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AMS ^{14}C MEASUREMENTS AT LABEC ON VIRI (FIFTH INTERNATIONAL RADIOCARBON INTER-COMPARISON) SAMPLES

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Abstract

Since May 2004, the Accelerator Mass Spectrometry (AMS) beam line of the new 3 MV Tandetron accelerator of LABEC laboratory in Florence has been in operation. The line, equipped with the necessary hardware for ^{14}C, ^{10}Be, ^{26}Al and ^{129}I measurements, has been used only for radiocarbon measurements so far. We have been involved both in measurements on test samples and in dating applications in collaboration with Universities and other Institutions.

After a brief description of the AMS beam line, we report on a set of radiocarbon measurements performed on samples of the Fifth International Radiocarbon Inter-comparison (VIRI) campaign. This campaign, coordinated by the Department of Statistics of the University of Glasgow, basically involves all the radiocarbon laboratories worldwide, both AMS and conventional beta-counting ones. Our data have been here compared to the statistical distributions of all collected data (average values and standard deviations).

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1 INTRODUCTION

The main facility of LABEC (LAboratorio di tecniche nucleari per i BEni Culturali) in Florence is a 3 MV Tandetron accelerator, manufactured by High Voltage Engineering Europe (HVEE)[1], which replaced the old 3 MV single-ended Van de Graaff KN3000. The new accelerator has been intended to strengthen the existing applications through Ion Beam Analysis (IBA) and to start a new activity of Accelerator Mass Spectrometry (AMS).

2 THE AMS BEAM LINE

Figure 1 shows a schematic layout of the Tandetron accelerator at LABEC; only the AMS beam line is reported below[2].
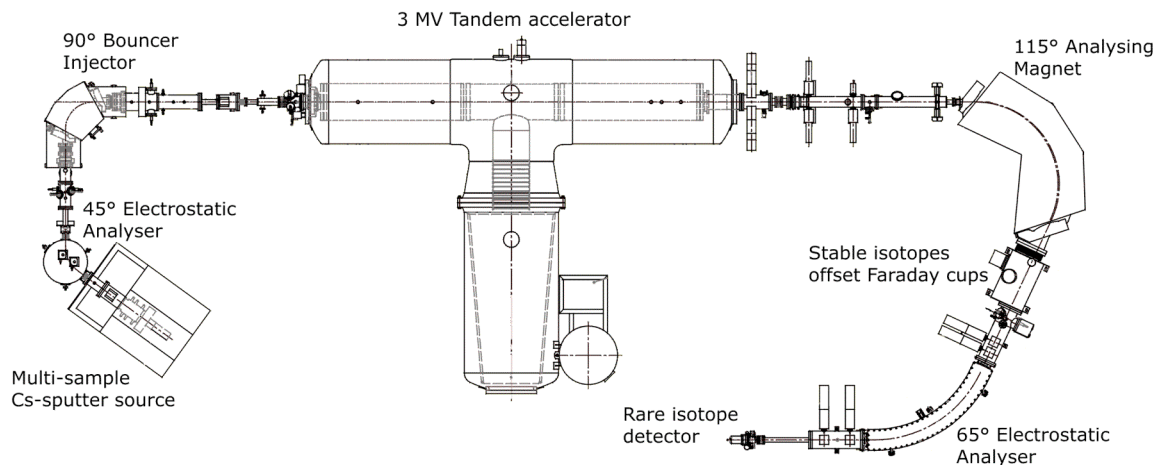

FIG. 1: Schematic layout of the AMS beam line of the new Tandetron accelerator in Florence: the main analyzing elements along the line are shown.

The AMS dedicated ion source is of the Cs-sputter type with a carrousel able to allocate up to 59 samples. Each sample, whose radiocarbon concentration has to be measured, is inserted in the source as a graphite pellet[1] on an aluminium holder. During sputtering process, samples are moved on a circular path in the plane that is transversal with respect to the Cs beam. This operation avoids the possible formation of craters and makes an average over the whole pellet surface (the total surface area of the sample is 2 mm^2). Negative carbon ions are then extracted from the source by a 35 kV voltage and first analysed (E/q = 35 keV/e) through a 45° electrostatic analyser: typical beam currents are about 25 μA.
Injection in the accelerator is accomplished by a sequential mechanism: the magnetic field of the 90° bouncer magnet (see figure 1) is kept fixed to transmit mass 13, a positive (~ 2.9 kV)

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[1] At LABEC, a sample preparation laboratory is also installed: raw materials to be dated are first purified, converted to gaseous CO_2 and then to elemental carbon (graphite) by chemical reaction with hydrogen. Since the overall process is quite time consuming, at present, we are implementing a fully automatic graphitisation line.

or a negative ($\sim$ -2.5 kV) voltage is applied to the electrically insulated magnet chamber to transmit, respectively, mass 12 and mass 14. Mass 14 is of course injected for most of the time; typical time windows are 6 μs for mass 12, 600 μs for mass 13 and 8.5 ms for mass 14. During mass 13 and mass 14 injections, also molecular isobars are injected in the accelerator tube and accelerated: ^{12}CH and the most problematic ^{13}CH and $^{12}CH_2$. The stripping process, a characteristic of the tandem accelerator mechanism, thus becomes a very important filter to remove such contaminants from the ^{14}C beam, since positive multiple charged molecules are no longer stable. At the high voltage terminal of the Tandetron, stripping is achieved by interactions with argon. Radiocarbon measurements are usually performed at 2.5 MV terminal voltage; voltage is stabilized using the generating voltmeter and the balance of the output signals from the two sides of the ^{13}C Faraday cup.

On the high energy side, the first analysis of the beam is performed by a 115° magnet, set to transmit C^{3+} ions. After the magnet, stable isotopes $^{12}C^{3+}$ and $^{13}C^{3+}$ are collected by two offset Faraday cups; measured $^{12}C^{3+}$ and $^{13}C^{3+}$ average currents (with bouncing on) are typically about 10 nA, corresponding to DC electrical currents of $\sim$ 20 μA and $\sim$ 0.2 μA, respectively. The residual beam enters a 65° electrostatic analyser (E/q = 10.035 MeV/$3e$), used to remove any other residual background due to different atomic species with various combinations of mass, energy and charge state, generated, for example, in possible charge-exchange processes occurring outside the high voltage terminal, along the acceleration tubes. Downstream the electrostatic analyzer, $^{14}C^{3+}$ ions are counted in a gas ionisation chamber, filled with butane (25 mbar), with a 125 μg cm^{-2} Mylar entrance window. A gate signal is used to acquire only during the time window in which ^{14}C is injected into the accelerator (with the proper delay, 4.5 μs, to take the time of flight of ions along the beam line into account).

3   RADIOCARBON MEASUREMENTS

Measurement of radiocarbon concentration is not absolute, since the measured $^{14}C/^{12}C$ isotopic ratios in unknown samples are normalised to measured ratios in samples whose ^{14}C concentration is certified. As standard reference material, we use Oxalic Acid II, provided by the US National Institute of Standard and Technology (NIST), whose concentration is (134.06 $\pm$ 0.04) pMC[2]. In this way, we can minimize systematic errors due, for example, to contaminations unintentionally introduced during sample preparation and isotopic fractionation effects that can occur in sputtering and stripping processes. Moreover, graphite pellets from nominally ^{14}C-free material are also prepared. These samples are measured together with unknown and standard samples, to check cleanliness of sample preparation procedures and to monitor the rejection of background events in the accelerator. Typical machine background value results to be of about 0.05 pMC, which corresponds to a radiocarbon age of $\sim$ 60000 years BP.

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[2] As international convention, radiocarbon concentration is usually expressed in pMC (percent of Modern Carbon), i.e. as ratio with respect to the atmospheric ^{14}C concentration in the reference year 1950.

3.1 The Fifth International Radiocarbon Inter-comparison (VIRI)

One of the most important applications of radiocarbon measurements is of course dating of archaeological artefacts. The need of archaeologists of comparing dates obtained in different laboratories has contributed to develop collaboration and exchanges among international laboratories. For this reason the international ^{14}C community periodically organizes some inter-comparison campaigns[3]. The importance of these campaigns is represented also by the fact that one of their aim is to establish a new set of standard reference materials. These materials will be later used by all laboratories worldwide to check the accuracy of their routine measurements.

We have just participated to the recently concluded first phase of the VIRI campaign, the Fifth International Radiocarbon Inter-comparison, coordinated by the Department of Statistics of University of Glasgow. In this first phase, four different materials, as indicated in table 1, were dispatched to the laboratories worldwide.

3.2 Results at LABEC

After chemical pre-treatment, different portions of each material A, B, C and D were converted to graphite pellets, obtaining either two or three samples from each of them.

Table 1 shows the results of our measurements; data of samples prepared from VIRI materials A and C are expressed as radiocarbon concentration in pMC[3]; the other samples (VIRI materials B and D) are expressed as radiocarbon age in years BP, i.e. years Before Present, with "Present" being conventionally 1950. Data are quoted with 1 σ uncertainty. Errors on measured concentrations are essentially due to statistics in ^{14}C counts and are of the order of 0.3 – 0.6 %[4].

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[3] These samples have a radiocarbon concentration larger than the atmospheric concentration conventionally taken as a reference (see note 2).

[4] An error of 0.5% in the measurement of ^{14}C concentration corresponds to an absolute error of ± 40 years on the radiocarbon age.

TAB. 1: VIRI samples measured at LABEC.

VIRI code	Description	Lab samples	Measured data
A	Barley mash from a Scotch whisky manufacture	14Fi0256 14Fi0261 14Fi0266	(108.84 ± 0.32) pMC (108.88 ± 0.36) pMC (108.98 ± 0.38) pMC
B	Seeds from an archaeological excavation in Israel	14Fi0245 14Fi0248	(2824 ± 38) BP (2803 ± 40) BP
C	Barley mash from a Scotch whisky manufacture	14Fi0269 14Fi0272	(110.47 ± 0.30) pMC (111.01 ± 0.63) pMC
D	Seeds from an archaeological excavation in Israel	14Fi0249 14Fi0250 14Fi0257	(2805 ± 27) BP (2862 ± 36) BP (2833 ± 32) BP

3.3   Summary of the results

The raw data collected from all the participant laboratories (about 80 worldwide) have been analysed by the Glasgow group and have been presented in the last International Radiocarbon Conference in April 2006[4]. Figure 3 shows the distributions of all collected results. The presence of some outliers is evident; for each material, in figure 3, the weighted average of our data is also shown – in the box – giving the idea of the "quality" of our measurements.

All collected data have been analysed to evaluate a consensus value for each of the materials. First, outliers were removed and then weighted averages over the remaining data were calculated[5].

Figure 4 summarizes the comparison of our experimental data with the calculated consensus values. The standard deviation of the distribution obtained after rejecting the outliers is also reported as dotted lines in figure 4.
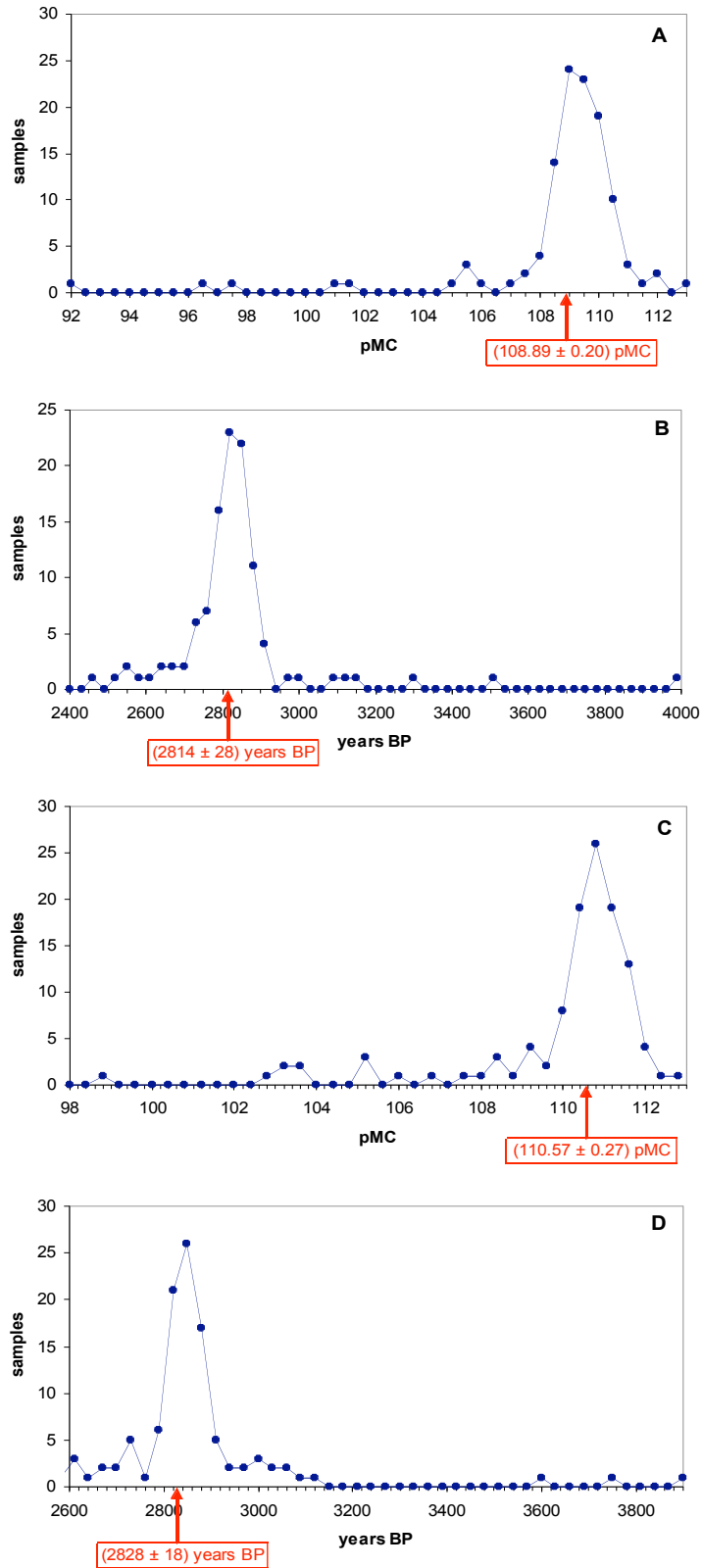
FIG. 3: Distributions of data collected from all the participant laboratories; the presence of a small number of outliers is evident. For each material, the weighted average of our data is reported in the box.
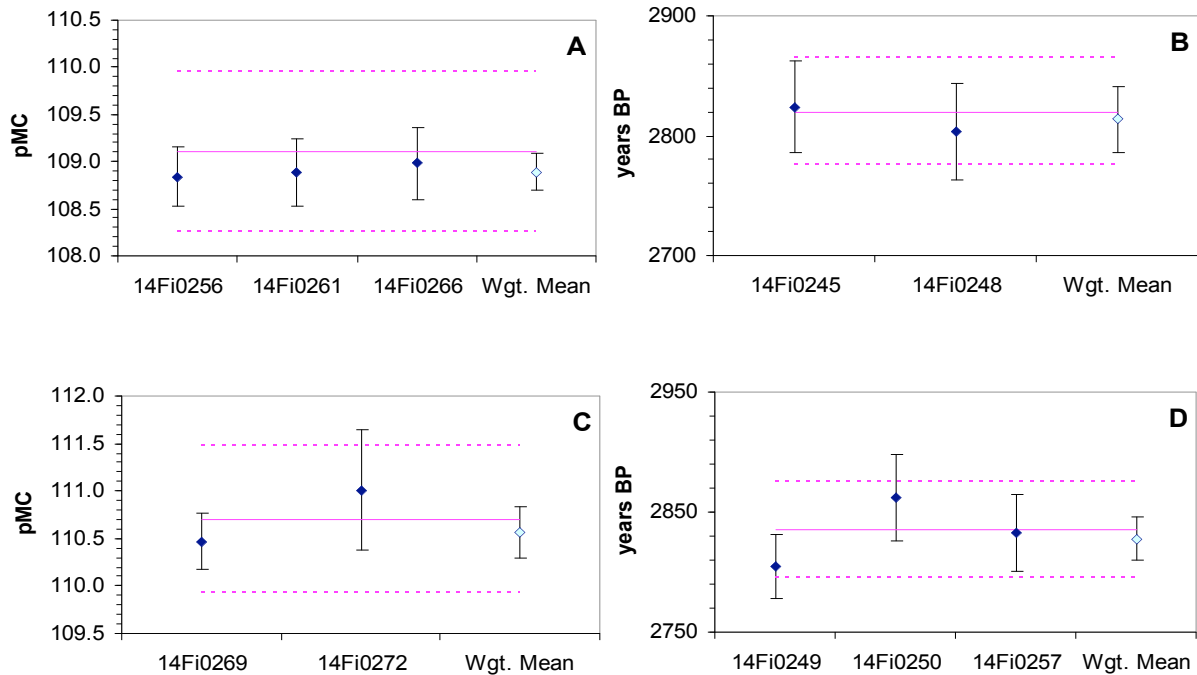
FIG. 4: Radiocarbon measurements on VIRI samples: our experimental data, measured samples (full dots) and their weighted averages (open dots), are compared to the calculated consensus values (straight line); for each VIRI material, the standard deviations of the distribution of data used to calculate the consensus values are indicated as dotted lines.

The agreement of our data with the calculated consensus values is quite well satisfactory, since the data, and their weighted averages, are consistent with consensus values well within the experimental error: this shows the good accuracy in our measurements. By comparing our quoted error with the width of the distributions of all the results, we can also notice our good precision.

At the moment, we are going to participate to the new phase of the VIRI project concerning radiocarbon measurements on bone samples, one of the most important – and critical – archaeological materials.

4   REFERENCES

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