

PRECISION OF ^{14}C DATING IN GLIWICE RADIOCARBON LABORATORY. FIRI PROGRAMME

ANNA PAZDUR, MARIUSZ FOGTMAN, ADAM MICHCZYŃSKI and JACEK PAWLYTA

*Department of Radioisotopes, Institute of Physics, Silesian University of Technology,
Krzywoustego 2, 44-100 Gliwice, Poland (e-mail: pazdur@polsl.gliwice.pl)*

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Abstract: In this paper the precision and accuracy of radiocarbon dating in Gliwice Radiocarbon Laboratory on the background of intercomparison programs is discussed. Here are briefly presented results of individual comparisons between laboratories from eight countries and three international intercomparison programmes: ISC Programme (1986), TIRI Programme (1994) and FIRI Programme (1999). Moreover the short description of Gliwice Radiocarbon Laboratory is presented. The main stress is laid on the description of FIRI Programme – types of samples included in Programme and methods of calculation of consensus values, but first of all the participation of our Laboratory in the programme is presented: pretreatment procedures of samples, results obtained in Gliwice and statistical analysis of these results. The most important conclusion, which may be drawn from this paper, is that Gliwice Radiocarbon Laboratory dating results are not biased by systematic error.

1. INTRODUCTION

Intercomparison Programs (IP) history

Presently there are above three hundred laboratories all over the world which take advantage of ^{14}C dating. There are three measurement techniques used in ^{14}C concentration determination:

- gas proportional counters (GPC) which uses proportional counters filled by CO_2 or methane as a counting medium,
- liquid scintillation counting (LSC) or rather liquid scintillation beta spectrometry which uses benzene as a counting medium and diluent of a solid state scintillator,
- accelerator mass spectrometry (AMS) which uses atom counting approach for ^{14}C concentration determination.

Scientists are pursuing to unification of results obtained with use of all these methods for the sake of pretreatment, age or activity determination and interpretation of results. This is the reason for introducing Intercomparison Programs (IP).

The first comparison between laboratories took place in the 70's. At the same time all ^{14}C laboratories in UK carried out a precision control. In 1980 Glasgow Laboratory initiated the first International Radiocarbon Intercomparison Program.

The International Collaborative Study program (ICS) was established during XII International Radiocarbon

Conference in Trondheim in 1986 (Pazdur *et al.*, 1990). This program was coordinated by a group from Glasgow University. ICS was split into three parts and 60 laboratories took part in this program. 16 samples were sent to every laboratory within the confines of ICS and some of the samples were the same, but that information wasn't known to the laboratories.

The next program took place in May of 1990. 137 laboratories took part in IAEA (International Atomic Energy Agency) coordinated program. Laboratories made activity/age determination for 5 samples (carbonates, cellulose, woods and sucrose). In all 69 results: 38 were obtained by LSC, 25 by GPC and 6 by AMS technique. A summary of the results is given in **Table 1**.

The Third International Radiocarbon Intercomparison (TIRI) started in 1994. About 60 laboratories sent the results of ^{14}C dating of 13 samples. A description of these samples and the consensus values are presented in **Table 2**.

The latest comparison program was the Fourth International Radiocarbon Intercomparison (FIRI). This program was managed by Department of Statistics, Glasgow University. Ten samples were sent to each of the participating ^{14}C laboratories in September 1999 and the results from the measurements were collected in the end of August 2000 (Scott, 1999).

The description of the FIRI samples is presented in chapter four of this paper.

Table 1. Results of ^{14}C activity determination in IAEA Programme (Rózański et al., 1992). Values in parenthesis are numbers of results of all laboratories, values beside were considered as correct.

Sample code	Material	Number of measurements	Expected value (pMC)	Standard deviation (pMC)
C-1	Carbonate	36 (73)	0.02	0.02
C-2	Carbonate	64 (92)	41.14	0.03
C-3	Cellulose	49 (84)	129.41	0.06
C-4	Wood	36 (79)	0.20 – 0.44	–
C-5	Wood	49 (75)	23.05	0.02
C-6	Sucrose	22 (39)	150.61	0.11

Table 2. Samples from TIRI programme with results (Gulliksen and Scott, 1994).

Sample code	Material	Consensus value ^{14}C Age (BP)	Estimated Precision (years)
TIRI A	Barley mash	116.35 pMC	0.0084 pMC
TIRI B	Belfast pine	4503	6
TIRI C	IAEA cellulose	129.7 pMC	0.008 pMC
TIRI D	Hekla peat	3810	7
TIRI E	Ellanomore humic	11,129	12
TIRI F	Icelandic doublespar	46,750	12
		0.18 pMC	0.006 pMC
TIRI G	Fuglaness wood	39,784	620
TIRI H	Ellanomore whole peat	11,152	23
TIRI I	Travertine	11,060	17
TIRI J	Crannog wood	1605	8
TIRI K	Turbidite carbonate	18,155	34
TIRI L	Whale bone	12,788	30
TIRI M	Icelandic peat	1682	15

Purposes of IP

The most essential points in dating are precision, maximum determinable age and counting efficiency. An important factor is also the amount of measurements which may be carried out in the laboratory per year. When we want to determine the precision of sample age, we should:

- eliminate any contamination during chemical pretreatment,

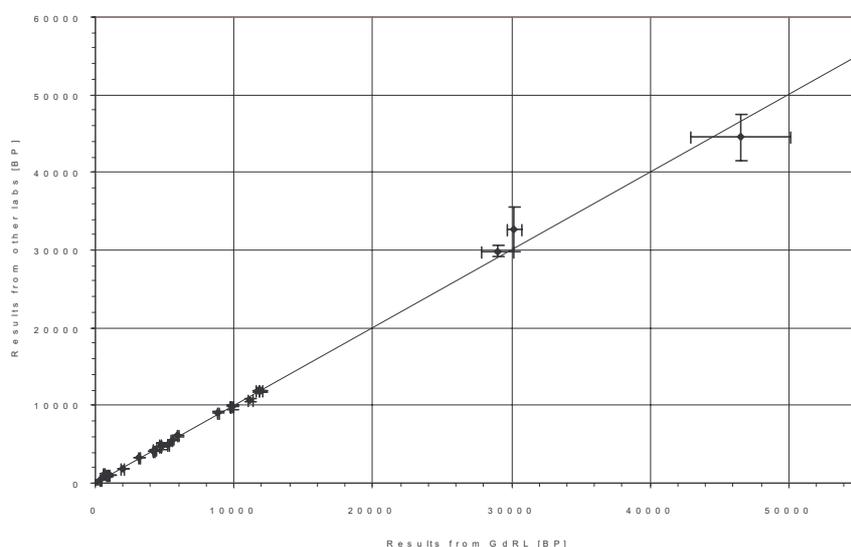
- carefully purify the counting medium,
- take $\delta^{13}\text{C}$ corrections into consideration,
- calculate correctly the concentration of ^{14}C in the sample and consequently age,
- calculate correctly a final uncertainty.

In most cases because of sample size we are not able to double ^{14}C age determination for ordinary sample. Then the only one possibility of getting comparable results from different laboratories is to make a crosscheck with use of intercomparison programs.

2. GLIWICE RADIOCARBON LABORATORY IN IP

Comparison between laboratories

Laboratories in: Gliwice, Łódź, Groningen, Hanover, Lyon, Uppsala, Lower Hutt and Bratislava took part in an interlaboratory comparisons of ^{14}C dating. The results of this comparison and type of dating material are presented in **Table 3** (see also **Fig. 1**). The samples presented in **Table 3** represent most of important dating materials, in principle. Some samples are modern and others have age close to the range of dating technique. The results for sample 7 obtained in Gliwice Radiocarbon Laboratory (GdRL), Gd-560 (685 ± 55 BP) and in Hanover Laboratory Hv-9105 (1230 ± 65 BP) are different, which is probably caused by unknown gross error.

**Fig. 1.** Comparison of dating age for samples dated in Gliwice Radiocarbon Lab and others laboratory - straight line is shown the equality of ages. (see Table 3 and 4).

**Comparisons based on information
from another laboratory**

Many laboratories have obtained information about dating results from sample submitters who have sent the same sample to more than one laboratory. Our results and results from laboratories in Berlin and Groningen are presented in **Table 4** (see also **Fig. 1**). Results from Gliwice Radiocarbon Laboratory (GdRL) are consistent with results from other laboratories. Comparison of values obtained in GdRL and other laboratories shows that most of them are identical when taking into the account uncertainty range.

ICS Programme

As mentioned, the ICS Programme consisted of three stages. In the first stage all laboratories obtained a carbonate sample with different ^{14}C concentration. These samples didn't require pretreatment. The purpose of this stage was to check the calibration of the measurement systems.

In the second stage laboratories made ^{14}C analysis of two cellulose and two humic acid samples. In this case the methods of production and purification of CO_2 from organic samples and measurement systems of ^{14}C concentration were checked.

Table 3. Results of individual comparison between laboratories (Pazdur et al., 1990).

No.	Sample name	Material	GdRL code Gd -	^{14}C Age (BP)	Laboratory code	^{14}C Age (BP)
1	Iwanie	Charcoal	567	3190 ± 45	GrN - 5250	3235 ± 35
2	Radziejów	Charred grains	574	4720 ± 55	GrN - 5045 M - 1846 Lod - 1	4710 ± 40 4860 ± 200 4670 ± 380
3	NLBH - 1	Wood	558 1003	11,940 ± 120 11,685 ± 105	Hv - 6958	11,850 ± 110
4	NLBH - 2	Wood	559	9805 ± 105	Hv - 6960	9915 ± 95
5	Miodowice	Peat	541	11,190 ± 175	GrN - 8890	10,710 ± 150
6	Kluki/74	Peat	558	9865 ± 105	Hv - 9104	9855 ± 315
7	Stolpie	Charred grains	560	685 ± 55	Hv - 9105	1230 ± 65
8	NZ - 1	Charcoal	1044	8870 ± 95	R - 5590	9105 ± 105
9	Jaureus sect. 20	Bone	1695	30,200 ± 500	Ly - 1938	32,630 ⁺²⁹⁰⁰ ₋₂₁₀₀
10	L'Amourette no. 3	Wood	3017	46,500 ⁺³⁶⁰⁰ ₋₂₆₀₀	Ly - 1322	44,500 ⁺³⁰⁰⁰ ₋₂₀₀₀
11	Tremble Bois 1963	Wood	2322	165.4 ± 0.8 pMC	Ly	170 ± 2 pMC
12	Tremble Bois 1964	Wood	2249	194.1 ± 1.7 pMC	Ly	193 ± 2 pMC
13	Tremble Bois 1964	Wood	2329	189.2 ± 1.9 pMC	Ly	193 ± 2 pMC
14	Młyniska s 748	Peat	2118	29,000 ± 1200	Ly	29,880 ± 740
15	Novograd nr 70	Wood	2143	870 ± 60	Ly	1000 ± 100
16	IW 31 - 40	Wood	2317	5250 ± 80	U	5000 ± 52
17	Kastelholms	Charcoal	2326	400 ± 60	U	430 ± 50
18	Cahuachi 88/6	Charcoal	3441	5535 ± 30	GrN - 16593	5555 ± 45

Table 4. Results of intercomparison based on information from another laboratories (Pazdur et al., 1990).

No.	Sample name	Material	GdRL code	^{14}C Age (BP)	Code of other labs	^{14}C Age (BP)
1	Grzegowice	Charcoal	Gd-259	1960 ± 140	Bln-1349	1810 ± 60
2	QS V/79	Charcoal	Gd-693	5960 ± 60	Bln-2335	6075 ± 50
3	QS 1/79 Gt. 145-150 cm	Charcoal	-	-	Bln-2333	5555 ± 60
	QS 1/79 Gt. 170-175 cm	Charcoal	Gd-1140	5540 ± 70	-	-
	QS 1/79 Gt. 175-185 cm	Charcoal	-	-	Bln-2334	5645 ± 55
4	Orle pal. 1	Wood	Gd-2331	990 ± 100	GrN - 12896	1070 ± 30
	Orle pal. 2	Wood	Gd-2328	1000 ± 100	-	-
5	Kierzkowo	Bone	Gd-4404	4230 ± 90	GrN-15411	4135 ± 40
6	Kierzkowo	Bone	Gd-4406	4310 ± 90	GrN-15412	4270 ± 40

In the third step laboratories dated four wood samples, shell and peat samples. The ages of the wood samples were determined independently by dendrochronology. The dendrochronological ages were only known to ICS organisers. In **Table 5** results from dating of these samples in GdRL are compiled.

GdRL results of the first stage were consistent with ICS results when taking uncertainty ranges into account. In the second stage, the GdRL ages of samples were about 300-350 years BP older than ICS values. The reason for these systematically older results was probably wrong estimation of the background counting rate. Another possible reason may have been improper purification of the CO₂ gas. GdRL results from the third stage are close to ICS conventional ages.

TIRI Programme

In 1995 in GdRL were dated some TIRI samples. Those measurements were carried out during LSC system commissioning and calibration process. For comparison purpose samples were also dated using GPC technique. Results of this comparison are presented in **Table 6**. In the round brackets a counter types are reported. The TIRI ages are consensus values from about 60 laboratories, which took part in TIRI Programme.

FIRI Programme

The broad geographical distribution of the participating laboratories is shown in the **Table 7**. In **Table 8** we can see the number of different techniques used in the laboratories (Scott, 2001B). In this programme 92 sets of results were obtained but several laboratories operate independent measurement systems, thus the total number of submitted results exceed the number of participating laboratories. An interesting issue is the background and modern standards samples, which were in use. **Tables 9** and **10** show the number of laboratories, which reported type of background and modern standard sample used.

Table 6. Results of TIRI samples dating in GdRL (Pazdur et al., 1999). L1a, L1b, L3, L4 and L5 are symbols of the GPC systems in GdRL.

Sample code	GPC ¹⁴ C Age (BP)	LSC ¹⁴ C Age (BP)	TIRI ¹⁴ C Age (BP)
TIRI H	11,300 ±80		11,152 ±23
TIRI I	11,070 ±70 (L1b) 11,280 ±90 (L1b) 10,880 ±100 (L3)	10,930 ±75	11,060 ±17
TIRI J		1530 ±50	1605 ±8
TIRI K	17,170 ±80 (L1a) 17,990 ±80 (L1b) 17,310 ±160 (L3) 17,000 ±470 (L4) 18,270 ±440 (L5)		18,155 ±34
TIRI L	13,330 ±90 (L1b)	13,090 ±170	12,790 ±30

Table 7. Geographical distribution of participating laboratories in FIRI programme.

Broad geographical description	Number of laboratories
Europe (EU)	35
Europe (non EU)	15
North America and Canada	13
South America	2
Asia and the Far East	15
Australia and New Zealand	4

Table 8. Laboratory type.

Laboratory type	Number participating
LSC	42
GPC	19
AMS	17
Target feeder for AMS	8
Direct absorption and LSC	4

AMS = Accelerator Mass Spectrometry, GPC = Gas Proportional Counting technique, LSC = Liquid Scintillation Counting technique.

Table 5. Results of samples dating within ICS Programme in GdRL (Pazdur et al., 1990). The numbers in brackets are mean Interquartile Range (IQR). ICS values in stages I and II are medians.

No.	Stage	Sample's code	Material	GdRL code (BP)	¹⁴ C Age (BP)	ICS Value
1	I	ICS 11B	Carbonate	Gd - 5041 Gd - 2575	3625 ±50 3570 ±80	3600 [3570, 3670]
2		ICS 110	Carbonate	Gd - 2604	3690 ±90	
3		ICS 11D	Carbonate	Gd - 2603	-80 ±80	-70 [-110, 0]
4		ICS 11	Carbonate	Gd - 2576	-120 ±70	
5	II	ICS 11N	Cellulose	Gd - 5164 Gd - 5171	2600 ±70 2600 ±60	2250 [2160, 2370]
6		ICS 11E	Cellulose	Gd - 5166	2390 ±50	
7		ICS 11L	Humic acid	Gd - 5165	3660 ±50	3390 [3290, 3450]
8		ICS 11F	Humic acid	Gd - 5163	3680 ±50	
9	III	ICS 11U	Wood	Gd - 3410	2165 ±30	2200 ±20
10		ICS 11R	Wood	Gd - 3412	2240 ±40	
11		ICS 11T	Wood	Gd - 3411	150 ±20	120 ±20
12		ICS 11G	Wood	Gd - 3413	275 ±30	305 ±20

Table 9. Background material.

Background classification	Number of laboratories
Anthracite	12
Benzene	17
Calcite	3
Coal	4
Graphite	3
Marble	25
Other	27

Table 10. Modern standard material.

Modern standard classification	Number of laboratories
ANU sucrose	9
Benzene	5
NBS Ox I	30
NBS Ox II	29
NBS 1/II	9
Other	5

Unfortunately not all laboratories reported this information.

We can notice that commercial dead benzene and marble are common and popular choices of background. In case of modern standard we can see that NBS Oxalic Acid are most commonly used. Over 60% of laboratories, which reported information about used standard sample use NBS Oxalic Acid.

3. GPC AND LSC SYSTEMS

Counting systems description

Gliwice Radiocarbon Laboratory now operates five custom designed gas proportional counters (GPC) and one commercially available liquid scintillation β spectrometer (LSC) Quantulus 1220TM. Comparison of our systems is presented in Pazdur *et al.* (2000). All of our GPC systems were used for FIRI measurements.

Pazdur A. and Pazdur M.F. (1986) described the design of GPC measurement systems used in GdRL. All GdRL GPC systems use CO₂ as counting gas. A detailed description of our GPC systems is presented in **Table 11**. Values in brackets are masses of pure carbon (in g) in sample needed for proportional counter filling when assuming no loss of carbon during carbon dioxide preparation.

Table 11. Parameters of proportional counter systems used in the Gliwice Radiocarbon Laboratory. Estimations of T_{max} (Stuiver and Polach 1977) were done for counting time $t=1000$ min. B_{est} was determined accordingly to Theodorsson (1991A) and FOM was calculated accordingly to Theodorsson (1991B).

GPC system name	V (l)	P(atm) (lg C)	S_0 (cpm)	B (cpm)	B_{est} (cpm)	B/ B_{est}	Eff (%)	FOM	T_{max} (years)
L1a	2.9	2.2 (3.4)	36.18±0.10	6.795±0.024	0.76	8.94	78	13.9	39,800
L1b	2.9	1.0 (1.55)	17.93±0.07	6.024±0.048	0.72	8.37	85	7.3	35,100
L3	1.5	1.0 (0.8)	7.813±0.025	2.255±0.012	0.45	5.01	72	5.2	33,100
L4	0.3	1.0 (0.16)	1.676±0.010	1.064±0.006	0.19	5.60	77	1.6	22,900
L5	0.3	1.0 (0.16)	1.686±0.013	0.963±0.003	0.19	5.06	77	1.7	23,700
L6	0.3	1.0 (0.16)	1.778±0.015	1.145±0.018	0.19				

V = volume of counter, p = pressure of gas in counter (mass of pure carbon), S_0 = standard counting rate, B = background counting rate, B_{est} = theoretical background counting rate, Eff = counting efficiency, FOM = Factor of Merit, T_{max} = maximum determinable age

Counters L1, and L3 are equipped with an outer active anticoincidence guards consisting of multiwire Geiger-Müller (GM) counters, while systems L4 and L5 are inserted in an anticoincidence guard made from independent GM counters.

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

T_{max} (Theodorsson, 1991B) values were estimated according to counting a time of $t=1000$ min. It is important to notify that 1000 min counting time was arbitrary chosen only to compare different counting systems. For “old samples”, which have radiocarbon age close to the maximum determinable age, counting times are about a few thousand minutes. For L1a real maximum determinable age is about 46,000 BP, while for the smallest detectors L4 and L5 T_{max} is about 32,000 BP. There are also B_{est} and FOM values presented in **Table 11**. B_{est} is a „theoretical” background counting rate calculated for our GPC counters while FOM is a Factor of Merit (Theodorsson, 1991A; Theodorsson, 1991B).

In GdRL, the Quantulus LSC operates in three counting geometries: 3 ml, 2 ml and 0.8 ml (Pawlyta *et al.*, 1998). 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 of no more than a few percent of the initial carbon. Efficiency (Eff. (%)) presented in **Table 12** means counting efficiency of ¹⁴C beta particles. For comparison purposes 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. Only 0.8 ml and 2 ml geometries were used for measurements of FIRI samples.

Uncertainty of radiocarbon age/radiocarbon activity determination

All calculations, which lead to determination of ¹⁴C activity and for most samples also to determination of conventional radiocarbon age and their uncertainties, are carried out according to the procedure given by Stuiver and Polach (1977) and revised by Mook and van der Plicht (1999).

Table 12. Parameters of QUANTULUS 1220TM LSC operated in Gliwice Radiocarbon Laboratory (Pawlyta et al., 1998). Estimations of T_{max} were done for counting time $t=1000$ min.

System	Vial	V (ml)	S_0 (cpm)	B (cpm)	Eff (%)	FOM	T_{max} (years)
QUANTULUS 1220	Glass	3	20.80	0.357	62.9	35	47,900
	Glass	2	12.39	0.252	56.3	25	45,100
	PTFE	0.8	5.27	0.061	59.6	21	43,900

V = volume of benzene, description of other symbols are given in Table 11.

Following uncertainties are included in radiocarbon activity and age uncertainty calculations in GdRL (Pazdur and Pazdur, 1986; Pazdur et al. 2000; Michczyński and Pazdur 1998)

GPC systems:

- Poisson uncertainty of counting rate for sample, background and standard samples,
- uncertainty of pressure of CO_2 in GPC determination (for sample, background and standard samples),
- uncertainty of determination of counting efficiency (for sample, background and standard samples),
- uncertainty of $\delta^{13}\text{C}$ determination for sample and standard sample.

LSC system:

- Poisson uncertainty of counting rate for sample, background and standard samples,
- uncertainty of determination of counting efficiency (for sample, background and standard samples),
- uncertainty of $\delta^{13}\text{C}$ determination for sample and standard sample.

Standard and background samples

Modern standard counting rate is determined during measurements of samples, which have well known ^{14}C activity. There are a few internationally accepted samples used for determination of modern standard counting rate (Curie and Polach, 1980; Mann, 1983). Two of them are used in Gliwice. National Institute of Standard and Technology SRM4990C (Oxalic Acid II or OXII) sample is used for S_0 determination for GPC systems and ANU Sucrose sample are used for S_0 for LSC system. ANU Sucrose (Polach 1976; Gupta and Polach, 1985) is preferred for LSC system because of its suitability for benzene preparation.

The background counting rates determination in Gliwice are based on anthracite and old carbonate samples for both GPC in LSC systems.

4. SAMPLES FOR ^{14}C DATING WITHIN FIRI PROGRAMME

In the FIRI Programme we obtained 10 samples, labelled from A to J. The materials were: wood, barley, humic acid, cellulose and carbonate. This chapter includes brief a description of the pretreatment undertaken before dispatch and instructions concerning their pretreatment (if any) before dating as given by Scott (1999).

Samples A and B were wood samples. These samples were subdivided to appropriate sample sizes (approx-

mately 50g for GPC and LSC laboratories and 5g for AMS laboratories) before being labelled and bagged. These samples were treated using the routine laboratory procedures for wood samples. These samples were considered as close to or beyond the limit of ^{14}C detection.

Sample C was turbidite carbonate. The material used in this study is derived from the middle ungraded deposit. The sample was supplied by Dr J. Thomson, Southampton Oceanography Centre. The sample was immediately oven dried (50°C), ground and fully homogenised before being bagged to size 100g for GPC and LSC laboratories and 10g for AMS laboratories. Finally samples were labelled. In laboratory this sample were fully hydrolysed and no fractions measured. This sample didn't require further pretreatment and was stored in a sealed container.

Sample D, F and H were dendro-dated wood samples. The dendro-dated samples (of 20 or 40 rings) were chiselled to appropriate sizes, at least 40g for GPC and LSC laboratories and at least 4g for AMS, before being labelled and bagged. These samples were treated using the routine laboratory procedures for wood samples.

Sample D was dated to the highest precision possible within the laboratory.

Sample E was a humic acid, which came from a coastal cliff deposit at St Bees Head in Cumbria, England. This sample has been exposed by erosion. In first step a large sample was digested in 2% KOH at 80°C . The alkali extracts were filtered and combined into a large container until over 150 l of solution were obtained. The solution was mixed and the humic acid precipitated by adjusting the pH to 3 by the stirred addition of 2M H_2SO_4 . Then the solid precipitate was recovered by filtration and given a preliminary wash with cold distilled water. Next it was re-dissolved, re-precipitated and dried. Finally the crystalline humic acid was washed free of sulphate inclusions with hot distilled water and re-dried. The size of this sample was 10g for GPS and LSC, and 1g for AMS laboratories. This sample requires no further pretreatment before dating.

Sample I was cellulose extracted from a dendro-dated wood. This wood was cut up finely and cellulose extracted using an acid-alkali-acid procedure. In the next step this cellulose was bleached using sodium chlorite. Then the extract was washed, dried at 40°C , physically mixed and packaged into samples of 10g for GPC and LSC, and 1g for AMS laboratories. This sample didn't require further pretreatment and was dated to the highest precision possible within the laboratory.

Samples G and J were barley mash, which was produced as a by-product of whisky manufacture. These

samples were considered as modern. These samples were force dried and physically mixed. Samples were bagged to size 50g for radiometric and 5g for AMS laboratories. These samples require no further pretreatment.

Table 13 contains information of all FIRI samples with their size and pretreatment procedure, which was carried out in Gliwice Radiocarbon Laboratory.

Table 13. Samples dated within the confines of FIRI with pretreatment procedure in GdRL. AAA – acid-alkali-acid procedure at 80°C.

Samples Code	Material	Mass (g)	Pretreatment in GdRL
FIRI A	Wood	50	AAA
FIRI B	Wood	50	AAA
FIRI C	Carbonate	100	No
FIRI D	Wood	50	AAA
FIRI E	Humic acid	10	No
FIRI F	Wood	50	AAA
FIRI G	Barley	50	No
FIRI H	Wood	50	AAA
FIRI I	Cellulose	10	No
FIRI J	Barley	50	No

5. RESULTS OF ^{14}C DATING BY GPC AND LSC TECHNIQUES

Results of all age or activity determinations carried out in Gliwice Radiocarbon Laboratory are presented in **Table 14**. Age determination results and corresponding uncertainties are presented in years BP while activity determination and corresponding uncertainties are presented in pMC. Presented uncertainties are 1σ . The uncertainty of $\delta^{13}\text{C}$ determination is better or equal to 0.1 ‰. Gd and GdS numbers are laboratory codes for GPC and LSC systems respectively.

6. STATISTICAL ANALYSIS OF DATING RESULTS WITHIN THE FIRI PROGRAMME

The results obtained from all laboratories, which participated in the FIRI Programme, were used for calculation of consensus values. Two individual methods of calculation were used – the first for samples C – J, and the second for samples A and B (Scott, 2001B).

Table 14. Results of ^{14}C dating determination for FIRI samples obtained in GdRL. Results are given in years BP except samples FIRI-G and FIRI-J for which results were given in pMC.

CS / Sample	L1b	L1a	L3	L4	L5	LSC 2ml	LSC 0.8ml	$\delta^{13}\text{C}$ (‰, PDB)
FIRI - A	39,250±1800 Gd-11523	>41,700 Gd-12192	39,000 ⁺⁵³⁰⁰ ₋₃₂₀₀ Gd-15030	>27,400 Gd-17004	>30,600 Gd-16005			-30.72
FIRI - B	41,500±1800 Gd-11524		>41,100 Gd-15057	>31,900 Gd-17001	>32,400 Gd-16002	>42,000 GdS-154		-30.98
FIRI - C	18,200±120 Gd-11530	18,990±280 Gd-12196				18,150±190 GdS-155	17,800±150 GdS-152	-2.42
FIRI - D	4370±45 Gd-11528	4510±55 Gd-12194					5630±160 GdS-153	-31.38
FIRI - E		12,140±140 Gd-12197	11,530±170 11,700±300 Gd-15056			11,460±120 GdS-156		-32.87
FIRI - F	4360±45 Gd-11522	4520±70 Gd-12190	4700±100 Gd-15058			4280±80 GdS-157		-32.18
FIRI - G	107.0±0.5 pMC Gd-11521	108.9±0.6 pMC Gd-12189				114.5±1.6 pMC GdS-158	111.15±0.75 pMC GdS-151	-33.12
FIRI - H	2180±40 Gd-11526	2220±60 Gd-12193		2230±150 Gd-13098	2310±150 Gd-14099	2110±70 GdS-159	2200±65 GdS-150	-31.13
FIRI - I			4870±100 Gd-15053 4470±110* Gd-15053*	5050±200 Gd-17000	5740±200 Gd-16001	5100±140 GdS-161 4760±135* GdS-161*		-21.69
FIRI - J	108.9±0.5 pMC Gd-11533					113.8±1.6 pMC GdS-160		-34.12

* = results recalculated after rejection of systematic error

CS = Counting System

Gd-, GdS- = Laboratory codes of date from GPC and LSC systems.

2ml, 0.8ml = benzene volume for LSC

Samples C - J

The procedure used in the calculation of the consensus values was an iterative procedure. The method of calculation of the consensus values splits into three steps (Róžański *et al.*, 1992; Scott, 2001B):

Step 1:

Gross outliers (in age or pMC) were rejected and preliminary consensus value (typically - the median) was evaluated using robust statistics. Outlying results were removed if they were either greater than $Q_3 + 3(Q_3 - Q_1)$ or less than $Q_1 - 3(Q_3 - Q_1)$, where Q_1 is lower quartile (25% of range) and Q_3 is upper quartile (75% of range; Fig. 2; Oktaba, 1974).

Step 2:

All results such that the interval result ± 2 sigma (uncertainty) includes the preliminary consensus value were identified.

Step 3:

The final consensus value based on weighted average of results from Step 2 was calculated.

The method of calculation of consensus values is considered for GPC, LSC and AMS laboratories separately. The final consensus values are calculated based on a weighted average of the sub-group results. The final consensus values and results from sub-groups are shown in Table 15. Results with large uncertainties were down

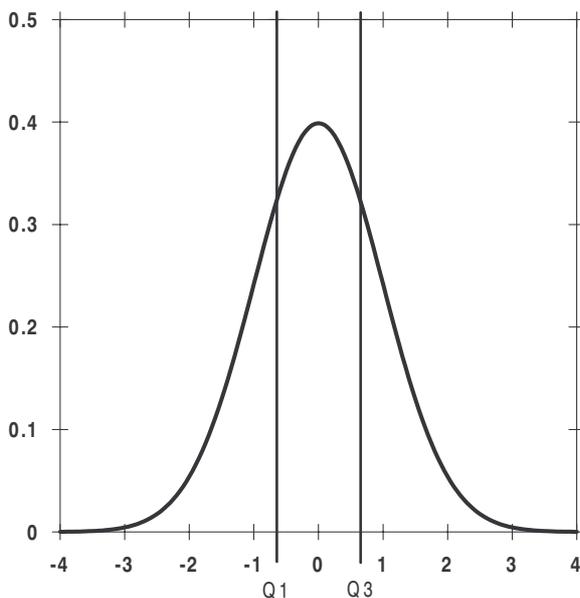


Fig. 2. Gaussian distribution with inter-quartile range IQR. Q_1 = lower quartile (25% of range), Q_3 = upper quartile (75% of range).

weighted in the calculation and therefore had a small impact on the final result. The final uncertainties are very small since the consensus values are based on a large number of results.

Samples A and B

The procedure described above could not be used for samples A and B because many laboratories did not quote finite ages and therefore an alternative approach was used. Because A and B were the same samples, all calculations were done for both together. The method of calculation of consensus value for samples A and B is described at points below:

- the results from tests suggested a range of 0.12 – 0.21 pMC,
- because many laboratories used various background and various pretreatment, the dating results formed broad range,
- finally the median amounted to 0.24 pMC, inter-quartile range 0.15 – 0.44 pMC and average amounted to 0.38 pMC – high discrepancy of results,
- some considerable variation in the results may be a function of laboratory background (estimation and material used) and limits of detection,
- many age results were reported as “older than” but the rest had a finite age,
- for results of dating samples A and B statistical test χ^2 (Oktaba, 1974) was carried out and a distribution of probability obtained. The final result for samples A and B was taken as 50% of this distribution,
- it may be noticed that AMS laboratories in general quoted older ages.

Distribution of probability, that age of samples is older than t for the three types of laboratories is shown in Fig. 3. The final results for samples A and B combined and for three types of laboratories are presented in Table 16. The result which is a mean of all laboratories in this table is the final value for samples A and B. This result was calculated on the basis of distribution of probability but for all laboratories altogether.

Table 16. Summary of ¹⁴C ages analysis by laboratory type.

Lab. type	Mean (BP)	Median (BP)	Q_1 (BP)	Q_3 (BP)
AMS	50,007	50,800	47,490	52,300
GPC	48,097	48,305	42,440	53,140
LSC	45,039	44,300	40,190	49,580
All laboratories	47,634	48,305	43,900	51,800

Table 15. Consensus values from sub-groups and weighted mean from all laboratories.

FIRI sample	Weighted Mean (all labs)	AMS ¹⁴ C Age (BP)	GPC ¹⁴ C Age (BP)	LSC ¹⁴ C Age (BP)
C	18,173 \pm 10,5	18,183 \pm 13	18,229 \pm 28	18,140 \pm 25
DF	4508 \pm 3	4519 \pm 4	4484 \pm 5	4507 \pm 6
E	11,778 \pm 7	11,805 \pm 9	11,738 \pm 19	11,707 \pm 17
GJ	110.69 \pm 0.04 pMC	110.52 \pm 0.05 pMC	110.85 \pm 0.07 pMC	110.82 \pm 0.08 pMC
H	2232 \pm 5	2238 \pm 6	2198 \pm 9	2233 \pm 9
I	4485 \pm 5	4483 \pm 7	4456 \pm 10	4499 \pm 11

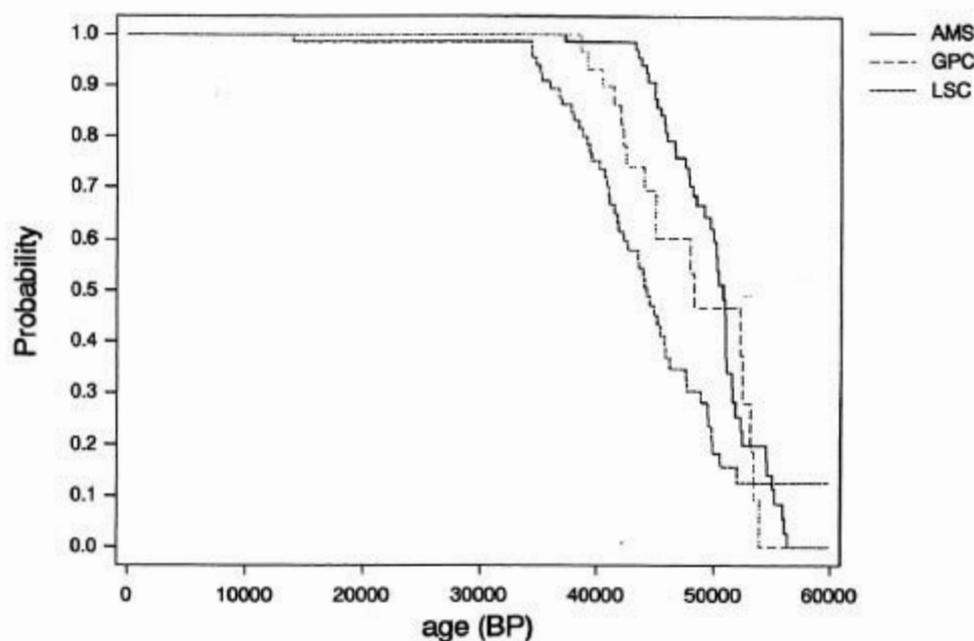


Fig. 3. Distribution of probability that ^{14}C Age of samples is older than "t" for three types of laboratories (Scott, 2001).

Dating of samples for tests and comparison

Samples C – J were dated in 9 laboratories very precise (Scott, 2001A). Laboratories which took place in tests: LSC – SUERC, NERC, KIK Brussels, Weizmann Institute, UCD Dublin.

AMS – Aarhus University, Uppsala University, CIO Groningen.

GPC – University of Trondheim.

The results from tests and consensus value calculations are compared in **Table 17**. It may be noticed that they have very similar values.

Gaussian distributions of results

Gaussian distributions of age / activity determination of the FIRI samples in Gliwice are presented in **Fig. 4**. Symbol Q denotes LSC system while number beside Q is geometry volume, in ml.

Gliwice Radiocarbon Laboratory results on the background of FIRI data

Comparison of Gliwice Radiocarbon Laboratory results with consensus values of FIRI Programme is presented in **Table 18**. There are collected results submitted by GdRL to FIRI Programme, weighted means calculated for results of all measurements performed in Gliwice (*total weighted mean*) and consensus values reported in final

Table 17. Comparison of ^{14}C ages from test and consensus values.

FIRI samples	Test ^{14}C Age (BP)	Consensus values ^{14}C Age (BP)
C	18,073 \pm 58	18,173 \pm 10.5
DF	4495 \pm 9	4508 \pm 3
E	11,905 \pm 62	11,778 \pm 7
GJ	110.8 \pm 0.4 pMC	110.69 \pm 0.04 pMC
H	2215 \pm 14	2232 \pm 5
I	4471 \pm 8	4485 \pm 5

FIRI Report (Scott, 2001b). Moreover the table contains weighted means of FIRI samples' results calculated separately for measurements performed by gas proportional counters (*GPC weighted mean*) and liquid scintillation spectrometer (*LSC weighted mean*). The results for sample FIRI "I" need additional comments. During measurement process using L3 counter inactive carbon dioxide was added to sample, but this fact was not properly noted down in laboratory register. This mistake was noticed after we had submitted results to FIRI Programme - consequently the submitted values have a systematic offset. Tables and figures present these original values and corrected values recalculated on account of our mistake. **Table 19** presents values of scaled deviation of declared results and total weighted mean for GdRL. Scaled deviation for weighted mean was calculated as a function, which tests the difference between mean values and is described by following formula:

$$\text{Scaled deviation} = \frac{W_m - C_v}{\sqrt{\sigma_{w_m}^2 + \sigma_{c_v}^2}} \quad (6.1)$$

where: W_m – total weighted mean, C_v – consensus value, σ_{w_m} – uncertainty of weighted mean and σ_{c_v} – uncertainty of consensus value.

Scaled deviation of declared results was calculated according to Appendix 2, FIRI Further Statistical Analysis (Scott, 2001b), without regard to uncertainty of consensus value ie. as the distance between result and consensus value divided by uncertainty of result. The values presented in **Table 19** are shown graphically in **Figs 5** and **6**.

The analysis of **Tables 18** and **19** and **Figs 5** and **6** enables to notice good agreement between GdRL results and consensus values. Total weighted mean agrees excellent with consensus value for samples FIRI C, D and E (scaled deviation less than 1) and quite good for FIRI F, H and J (scaled deviation greater than 1 but less than 3). Too large differences are observed only for sample FIRI G

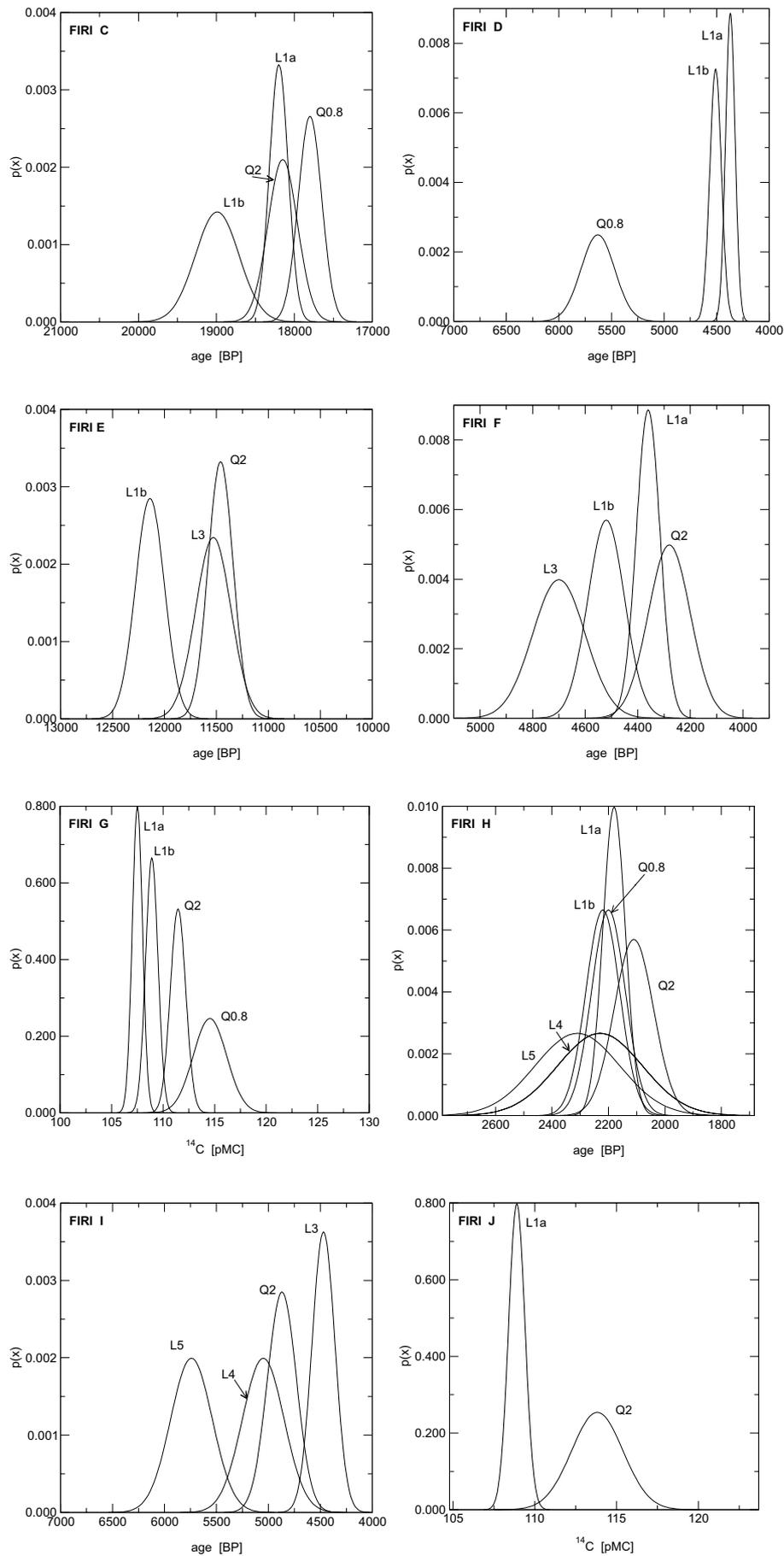


Fig. 4. Gaussian distributions for ^{14}C dating results obtained for FIRI: C, D, E, F, G, H, I and J samples. L1a, L1b, L3, L4 and L5 are symbols of GPC systems in GdRL. Qx is symbol of LSC system, so that 'x' is volume of benzene, in ml.

Table 18. Comparison of Gliwice Radiocarbon Laboratory results with consensus results of FIRI samples. The values in brackets indicate numbers of results used for calculation of mean. Gliwice Laboratory results for sample FIRI "I" are presented twice: values in roman are corrected on account of mistake in calculation procedure which was founded after we had submitted results to FIRI Programme, values in italic are original (without correction).

Sample	Submitted results (BP)	Weighted mean			Consensus values (BP)
		GPC (BP)	LSC (BP)	Total (BP)	
FIRI C	18,200 ± 120	18,150 ± 190	17,934 ± 118	18,141 ± 80	18,173 ± 11
	18,323 ± 110	(2)	(2)	(4)	
FIRI D	4370 ± 45	4426 ± 35	5630 ± 160	4481 ± 34	4508 ± 3
		(2)	(1)	(3)	
FIRI E	11,530 ± 170	11,460 ± 120	11,460 ± 120	11,699 ± 80	11,778 ± 7
	11,893 ± 108	(2)	(1)	(3)	
FIRI F	4360 ± 45	4444 ± 35	4280 ± 80	4417 ± 32	4508 ± 3
	4280 ± 80	(3)	(1)	(4)	
FIRI G	107.0 ± 0.5 pMC	107.78 ± 0.38 pMC	111.80 ± 0.72 pMC	108.66 ± 0.34 pMC	110.69 ± 0.04 pMC
		(2)	(2)	(4)	
FIRI H	2180 ± 40	2199 ± 32	2162 ± 46	2187 ± 26	2232 ± 5
	2110 ± 70	(4)	(2)	(6)	
FIRI I	4470 ± 110	4819 ± 87	4760 ± 130	4801 ± 72	4485 ± 5
	4760 ± 130	5045 ± 82	5100 ± 140	5059 ± 71	
	4870 ± 100	(3)	(1)	(4)	
	5100 ± 140				
FIRI J	108.9 ± 0.5 pMC	108.90 ± 0.50 pMC	113.80 ± 1.60 pMC	109.34 ± 0.48 pMC	110.69 ± 0.04 pMC
		(1)	(1)	(2)	

Table 19. Scaled deviations of submitted results and total weighted mean for Gliwice Radiocarbon Laboratory. Scaled deviation for sample FIRI "I" are presented twice: values in roman are calculated basing on results corrected on account of mistake in calculation procedure which was founded after we had submitted results to FIRI Programme, values in italic are calculated basing on results without correction.

Sample	Scaled deviation of submitted results	Scaled deviation of total weighted mean
FIRI C	0.225	-0.392
	-0.121	
FIRI D	-3.067	-0.802
FIRI E	-1.459	-0.976
	-2.650	
FIRI F	-3.289	-2.806
	-2.850	
FIRI G	-7.380	-5.936
FIRI H	-1.300	-1.695
	-1.743	
FIRI I	-0.136	4.360
	2.115	8.117
	3.850	
	4.393	
FIRI J	-3.580	-2.827

and FIRI I. The most important conclusion, which may be drawn from the data, is that GdRL dating results are not biased by systematic error. It was confirmed by value of estimated laboratory offset presented in Appendix 3, FIRI Further Statistical Analysis. The laboratory offset for GdRL has very low value -0.02 (only 21 of 92 laboratories have absolute value of offset less than 0.1).

The comparison LSC weighted means and GPC weighted means clearly shows, that there is no distinct systematic offset between gas proportional counters results and liquid scintillation results. This observation is confirmed by GPC-LSC scaled deviations calculated for GPC weighted means and LSC weighted means in accordance with formula:

$$\text{GPC_LSC scaled deviation} = \frac{W_{\text{GPC}} - W_{\text{LSC}}}{\sqrt{\sigma_{\text{GPC}}^2 + \sigma_{\text{LSC}}^2}} \quad (6.2)$$

where: W_{GPC} – GPC weighted mean, W_{LSC} – LSC weighted mean, σ_{GPC} – uncertainty of GPC weighted mean and σ_{LSC} – uncertainty of LSC weighted mean.

Mean value of GPC-LSC scaled deviations for all FIRI samples is equal to 0.126, consequently we may assume that the offset between GPC and LSC results do not occur and we do not observe influence of radiocarbon standard material (NBS or ANU) on dating results.

SUMMARY AND CONCLUSIONS

The precision and accuracy of radiocarbon dating in Gliwice Radiocarbon Laboratory were discussed above on the background of several intercomparison programs, which were organised in the past (ISC Programme, TIRI Programme and FIRI Programme) as individual comparison between laboratories. The main stress was laid on the results of the FIRI Programme. The most important elements of the Programme – types of included samples and methods of calculation of consensus values - were described, but the paper focused on the results obtained by

Gliwice Radiocarbon Laboratory (GdRL) and statistical analysis of these results.

The confrontation of radiocarbon dates from GdRL and dates obtained in another laboratories or final values of ISC and TIRI Programmes (see Table 3, 4, 5 and 6) shows good agreement between them. The analysis of GdRL and FIRI results (Table 18, Figures 5 and 6) also enables to notice good and quite good agreement between our results and consensus values. Consequently very important conclusion, which may be drawn, is that GdRL dating results are accurate and distinct systematic errors are not observed. However the analysis of GdRL results on the background of FIRI data shows a little too large dispersion of our results in comparison with the values of laboratory uncertainty (Table 19, Figures 5 and 6). This dispersion of results may be produced by fluctuation in the concentration of electronegative impurities in carbon

dioxide counting gas. The occurrence of such fluctuation was ascertained, when application of pulse rise-time discrimination of background reduction was tested (Michczyński and Pazdur, 1998). The gas purity control and counting efficiency system applied in Gliwice Laboratory compensates effect of electronegative impurities based on average dependence of background and standard counting rate on purity control parameter (Pazdur, Walanus and Mościcki, 1978). However statistical fluctuation of counting rate occurring around the average relationship may produce additional spread of results.

The comparison between LSC results and GPC results from our Laboratory clearly shows that the offset between GPC and LSC results do not occur, therefore we do not observe influence of radiocarbon standard material (NBS or ANU) on dating results.

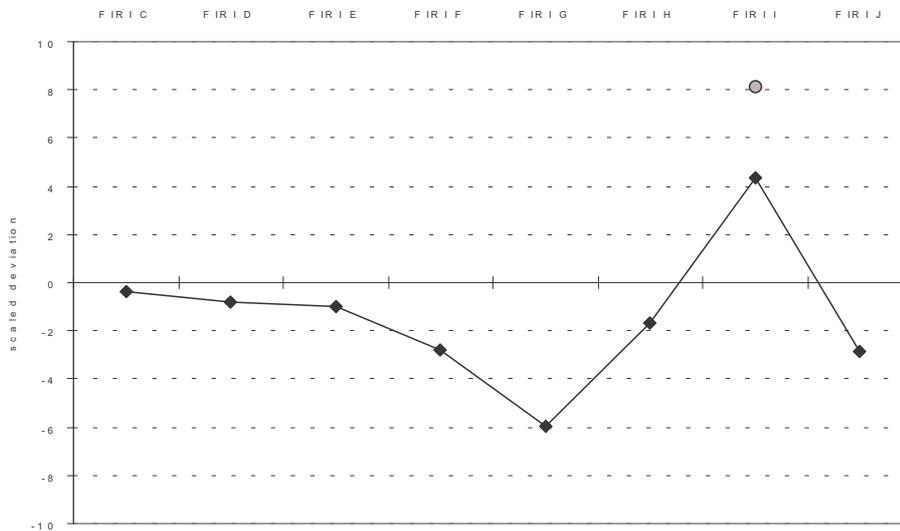


Fig. 5. Scaled deviation of total weighted mean (see formula 6.1 and 6.2) for GdRL results. Grey circle shows deviation of sample FIRI "I" calculated on results without correction on mistake in calculation procedure.

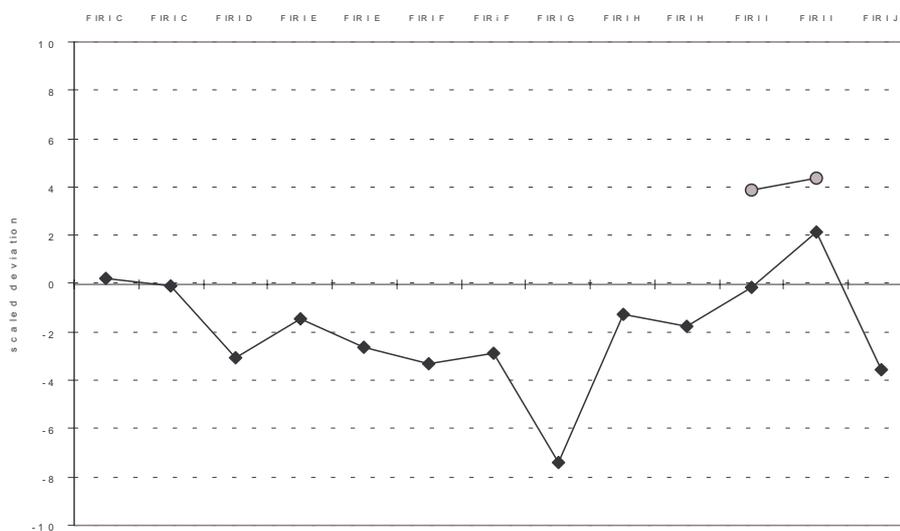


Fig. 6. Scaled deviation of results (see formula 6.1 and 6.2) submitted by GdRL to FIRI Programme. Grey circle shows deviation of sample FIRI "I" calculated on results without correction on mistake in calculation procedure.

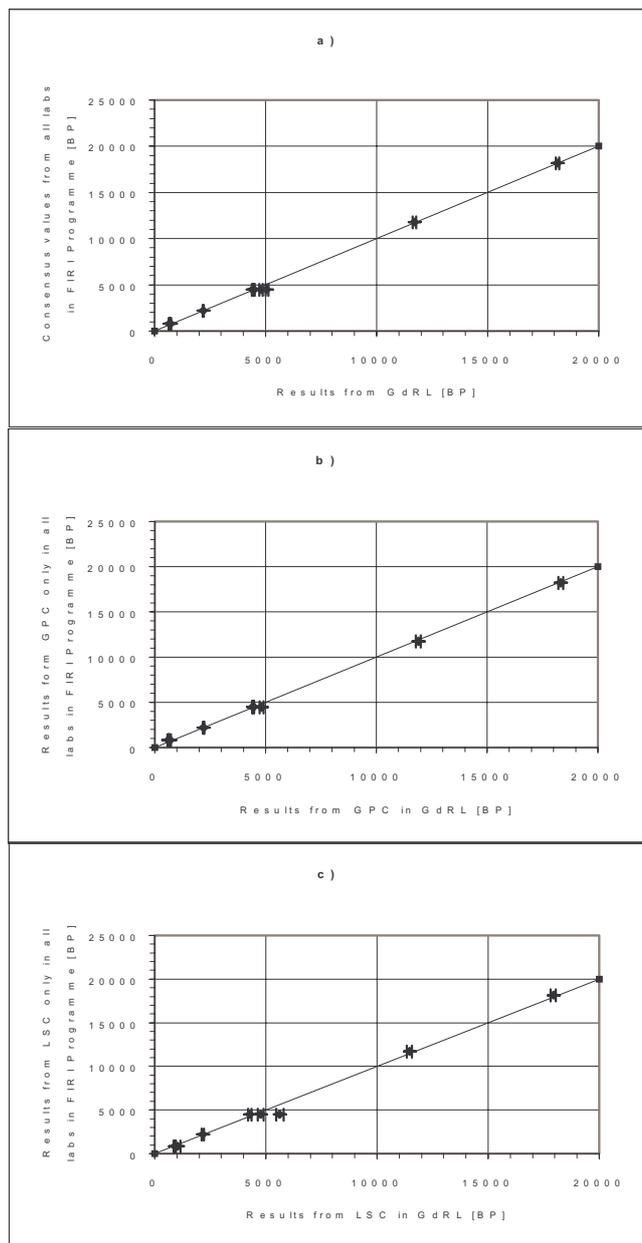


Fig. 7. a) Comparison of ^{14}C dating results of FIRI samples (C - J) in GdRL (axis X) and consensus values (C - J) calculated for all laboratories (axis Y), which took part in FIRI Programme. The results of GdRL are weighted mean for GPC and LSC systems, b) The same comparison but only results from GPC (in GdRL and another GPC laboratories), c) The same comparison but only results from LSC (see Table 15 and 18).

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