

## MEASUREMENT OF LOW $^{14}\text{C}$ ACTIVITIES IN A LIQUID SCINTILLATION COUNTER IN THE ZAGREB RADIOCARBON LABORATORY

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**ABSTRACT.** Two methods of chemical preparation of radiocarbon samples are implemented in the Zagreb Radiocarbon Laboratory for measurement by a new liquid scintillation counter (LSC), Quantulus 1220<sup>TM</sup>: a  $\text{CO}_2$  absorption method (LSC-A) and a benzene synthesis method (LSC-B). For samples prepared by both methods, the optimal counting windows for measurement in LSC were determined. The total efficiency of LSC-A is 65% and that of the LSC-B is 83%, while the corresponding  $^{14}\text{C}$  dating limits are 31,800 yr and 52,160 yr, respectively.

$^{14}\text{C}$  activities measured by the LSC-A and LSC-B methods were compared with those measured by the gas proportional counter (GPC) method (efficiency 75%,  $^{14}\text{C}$  dating limit 37,500 yr). The results obtained by the LSC-A method have larger errors than those measured by the GPC method, but LSC-A is quick, inexpensive, simple, and requires less carbon than the GPC method. Thus, LSC-A is suitable for  $^{14}\text{C}$  measurements of geological, hydrological, and environmental samples. On the other hand, the results obtained by the LSC-B method give smaller errors and a larger  $^{14}\text{C}$  dating range. Therefore, LSC-B is more suitable for  $^{14}\text{C}$  dating of archaeological samples.

### INTRODUCTION

Radiocarbon activity in archaeological, geological, environmental, and hydrological samples has been measured in the Zagreb Radiocarbon Laboratory at the Rudjer Bošković Institute since 1968 by the gas proportional counter (GPC) technique. In order to improve the capability of low-level  $^{14}\text{C}$  measurement in our laboratory, we recently obtained a new liquid scintillation counter (LSC), Quantulus 1220<sup>TM</sup>, which is placed in the same ground-floor room with the GPC system, where we can control environmental parameters.

Sample preparation methods for the GPC technique and our participation in international intercomparison studies have been described previously (Srdoč et al. 1971; Horvatinčić et al. 1990, 1995; Krajcar Bronić et al. 1995). Briefly, after pretreatment by the acid-base-acid method, organic samples are combusted in a stream of pure oxygen. Carbonate samples are dissolved by acid ( $\text{HCl}$  or  $\text{H}_3\text{PO}_4$ ). The obtained and purified  $\text{CO}_2$  is then catalytically converted to methane, which is used as the counting gas in GPC.

Two methods of chemical preparation of samples for  $^{14}\text{C}$  activity measurement by LSC are implemented: a  $\text{CO}_2$  absorption method (LSC-A) and a benzene synthesis method (LSC-B). The preparation lines have been constructed following the descriptions of similar lines in previous literature (*LSC-A*: Qureshi et al. 1989; Rao and Killey 1994; Aravena et al. 1989; Nair et al. 1995; Woo et al. 1999; Momoshima et al. 1993; *LSC-B*: Noakes et al. 1965; Tamers 1975; Belluomini et al. 1978; Gupta and Polach 1985; McCormac et al. 1993; Enerson et al. 1998; Muraki et al. 1998; Pawlyta et al. 1998; Cook 2002, personal communication) with some modifications. In this paper, we describe the procedures for the absorption method and for the benzene synthesis, as well as different tests that were performed during the implementation of both methods. We have determined the optimal parameters for measurements in LSC for samples prepared by both methods, e.g.  $^{14}\text{C}$  window, efficiency, and figure of merit. Finally, we discuss the results of  $^{14}\text{C}$  activity measurements by both LSC-A and LSC-B methods and compare them with those obtained by the GPC method.

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For all tests, we used CO<sub>2</sub> borehole gas containing no <sup>14</sup>C ( $a^{14}\text{C} = 0$  pMC), which has been used as background gas also for the GPC technique, and carbonate obtained from recent shells from the Adriatic Sea ( $a^{14}\text{C} = 100$  pMC,  $\delta^{13}\text{C} = 0\text{‰}$  VPBD), the activity of which has been determined previously by GPC. The <sup>14</sup>C activity of all prepared samples was measured by LSC and the quenching effect was assessed with an index called the Standard Quench Parameter, SQP(E) (hereafter “SQP”), which represents the end-point of the external standard spectrum, i.e., the channel number beyond which 1% of the total counts are found. As an external standard, we used a built-in 37-kBq <sup>152</sup>Eu capsule. The LSC running and data acquisition were performed by using Wallac WinQ Windows software for controlling Wallac 1220 Quantulus™ (Version 1.2), and for data processing we used the Wallac EASY View Spectrum Analysis Program (Version 1.0).

## SAMPLE PREPARATION

### Method LSC-A

The vacuum line for CO<sub>2</sub> absorption (Figure 1) consists of the following: (1) a steel container with a CO<sub>2</sub> sample; (3) a U-tube with silica-gel for CO<sub>2</sub> purification; a manometer and (2) a needle valve for CO<sub>2</sub> flow regulation; (4) a 20-mL low-potassium glass vial with absorption mixture (*Carbosorb E*® + *Permafluor E*®) cooled with ice; and (5) a flow meter/bubbler. The amount of CO<sub>2</sub> absorbed in the absorption mixture is determined by weighing the glass vial with the mixture before and after the absorption.

In order to obtain optimal conditions for sample preparation, we performed tests by varying the CO<sub>2</sub> flow rate and the composition of the absorption mixture. For all prepared samples, the SQP and count rate have been determined by liquid scintillation counting.

The CO<sub>2</sub> flow rate in the absorption system was varied by the needle valve. Taking into account the reproducibility of the loaded CO<sub>2</sub>, we chose a medium flow rate of about 70 mL CO<sub>2</sub> per min for routine sample preparation. Under such a flow rate, it takes about 15 min until the bubbles appear in the bubbler at the end of the line, indicating that the absorption mixture is almost saturated with CO<sub>2</sub>. Some CO<sub>2</sub> can still be absorbed after the first bubbles have appeared; therefore, we continued the overflow of CO<sub>2</sub> for 10 min to assure saturation. It was established that the samples with no saturation of absorption mixture by CO<sub>2</sub> show stronger quenching, i.e., have lower SQP values (Figure 2) and as such are not suitable for measurement. Stronger quenching of not-completely-loaded samples was also observed by Rao and Killey (1994), while Qureshi et al. (1989) used the quenching parameter as an indirect method to estimate the amount of absorbed CO<sub>2</sub> instead of direct weighing. The best SQP value was obtained for about 2.15 g of the absorbed CO<sub>2</sub> in a mixture consisting of 10 mL *Carbosorb E* and 10 mL *Permafluor E*. In some cases, we obtained overloaded samples, i.e., the amount of absorbed CO<sub>2</sub> was higher than given theoretically by the manufacturer's specification (0.22 g CO<sub>2</sub> per 1 mL of *Carbosorb*) and the SQP of such samples decreased again (Figure 2). Nair et al. (1995) also observed stronger quenching in samples overloaded by CO<sub>2</sub>. Therefore, the SQP of a sample for <sup>14</sup>C activity measurement prepared by the absorption method can serve as an indicator of the amount of absorbed CO<sub>2</sub>. For <sup>14</sup>C activity calculation, we use only samples saturated but not overloaded with CO<sub>2</sub>, with an SQP in the range of 710–725 (Figure 2).

To determine the best composition of the absorption mixtures, we performed test samples setting the ratio of *Carbosorb E* to *Permafluor E* to 9:11, 10:10, 11:9, 12:8, 13:7, 14:6, and 15:5. All samples were prepared by the adopted standard procedure, keeping the CO<sub>2</sub> flow rate constant (about 70 mL/min) with a 10 min overflow, and keeping the total volume of the absorption mixture equal to 20 mL.

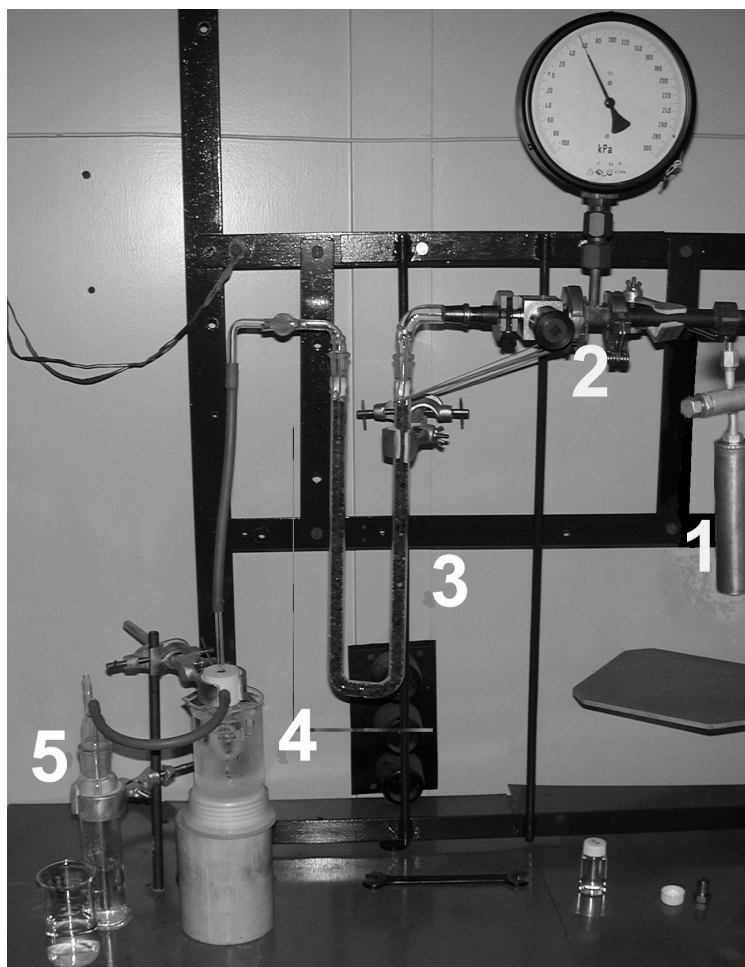


Figure 1 Preparation line for the  $\text{CO}_2$  absorption: 1—metal container with  $\text{CO}_2$  sample; 2—needle valve; 3—U-tube with silica-gel; 4—vial with absorption mixture (Carbosorb E + Permafluor E) immersed in mixture of ice and water; 5—bubbler.

The amount of  $\text{CO}_2$  absorbed in the mixture increases with the amount of Carbosorb E, but the relative amount of  $\text{CO}_2$  per mL of Carbosorb E remains constant ( $\sim 0.21 \text{ g/mL}$ ). The SQP decreases as the quantity of Carbosorb E increases because Carbosorb E is a strong quencher (Qureshi et al. 1989; Rao and Killey 1994; Woo et al. 1999). The count rate of background samples does not depend on the amount of Carbosorb E; the count rate of the active sample shows a maximum for approximately 12 mL Carbosorb E in the absorbing mixture. The counting efficiency (Figure 3)—determined as the ratio of the measured count rate, expressed in counts per minute (cpm), to the sample activity, expressed in disintegration per minute (dpm)—shows a maximum of about 62% for the mixture containing 10 mL of Carbosorb E. A similar counting efficiency (60%) was obtained also by Qureshi et al. (1989) and Nair et al. (1995) for the component ratio 1:1 in the absorption mixture. Taking into account all these findings, we decided to use the mixture of 10 mL Carbosorb E and 10 mL Permafluor E in a routine sample preparation.

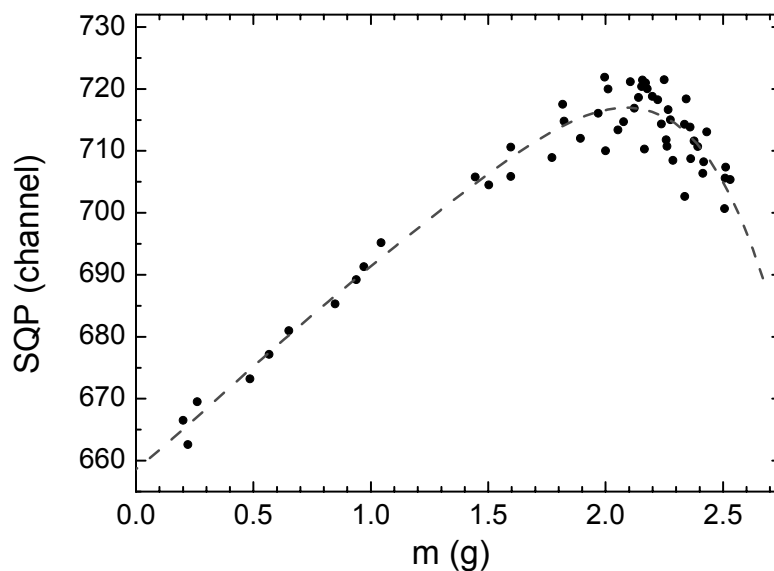


Figure 2 Standard Quench Parameter (SQP) as a function of the amount of the absorbed  $\text{CO}_2$  in adsorption mixtures consisting of 10 mL Carbosorb E and 10 mL Permafluor E. Symbols: measurements; dotted line: polynomial fit.

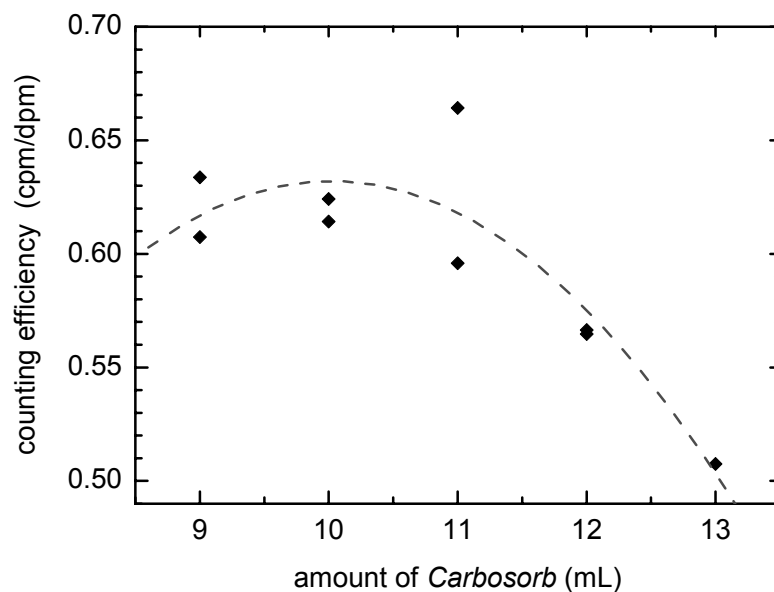


Figure 3 Counting efficiency as a function of the amount of Carbosorb in the absorbing mixture. The remaining of the total volume of 20 mL is Permafluor. Symbols: measurements; dotted line: polynomial fit.

To test the reproducibility of the procedure, we repeated the absorption of the  $\text{CO}_2$  obtained from the same sample (replicate sample preparation). We found that the process gives reproducible results (SQP, count rate, efficiency,  $^{14}\text{C}$  activity) if the saturation of the absorption mixture with  $\text{CO}_2$  has been achieved.

**Method LSC-B**

For the LSC-B method, the vacuum line for benzene synthesis has been constructed (Figure 4). The first step involves the reaction of  $\text{CO}_2$  with lithium at 700–900 °C to produce lithium carbide.  $\text{CO}_2$  stored in glass bulbs (2) is successively added into a stainless steel reactor (1) containing metallic lithium in stoichiometric quantity with an excess of 30%. The reaction is controlled by  $\text{CO}_2$  pressure in the reactor and monitored through a glass window on the top of the reactor. After cooling and pumping of the reaction vessel, the lithium carbide is subsequently hydrolyzed to acetylene by slowly adding distilled water (15). The obtained acetylene passes through a water trap cooled to –50 °C (5) and is frozen in the next 2 traps (6, 7), which are cooled by liquid nitrogen under a dynamic vacuum. The purification of acetylene is realized by passing through a trap containing phosphoric acid with glass beds (8) in order to remove nitrogen compounds, and a cold trap (9) for water removing. Trimerization of acetylene to benzene is performed on the vanadium catalyst supplied from the Kyiv Laboratory (according to the procedure in Arslanov et al. 1993). Before reaction, the catalyst is activated in an oven (13) at 350 °C for 10 hr. Acetylene from bulbs (11) slowly sublimates on the catalyst (13) while the temperature of the reaction (monitored by thermocouple 14) has been kept below 90 °C by immersing the catalyst vessel into the mixture of water and ice. The obtained benzene is extracted into a glass finger (12) by heating the catalyst to 150 °C and simultaneously cooling the finger with liquid nitrogen.

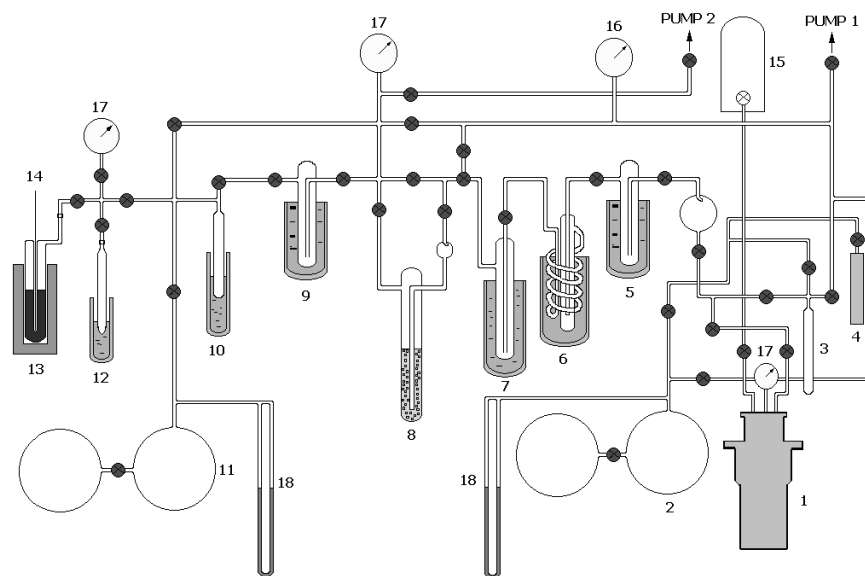


Figure 4 Benzene synthesis line: 1–reaction vessel; 2–bulbs for  $\text{CO}_2$  storage; 3–glass finger for  $\text{CO}_2$ ; 4–metal container for  $\text{CO}_2$ ; 5,9–water traps cooled with mixture of ethanol and liquid nitrogen; 6,7– $\text{C}_2\text{H}_2$  traps cooled with liquid nitrogen; 8–trap with  $\text{H}_3\text{PO}_4$  and glass beds; 10–glass finger for  $\text{C}_2\text{H}_2$  cooled with liquid nitrogen; 11–bulbs for  $\text{C}_2\text{H}_2$  storage; 12–glass finger for  $\text{C}_6\text{H}_6$  cooled with liquid nitrogen; 13–vanadium catalyst heated by oven; 14–thermocouple; 15–reservoir with distilled water; 16–Pirani gauge; 17–Bourdon gauges; 18–Hg manometers.

Several tests for benzene synthesis were performed: duration of carbide and hydrolysis reaction, type of  $\text{C}_2\text{H}_2$  purification, and duration and temperature of catalytic trimerization. The test results showed that the optimal time of the carbide and hydrolysis reaction is 20 min and 30–40 min, respectively. The temperature of the catalytic reaction is between 60–90 °C, with a duration of 1–2 hr, depending

on the quantity of acetylene. The acetylene yields range from 89% to 98% and benzene yields range from 77% to 90%. The purification process described above gives benzene of purity 98.9% to 99.5%, as determined by gas chromatography. The main impurity in all benzene samples is toluene.

To prepare the scintillation cocktail for LSC measurements, the recommended quantity of 15 mg of butyl-PBD per 1 g of benzene is added (Gupta and Polach 1985). The cocktail is then put into 7-mL low-potassium glass vials (pico-vials). To test the sensitivity of the cocktails on the amount of added butyl-PBD, we prepared cocktails with 7 mg and 22 mg butyl-PBD per 1 g of benzene (i.e. 50% and 150% of the recommended amount). We observed no significant changes in either count rate or SQP.

## MEASUREMENTS IN LSC

We determined the optimal parameters for  $^{14}\text{C}$  activity measurement by LSC for samples prepared by both the LSC-A and LSC-B methods. By comparing the standard deviation of the measured count rate with the number of 30-min cycles, we established the number of cycles in a run to 30 (or more), resulting in 900 (or more) min per sample measurement.

The counting efficiency ( $E$ ) was determined from the ratio of measured (net) count rates ( $A_{\text{meas}}$ , expressed in cpm) and the known  $^{14}\text{C}$  activity of the standard ( $A$ , expressed in dpm):

$$E = A_{\text{meas}} / A \quad (1).$$

Typical spectra for inactive and active standard prepared by the LSC-A and LSC-B methods are illustrated in Figure 5. The area of spectrum containing the  $^{14}\text{C}$  spectrum, the so-called “ $^{14}\text{C}$  window” (between the dashed lines in Figure 5), encompasses the channels between 109 and 431 and between 127 and 580 for LSC-A and LSC-B, respectively. The counting efficiencies in these areas are 70% and 90%, respectively.

Optimization of the counting system consists of moving the boundaries of the  $^{14}\text{C}$  window during the processing of spectra in order to decrease as much as possible the background count rate ( $B$ ), and at the same time not to lose the essential part of the  $^{14}\text{C}$  spectrum ( $A_{\text{meas}}$ ). The optimal measuring window for the LSC-A technique was established to be between channels 144 and 372 (the area between the full lines in Figure 5), which encompasses 93% of the total  $^{14}\text{C}$  spectrum and 77% the background spectrum. In such a way, we determined the total efficiency for LSC-A to be 65%. The figure of merit ( $FM = A_{\text{meas}}^2/B$ ) has been improved from 16 to 18.4 (Table 1).

Optimization of the counting window for the LSC-B technique resulted in background reduction to 64% of that in the  $^{14}\text{C}$  window, while 92% of the  $^{14}\text{C}$  spectrum has remained in the window. Therefore, the total efficiency of the LSC-B technique is 82.4% and the figure of merit is considerably improved (from 2200 to 2908). Comparison of some basic parameters of the measurement of  $^{14}\text{C}$  in the counting windows is shown in Table 1, where data for our GPC system are also shown for comparison.

Several samples prepared by the LSC-A method have been measured repeatedly during longer periods of time (4 months) to test the stability of the prepared samples. Since no significant changes in either count rate or SQP have been noticed, we concluded that measurements can be performed also some time after the sample preparation.

When the sample is measured immediately after preparation, the presence of radon may influence the count rate. However, radon can be easily detected in the upper part of the spectrum. We control the count rate in the so-called “radon window” (channels 450–700 for the LSC-A samples) for routine measurement.

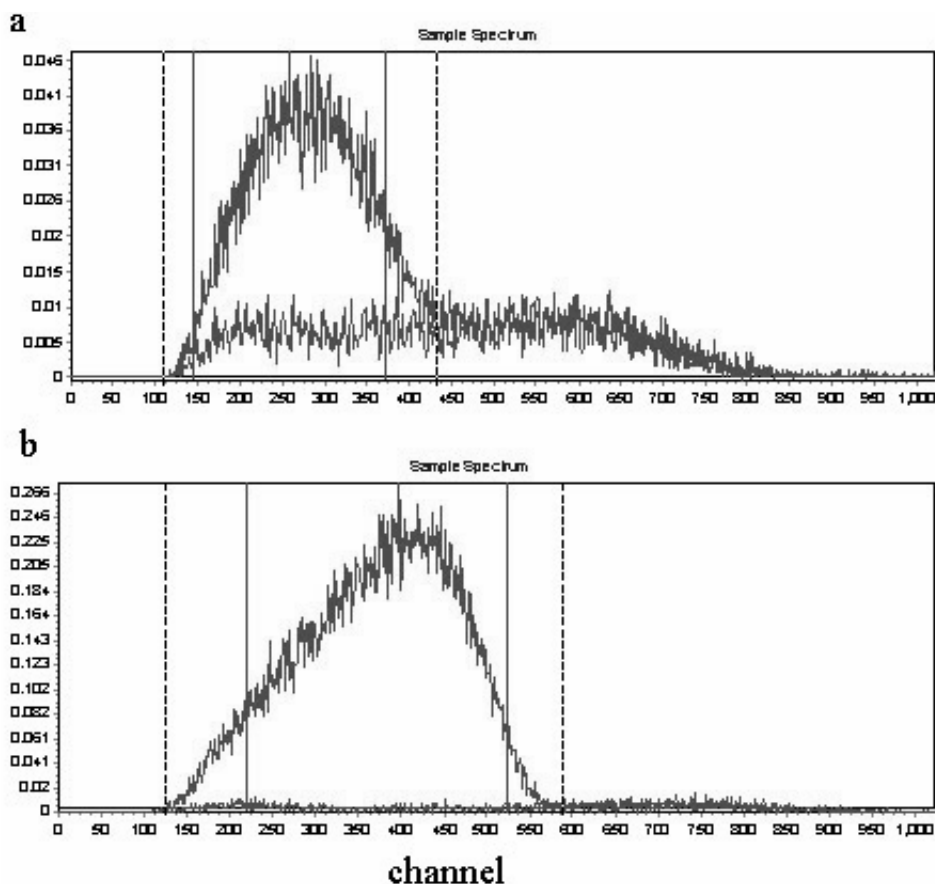


Figure 5 Characteristic  $^{14}\text{C}$  spectra obtained in LSC. a) LSC-A preparation method (absorption of  $\text{CO}_2$ ). b) LSC-B preparation method (benzene synthesis). Upper spectra: modern shells (100 pMC); bottom: background. Dashed lines: limits of the  $^{14}\text{C}$  windows; full lines: limits of the counting windows.

Table 1 Comparison of characteristic parameters of all 3  $^{14}\text{C}$  measurement techniques. LSC-A: absorption of  $\text{CO}_2$  and LSC measurement; LSC-B: benzene synthesis and LSC measurement; GPC: methane preparation and gas proportional counting. The data for LSC-A and LSC-B technique correspond to the optimized counting windows.

Value	Symbol (unit)	LSC-A	LSC-B	GPC
Amount of carbon	$m$ (g)	0.59	4.5	2.01
Spectrum area (counting window)	(channel)	144–372	219–525	—
Real activity of standard (100 pMC)	$A$ (dpm)	7.98	61.06	27.34
Count rate of background	$B$ (cpm)	1.47	0.87	5.54
Net count rate of standard (100 pMC)	$A_{\text{meas}}$ (cpm)	5.20	50.30	20.47
Efficiency	$E = A_{\text{meas}} / A$ (%)	65	82.4	75
Figure of merit	$FM = A_{\text{meas}}^2 / B$	18.4	2908	75.7
Maximum age ( $t_{\text{meas}} = 1200$ min)	$T_{\text{max}}^a$	31,800	52,160	37,500

$$^a T_{\text{max}} = 8033 \times \ln(0.3546 \times A_{\text{meas}} \times \sqrt{t_{\text{meas}}/B})$$

We compared the benzene background count rate and the count rate of a spike sample in glass pico-vials and in special low-background teflon-copper vials (Wallac-Perkin Elmer). The use of special teflon-copper vials reduces the background count rate significantly (and the figure of merit is better, 9000, in teflon-copper vials), but the difference in the  $^{14}\text{C}$  spectra shape and count rates of the spike sample is negligible. In both types of vials, the background count rate (5 mL of commercial petrochemical benzene, counting window 219–525 channels) was stable in the period of 6 months, and the values were  $0.80 \pm 0.05$  cpm in pico-vials and  $0.28 \pm 0.03$  cpm in teflon vials. Due to the limited number of teflon vials and their rather high price, we performed all test measurements in pico-vials.

The quenching correction curve was determined for the counting geometry of 5 mL of benzene in pico-vials. A small amount of acetone was added to the spike benzene and the SQP and the count rate of such samples was measured. The obtained quenching curve is shown in Figure 6, where the relative efficiency is calculated as the ratio of the count rate in the counting window of the “poisoned” samples to the count rate of the pure spike sample. Our synthesized benzene samples of purity 98.9%–99.5% resulted in SQP values above 835; therefore, the efficiency correction due to quenching was less than 1%.

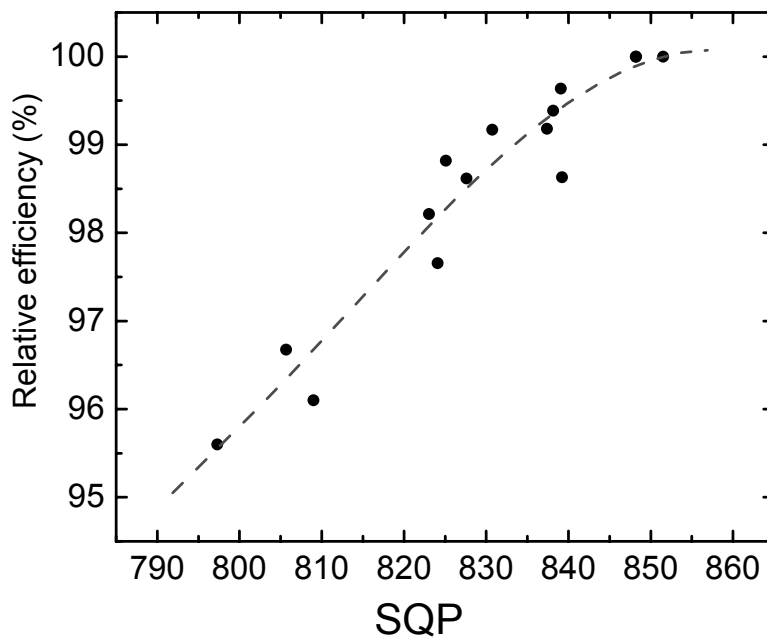


Figure 6 Quenching curve. Symbols: measured data; dashed line: polynomial fit.

## RESULTS

The comparison of conventional  $^{14}\text{C}$  ages (Stuiver and Polach 1977; Gupta and Polach 1985) of benzene samples prepared by the LSC-B method and  $^{14}\text{C}$  ages of the same samples measured by GPC are shown in Figure 7. The LSC-B ages were corrected also for different quenching by using the quenching curve shown in Figure 6. The agreement between the LSC-B and GPC ages is good, giving the slope of the fitted line equal to  $1.01 \pm 0.01$ . No systematic difference between the 2 sets is observed, as shown also by the intercept of the fitted line equal to  $39 \pm 41$  yr.



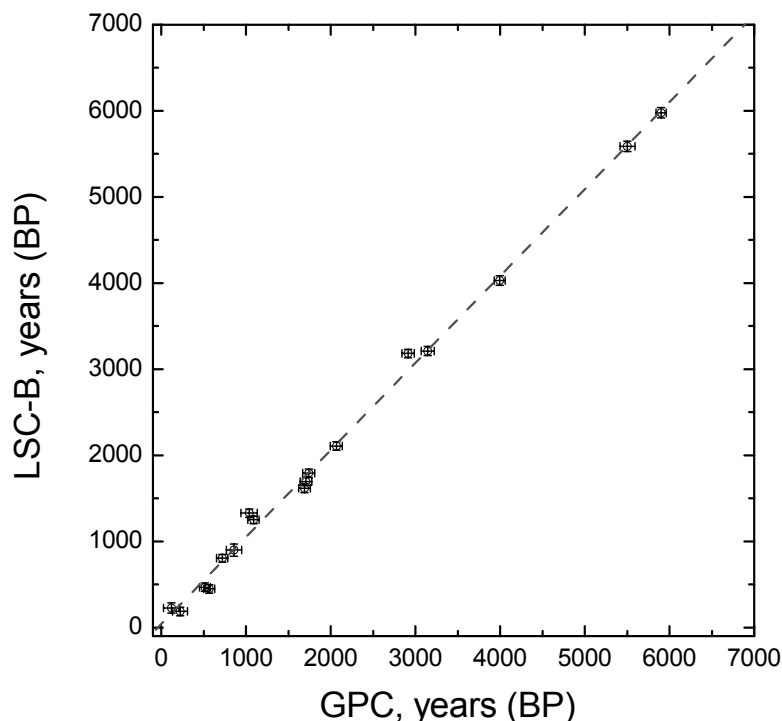


Figure 7 Comparison of conventional  $^{14}\text{C}$  ages measured by LSC-B and GPC methods. Symbols: measured ages with corresponding 1- $\sigma$  errors; line: linear fit to the measured data, slope  $1.010 \pm 0.015$ , intercept  $39 \pm 41$  yr,  $N = 17$ ,  $R = 0.998$ .

To check the background of samples that pass different procedures of  $\text{CO}_2$  preparation (organic and carbonate samples) in addition to the old borehole  $\text{CO}_2$  gas that was used as a test gas in the development of the method, we synthesized benzene also from anthracite and marble. The measured count rate of all 3 kinds of background samples was the same. In Table 1, we give the mean value ( $0.87 \pm 0.02$ ) of all background samples in the same geometry. However, as mentioned previously, a commercially available benzene from a petrochemical source shows a slightly lower count rate ( $0.80 \pm 0.05$ ) under the same counting conditions.

Under the adopted counting condition, the  $^{14}\text{C}$  dating limit (Table 1) is 52,160 yr (5-mL samples measured 1 day). The limit can be improved to 56,730 yr by using special low-background teflon-copper vials (5-mL samples measured 1 day). A larger amount of benzene (e.g., 7 mL, if the quantity of available sample allows it) would also improve the dating limit to 54,800 yr and 59,400 yr in pico and teflon vials, respectively. A longer counting time will also increase the maximal age that can be determined (57,600 yr and 62,100 yr for 7-mL samples measured 2 days in pico and teflon vials, respectively).

A comparison of  $^{14}\text{C}$  activities (expressed in pMC) obtained by the GPC and LSC-A methods is presented in Figure 8. The agreement between the 2 sets of data is again very good (the slope of the fitted line is 1), but the uncertainties of the LSC-A results are 2–3 times larger than those of the GPC method for the same measuring time (1 day per sample). Due to the high background count rate and low efficiency (Table 1), the maximal determinable  $^{14}\text{C}$  age is 31,800 yr. However, these characteristics are good enough for certain applications that do not require high precision and also for samples having very high  $^{14}\text{C}$  activity.

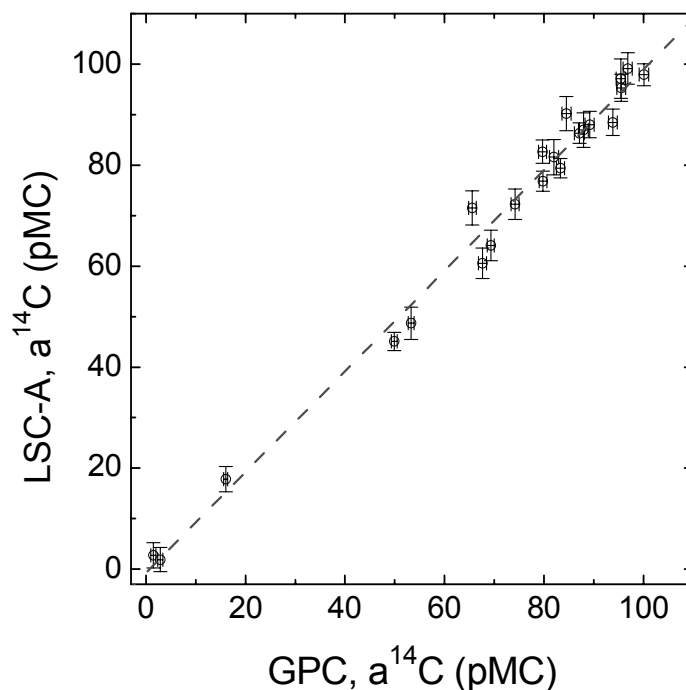


Figure 8 Comparison of  $^{14}\text{C}$  activities measured by LSC-A and GPC methods. Symbols: measured activities with corresponding 1- $\sigma$  errors; line: linear fit to the measured data, slope  $0.997 \pm 0.026$ , intercept  $-0.7 \pm 2.0$  pMC,  $N = 22$ ,  $R = 0.993$ .

As in the case of the LSC-B method, the count rate of various background materials (anthracite, marble, borehole  $\text{CO}_2$ ) did not show any difference.

## CONCLUSION

By introducing a liquid scintillation counter for  $^{14}\text{C}$  activity measurement in our laboratory, we implemented also 2 new sample preparation techniques: 1) absorption of  $\text{CO}_2$  in an absorption mixture consisting of Carbosorb E and Permaflor E (LSC-A), and 2) benzene synthesis (LSC-B). The presented methods differ in complexity, time consumed, price, and in the precision of measured results. The characteristic features of all 3 techniques—GPC, LSC-A, LSC-B—of  $^{14}\text{C}$  measurements are compared in Table 1 and the measured activities are compared in Figures 7 and 8.

The simplest preparation method, absorption of  $\text{CO}_2$  followed by liquid scintillation counting (LSC-A), is fast and requires only about 1 g of carbon. Its characteristics are high background, low efficiency, low  $^{14}\text{C}$  dating limit, and large errors. However, it is accurate enough for certain applications (e.g., geological, hydrological, and environmental samples). It could be used also for quick determination of increased environmental  $^{14}\text{C}$  contamination, e.g., in the case of a nuclear accident.

The best  $^{14}\text{C}$  dating features are obtained by benzene synthesis and liquid scintillation counting (LSC-B): low background, high efficiency, high dating limit, and good precision. The features could be improved by using special low-background teflon-copper vials, by increasing the amount of benzene, and by prolonging the counting time. Due to these good characteristics, the LSC-B method is suitable for  $^{14}\text{C}$  dating of archaeological samples and all other samples that require high precision or are close to the limit of the  $^{14}\text{C}$  dating method.

The features of the GPC technique lie in between the 2 LSC techniques. The method gives accurate results, as justified by participation in the international  $^{14}\text{C}$  intercomparison studies.

All 3 methods of  $^{14}\text{C}$  activity measurement in our laboratory allow us to choose the preparation and counting technique which best meets the need for accuracy and precision of different kinds of samples. The 3 methods also enable a higher sample through-put.

## ACKNOWLEDGEMENTS

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