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Status report on the Zagreb Radiocarbon Laboratory – AMS and LSC results of VIRI intercomparison samples

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ABSTRACT

A new line for preparation of the graphite samples for ^{14}C dating by Accelerator Mass Spectrometry (AMS) in the Zagreb Radiocarbon Laboratory has been validated by preparing graphite from various materials distributed within the Fifth International Radiocarbon Intercomparison (VIRI) study. ^{14}C activity of prepared graphite was measured at the SUERC AMS facility. The results are statistically evaluated by means of the *z*-score and *u*-score values. The mean *z*-score value of 28 prepared VIRI samples is (0.06 ± 0.23) showing excellent agreement with the consensus VIRI values. Only one sample resulted in the *u*-score value above the limit of acceptability (defined for the confidence interval of 99%) and this was probably caused by a random contamination of the graphitization rig. After the rig had been moved to the new adapted and isolated room, all *u*-score values laid within the acceptable limits. Our LSC results of VIRI intercomparison samples are also presented and they are all accepted according to the *u*-score values.

1. Introduction

A new rig for graphite target preparation for ^{14}C dating by Accelerator Mass Spectrometry (AMS) was implemented in the Zagreb Radiocarbon Laboratory in 2008. Technical details of the new rig and the results from the test and validation series of the first hundred prepared graphites have already been presented [1]. Prepared graphite-iron powders are sent to the Scottish Universities Environmental Research Centre (SUERC, East Kilbride, Scotland), where they are pressed into aluminium carriers (targets) and measured for ^{14}C at the AMS facility [2]. The results of a validation phase showed a successful implementation of the new technique with a slight bias of less than 0.4 pMC towards more positive values [1]. Afterwards, the bias has been carefully investigated and some improvements in the sample preparation have been performed. In this paper we present the improvements performed and the results of measurement of samples within the VIRI (Fifth International Radiocarbon Intercomparison) study obtained by both AMS and radiometric (Liquid Scintillation Counting – LSC) measurement techniques in our laboratory. The LSC measurement technique with benzene synthesis has been described in detail in [3] and it has been continuously used for dating of large enough samples.

Parallel with the introduction of the LSC measurement techniques of radiocarbon [3] and graphite preparation for AMS [1] a new relational database ZAGRADA (ZAGreb RAdiocarbon DAtabase) was developed [4]. ZAGRADA enables processing and storing of data obtained by different preparation and measurement techniques at the Zagreb Radiocarbon Laboratory. The samples are identified by a laboratory number Z and by an additional code number associated with the measurement techniques, such as B for benzene synthesis or A for AMS. Therefore, a sample having unique Z number can be prepared and measured by different techniques and there is also a possibility of multiple preparations by the same techniques, e.g., to check the reproducibility.

Measured values are here expressed as ^{14}C activity ratio $^{14}a_N$, following the definitions and notation defined in [5]:

$$^{14}a_N = {}^{14}A_{sample}/{}^{14}A_{ref} \quad (1)$$

where $^{14}A_{sample}$ and $^{14}A_{ref}$ are specific ^{14}C activities (in Bq/kg of carbon) of a sample and of the standard reference activity sample, respectively. The standard reference activity was defined as 95% of the activity of the specific batch of NIST Oxalic Acid I in AD 1950 [5] and it equals the specific activity of 226 Bq/kg C. Both activities in Eq. (1) are decay-corrected to AD 1950 and are normalized to the defined ^{13}C content as defined in Eq. (3) of [5] and conventionally used in reporting radiocarbon data. The activity ratio is expressed in units of pMC, percent of modern carbon, and from the definition (1) it follows that 100 pMC = 226 Bq/kg C. In the following text we use the term "^{14}C activity" for the normalized ratio of specific activities, $^{14}a_N$, and all results are expressed in units of pMC.

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2. Sample preparation

A glass vacuum line for graphite preparation was installed in the Zagreb Laboratory with the help of the SUERC Radiocarbon Laboratory [1]. Organic samples, such as charcoal or wood, are pre-treated by the standard ABA (acid/base/acid) method [3]. The collagen from the bone samples is obtained by the modified Longin method [6]. Compact carbonate samples (e.g., shells) are pre-treated by etching about 20% of the sample mass from the surface with hydrochloric acid. Standard material samples, both background samples and reference activity sample (NIST SRM4990C Oxalic Acid II, OxAII further on) were used for graphite preparation without chemical pre-treatment [1].

CO_2 is obtained either by oxidation of organic samples with CuO on 850 °C in pre-baked, evacuated and sealed quartz tubes or by hydrolysis of carbonate samples with HCl in Pyrex glass vials with rubber septa mounted on the glass vacuum line. The amount of CO_2 corresponding to 1.5 mg of carbon is then converted/reduced to graphite in reaction with Zn on 450 °C and iron powder at 550 °C as a catalyst. The graphitization yield has been high (>95%) for all four graphitization units and no memory effect was observed. Details on the sample preparation are given in [1].

3. Improvements

During the test and validation phase presented in [1] we found a systematic positive deviation of less than 0.4 pMC in comparison with the expected ^{14}C activities of various samples used as standard or control samples: the average difference between the measured and the expected activities were 0.32, 0.21, and 0.36 pMC, for anthracite, marble and OxAII, respectively [1]. Such a bias indicated the source of possible contamination somewhere in the combustion/hydrolysis/graphitization stage. The deviations were equal for both the background and active reference material, leading to the assumption that there would be no significant deviation from the ^{14}C activities/ages obtained for the samples prepared in our laboratory if the referent values used for calculation of ^{14}C activities/ages are obtained from our reference materials. However, we performed careful investigation of our system to identify the source of the contamination.

We also noticed that increased background levels may be caused by an inappropriate position of the graphitization rig in the entrance area of the laboratory with intense movements of laboratory staff and visitors. Therefore, the first step was to move the rig into an adapted and isolated "clean" room dedicated to the AMS sample preparation. The new room has its own air-conditioning system and is entered only when the designated laboratory personnel is preparing AMS samples. Further more, an additional room was cleaned and dedicated solely for AMS sample storage and weighting.

Each step in graphite preparation was then separately tested using background materials in different forms: borehole CO_2 gas, anthracite, Carrara marble and the "Heidelberg wood". The first three types of background samples have been used in our laboratory since its establishment in 1968. Also, Carrara marble was one of the samples (code Carbonate C1) in the IAEA ^{14}C intercomparison exercise 1990 [7] with the consensus value of (0.00 ± 0.02) pMC. Our laboratory participated in this intercomparison with the reported value (0.1 ± 0.6) pMC [8]. The "Heidelberg wood" sample has been routinely used in SUERC-AMS laboratory as background sample since 2003, and in fact this is an interglacial wood used in the VIRI intercomparison study under the code VIRI K [9]. By graphitization of a borehole CO_2 we tested the graphitization part of the rig only, while by Carrara marble both the hydrolysis and graphitization steps can be tested and monitored. Antracite and the "Heidelberg wood" are used for testing and monitoring the combustion and graphitization steps, and the latter is also used for cross-check with the SUERC backgrounds. The graphite targets prepared from the reference material OxAII showed the same quality and ^{14}C content as the corresponding targets prepared by SUERC and were included in the batch of reference targets used for calculation of unknown ^{14}C activities. Therefore, the batch of background and standard samples prepared in the "clean room" proved that the new location was suitable for producing contamination-free graphite powders for ^{14}C AMS measurements showing detection limit of 51,000 years BP (corresponding to 0.17 pMC) and the routine AMS measurements of unknown samples could commence. Since all standard materials are fully compliant with the SUERC standard materials, we use the same method of error estimation as SUERC [9].

In addition, the prescribed procedures of sample handling and handling quartz glassware were strictly adhered to, and the procedures involving gas handling at the vacuum lines were optimized. Sample pre-treatment techniques including collagen extraction from bone samples were scrutinized by preparing several samples already measured in the laboratory by the LSC technique.

4. Intercomparison results

For final validation a set of graphite targets was prepared from various types of samples distributed among the ^{14}C laboratories within the Fifth International Radiocarbon Intercomparison (VIRI) study (Table 1). Details on the samples distributed among radiocarbon laboratories in 3 stages of the VIRI study, the statistical analysis and the consensus values are presented elsewhere by the VIRI organizers [10,11]. Our laboratory participated officially in the VIRI intercomparison with the radiometric LSC results only, since at that time our graphitization rig was not in operation. We stored a certain amount of each sample for validation of the AMS measurements. The samples of wood (K, L, M), cellulose (O), murex shell (R), barley mash (S), humic acid (U) and charcoal (P) were prepared and measured by both LSC and AMS techniques, while the humic acid (T) and various bone samples (F: horse bone, I: whale bone, H: whale bone, E: mammoth bone) [10,11] were prepared by AMS technique only since the sample size did not meet the routine requirements for LSC measurements. To check the reproducibility of the graphite preparation rig, some VIRI samples were prepared in duplicates or more, as indicated by different A code numbers in Table 1.

Samples O, S, U and T were not chemically pre-treated, as well as OxAII used as a reference activity sample ($^{14}a_{OXAII} = 134.07$ pMC). Other organic samples were pre-treated by the ABA method including bone sample E prior to collagen extraction. The bone sample were used to evaluate AMS collagen preparation. Sample T (Humic acid) has been used in our laboratory as the control sample for the graphitization process since October 2010 following the SUERC laboratory practice.

The numerical results of the consensus VIRI values and our measurements, both AMS and LSC, are shown in Table 1, while the comparison of our results with the consensus VIRI values is presented in Fig. 1. Generally, the agreement between our and the consensus values is good. The linear regression lines, shown in the lower part of Fig. 1, can be described as:

$$^{14}a_{LSC} = (0.996 \pm 0.003)^{14}a_{VIRI} + (-0.1 \pm 0.1), N = 8, \quad R = 0.9998 \tag{2}$$

and

$$^{14}a_{AMS} = (0.999 \pm 0.001)^{14}a_{VIRI} + (0.08 \pm 0.08), N = 28, \quad R = 0.99995 \tag{3}$$

Table 1
^{14}C activity ratios ($^{14}a_N$) of the VIRI intercomparison samples measured in the Zagreb Radiocarbon Laboratory by the AMS and LSC techniques and the consensus values from the VIRI study [10,11]. For each result, the *z*-score and *u*-score values are determined according to Eqs. (4) and (5), respectively. Z-code number is the identification number of a sample in the Zagreb Radiocarbon Laboratory, and A-code and B-code numbers are the laboratory codes for the AMS and LSC (benzene synthesis) measuring techniques [4], respectively.

Sample code and type	VIRI [6,7]		Z-code	AMS					LSC				
	$^{14}a_{VIRI}$ (pMC)	σ VIRI		A-code	$^{14}a_{AMS}$ (pMC)	σ_{AMS}	z_{AMS}	u_{AMS}	B-code	$^{14}a_{LSC}$ (pMC)	σ_{LSC}	z_{LSC}	u_{LSC}
K wood	0.0576	0.0062	Z-3882	A80	0.09	0.17	0.19	0.19	B426	−0.08	0.12	−1.15	1.15
				A81	−0.06	0.17	−0.69	0.69					
L wood	75.719	0.0395	Z-3883	A82	75.15	0.36	−1.58	1.57	B425	75.64	0.65	−0.12	0.12
				A83	75.71	0.36	−0.03	0.02					
M wood	73.900	0.0322	Z-3884	A84	74.4	0.35	1.43	1.42	B427	73.16	0.62	−1.19	1.19
				A85	74.05	0.33	0.45	0.45					
O cellulose	98.457	0.0385	Z-3885	A72	97.81	0.44	−1.47	1.46	B423	97.99	0.74	−0.63	0.63
				A73	98.84	0.44	0.87	0.87					
R murex shell	73.338	0.0368	Z-3886	A78	73.94	0.35	1.72	1.18	B428	73.83	1.11	0.44	0.42
				A79	73.42	0.33	0.25	0.25					
S Barley mash	109.96	0.0417	Z-3887	A74	109.56	0.49	0.82	0.81	B424	108.59	0.77	−1.78	1.78
				A75	109.47	0.49	−1.00	1.00					
U humic acid	23.079	0.0155	Z-3888	A76	23.00	0.19	−0.42	0.41	B422	23.05	0.30	−0.10	0.10
				A77	22.98	0.19	−0.52	0.52					
P charcoal	80.457	0.0862	Z-3889	A86	81.68	0.36	3.40	3.30	B429	80.52	0.68	0.09	0.09
				A87	80.99	0.35	1.52	1.48					
				A240	80.62	0.35	0.46	0.45					
E mammoth bone	0.75	0.01	Z-4013	A269	1.02	0.17	1.59	1.59					
F horse bone	73.13	0.05	Z-4014	A239	73.16	0.32	0.09	0.09					
I whale bone	35.45	0.03	Z-4016	A247	35.59	0.17	0.82	0.84					
H whale bone	30.54	0.03	Z-4015	A244	30.84	0.17	1.76	1.79					
T humic acid	65.821	0.033	Z-4700	A257	65.67	0.21	−0.70	0.69					
				A272	65.74	0.17	−0.48	0.49					
				A279	65.64	0.19	−0.98	0.96					
				A303	65.86	0.24	0.16	0.16					
				A304	65.54	0.26	−1.07	1.06					
				A310	65.60	0.26	−0.84	0.84					
				A312	65.19	0.26	−2.43	2.40					

The Student's *t*-test applied to paired sets of data [12] resulted in p value >0.05 for both AMS-VIRI ($p = 0.23$) and LSC-VIRI ($p = 0.10$) pairs of data, meaning that the compared sets of data are not different.

For more detailed statistical analysis we used *z*-score and *u*-score values [10,11]. The *z*-score value represents the deviation of the measured value from the consensus VIRI value in units of laboratory error σ_{lab}:

$$z = \frac{^{14}a_{lab} - ^{14}a_{VIRI}}{\sigma_{lab}} \quad (4)$$

where $^{14}a_{lab}$ and σ_{lab} are the measured relative specific ^{14}C activities and the corresponding laboratory errors, respectively, "lab" refers to either AMS or LSC, and $^{14}a_{VIRI}$ is the consensus VIRI value [10,11]. It is commonly assumed that *z*-score should have a normal distribution with zero mean and variance 1, and a *z*-score value near zero implies a perfect result. A *z*-score value between −2 and +2 is generally considered as complying with fitness for purpose, while a *z*-score value outwith −3 or +3 would need further investigation [11,12].

The *u*-score values are calculated as:

$$u = \frac{|^{14}a_{lab} - ^{14}a_{VIRI}|}{\sqrt{\sigma_{lab}^2 + \sigma_{VIRI}}} \quad (5)$$

where σ_{VIRI} is the standard deviation of the VIRI consensus value [10,11]. The calculated *u*-score value is then compared with the critical value listed in the *t*-statistics tables to determine if the reported result differs significantly from the expected value at a given level of probability, i.e., the result is acceptable if the *u*-score value is lower then some predetermined value that corresponds to a chosen confidence interval. In this case, we have decided to take the confidence interval of 99%, and therefore the *u*-score values should be $u < 2.58$ [12] to accept the result of measurement.

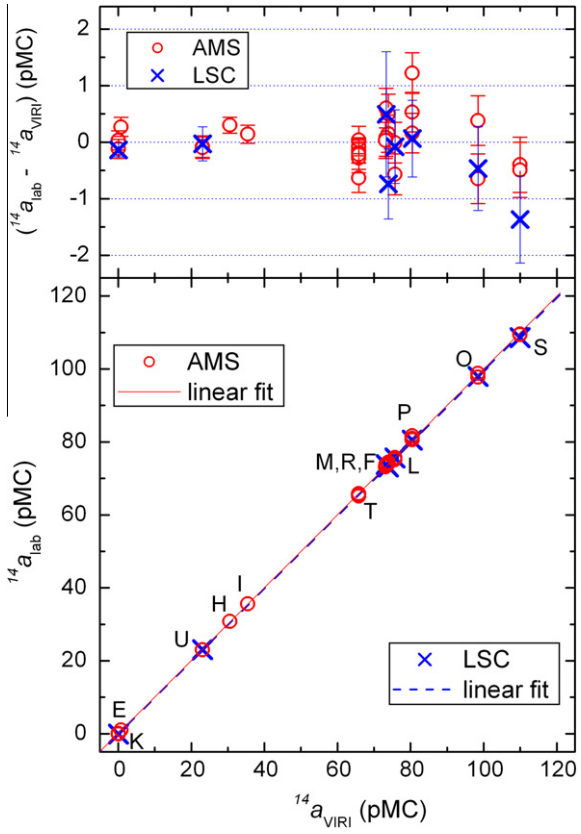

Fig. 1. Comparison of our individual AMS and LSC results (ratio of ^{14}C activities, $^{14}a_{lab}$) with the consensus VIRI values, $^{14}a_{VIRI}$. Data points are labeled by the VIRI sample codes given in Table 1. The upper part shows the difference between measured and consensus values, $^{14}a_{lab} - ^{14}a_{VIRI}$.

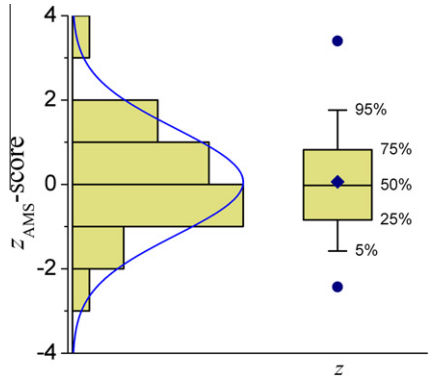

Fig. 2. Statistical plots of the z_{AMS}-score values of VIRI samples. Left: histogram of the z-score values with the fitted normal distribution (full line). Right: box-plot of the z_{AMS} with indicated mean value (diamond), percentile values and the two outliers (circles).

Because σ_{VIRI} values are much lower than the laboratory errors σ_{lab}, the calculated u-score values for each sample are very close to the absolute values of the z-score values, see Table 1.

All z-score values for LSC results (Table 1) lie between −1.78 and 0.44 indicating deviations less than 2 σ_{LSC} from the consensus VIRI values. The mean (−0.55) and the median (−0.64) values point to a negative bias of approx. one half a σ_{LSC} value. However, all u-score values lie below the here predefined acceptability limit, $u_{LSC} < 2.58$, therefore, all results are accepted. Comparison with the boxplots of z-scores obtained from all laboratories participating in VIRI for all samples (Fig. 3 in [11]) shows that all our LSC results lie in the interquartile range, i.e., they lie in either Q2 or Q3 quartiles [11,12].

The statistical plots of the distribution of the z-score values for AMS results and the box-plot are shown in Fig. 2. The mean and median z-score values are 0.06 and 0.03, respectively, indicating practically no bias to the VIRI consensus values. Out of total of 28 AMS results (Table 1), 15 have positive z-score values and 13 negative ones. The distribution of the z-score values resembles well the normal distribution (Fig. 2): 18 or 64.3% results lie within ±1 σ_{AMS}, 26 or 92.8% lie within ±2 σ_{AMS}, and only 1 result (A86) deviates more than 3 σ_{AMS}. The reason for deviation of A86 ($z = 3.4$) is probably an accidental/random contamination in the graphitization stage, since both graphite samples A86 and A87 were prepared from the same CO_2. The repeated preparation of the same sample (A240) after the graphitization rig had been moved to the new locations resulted in an acceptable result.

Comparison of z-score values for graphite samples prepared before and after the rig was moved to the new location showed no significant difference between the two sets of data.

5. Conclusion

In the Zagreb Radiocarbon Laboratory a new isolated and "clean" room has been adapted for the graphite preparation line and the pre-treatment procedures. After the line had been moved to the new location, a careful testing of each part of the line by using different types of background samples was performed. The background samples were contamination-free and the measured ^{14}C activities were fully compliant with the values obtained in the SUERC, where the graphites prepared in Zagreb have been measured.

Final validation of the graphitization rig was performed by preparing various samples from the VIRI intercomparison study. The analysis of the results in terms of the z-score and u-score values showed that there is no deviation observed between our and the VIRI consensus values. Therefore, we may conclude that complete procedure of sample handling (pre-treatment, combustion or hydrolysis, and graphitization) is free of contamination and that the laboratory is ready for routine measurement of ^{14}C activity by the AMS technique.

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