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COMPARISON OF THE RADIOCARBON DATING METHODS USED IN THE GLIWICE RADIOCARBON LABORATORY

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Abstract. In the Gliwice Radiocarbon Laboratory the technique of gas proportional counters (GPC) filled with CO_2 has been used since the beginning of 70ties. In 1994 the Gliwice Radiocarbon Laboratory started the operation of a liquid scintillation spectrometry system (LSC technique) which consists of a Quantulus 1220 spectrometer and two vacuum rigs for benzene production. The work on the calibration of the Quantulus 1220 for the purpose of radiocarbon dating in three different counting geometries was undertaken. This paper presents characteristic parameters (background and standard counting rates) of facilites working on the basis of the methods above (GPC and LSC), and a comparison of results of radiocarbon dating obtained using other GPC and LSC facilities. Assessment of the analytical accuracy and precision achieved in routine liquid scintillation counting was based on the results of ^{14}C measurements for TIRI intercalibration samples (and other samples), and on the comparison with the results obtained with the well established gas proportional counting method performed in the Gliwice Laboratory.

1. INTRODUCTION

Precision and range of the radiocarbon dating are limited by low ^{14}C concentration in different carbon reservoirs. These concentration decrease in time according to radioactive decay law. Decrease is determined by half life of the ^{14}C and begins at the moment of death of living organism or sedimentation of mineral material. Especially decrease begins at crystallisation of calcite.

Other limitations of radiocarbon dating method has its source in the very low value of ^{14}C decay constant (λ=2,368x10^{-10} min^{-1}) and low maximum energy of β particles emitted in the decay of ^{14}C which is equal to 156 keV.

Conventional radiocarbon age of sample is commonly denoted as years BP, yrs BP, conv BP or simply BP. This age means the time, which elapsed from the moment when carbon exchange between dated material and its environment was stopped to arbitrary chosen year 1950 AD. It is stipulated calendar year, which ends the period of 50,000 years without human interference into the atmospheric ^{14}C concentration. This interference has valuable influence on choose of the standard of the ^{14}C concentration in the biosphere.

Assumed constant value of ^{14}C concentration in the biosphere (S_0) in the period of range of radiocarbon dating method allows to calculate conventional radiocarbon age. When contemporary radiocarbon concentration of investigated sample is known, radiocarbon age of sample may be calculated using formula:

$$T = 8033 \ln \frac{S_0}{S} \qquad (1.1)$$

Due to isotopic fractionation of carbon in the assimilation and geochemical processes, there is a need to apply appropriate correction (using $\delta^{13}C$ value) to the measured ^{14}C concentration in the standard and sample. Correction should be applied using formula (Stuiver and Polach, 1977):

$$S = S_m \left[1 - \frac{2(\delta^{13}C + 25)}{1000} \right], \qquad (1.2)$$

where S_m means measured ^{14}C concentration in the sample. $\delta^{13}C$ value is determined independently using mass spectrometry method. $\delta^{13}C$ is equal about -25‰ for organic samples and vary from small positive values for some carbonate sediments to -40‰ for plants which assimilate CO_2 in the C3 photosynthesis cycle.

2. PRECISION AND RANGE OF RADIOMETRIC RADIOCARBON DATING

There are two main radiometric radiocarbon dating methods: gas proportional counting (GPC) and liquid scintillation counting (LSC). All these techniques needs to determine background counting rate (also called background). Background is the counting rate for sample which in the radiocarbon dating point of view has unlimited age. Sources of that counting rate are different in different counting techniques.

Other measured quantities which are necessary to calculate radiocarbon age (see equation 1.1) are: counting rates for the investigated sample (S) and standard of contemporary biosphere (S_0). Both counting rates are proportional to the concentration of radiocarbon in sample and standard respectively.

Directly it is only possible to determine S_0+B, $S+B$ and B values. Commonly samples which fulfil condition $S>>B$ are called „young samples". Their ages are usually younger than 10,000 BP. While samples for which $S<<S_0$ are commonly called „old samples". Age for such samples is always older than 20,000 BP. ^{14}C concentration in standard and samples are obtained with accompanying error which determine laboratory error of conventional radiocarbon age:

$$\Delta T = 8033\left[\left(\frac{\Delta S}{S}\right)^2 + \left(\frac{\Delta S_0}{S_0}\right)^2\right]^{1/2}, \qquad (1.3)$$

where ΔS and ΔS_0 are errors of determined S and S_0 respectively. ΔS and ΔS_0 are proportional to $t^{-1/2}$ where t is a counting time.

Factor of merit which characterise maximum determinable age is given by equation:

$$FOM = \frac{S_0}{\sqrt{B}} \qquad (1.4)$$

Maximum determinable age for given counting time on measurement system characterised by FOM value may be calculated using formula:

$$T_{max} = 8033 \ln(0{,}3546\ FOM\ t^{1/2}). \qquad (1.5)$$

Increase of maximum determinable age of system used for the radiometric radiocarbon dating is only possible by enlarging the counting time or by use of a few detectors with the same FOM value.

3. GAS PROPORTIONAL COUNTERS

Background counting rate for a properly designed proportional counter may be estimated using simplified model and its empirical equation:

$$B_{st} = 0{,}0081\ M + 5A \times 10^{-4} \qquad (1.6)$$

where M is a mass of gas in grams and A is the inner area of the counter [in cm^2]. Low B_{est} value in a given counter geometry demonstrates the absence of radioactive contamination of material used for counter construction. Detailed study of factors which may influence the background counting rate of proportional counters are presented by Theodorsson (1991, 1998). **Table 1** contains description of proportional counter systems used in the Gliwice Radiocarbon Laboratory.

Design of GPC measurement systems used in the Gliwice Radiocarbon Laboratory was described by A. Pazdur and M.F. Pazdur (1986). All GPC systems used for radiocarbon dating are filled with CO_2.Values in brackets are masses of pure carbon (in g) in sample needed for filling proportional counter when assuming no loss of carbon during carbon dioxide preparation.

Counters L1, L2, L3 are equipped with outer active anticoincidence guard consisting of multiwire GM counters, while systems L4 and L5 are inserted in the same anticoincidence guard made from the independent GM counters.

Counters L2, L3 operates in horizontal position. L3 is also equipped with a 2 cm thick mercury passive shield which is situated close to the counters wall. Since A. Pazdur and M.F. Pazdur (1986) publication counter L4 and L5 were redesigned and now their volume is about half of the previous one.

T_{max} values were estimated according to counting time t=1000 min. It is important to notify that counting time t=1000 min was arbitrary chosen only to compare different counting systems. For "old samples", which have radiocarbon age close to the maximum determinable age

Table 1. *Parameters of proportional counters systems used in the Gliwice Radiocarbon Laboratory. Abbreviation PRA means registration mode with active pulse rise time analysis (Michczyński et al., 1995, 1998). Estimations of T_{max} were done for counting time t=1000 min.*

GPS System name	V [l]	p[atm] ([g C])	S_0 [cpm]	B [cpm]	B_{est} [cpm]	B/B_{est}	FOM	T_{max} [years]
L1a	2.9	2.2(3.5)	36.18±0.10	6.795±0.024	0.76	8.94	13.9	39,800
L1b	2.9	1.0(1.5)	17.93±0.07	6.024±0.048	0.72	8.37	7.3	35,100
L1a,PRA	2.9	2.2(3.5)	29.65±0.05	2.832±0.018	0.76	3.73	17.6	42,500
L2	3.8	2.2(4.5)	48.234±0.16	5.667±0.035	0.99	5.72	20.3	43,600
L3	1.5	1.0(1)	7.813±0.025	2.255±0.012	0.45	5.01	5.2	33,100
L4	0.3	1.0(0.3)	1.676±0.010	1.064±0.006	0.19	5.60	1.6	22,900
L5	0.3	1.0(0.3)	1.686±0.013	0.963±0.003	0.19	5.06	1.7	23,700

counting time is about a few thousand minutes. For the L2 counter for example it means that maximum determinable age is about 50,000 BP. For L1a maximum determinable age is about 46,000 BP, while for smallest detectors L4 and L5 T_{max} is about 32,000 BP.

4. LIQUID SCINTILLATION β SPECTROMETRY (LSC)

Commonly used in radiocarbon laboratories are commercially available liquid scintillation spectrometers Packard and Quantulus. Comparison of maximum determinable age for this type of spectrometers is presented in **Table 2** (Polach *et al.*, 1988; Pawlyta *et al.*, 1998).

Lowest background counting rates for these systems are obtained when using teflon vials. Commonly 3 ml volume of sample benzene is used for counting. For everyday use disposable low potassium glass vials are preferred.

In the Gliwice Radiocarbon Laboratory Quantulus LSC operates also in two other counting geometries: 2 ml and 0.8 ml. 3 ml, 2 ml and 0.8 ml of benzene may be obtained from samples containing respectively 2.43 g, 1.62 g and 0.65 g of pure carbon when assuming no loss of carbon during benzene preparation. However properly processed procedures of benzene preparation may cause loss no more than a few percent of initial carbon. Efficiency (Eff. [%]) presented in the **Table 2** means counting efficiency of ^{14}C beta particles. For comparison counting time t=1000 min was used when estimating T_{max} for LSC operated in Gliwice. Real counting time for small and "old" samples is about 3000 to 5000 min.

5. LABORATORY ERRORS IN GPC AND LSC METHODS

As it was written before, the increase of counting time leads to reduction the laboratory error of obtained conventional radiocarbon age. Comparison of estimated laboratory errors for different counting time and different counting systems (L1a and Quantulus 1220 operated in Gliwice) are presented in **Table 3**.

Estimation of error was done for maximum ^{14}C concentration, which corresponds to the ^{14}C concentration in the contemporary biosphere and for 3 ml counting geometry. Results presented in **Table 3** show, that error for GPC system L1a are a bit lower than for LSC system. It is also evident that enlarging the counting time beyond 2000 minutes practically has no influence on laboratory error. Value of laboratory error of conventional radiocarbon age depends on ^{14}C concentration in the investigated sample and therefore on sample age. That dependence is illustrated in **Table 4**.

***Table 3**. Comparison of laboratory errors (ΔT) of conventional radiocarbon age for GPC system L1a and LS spectrometer QUANTULUS 1220 (Gliwice Radiocarbon Laboratory).*

t [min]	L1a, ΔT [years]	Q1220, ΔT [years]
1000	50	65
2000	40	50
3000	35	40
4000	30	40
5000	30	35

***Table 4**. Laboratory errors of conventional radiocarbon age as a function of sample age. Comparison of measurement precision for Gliwice Radiocarbon Laboratory and Waikato Radiocarbon Laboratory in New Zeland (Pazdur et al., 1999).*

Sample age [yrs BP]	A L1a	B Q, Gliw.	C NZ,hp	D NZ,st.	E NZ, mp
500	50	60	25	50	120
1000	55	65	25	50	120
5000	70	80	30	65	150
10 000	110	110	40	85	200
20 000	300	220	70	170	390
30 000	940	490	150	350	870
40 000	3200	1300	400	900	2400
50 000	–	4200	1300	2700	–

Explanation of symbols used in Table:

A, B, C, D, E – laboratory errors ΔT, [yrs]. Symbols: hp, st i mp denotes respectively dating in high, standard and medium precision.

A – GPC system L1a, Gliwice, required 3.5 g of C

B – QUANTULUS 1220, Gliwice, required 2.4 g of C

C – high precision, required 50 g of C

D – standard precision, New Zeland, required 8-12 g of C

E – standard precision, small sample, required 1g of C

NZ=*New Zealand, information from Internet* (http://www2.waikato.ac.nz/c14/)

***Table 2**. Comparison of commercial spectrometers PACKARD and QUANTULUS (Polach et al., 1988, Pawlyta et al., 1998) (*)= with active anticoincidence guard and thicker passive lead shield.*

System	Vial	V [ml]	S_0 [cpm]	B [cpm]	Eff. [%]	FOM	T_{max} [BP]
PACKARD 2000	Glass	3	17.9	1.01	54.2	18	42,600
PACKARD 2060	Teflon	3	23.6	0.69	71.4	24	45,000
QUANTULUS	Teflon	3	25.2	0.21	76.4	55	51,600
QUANTULUS(*)	Teflon	3	23.1	0.14	70.0	62	52,600
Gliwice							
QUANTUL.1220	Glass	3	20.80	0.357	62.9	35	47,900
	Glass	2	12.39	0.252	56.3	25	45,100
	Glass	0.8	5.27	0.061	59.6	21	43,900

Parameters for two before measurement described systems used in the Gliwice Radiocarbon Laboratory are accompanied by data published in the Internet by Waikato Radiocarbon Laboratory in New Zealand. Waikato Radiocarbon Laboratory is making ^{14}C analysis from many years using all available measurement methods.

The precision of radiocarbon dating is described by the error given together with dating result. **Table 5** presents conventional radiocarbon age of randomly selected samples which were then dated using GPC and LSC systems in Gliwice. There are also results of dating of special series of samples – TIRI. Every few years there are interlaboratory comparison projects organised that, involve many of radiocarbon laboratories. All of them date the same samples that have different origin and age. Previously organised project with codename TIRI ended in the 1994 by publication of results during International Radiocarbon Conference in Glasgow. In the year 1995 Gliwice Radiocarbon Laboratory has done few radiocarbon analysis for samples from TIRI project mainly to calibrate commissioned LSC system. For comparison between GPC and LSC systems in Gliwice the same samples were dated using GPC. Dates presented in GPC column in **Table 5** were obtained using one of GPC system (L1a, L1b, L2, L3, L4 or L5). Values presented in TIRI column represent mean consensus values obtained by 60 radiocarbon laboratories which used GPC or LSC systems (Gulliksen and Scott, 1995). Error presented in that column corresponds to the spread of data obtained from all laboratories involved in the project.

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***Table 5.** Comparison of ^{14}C ages obtained by GPC and LSC systems in the Gliwice Radiocarbon Laboratory (Pazdur et al., 1999). TIRI samples comes from Third International Radiocarbon Intercomparison (Gulliksen and Scott, 1995).*

Sample name	LSC [BP]	GPC [BP]	TIRI [BP]
CAH 91/30	1750 ± 70	1710 ± 50	
CAH 91/31	1730 ± 70	1840 ± 50	
CAH 91/32	2045 ± 70	2045 ± 50	
Strzegocice	1200 ± 80	970 ± 30	
OB34535 ± 80	4500 ± 60		
NASZ581020 ± 110	1020 ± 40		
M17A/27135 ± 130	7320 ± 80		
TIRI H		11300 ± 80 (L1b)	11152 ± 23
TIRI I	10930 ± 75	11070 ± 70 (L1a)	11060 ± 17
		11280 ± 90 (L1b)	
		10880 ± 100 (L3)	
TIRI J	1530 ±50	–	1605 ± 8
TIRI K		17170 ± 80 (L1a)	18155 ± 34
		17990 ± 80 (L1b)	
		17310 ± 160 (L3)	
		17000 ± 470 (L4)	
		18270 ± 440 (L5)	
TIRI L	13090 ± 170	13330 ± 90 (L1b)	12790 ± 30

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