INVESTIGATION OF PERFORMANCE OF THE RADIOCARBON DATING SYSTEM AT THE PONTIFICIA UNIVERSIDAD CATOLICA DEL PERU

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INTRODUCTION

Radiocarbon dating, developed 40 years ago by W.F. Libby, is now significantly improved and is widely applied as one of the fundamental dating methods in archaeology and earth sciences. Besides of dating, radiocarbon measurements have numerous important aplications in oceanography, hidrology and environmental studies. The reviews of applications of the radiocarbon method and technical and methodical improvements can ben found in the proceedings of recent international radiocarbon conferences [1], [2], [3].

Two classical methods are used for the determination of the radiocarbon content in organic samples, namely the liquid scintillation method and the gas counting method. The first method is used in the laboratory at the PUCP, the second one in the laboratory of the Solesian Technical University in Gliwice, Poland. In the liquid scintillation method the carbon dioxide obtained from the dated sample is converted first to acethylene and then to benzene, which is used for counting the beta particles emitted by radiocarbon decays. In the gas counting method counting is performed either directly on carbon dioxide or acethylene or methane. Both liquid scintillation and gas counting methods have their specific advantages and drawbacks; actually about 40% of all active radiocarbon dating laboratories are working with gas counting, and 60% with liquid scintillation counting. In recent years an important development was

archieved in the field of accelerator mass spectrometry (AMS) and its application to radiocarbon dating. Actually more than 10 radiocarbon dating laboratories are using this technique.

The Radiocarbon Laboratory at the PUCP, establisahed in the late seventies, is equipped with the vacuum line for producing carbon dioxide and converting it to benzene, and a liquid scintillation counting unit. The fundamentals of the chemistry involved in obtaining benzene from dated samples were described in detail [4]; however, no sufficiently detailed description is available for the physical problems of dating with this system. The present paper is devoted to give a short description of the counting system, to analyse the results of some measurements recently performed, and to estimate the accuracy of dating actually available.

PHYSICAL BACKGROUND OF LIQUID SCINTILLATION COUNTING

In liquid scintillation counting the sample form of benzene is mixed with an appropiate amount of scintillator (PPO and POPOP) and placed in a counting vial made of glass or teflon. Beta particles from radioactive decays of radiocarbon produce very weak and fast light pulses, which are detected by photomultipliers surrounding the vial, and converted into electric signals. The magnitude of the electric pulse is proportional to the amount of light emitted by the scintillator, which is proportional to the energy of beta particles. Therefore, the shape of the spectrum of electric pulses is similar to the shape of the energetic spectrum of beta particles. There are two main difficulties inherently associated with liquid scintillation counting of radiocarbon samples; the first is caused by the presence of hydrogen atoms in the molecule of benzene. Because one of the hydrogen isotopes (tritium-T or H3) is radioactive, and emits beta particles like radiocarbon, there is a possibility that the observed counts can be caused by beta decays of both radiocarbon and tritium. Elimination of counts produced by tritium is achieved in two ways: the first is using tritium-free water for producing acethylene, the second by counting only those beta particles which have an energy greater than the maximun energy of tritium beta decays. The first way is difficult and expensive, therefore the most widely applied method is the second one. In practice, this method is achieved by counting only those electric pulses which have amplitudes greater than an appropiately selected level (the so called lower discrimination level L.).

The second difficulty of liquid scintillation counting is caused by shifts in wavelenght of the light emitted by the scintillator and decrease of the amount of light emitted by the scintillator and decrease of the amount of light

emitted. These effects are associated with some impurities of the counting "cocktail" and are known as "quenching effects". The quenching effects cause distortion of the spectrum of electric pulses which may have an important influence on the accuracy of determination of the radiocarbon content in the dated sample, and, consequently, on the estimated age of said sample.

The main advantage of liquid scintillation counting is connected with the presence of six carbon atoms in the molecule of benzene. Moreover, because the counted sample is in the liquid state its volume is ca. 1000 times smaller than the corresponding volumes of gaseous samples used in gas counting method. In consequence, the shields for eliminating counts caused by cosmic radiation and environmental radioactivity are much simpler than those used in gas counting. In order to eliminate the counts caused by high energy cosmic and environmental radiation most counting systems are supplied with the so-called upper discrimination level U. Therefore, the counting is performed in a window between two appropiately chosen levels, L and U.

The significance of the proper setting of the counting window is explained in Figures 1A-C. The counting window determines the appropiate part of all electric pulses produced by photomultipliers (PM in Fig. 2). In regime "L-U" are counted such pulses which are below the upper level (U) and above the lower level (L). In regime "L-α" are counted all pulses that are above the level L, and in regime "U-α" only pulses that are above upper level U. Proper setting of the counting window is shown in Figure 1A. Location of the upper and lower levels is shown by the vertical bold lines L_o and U_o. The solid curve shows the shape of the pulse height spectrum in an ideal case. With such setting of levels L and U the efficiency of counting should be ca 80-90%. The effect of small fluctuations of the lower level is shown by the dashed area between two outlying positions of the lower level, marked with dashed lines L′ and L″. The effect of similar fluctuations of the upper level U, determined by the dashed lines U ′ and U ″, is in such case negligible. The dashed curve shows the shape of the pulse height spectrum distorted by a quenching effect. With proper setting of the levels L and U small distortion of the shape of the pulse height spectrum by quenching, the resulting change of the number of counts within the counting window should be negligible. The obvious relation is valid:

(counts in "L-α") = (counts in "L-U") + (counts in "U-α").

Figure 1B explains the effect of inappropiate setting of the counting window. The counting window is too narrow; therefore a significant part of the pulses is not counted. This causes decrease of counting efficiency and in-

crease of the error of age determination. The effect of fluctuations of the lower level L, marked by L ´ and L ´´, is approximately the same as in Figure 2A; the effect of similar fluctuations of the upper level, determined by U ´ and U ´´, is in this case much higher than before, and is comparable to that of L. Therefore, in such a case, the influence of instabilities may be ca. 2 times greater than in case of proper setting of the counting window. Because counting efficiency is also significantly lower, the overall efect may be seen as a distinct increase in the error of dating. Figure 1C shows the influence of the quenching effects in case of inappropiate setting of the counting window. The number of counts obtained with distorted shape of pulse height spectrum may be significantly lower, and the age calculated without correcting for this effect may be significantly older.
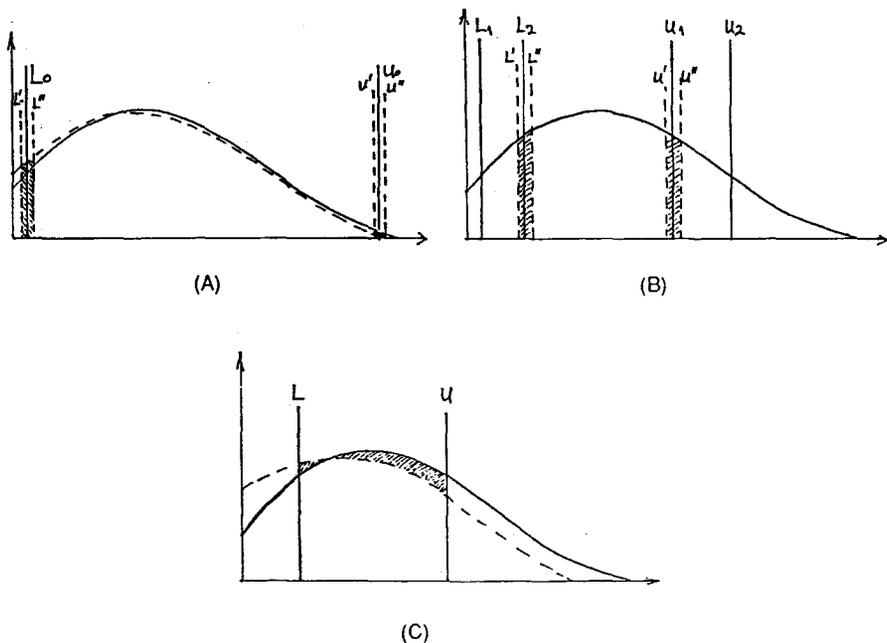

(A)

(B)

(C)

Fig. 1. Illustration of the effect of setting the counting window on the counting efficiency, instabilities of counting results and influence of quenching.
A - proper setting of counting window - high efficiency (ca 80-90%, moderate effect of instabilities and idstortion of pulse height spectrum by quenching.
B - counting window too narrow - decrease of counting efficiency, increased effect of instabilities.
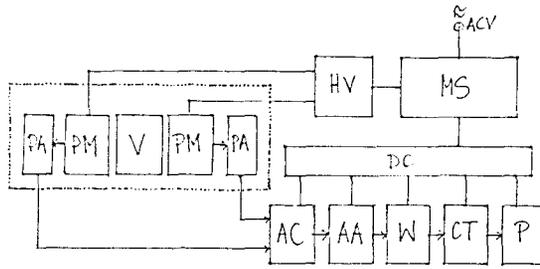C - counting window too narrow - decrease of counting efficiency, increased effect of quenching.

Fig. 2. Schematic diagram of counting system. Dotted line markes the elements in side the measunng hourse.
Abbreviations: ACV - 220V supply, MS - main supply unit, HV - high voltage supply, V - counting vial, PM - photomultiplier tubes, PA - preampiifiers, AC adjusting circuit and anticoincidence unit, AA - amplifier and anlyser, W - window setting unit, CT - counter/ timer, P - printer.

TECHNICAL DESCRIPTION OF THE DATING SYSTEM

The dating system, installed in 1976 with the financial support of the Stiftung Volkswagenwerk, consists of a vacuum line for producing benzene and the liquid scintillation counting unit. Other facilities include: chemicals and laboratory equipment for pretreatment of the samples (electric oven, refrigerator, etc.).

The vacuum line is made of glass with either glass or plastic tube connections. It enables production of carbon dioxide from organic samples by direct combustion in a stream of oxygen or by wet oxidation, and from carbonates by evolving with HCl. Carbon dioxide is converted to acethylene, which is then trimerized to benzene.

The counting system consists of two parts: measuring house and counting electronics. The measuring house shielded with lead contains two photomultipliers (PM) with preamplifiers (PA), surrounding the vial (V) with the sample. The electronics is manufactured by Nuclear Chicago and contains 3 general-purpose commercial blocks manufactured by CANBERRA (supply blocks (MS and DC), counter/timer (CT) and printer (P)), and three other blocks specially designed for radiocarbon counting. These blocks include: adjusting and anticoincidence unit (AC), amplifier and analyser (AA) and window setting unit (W). The pulses produced by C-14 beta particles and background radiation are recorded in a single channel, in a window between the lower (L) and upper (U) discrimination level. Results are printed on paper tape in equal intervals of time. Three counting regimes should be available with this electronic hardware: in window "L-U", and two infinite windows "L-α" and "U-α".

RESULTS OF TESTING OF THE COUNTING EQUIPMENT

1.   Analysis of long-term stability of the counting system.

The analysis was performed using the results of measurements of an oxalic acid sample and background, available in laboratory records, and the results obtained during testing the counting system. The first series of results was from the time period between november, 1988, and january, 1989; a second series of results was initiated in the end of february, 1989, and lasted till the 20th of april, 1989.

Results of background counting rate measurements are shown in Figure 3. Dots indicate mean valued of individual series, consisting of approximately 10-13 partial results of 100 min duration. Vertical bars denote one-sigma standard deviations, estimated from Poisson statistics.

Results of exalic acid measurements are shown in Figure 4 in the same way as for the background. Error bars are indicated for all results obtained after march 20th, 1989, and for a few earlier results in order to show the magnitude of the instabilities.

In the plots shown in Figure 3 and 4 are clearly visible three periods of quite different behaviour of results. The results on both plots are similar and are obviously correlated. In the period november 1988 - january 1989 there is relatively good stability of both background and oxalic acid counting rates. Mean values are:

background: $B = 4.98 + 0.10$ counts/minute
oxalic acid: $U = 12.45 + 0.26$ counts/minute

Errors quoted are mean square standard desviations estimated from real scatter in analysed assuming Poisson statistics are:

for background: $S_p = 0.07$ cpm.
for oxalic acid: $S_p = 0.11$ cpm

Comparison of these two estimates of errors gives the measure of the long-term instability of the counting equipment, which can be expressed by the parameter:

$$w = s_s/s_p$$

The value of this parameter is:
for background measurements: $w = 1.38$
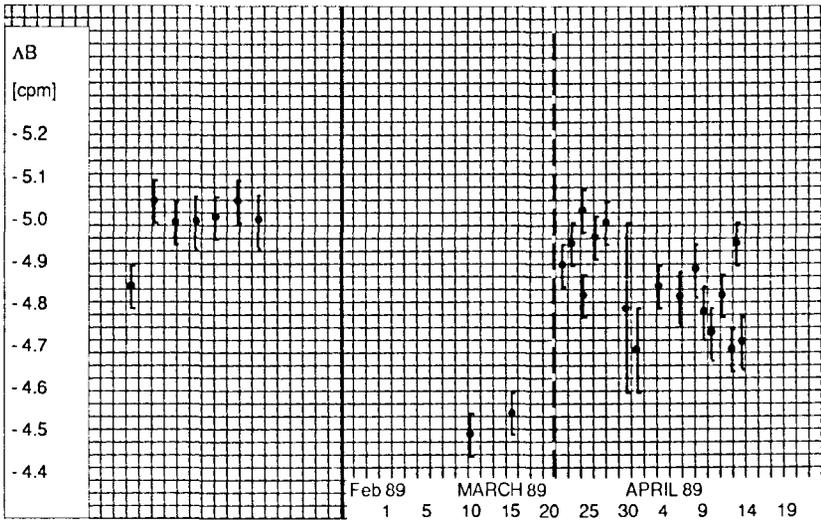for oxalic acid measurements: $w = 2.32$

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Fig. 3.   Results of background counting rate measurements. Dashed vertical line marks the beginning of the period with relatively good stability of background. Vertical bars denote standard errors of background counting rates.
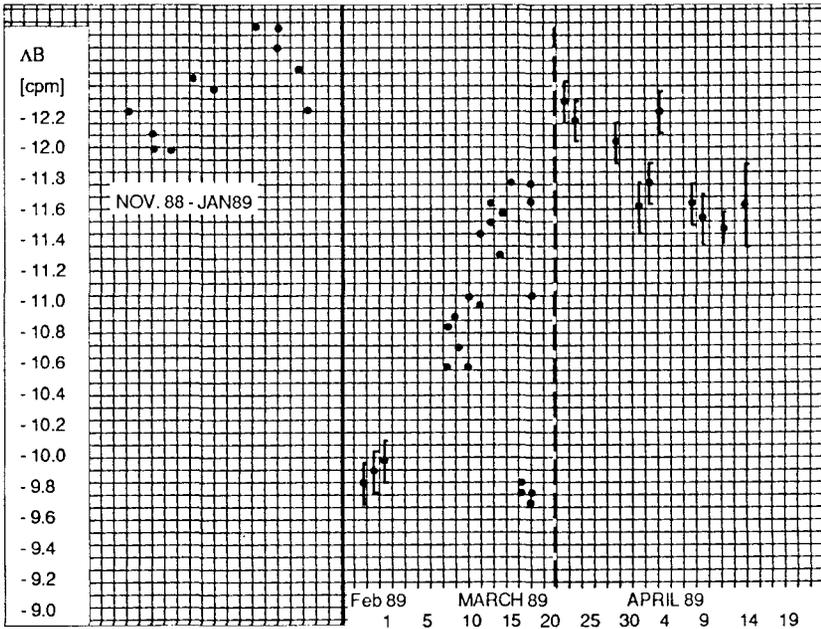

Fig. 4.   Results of measurements of oxalic acid sample. For explanation see Fig. 3

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The second period, between the end of february and march 20th, 1989, is characterized by highly unstable results, which are moreover much lower than those previously obtained. There is also a systematical trend in both background and oxalic acid results. The variability of oxalic acid results is ca. 20% of the previous value. The reasons for such highly unstable results were not explained as detailed laboratory records are not available.

The results obtained in the third period, stanting on march 20th, 1989 show reasonable stability with a slight systematic trend and some excessive fluctuations, which, however, may be accepted and accounted for in attempts at dating some unknown samples. The results for this period are summarized in Table 1. It should be pointed out that for accurate measurements it is necessary that both the background and sample counting rates must be much more stable. The reasonable value of the coefficient of instability w for reliable dting with satisfactory accuracy should not exceed a maximun value of ca. 1.25.

Table 1.- Long-term stability of counting equipment

	background	oxalic acid
Mean counting rate	4.831 cpm	12.01 cpm
Number of results	14	9
Theoretical dispersion S_p	0.070	0.110
Experimental dispersion S_s	0.111	0.202
Coefficient of instability w	1.59	1.84

2. Analysis of short-term stability of counting system

Analysis of short-term stability indicates if the counting conditions are stable within a single series of measurements of approximately 1 day duration. As a rule, such series consists of ca. 11-16 partial results with 100 min. counting time.

The results of this analysis are shown in Figure 5 for background and in Figure 6 for oxalic all measurements made after march 20th, 1989. All histograms shown in figure 5 give evidence for a relatively good stability of back-

ground counting rate; the results of oxalic acid measurements reveal similar instabilities in all series. Numerical data are listed in Table 2.
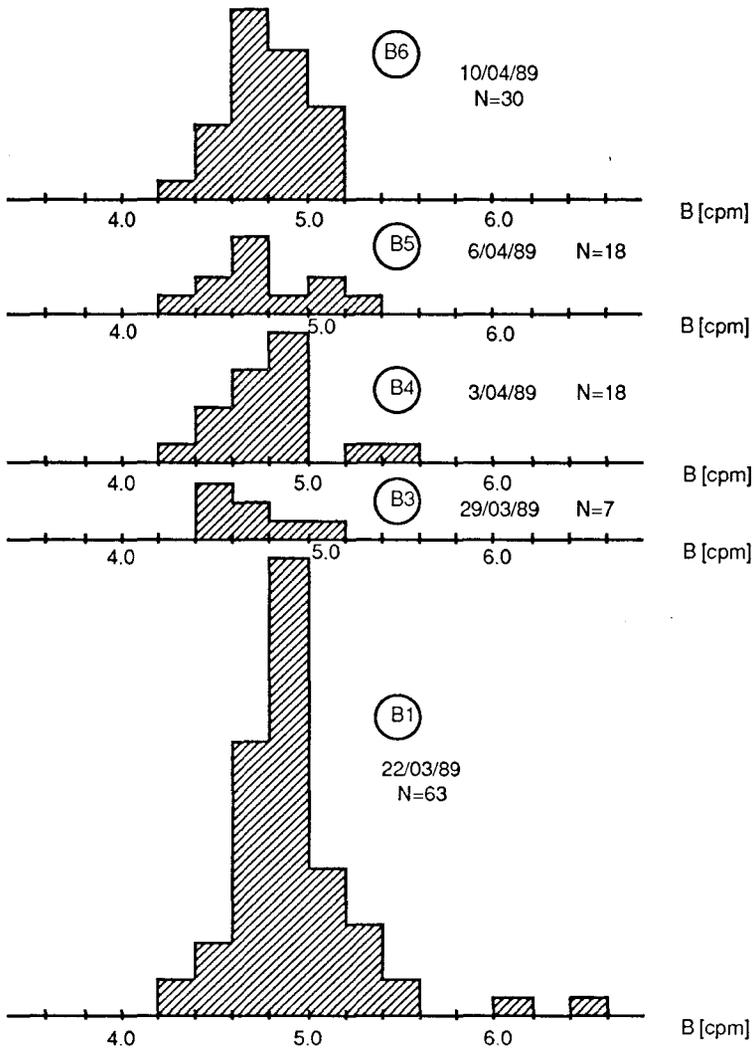

Fig. 5. Histograms showing the fluctuations of background counting rate in measurements performed between March 20 th and April 12, 1989. Duration of single partial measurements is 100 minutes. Number of partial measurements in each series is indicated. Two outlying results in series B1 are crossdashed.

An additional check for the short-term stability and the presence of outliers connected with the effect of electromagnetic disturbances was obtained by counting the background sample in short intervals of 20 minutes duration. Four series of measurements were performed for detailed statistical analysis, each consisting of ca. 60 partial results. The results listed in Table 3 indicate similar stability as that observed with 100 min. measurements. Few outlying results were noted in series B8 and B9. After rejecting these results the coefficients of instability were respectively 1.06 and 0.98, indicating good stability of the counting system. The occurence of outlying results may be connected with either the faults of the electronics, or, what seems more probable, with malfunctioning of the printer. The histograms obtained in 4 series of background counting in 20-min intervals are shown in Figure 7.
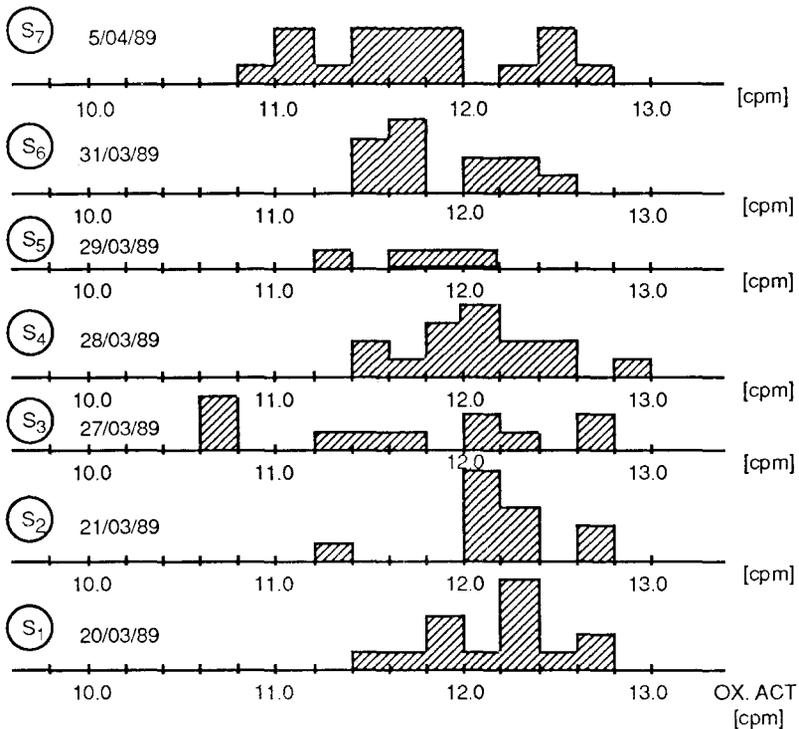

Fig. 6.   Histograms showing the fluctuation of counting rate in measurements of oxalic acid sample, performed between March 20 th and April 6 th, 1989. Duration of single partial measurements is 100 minutes. No outlying results were found.
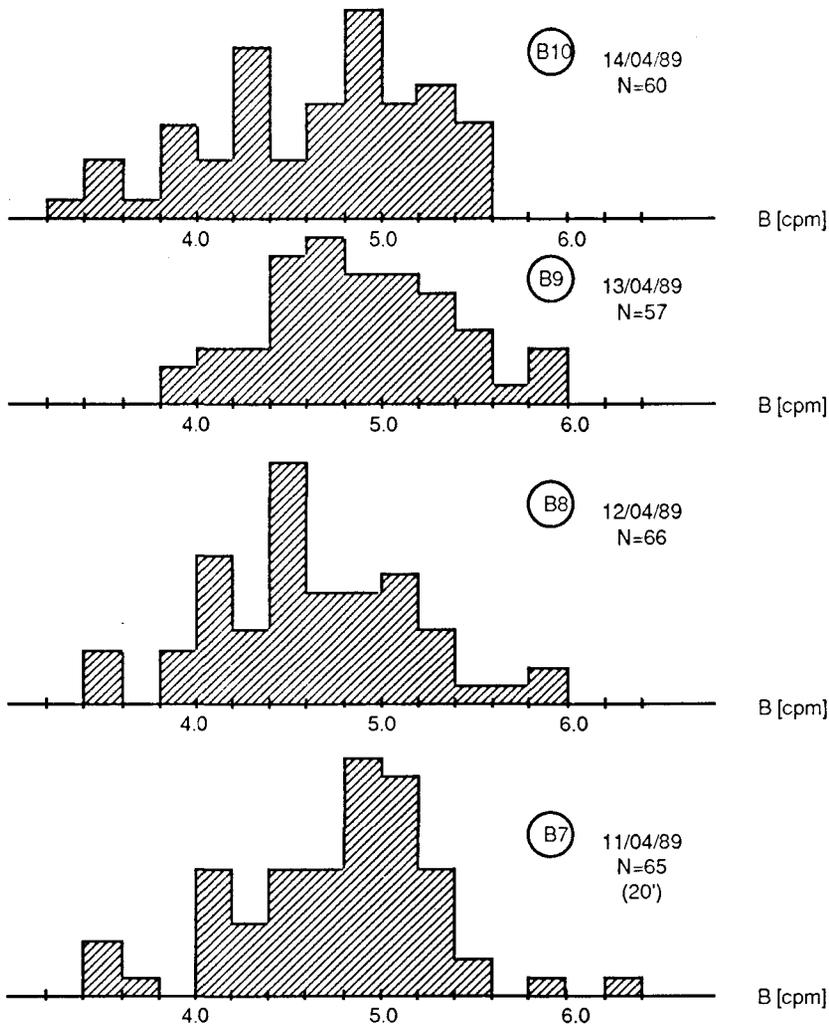
Fig. 7. Histograms showing flu. ·.ations of background counting rate in measurements performed in 20 minute counting intervals. Number of partial results in each series is indicated. Few outlying results not shown in histograms were found in series B8 and B9.

Table 2.- Analysis of short-term stability of the counting system based on partial measurements of 100 minutes duration.

Sample	N	dispersion experimental Ss	theoretical Sp	coeff. of instability actual w	mean
B1	61	0.249	0.219	1.14	
B2	7	0.177	0.217	0.82	
B3	18	0.290	0.219	1.32	1.11
B4	11	0.323	0.218	1.48	
B5	28	0.216	0.218	0.99	
OX1	13	0.338	0.348	0.97	
OX2	11	0.370	0.349	1.06	
OX3	13	0.430	0.350	1.23	
OX4	15	0.369	0.347	1.06	
OX5	4	0.398	0.342	1.16	1.16
OX6	12	0.372	0.345	1.08	
OX7	16	0.575	0.343	1.68	
OX8	14	0.345	0.342	1.01	
OX9	10	0.400	0.344	1.16	

Table 3.- Analysis of short-term stability of the counting system based on partial measurements of 20 minutes duration.

Sample	N	dispersion experimental Ss	theoretical Sp	coeff. of instability actual w	mean
B7	65	0.547	0.490	1.12	
B8	68	0.506	0.482	1.06	1.08
B9	57	0.482	0.494	1.06	
B10	60	0.565	0.483	1.17	

ESTIMATES OF THE ACCURACY OF RADIOCARBON DATES
AVAILABLE WITH ACTUAL EQUIPMENT

The results of analysis of the long-term stability of background counting rate described above indicate the presence of significant instabilities of the counting conditions, which must be taken into account as they set the important limits on the accuracy of dating. The accuracy of dating is also determined by the counting efficiency, or, more, simply, by the counting rate obtained with the sample of modern C-14 activity. Such a sample was not available for precise testing, so for the purpose of rough estimation of the dating accuracy available with the actual equipment two realistic cases were considered:

Case a: overall counting efficiency 60%
coefficient of instability w=1.8
Case be: overall counting efficiency 50%
coefficient of instability w=2.5

The results are shown in Figure 8 in the form of plots of the error of sample age for ages younger than 5,000 BP. An important assumption necessary for obtaining this estimate was that the measurements are performed strictly according to the regime described in Table 4, i.e. the sample is counted for 4000 minutes, and background and exalic acid standard are counted for ca. 6000 minutes. For case a (curve PUCP (a)) the predicted theoretical error of dating can be 90 yr for recent samples and for older samples increase to ca. 130 yr. For case b (curve PCP(b)) the minimun predicted error for recent samples is ca. 140 yr, and for a sample 5,000 yr old is equal to ca. 200 yr. For comparison, in Figure 8 are also shown the corresponding plots for counting systems used in the Radiocarbon Laboratory of the Silesian Technical University in Gliwice. Curves denoted as GdLi show the magnitude of the dating error for a large counter (L1) and curves GdL3 for a small counter (L3). For each counter two curves are plotted, showing the errors for 2 days (ca. 2500 minute counting lower curves marked as a) and for 1 day counting (ca. 1200 minutes, upper curves marked as b).

Table 4.- Counting regime in presence of instabilities.

Basis for the counting cycle: 2 weeks
Duration of single partial counting unit: 100 minutes
Abbreviations: B - background
               ST - standard of modern C-14 activity
               U1, U2 - unknown samples

Day	Start at; counted	Number Sample results	Counting of partial (minutes)	time
Monday	morning	B	4	400
"	evening	U1	10	1000
Tuesday	morning	B	4	400
"	evening	U2	10	1000
Wensday	morning	ST	4	400
"	evening	U1	10	1000
Thursday	morning	B	4	400
"	evening	U2	10	1000
Friday	morning	ST	4	400
"	evening	B	38	3800
Monday	morning	U1	4	400
"	evening	U2	10	1000
Tuesday	morning	ST	4	400
"	evening	U1	10	1000
Wensday	morning	U2	4	400
"	evening	B	10	100
Thursday	morning	U1	4	400
"	evening	ST	10	1000
Friday	morning	U2	4	400
"	evening	ST	38	3800

Total counting times:

  B : 6000 minutes (5 series with 60 partial results)
ST : 6000 minutes (5 series with 60 partial results)
U1 : 3800 minutes (5 series with 38 partial results)
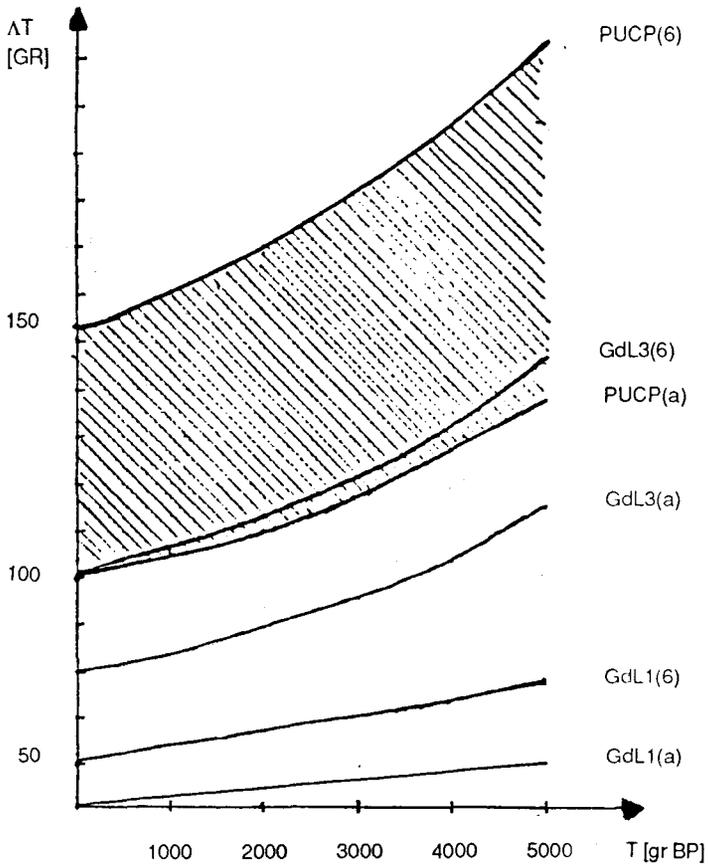U2 : 3800 minutes (5 series with 38 partial results)

Fig. 8. ed theoretical accuracy of age determination for the PUCP counting unit compared with accuracy of dating available at Gliwice Radiocarbon Laboratory. Detailed explanations in the text.

For testing the overall efficiency of counting and estimating the approximate value of the counting rate of the modern C-14 activity, benzene obtained from combustion of the recent wood collected in the center of the university area was prepared. The wood was grown most probably during the last two-three years (vegetation seasons 1987-1989) and its C-14 activity can be roughly estimated as 5-10% higher than the activity of the contemporary uncontaminated biophere. The counting rate obtained with this sample is equal to:

$$S = 8.59 \pm 0.16 \text{ cpm/1gC.}$$

with the known theorical counting rate of the modern C-14 activity standard sample, equal to 13.56 cpm/1gC, it is easy to estimate the counting efficiency available with the actual equipment of the radiocarbon laboratory of PUCP. The counting efficiency is equal to 63%, that is close to the value assumed in case a and therefore it may be concluded that the estimate of the theoretical error of dating with the actual equipment should be close to the level indicated by curve PCP(a) in Figure 8. Using this value it is possible to estimate that the counting rate which can be expected for the 3 ml sample of NBS OXALIC ACID STANDARD will be ca 22.7 counts per minute.

In the field of radiocarbon dating the quality of the counting system is commonly described by quoting three related parameters: background counting rate B, factor of merit F, and range of dating, i.e. maximun age of sample which can be measured, Tmax. The factor of merit is defined as

$$F = \frac{S_o}{\sqrt{B}}$$

where So is counting rate of standard of modern C-14 activity. The maximum theoretical measurable age, estimated on assumption of stability of background counting rate, is determined by the equation

$$T_{max}^{theor} = 8033 \ln \frac{S_o}{k\sqrt{B/\tau}}$$

where τ denotes measuring time and the value of k, which determines the confidence level, is taken usually as equal to 2,3 or 4. In case of very high long-term stability of the counting equipment it is accepted that k=2, in the presence of some fluctuations k is taken equal 3 or 4. After substituting the expression for F we obtain

$$T_{max}^{theor} = 8033 \ln \frac{F}{k\sqrt{\tau}}$$

Assuming $S_o = 22.7$ cpm, as was indicated by counting the sample of modern wood, and counting time $\tau = 4000$ minutes, we obtain that the factor of merit of the counting system, in the actual status, is equal to ca. 10, and is comparable with the corresponding parameter of the counting unit L3 of the Gliwice Radiocarbon Laboratory.

Theoretical range of dating may be estimated as equal to 35,000 yr BP. However, because of significant fluctuations of the background counting rate, the real range of dating is remarkably lower. It can be estimated accounting for the real fluctuations of background counting rate from the equation [5].

$$T_{max}^{exp} = 8033 \ln \frac{S_o}{k\,S_B}$$

where S_B is the real scatter of the background counting rate observed in a reasonably long time. Assuming $S_B = 0.11$ cpm, as is indicated by real scatter of background counting rate values obtained in a series of measurements performed during one month (cf Table 1), we obtain the estimate of real range of dating as equal to 28,000 yr BP.

The comparison of the physical parameters of the dating system of the Radiocarbon Laboratories of PUCP and Silesian Technical University is given in Table 5. It may be concluded, that the actual parameters of the liquid scintillation counting system of PUCP are comparable to those of small proportional counters of the Gliwice Radiocarbon Laboratory.

Table 5.- Comparison of physical parameters of dating units at PUCP and Gliwice Radiocarbon Laboratory.

Unit	Volume of sample	Mass of carbon	B cpm	S_o cpm	F	T_{max} min	T_{max} kyr BP
GdL1	2.5 l	4 g	7.00	36.65	14	2500	45
GdL2	4.5 l	6 g	6.00	49.50	20	5000	55
GdL3	1.5 l	1 g	1.95	10.25	7	2500	38
GdL4	0.5 l	0.8 g	2.40	6.55	4	5000	30
GdL5	0.5 l	0.8 g	2.25	6.55	4	5000	30
GdL6	0.5 l	0.8 g	2.55	6.55	4	5000	30
PUCP	3.0 ml	8 g	4.83	22.70	10	4000	32

Dating unit GdL2 is especially constructed and calibrated and is used exclusively for high-accuracy dating of charcoal and wood for archaeological and dendrochronological studies. The dating accuracy available with quoted parameters is ca. 25 yr for samples younger than 5,000 BP [6].

CONCLUSIONS

It should be pointed out that the estimates presented in Figure 8 and in Table 5 do not account for some other sources of errors, and in particular, do not account for the systematic errors caused by possible fractionation during systhesis of benzene samples, as well as for the errors connected with the quenching effects, illustrated in Figures 1A and 1C. The magnitude of these errors should be carefully determined before any attempts of radiocarbon dating with the equipment actually available at the PUCP are carried out. It should be also noted in Figure 8 the importance of slight improvements of the counting system. Increasing the counting efficiency from 50 to 60% and decreasing the instabilities from level w = 2.5 to the level w = 1.8 causes an important decrease of the dating error.

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