Nuclear Instruments and Methods in Physics Research B 361 (2015) 322–326

Contents lists available at ScienceDirect

Nuclear Instruments and Methods in Physics Research B

journal homepage: www.elsevier.com/locate/nimb

# $^{14}$C SIRI samples at CNA: Measurements at 200 kV and 1000 kV

Francisco-Javier Santos Arévalo *, Isabel Gómez Martínez, Lidia Agulló García

*Centro Nacional de Aceleradores (Universidad de Sevilla, Consejo Superior de Investigaciones Científicas, Junta de Andalucía), Thomas Alva Edison 7, 41092 Seville, Spain*

ARTICLE INFO

*Article history:*
Received 14 November 2014
Received in revised form 18 March 2015
Accepted 19 March 2015
Available online 30 March 2015

*Keywords:*
Radiocarbon
AMS
Intercomparison

ABSTRACT

The Sixth International Radiocarbon Intercomparison (SIRI) exercise has taken place during late 2013 and 2014. 13 samples were distributed for AMS (Accelerator Mass Spectrometry) and 5 for radiometric laboratories, including one sample exclusively for radiometric laboratories. Being the first opportunity for our laboratory to participate actively in an intercomparison exercise, we have prepared and measured the samples in the two existing AMS dedicated facilities at the Centro Nacional de Aceleradores (CNA): SARA (Spanish Accelerator for Radionuclide Analysis), a 1 MV multielemental AMS system from HVEE, and Micadas, a 200 kV radiocarbon dating system designed by ETH. Results are presented for the two systems, together with a description of both the sample preparation and measurement procedures.



## 1. Introduction

The Sixth International Radiocarbon Intercomparison (SIRI) follows the previous intercomparison exercises as the TIRI, FIRI and VIRI [1–3] or the IAEA intercomparison exercise [4] and provides the latest set of samples for laboratories to check their procedures and compare the results of different laboratories which may work under different conditions and use different laboratory protocols. It is a clear opportunity for the involved radiocarbon facilities to detect systematic offsets in their results, if any, and undertake the necessary investigation to correct any detected problem.

The radiocarbon laboratory at CNA started its operation in 2007 after the installation of the multielemental 1MV AMS facility by HVEE, SARA [5,6]. In 2012, a 200 kV Micadas facility [7] was installed, and routine radiocarbon measurements at CNA moved from the SARA to the Micadas facility to leave more beam time free for other isotopes at SARA. At this moment, radiocarbon measurements at CNA are performed at SARA only for testing, as in this exercise, or in case of long term maintenance of the Micadas system.

The SIRI exercise is the first intercomparison exercise in which our laboratory can participate actively, and it appeared as a great opportunity to compare the performance of both systems, which work under different conditions. In this paper we review the sample preparation procedures used at CNA for the samples from the SIRI exercise and the major operation differences between the two facilities. Finally, we show the results obtained in both systems and compare with the first published data.

## 2. Materials and methods

The set of SIRI samples was distributed among the interested laboratories by September 2013 and included a total of thirteen samples: seven wood samples, two bone samples, and one each of barley mash, charcoal, carbonate and humic acid. Four of the samples (two wood samples, one bone and the carbonate sample) were known to be free of $^{14}$C. Table 1 shows the most relevant information about the set of samples together with the results obtained in both systems. First deadline was January 2014 and a brief report was presented in the AMS-13 conference.

### 2.1. Sample preparation

Targets of each sample were prepared individually for each system. That is, each final result includes the whole sample preparation and measurement. Samples were prepared following routine procedures used in our lab, as follows:

(a) *Wood:* Wood samples are prepared following one of the methods presented in [8]. The procedure is a variation of the acid–base–acid method to obtain holocellulose, which is a very stable part of the wood. 15 mg of the sample is washed overnight in a 4% NaOH solution. Samples follow the acid–base–acid procedure, which consists on a first wash with HCl 0.5 M followed by a wash with NaOH 0.1 M. Both steps last about 24 h. The final acid wash lasts 15 min. All

* Corresponding author. Tel.: +34 954460553.
*E-mail address:* fj.santos@csic.es (F.-J. Santos Arévalo).

http://dx.doi.org/10.1016/j.nimb.2015.03.058
0168-583X/

**Table 1**
Results of SIRI samples for the two AMS facilities of CNA, i.e. SARA and Micadas. SIRI-M was for radiometric laboratories alone. UF indicates ultrafiltration of bone samples. Uncertainties represent 1 sigma.

| Material | SIRI | Comments | Micadas | | SARA | |
|---|---|---|---|---|---|---|
| | | | $F^{14}C$ (x100) | $\delta^{13}C$ | $F^{14}C$ (x100) | $\delta^{13}C$ |
| Wood | A | Background (Miocene) | 0.31 ± 0.01 | −20.2 | 0.26 ± 0.02 | −23.2 |
| Bone | B | Sea mammal bone (Pleistocene) | 0.99 ± 0.04 | −23.6 | 1.12 ± 0.02 | −24.5 |
| Bone | B | Sea mammal bone (Pleistocene) (UF) | 1.00 ± 0.04 | −21.5 | NA | NA |
| Bone | C | Background | 0.66 ± 0.02 | −22.3 | 0.93 ± 0.02 | −24.0 |
| Bone | C | Background (UF) | NA | NA | 0.35 ± 0.01 | −21.1 |
| Barley mash | D | | 103.95 ± 0.41 | −29.5 | 104.56 ± 0.42 | −32.5 |
| Wood | E | Decadal rings | 25.81 ± 0.15 | −23.9 | 25.80 ± 0.12 | −19.1 |
| Wood | F | Medieval | 95.52 ± 0.38 | −23.2 | 95.11 ± 0.35 | −21.1 |
| Wood | G | | 95.87 ± 0.41 | −24.7 | 95.10 ± 0.35 | −24.3 |
| Wood | H | | 95.65 ± 0.39 | −22.5 | 95.12 ± 0.35 | −24.1 |
| Wood | I | Single ring (Younger Dryas) | 28.84 ± 0.16 | −24.4 | 28.59 ± 0.11 | −21.0 |
| Charcoal | J | Paleolithic | 2.50 ± 0.05 | −24.0 | 2.87 ± 0.04 | −26.3 |
| Carbonate | K | Doublespar Background | 0.23 ± 0.01 | −3.6 | 0.16 ± 0.01 | −3.4 |
| Wood | L | Background | 0.43 ± 0.01 | −21.0 | 0.27 ± 0.01 | −25.0 |
| Humic acid | N | <1 half-life | 65.83 ± 0.29 | −28.6 | 65.53 ± 0.24 | −33.6 |

the steps are at 80 °C, except for fragile samples at room temperature. A final bleaching with 10% $NaClO_2$ in acid conditions for 60 min at 80 °C plus 15 min at room temperature in an ultrasonic bath dissolves components other than the holocellulose, which is washed with water prior to graphitization. Samples are washed with ultrapure water until neutral between subsequent steps.

(b) *Bone:* Bone samples were prepared twice in order to test the effect of the ultrafiltration process, which was being implemented at our laboratory at the time of the SIRI exercise. Thus, each of the two bone samples was first prepared two times (one target for each AMS system) without the ultrafiltration step, and after the implementation of the ultrafiltration procedure was finished, additional targets were prepared including this step. In this case, they were only prepared for one of the systems. Either with or without the ultrafiltration step, the preparation protocol is a modified version of the Longin procedure [9] to obtain the collagen. About 1 g of clean and dry bone is powdered and demineralised with cold HCl 1 M in the fridge, until all the carbonate part of the bone has dissolved. Working at low temperatures about 5–8 °C makes the demineralisation reaction less violent, which can potentially be a problem when working with powdered bones. Besides, the low temperature helps preserve collagen during the treatment. The remaining gelatine is neutralised with ultrapure water, and washed with NaOH 0.2 M for 15 min at room temperature, to eliminate possible contamination from humic acids, and then neutralized. The steps to purify the gelatine are different depending whether the ultrafiltration is applied or not. If it is not applied, pH = 3 HCl solution is added to the gelatine to stay overnight at 80 °C. This way the collagen in the gelatin dissolves in the acid. The undissolved gelatine and other parts of the bone are eliminated by centrifugation. The remaining solution is dried in the oven until the collagen precipitates and dries. If ultrafiltration is applied, HCl $10^{-2}$M is added and pH adjusted to 2.0–2.5 to stay at 58 °C for two days. Ezee-filters™ (Elkay Laboratory Products, 9 ml, 60–90 μm) are used instead of centrifugation to eliminate undissolved material. The dissolved collagen is transferred to previously cleaned ultrafilters (Amicon Ultra-4, Millipore, 30 KDa), and centrifuged to eliminate the short collagen molecules which may be degraded and contaminated [10,11]. The final product after ultrafiltration is freeze-dried. Depending on the drying process used in each case, the final product looks quite different. If the collagen is dried in the oven, it will crystallise and will be hard and brown colored, meanwhile the product after freeze-drying is white, porous and soft and easier to manipulate afterwards.

(c) *Barley mash, charcoal:* For these materials, a simple acid–base–acid procedure at 80 °C is used to eliminate possible carbonates or humic acids.

(d) *Humic acid:* No pre-treatment was done to this sample prior to direct graphitization.

(e) *Carbonate:* Carbonate samples differ from organic samples in the sense that $CO_2$ is not obtained through combustion, but by complete dissolution of the carbonate in $H_3PO_4$. The only pre-treatment they follow is a soft leaching at room temperature for some minutes with HCl 0.1 M in order to dissolve the external and potentially contaminated surface layer. This leaching is not done for small or fragile samples.

Organic samples were all graphitized with an AGE system [12] which couples an elemental analyzer to the graphitization line. The necessary amount of sample to obtain ca. 1 mg of carbon is wrapped in tin foils and combusted in the elemental analyzer, and the different gases are trapped in a chromatographic column. Gases are released sequentially by increasing the temperature of the column, and the software controlling the process manipulates the appropriate valves, releasing nitrogen to atmosphere and transferring the $CO_2$ to the corresponding reactor of the graphitization line. $H_2$ is added to the reactor, where Fe is used as catalyst, and heating ovens at 580 °C enable the reducing reaction to transform $CO_2$ to graphite. Water that is generated in the reaction is trapped using Peltier coolers. The system allows the preparation of seven samples in parallel in an automatic way after loading the samples in the elemental analyzer, with a total time of about four hours for the whole process.

The carbonate samples cannot be combusted properly and the AGE system needs a special carbonate handling system to be used with such samples. Thus, we prepared the SIRI-K sample in our manual graphitization line [13] which was the one in operation for all kind of samples before the AGE system was installed in 2012. This manual line uses the same concept, but $CO_2$ has to be produced offline, (e.g., by combustion of the sample in a vacuum-sealed ampoule in the case of organic samples), and gases are transferred in the graphitization line using liquid nitrogen to freeze $CO_2$ in the corresponding reactor. As a result, it is a much more time consuming system, and currently we are only using this line for carbonate samples. Carbonate samples are prepared in special vacuum ampoules with two separate compartments, for the sample and phosphoric acid respectively. They are kept separated