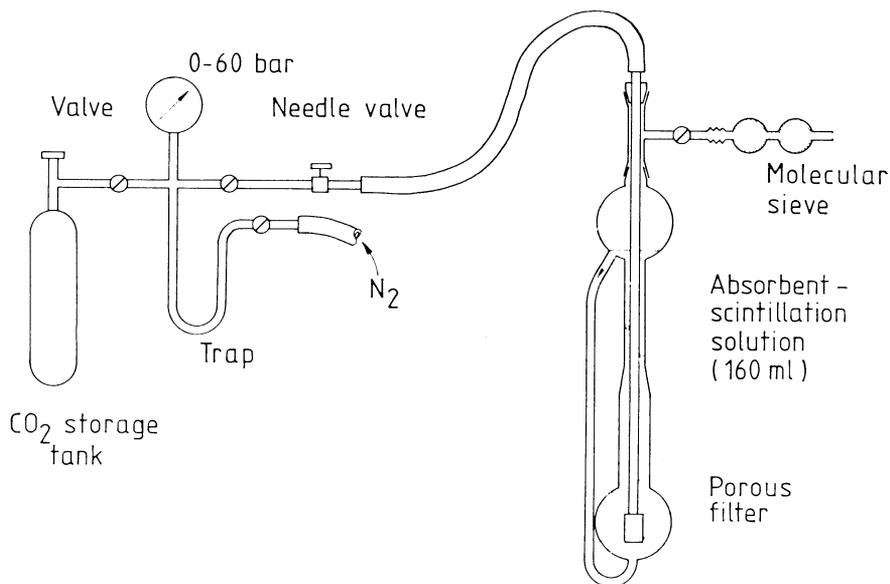


Fig 3. Set-up for the absorption of CO₂ in an absorbent-scintillation solution. The glass device containing the solution, can be cooled in a water bath during CO₂ absorption.

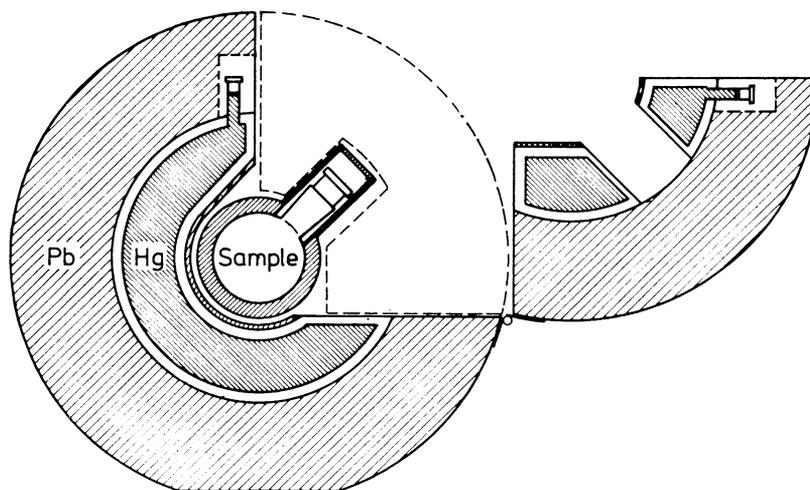
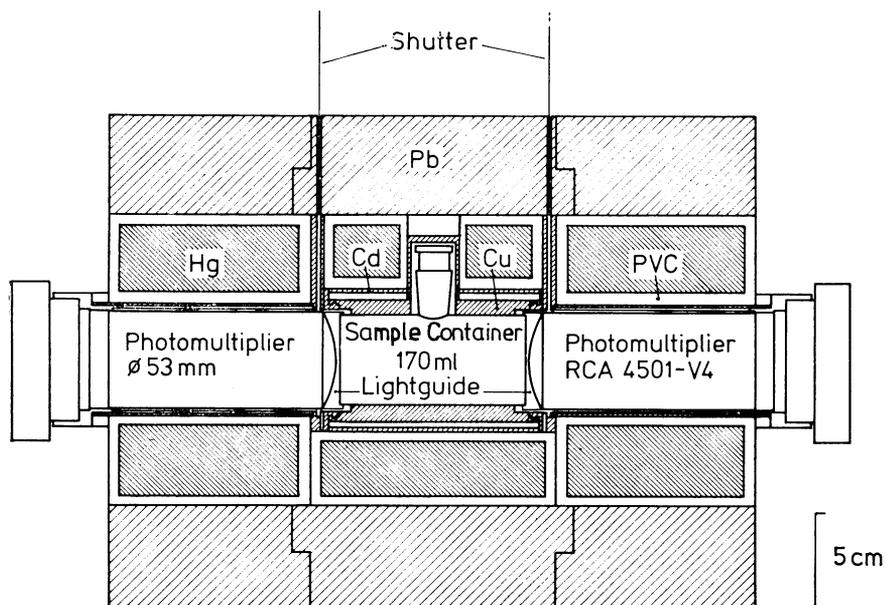


Fig 4. Measuring chamber for liquid scintillation counting of samples in a 170ml quartz cuvette. As shown in the cross-section at the bottom, a segment of the shield is opened to change the sample manually.

taining 5.3g of carbon. No drift of counting rates was noted during counting of a limited number of samples for 7000min. Nevertheless, the problem of long-time measurements requires further study, as in the case of benzene samples.

With the use of the special measuring chamber, very low detection limits³ can be expected for ¹⁴C if large amounts of carbon are available and if large volumes of benzene can be synthesized in a simple manner. Arslanov and others (1968) give some indication that this has already been attempted. It may be worth noting that the direct determination of ³H in 75ml of water mixed with 85ml of Instagel scintillator (Packard Co) gave an experimental detection limit of 4 TU⁴ ($P = 97.5\%$, $\tau = 1000\text{min}$) with a calibration factor of 9.2 TU/cpm and a blank count rate of 10.4cpm. This is comparable to the theoretical detection limit of about 5 TU derived for the only commercially available liquid scintillation counter for large volumes, manufactured by Aloka, Japan (Iwakura and others, 1979).

Anticoincidence arrangement

Four large-area counters of the flow-through type operated with methane were available for preliminary investigations with an anticoincidence shielding of the large-volume measuring chamber⁵. Two counters measured $70 \times 30 \times 3\text{cm}^3$ and the other two counters, $35 \times 30 \times 3\text{cm}^3$. Used for ¹⁴C blank counting were 150ml reagent-grade benzene mixed with 10ml of Permafluor I, whilst ³H blank counting was done on 75ml of tritium-free water mixed with 85ml of Instagel scintillator. The maximum reduction of blank count rates was 33 percent in the ¹⁴C window and 23 percent in the ³H window, with all four large-area counters positioned above the measuring chamber. With this arrangement whose geometry and response probability is not optimum, the detection limits for ¹⁴C can be reduced only by 20 percent if compared to measurements without anticoincidence shielding.

Crosstalk discrimination

Light flashes originating on the photocathode of one photo-tube and registered by the other represent the crosstalk fraction of the blank count rate. Experiments with the large-volume measuring chamber indicate that the fraction of the crosstalk in the blank count rate lies between 20 and 30 percent in the ¹⁴C window and by 10 percent in the ³H window. Liquid scintillation counter of the type Mark II (Searle Co) eliminate the crosstalk effect through a discriminator (Laney, 1971), thereby reducing the count rate of blanks in usual 25.5ml vials in the ¹⁴C window to less than half the value obtained without discriminator. No reduction is obtained when connecting the large-volume measuring chamber to

³The following data were obtained from a measurement of reagent-grade benzene and ¹⁴C-labelled benzene in our large-volume chamber, containing an equivalent of 130g C: $n_o = 25\text{cpm}$, $\eta = 86\%$, $n_{st} = 1516\text{cpm}/100\%$ modern, $c_{min,es} (97.5\%, 1000\text{min}) = 0.03\%$ modern.

⁴1 TU = 0.119 Bq ³H/1 liter of water = 3.21 pCi ³H/1 liter of water.

⁵The support of Laboratorium Prof Dr Berthold, Wildbad, is appreciated.

electronics with, instead of without, a crosstalk discriminator. Presumably, the light output of crosstalk events is diminished by multiple reflection at the wall of the extended sample container to such an extent that pulse shape discrimination is no more effective.

CONCLUSION

Figure 2 and table 1 allow comparison of reproducibilities and detection limits of different ^{14}C analysis techniques, including those that are not routinely used in our laboratory. When comparing, it must be remembered that the data and curves presented depend on the special measuring conditions and partly on the different numbers of samples of the type that were measured. Nevertheless, the following conclusions can be drawn in addition to those already mentioned:

— The accuracy of ^{14}C analyses carried out by simple CO_2 absorption and large-volume liquid scintillation counting might be adequate to the requirements of many hydrogeologic investigations. According to preliminary measurements, attempts to also improve the measurement of small carbon amounts in usual small-volume liquid scintillation counters seem worthwhile.

— The relatively low reproducibility of measuring results obtained on very small benzene samples can possibly be improved when suitable CO_2 is admixed prior to sample preparation and/or by counting in self-made vials with small sample volumes.

— Further work is required to examine the possibility of further decreasing the experimental detection limit below 0.1 percent modern by extension of counting time, in particular for 24ml benzene samples.

The efforts that would have to be spent on preparing benzene from samples, for liquid scintillation counting in a large-volume chamber, have to be compared with the work required for enrichment of ^{14}C prior to gas counting.

ACKNOWLEDGMENTS

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DISCUSSION

Oeschger: Your work is very impressive. Still, I would like to draw your attention to the considerable additional background reduction possible by placing such equipment into a laboratory which is say 30m underground.

Rauert: We have thought about such a possibility, and we estimate that the detection limit could be lowered roughly by half by placing our large-volume counter, eg, in your Bern underground laboratory.

Harkness: Over what period can benzene be stored in the nylon vials without incurring measurable loss?

Rauert: Our benzene can be contained in nylon vials over a period of 4 weeks or even longer, at a temperature of about 6°C.

Harkness: I would suggest that the lower background of nylon relative to that of impervious low potassium glass vials is marginal.

Radnell: Is there any special sealing technique used for your nylon vials? Our experience has been that the softness of nylon allows for, in some cases, large leakage rates.

Rauert: A special sealing technique is not used for our nylon vials, but the vial caps are tightened again one day after the vials have been put in the (cooled) liquid scintillation counter for counting. Each vial is weighed before and after counting, and leakage was only observed in a few cases where the vial caps had not been properly closed.

Gove: Since you mentioned the question of cost compared with dedicated accelerators, what is the cost of your large volume scintillation counters?

Rauert: I cannot give you an exact figure, because our large volume measuring chamber has been built in our institute workshop, but the cost should not be much higher than that of a purchasable liquid scintillation counter with cooling and manual change of samples.

Hewson: You mentioned that you have seen no drift in count rate in 7000 minutes of counting of your 160ml samples. Have you any evidence of CO₂ exchange with the atmosphere during the counting period?

Rauert: CO₂ exchange is unlikely because the quartz cuvette holding the sample can be closed tightly, and an increase of the blank count rate has not been observed.