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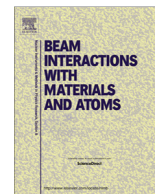
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Radiocarbon measurements at LAC-UFF: Recent performance

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A B S T R A C T

In 2012 a single stage accelerator mass spectrometer from NEC was installed at the Radiocarbon Laboratory of Universidade Federal Fluminense (LAC-UFF), Niterói, Brazil. Here, we present a status report of our facility. We discuss some modifications applied to our combustion protocol in an attempt to reduce our procedural blank, mostly to processed organic samples. Measurements of reference materials indicate low precision and accuracy that are partially related to beam optics through the acceleration tube. We observed that once the beam current intensity increases the measured $^{13}C^+/^{12}C^+$ becomes erratic. Therefore, in order to maintain the AMS-δ^{13}C values within reasonable values, so that fractionation corrections using the spectrometer $^{13}C^+/^{12}C^+$ values does not affect the final ^{14}C results, we are forced to limit the $^{12}C^-$ beam intensity to $\leqslant 30$ μA. This requirement was confirmed during our accuracy tests, when measuring selected annual tree-rings wood samples from a Parana pine (*Araucaria angustifolia*) between 1927 and 1997 previously measured at the Keck Carbon Cycle AMS Facility (KCCAMS), at the University of California, Irvine (UCI). At the LAC-UFF tree-ring wood samples were processed and measured in 4 different batches during a period of about 5 months. The ^{14}C results were later compared to the high-precision data obtained at KCCAMS/UCI and reached a good agreement. Recently a problem associated with graphitization yield were finally identified and new measurements with secondary standards are promising.

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1. Introduction

In 2012 a NEC 250 kV SSAMS (single stage) system was installed in our laboratory to complement the radiocarbon sample preparation laboratory at the Universidade Federal Fluminense (UFF), Niterói, Brazil, operating for over 3 years [1]. Similar AMS systems have been adopted in other facilities worldwide [2–4]. Since we started operating the SSAMS system, the facility has processed and measured about 3,200 samples, including reference materials (such as, HoxII, IAEA-C6, IAEA-C5, IAEA-C2 and Alfa-Aesar synthetic graphite as blank). Typical unknown materials prepared in our sample preparation laboratory are soil, sediment, woods, charcoals, shells and otoliths from a fairly wide range of multidisciplinary research projects.

In order to evaluate our overall performance, a ^{14}C inter-comparison exercise was carried out involving the LAC-UFF, the Center for Applied Isotope Studies at the University of Georgia, USA (UGa; AMS method) and the Centro de Energia Nuclear na Agricultura at the Universidade de Sao Paulo, Brazil (CENA; scintillation counting method) laboratories [5]. This exercise was not intended to be overwhelming, however it showed that although our ^{14}C results were in good agreement (within uncertainties) our precision (and possibly accuracy) was lower than the one achieved by the University of Georgia. High-precision ($\leqslant 0.3\%$) and accuracy are mandatory, for instance, to produce high-quality ^{14}C dating by means of the wiggle-matching or single-event matching [6] and to develop studies on the dynamics of the global carbon cycle [7,8].

Here, we present a status report of our facility based on ^{14}C measurements performed between 2013 and April, 2015. This contribution is structured as follows. In the first part, we show ^{14}C results for reference and blank materials when we operate the spectrometer under system's typical conditions. Secondly, we show the effects of beam current to the spectrometer transmission and the online $^{13}C^+/^{12}C^+$ values. Third, we discuss some modifications implemented on the combustion protocol, as an attempt to reduce the exogenous carbon contamination on processed organic

materials. Finally, we present bomb-pulse ^{14}C results of selected wood rings from a single Parana pine (*Araucaria angustifolia*) previously measured at KCCAMS/UCI [9], as a way to identify and improve the SSAMS performance. Quite recently it has been identified the uncompleteness of graphitization yield [10] and ^{14}C results from new graphites of HoxII produced so far are shown.

2. Typical operation

The LAC-UFF SSAMS system has a 40 MC-SNICS ion source. Typical settings of elements in the ion source are presented in Table 1. Under these settings, we normally extract 20–50 μA ^{12}C$^-$ beam current. It is our experience that before a new tuning by means of AMS can be started, graphite targets need to be "warm-up" (i.e. expose to the Cs beam) per ~3–6 min, or until stable-isotope beam currents are achieved (whichever comes first). Once this step is concluded, the system tuning can be started by searching the best setting conditions (within the parameters shown in Table 1) to optimize source output.

The acceleration tube operates at 240.2 kV (with 105–120 μA in the H.V. supply). The stripper is filled with argon 99.999% at 0.95 sccm. At those settings, overall beam transmission vary between 32% and 34% although it is dependent on the ^{12}C$^-$ beam current, as it will be discussed later. Measurements of each cathode are performed in 20 runs of 60 s warm-up and 140 s acquisition.

The full extent of precision and accuracy offered by a carbon-based AMS system is based on a long term of multiple measurements of several reference materials. Randomly selected ^{14}C data of graphite targets produced from the reference materials IAEA-C2 chalk (pMC = 41.14 ± 0.03), IAEA-C6 sucrose (pMC = 150.61 ± 0.11) and blanks of inorganic and organic origins (pMC ≅ 0) are presented in Fig. 1. Graphites that yielded low beam currents (<3 μA ^{12}C$^-$) are not considered. Those samples were measured as secondary standards in multiple wheels, and were normalize by a set of 4 graphite targets of HoxII (oxalic acid II, used in our facility as the primary normalizing standard). Initial precision of 2.8% and 1.2% was obtained from multiple measurements of IAEA-C6 (n = 23) and IAEA-C2 (n = 25), respectively, which reflects the combustion and graphitization procedures coupled with spectrometer measurement variability. Spectrometer background was evaluated by measuring non-processed Alfa Aesar (mesh -200) graphite targets, the ^{14}C/^{12}C obtained from these measurements are equivalent to ca. 50,000 ^{14}C years while for organic and inorganic processed blanks are ca. 35,000 and 38,000 ^{14}C years, respectively (see Fig. 1b). Note that machine background have not been subtracted from those values.

Mass-14 interference in the accelerator, such as CH$^-$ and CH$_2^-$ not properly dissociated at the stripper channel, can also mask the results of our blanks. We have tested the spectrometer transmission and blanks by varying the amounts of argon in the stripper channel but no improvement on the organic procedural blank had been observed.

Recent report from the AMS group of the Scottish Universities Environmental Research Center (SUERC) indicates that ^{13}C particles, when dissociated from ^{13}CH molecule, can cause mass-14 interference since a fraction of these particles can exit from the stripper channel with the same magnetic rigidity as for the ^{14}C [11]. An offset on the electrostatic spherical analyzer (ESA) should be enough to get rid of those undesirable particles and allow for a better background. In our case we still need a long-term database to confirm that.

2.1. The ^{13}C$^+$/^{12}C$^+$ measured in the spectrometer

The ion source introduces partial separation of the different isotopes that usually results in the enrichment of one isotope relative to the other [12]. In addition, Prasad et al. [4] reported a deviation of ±0.5% of spectrometer online-δ^{13}C relative to standard stable isotope δ^{13}C values, when measuring samples in their SSAMS system at UGa. Skog et al. [2] also reported that their SSAMS spectrometer has a beam current dependent ^{13}C$^+$/^{12}C$^+$ at the high-energy deck. At the LAC-UFF facility, the high-energy ^{13}C$^+$/^{12}C$^+$ *versus* ^{12}C$^-$ current plot from individual runs (i.e. averaged over 140 s of acquisition) with targets produced from HoxII (pMC = 134.07) are shown in Fig. 2. In some cases, the abnormally high scattering of ^{13}C$^+$/^{12}C$^+$ points are due to the targets produced from incomplete graphitizations and consequently very low beam currents. The large ^{13}C$^+$/^{12}C$^+$ scatter associated with individual targets delivering currents above 40 μA cannot possibly be from "failed" or incomplete graphite. We argue that in those case, the spectrometer were poorly tuned or other still unidentified effects played a role. All blue points corresponding to 12 HoxII graphite targets running in 2 independent wheels highlighted in Fig 2, were produced after the graphitization procedure was completely corrected (see Ref. [10]). Compared to our previous measurements of HoxII graphites, the new dataset still indicates a deviation on the online AMS ^{13}C$^+$/^{12}C$^+$ toward high values. From 16 to 25 μA ^{12}C$^-$, where ^{13}C$^+$/^{12}C$^+$ data are roughly independent on the ^{12}C$^-$ beam current, the standard deviation of the "raw" ratio about 0.4% (based on the new batches of HoxII).

We also have learned that the spectrometer transmission is affected by high ^{12}C$^-$ beam currents. Typical spectrometer transmission is 32–34% at ~30 μA ^{12}C$^-$, but tend to collapse to 28–29% for ~60 μA ^{12}C$^-$. Higher ^{12}C$^-$ beam currents tend to load the HV supply, i.e. drive current from it and pull down the high voltage. For 60 μA ^{12}C$^-$ beam current in direct mode, current of the HV supply saturates at 150 μA and voltage goes down to ~190 kV. A possible explanation is that negative beam deposits some fraction of electric charge on the stripper channel entrance and consequently drives away more current from the HV supply. This effect is not noticed in jumping mode, i.e. sequentially injecting mass 12, 13 and 14. However it may be responsible for some selective losses of carbon isotopes that result in very erratic ^{13}C$^+$/$^+$ (and possibly ^{14}C$^+$/^{12}C$^+$ as well) when measurements are performed in the high ion source beam current regime. Therefore, beam current higher than 30 μA ^{12}C$^-$ was completely discouraged in our facility until we better understand its cause.

2.2. Treatment of organic materials

The high background of our processed graphites (see Fig. 1b) from organic materials is a matter of concern. In a simple model, the ^{14}C/^{12}C ratio (R_{true}) of a sample can be influenced by ^{14}C-modern and ^{14}C-dead contaminants added throughout sample processing steps. The measured rare isotope ratio (R_{meas}) is given by:

$$R_{meas} = \frac{m_{true}R_{true} + m_{mod}R_{mod} + m_{old}R_{old}}{m_{meas}} + R_{mach} \tag{1}$$

Table 1
Typical parameters at the MC-SNICS ion source.

Element	Value
Cathode	−4.0 kV
Immersion lens	−3.8 kV
Cesium oven (temperature)	82°–88 °C
Ionizer (current)	20–22.0 A
Extractor	+10.0 to +14.0 kV
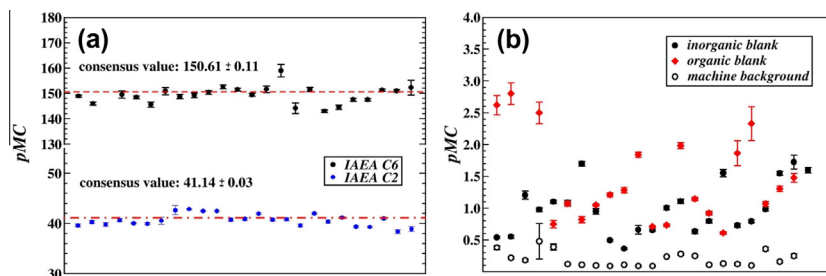
Fig. 1. Randomly selected data for IAEA-C6 and IAEA-C2 graphite targets, and blank materials. Spectrometer background was evaluated with non-processed Alfa Aesar graphite targets, while organic procedural blanks were determined by measuring the same material after combustion and graphitization procedures. Optical calcite were used as inorganic procedural blank. The X axis is in arbitrary unit. Standard deviations for IAEA-C6 ($n = 23$) and IAEA-C2 ($n = 25$) are 2.8 and 1.2 pMC, respectively.
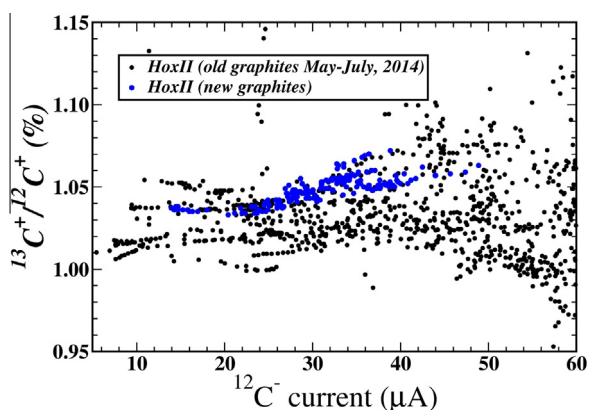
Fig. 2. Raw $^{13}C^+/^{12}C^+$ against beam current measured during single runs of HoxII graphites. The results in black are associated with the graphites measured from May to July, 2014. Blue results are associated to HoxII graphites produced under optimum graphitization conditions. See text. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

R_{mod} and R_{old} are the $^{14}C/^{12}C$ ratio of ^{14}C-modern and dead contamination sources, respectively. m_i (with i = meas, true, mod, old) are their masses. R_{mach} accounts for ^{14}C signal interferences in the machine.

To evaluate the blank introduced from combustion, graphitization and spectrometer contributions, we normally processed aliquots of the Alfa Aesar synthetic graphite. Once 1.5 mg of Alfa Aesar graphite (whose $R_{true} < 1.0 \times 10^{-15}$ $^{14}C/^{12}C$) is processed by the steps above and pressed in a target holder, the measured activity is typically 1.2×10^{-14} $^{14}C/^{12}C$ (equivalent to just 35,000 years BP). Neglecting sources of ^{14}C-dead contaminations, we estimate about 12 µgC of modern contamination (R_{mod} ~1.1×10^{-12} $^{14}C/^{12}C$).

Leakage of atmospheric-CO_2 into the evacuation lines (combustion and/or graphitization) alone cannot account for this background. Moreover radiocarbon measurements on non-processed graphites indicate that the graphite pressing step into aluminum target holders is not a major source of contamination (see Fig. 1b). Here we restrict ourselves to evaluate our combustion protocol since potential doorways to contamination may come from the walls of the quartz tubes [13], the CuO reagent [14] and/or vacuum components [15].

Our former combustion protocol is summarized as follows:

(a) Cleaning of quartz tubes (both ends open) with Sodium Lauryl Sulfate with a final rinse with ultra-pure water and drying at 90 °C.
(b) Closure of one end of quartz tubes using a torch and storage in an air-tight box.

(c) Loading the closed-end quartz tube with 10–30 mg Ag powder and 60–80 mg CuO and baking for 3 h at 900 °C.
(d) After the baking step, tubes are wrapped up in aluminum foil and stored in a climatic chamber.
(e) Then samples are loaded into the clean quartz tubes and sealed under vacuum better than 1.0 mTorr.
(f) Baking the vacuum sealed quartz tubes at 900 °C for 3 h to produce CO_2.

Influenced by established protocols at KCCAMS/UCI [16] and at Centre for Isotopic Research for Cultural and Environmental Heritage (CIRCE) laboratory in Caserta, Italy [17] with outstanding performance, we have introduced the following modifications:

(1) No cleaning with Sodium Lauryl Sulfate, since the organic impurities on the walls of the quartz tube can be eliminated by baking at 900 °C.
(2) Use of Ag wires instead of powder: contamination on reagents may be surface dependent, so that Ag wires potentially introduce less contamination than Ag powder.
(3) Closed-end quartz tubes and reagents are pre-conditioned aside at 900 °C for 3 h.
(4) Pre-baked CuO, Ag wire and sample are loaded into the clean quartz tube at the same time, prior to be evacuated.

These modifications did not translate to a significant improvement of our procedural organic blank. On the other hand, they allow us to reduce our typical turnover time of sample preparation. The steps 3 and 4 allow for large quantities of reagents and tubes be prepare in advance. As long as they are properly store, the ^{14}C results associated with the procedural organic blank is relatively stable. Therefore, we concluded that the combustion procedure step alone is not the major contributor of our organic blank.

Recently we identified and corrected a problem regarding low graphitization reaction yield due to an offset in one of our muffle furnace temperature settings. This subject is addressed in Ref. [10]. Generally, the yield of the graphitization reaction can be estimated from the pressure change during the reaction (i.e. during the reduction of CO_2 to filaments graphite on catalyst powder) [18]. However, we chose to produced graphite by the sealed Zn process [19] and therefore monitoring the pressure during graphitization reduction is not an option. Since we use more than one muffle furnace in our lab for graphitization purposes, the problem was difficult to be initially identified. For years we experienced inconsistent graphitization reaction yields, mostly observed by intermittent low beam currents and erratic carbon ratios. We want to note that some of the spectrometer measurement variability observed earlier could be in principal attributed to those intermittent low sample processing yields. But since not all of the graphite's we measured until 2014 were produced in the problematic muffle

furnace, some of the variability in precision could still be associated to the spectrometer performance, which was still under evaluation.

3. Measurements of annual tree-rings: performance test

As mentioned earlier, for a more in depth evaluation of spectrometer precision and accuracy, we also processed and measured selected tree-rings from a single tree of *A. angustifolia* cut down in 1998 from Camanducaia, Minas Gerais, Brazil (for more details see Ref. [9]).

We have measured 43 annual tree-rings, including 9 randomly selected duplicates. It should be highlighted here that those graphite targets were produced and measured before the incompleteness of graphitization (low graphitization yield) has been identified and corrected. Therefore, we suspect that some of the graphite targets measured was not of a high quality, as we initially expected.

Holocellulose fraction was extracted from subsamples of 5–10 mg of each growth ring, following an established procedure [20]. After bleaching, the holocellulose extract was rinsed with ultra-pure water 3 times and then dried at ∼60 °C per 24 h. A ^{14}C-dead (or ^{14}C-free) wood sample and two secondary standards (IAEA-C3 cellulose and IAEA-C5 two creeks) were added to those batches and treated in exactly the same way. After combustion, CO_2 was cryogenically purified under a vacuum better than 1.0 mTorr. Graphitization was performed following the modified Zn and TiH_2 reduction method, described in [20]. It should be highlighted that all samples in this exercise were in the problematic muffle furnace at 520 °C for 7 h [10]. Graphites were kept in the sealed reaction tubes until being pressed into the target holders.

In Fig. 3 we show the AMS-δ^{13}C measured for all 4 batches with values ranging from −75‰ to +20‰ while typical δ^{13}C signature for this type of samples lies between −22‰ and −26‰. Differences between AMS-δ^{13}C and the δ^{13}C of the original material are expected [16], if fractionation occurred during sample graphitization or the AMS measurement. However the anomalous range reported are beyond correction.

In Fig. 4 we show the *A. angustifolia* ^{14}C results (AMS-δ^{13}C corrected and background subtracted), compared to independent ^{14}C results obtained at KCCAMS/UCI [9]. An overall agreement is observed, but some of the results are 2-sigma deviation or more from the correct values (those are indicated with arrows in Fig. 4). Radiocarbon results from IAEA-C3 and C5 reference materials in all batches were within 3-sigma of their consensus values (those are not shown). We suspect that those ^{14}C offsets arised mostly from the isotopic fractionation correction using anomalous AMS-δ^{13}C values, although some cross contamination during
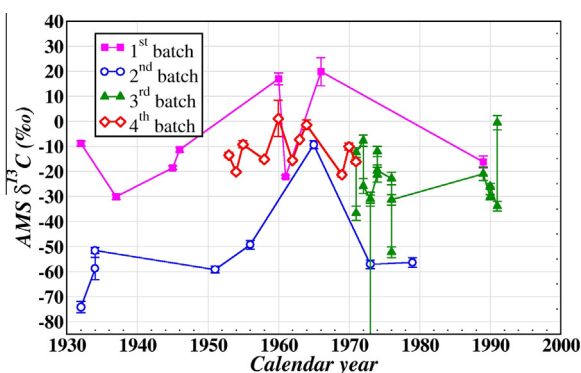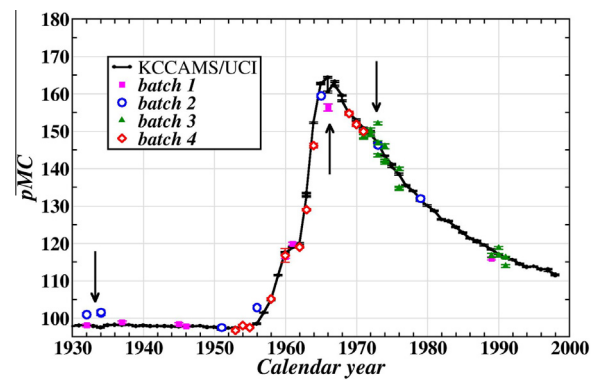

Fig. 4. Radiocarbon results for annual growth rings of *A. angustifolia* measured at LAC-UFF compared with KCCAMS/UCI results [9]. Arrows indicate points with more than 2-sigma deviation from their correct values.
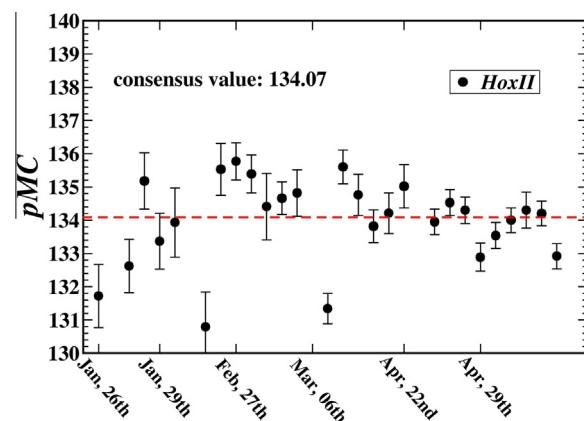

Fig. 5. ^{14}C results for some of our latest HoxII graphites measured in 2015. Graphites we produced according to [10] and measurements were carried out with good control of beam intensity. See text for details.

sample preparation and failed graphites cannot be ruled out. For the batch 4 (Fig. 3) we controlled the beam current intensity (e.g. less than 50 μA ^{12}C$^-$ at the time of measurements as explained in Section 2.1), and consequently the AMS-δ^{13}C yielded values from −22‰ to ∼0‰. Under this condition reasonable AMS-δ^{13}C values were achieved and a good agreement with the KCCAMS/UCI dataset were obtained. Nowadays, 30 μA ^{12}C$^-$ is a convenient upper limit for better accuracy of our measurements.

Recent measurements of graphites targets produced under proper graphitization reaction conditions are promising. In Fig. 5 we show the ^{14}C results for some HoxII graphites produced in 2015 measured so far. Each HoxII has been analyzed as unknown sample and normalized by their 4 standards neighbor in time in the wheel. Considering only measurements performed in April, 2015, we obtain a precision of 0.8% based on 11 targets. The processed background for organic samples (not shown here) seems to be better compared to Fig. 1. Nevertheless a long-term evaluation with the new graphites is required to draw conclusions on the reproducibility of our measurements.

4. Conclusions

Our procedural background is relatively high compared to values typically reported by other laboratories. The combustion procedure alone is unlikely to be the major contributor to the overall blank observed here, since no significant improvements were achieved after we modified our combustion protocol.

Fig. 3. Spectrometer online-δ^{13}C values for annual tree-rings of *A. angustifolia* measured at LAC-UFF into 4 independent batches. Typical δ^{13}C signatures of wood samples are in the range of −22‰ to −26‰. See text for details.

Recently the incompleteness of graphitization reaction has been identified and corrected. Nevertheless, a strong dependency between the spectrometer $^{13}C^+/^{12}C^+$ values and ion-source beam intensity has been observed. Such dependency imposes an ion-source beam intensity upper limit of $\sim$30 μA $^{12}C^-$ ($\sim$10 μA $^{12}C^+$) when measuring graphite targets. Above this limit the $^{13}C^+/^{12}C^+$ values become erratic, and the ^{14}C results corrected by the online AMS-$\delta^{13}C$ can also yield inaccurate values.

Precision and accuracy of ^{14}C results in our SSAMS have been evaluated by measuring reference materials and selected annual growth rings from a subtropical native pine measured at KCCAMS/UCI [9]. Comparison between our ^{14}C results and those from the KCCAMS/UCI facility identified some non-systematic behavior of both origins: (a) incomplete graphitizations [10], leading to low beam current intensities and further fractionation and; (b) erratic spectrometer online-$\delta^{13}C$ values associated with the beam transmission in our spectrometer, as mentioned above. Measurements done under controlled beam current (i.e. with $^{12}C^-$ beam lower than $\sim$30 μA) produced reliable AMS-$\delta^{13}C$ values and, consequently, a better agreement between the ^{14}C results at the LAC-UFF with those produced by high-precision at KCCAMS/UCI. Initial measurements with the new graphites are promising. Precision/accuracy based on recent batches of HoxIIs indicated that reproducibility of results is within 0.8%. Further improvements are needed to reduce this value.

Acknowledgements

References

[1] R.M. Anjos, K.D. Macario, P.R.S. Gomes, R. Linares, E. Queiroz, C. Carvalho, Nucl. Instr. Meth. B 294 (2013) 173.
[2] G. Skog, Nucl. Instr. Meth. B 259 (2007) 1.
[3] S.P.H.T. Freeman, A. Dougans, L. McHargue, K.M. Wilcken, S. Xu, Nucl. Instr. Meth. B 266 (2008) 2225.
[4] G.V. Ravi Prasad, J.E. Noakes, A. Cherkinsky, R. Culp, D. Dvoracek, Radiocarbon 55 (2013) 319.
[5] K.D. Macario, P.R.S. Gomes, R.M. Anjos, C. Carvalho, R. Linares, E.Q. Alves, F.M. Oliveira, M.D. Castro, I.S. Chanca, et al., Radiocarbon 55 (2013) 325.
[6] Q. Hua, Quat. Geochronol. 4 (2009) 378.
[7] G.M. Santos, AIP Conf. Proc. 1423 (2012) 311.
[8] A. Hogg, C. Turney, J. Palmer, E. Cook, B. Buckley, Radiocarbon 55 (2013) 2029.
[9] G.M. Santos, R. Linares, C.S. Lisi, M.T. Filho, Quat. Geochronol. 25 (2015) 96.
[10] K.D. Macario, F.M. Oliveira, C. Carvalho, et al., Nucl. Instr. Meth. B 361 (2015) 402.
[11] R. Shanks, P. Ascough, A. Dougans, P. Gallacher, P. Gulliver, D. Rood, S. Xu, S. Freeman. Performance of the rebuilt SUERC single-stage accelerator mass spectrometer. In: AMS-13 Conference, Aix en Provence – Book of Abstracts (2014) 236.
[12] M.J. Nadeau, W.E. Kieser, R.P. Beukens, A.E. Litherland, Nucl. Instr. Meth. B 5 (1984) 254.
[13] J.S. Vogel, D.E. Nelson, J.R. Southon, Radiocarbon 29 (1987) 323.
[14] K. Vandeputte, L. Moens, R. Dams, J. van der Plicht, Radiocarbon 34 (1998) 103.
[15] J. Czernik, T. Goslar, Radiocarbon 43 (2001) 283.
[16] G.M. Santos, R.B. Moore, J.R. Southon, S. Griffin, E. Hinger, D. Zhang, Radiocarbon 49 (2007) 255.
[17] F. Marzaioli, G. Borriello, I. Passariello, C. Lubritto, N. De Cesare, A. D'Onofrio, F. Terrasi, Radiocarbon 50 (2008) 139.
[18] G.M. Santos, M. Mazon, J.R. Southon, S. Rifai, R.B. Moore, Nucl. Instr. Meth. B 259 (2007) 308.
[19] X. Xu, S.E. Trumbore, S. Zheng, J.R. Southon, K.E. McDuffee, M. Luttgen, J.C. Liu, Nucl. Instr. Meth. B 259 (2007) 320.
[20] J.R. Southon, A.L. Magana, Radiocarbon 52 (2010) 1371.