

DEVELOPING ULTRA SMALL-SCALE RADIOCARBON SAMPLE MEASUREMENT AT THE UNIVERSITY OF TOKYO

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ABSTRACT. We have developed accelerator mass spectrometry (AMS) measurement techniques for ultra small-size samples ranging from 0.01 to 0.10 mg C with a new type of MC-SNICS ion source system. We can generate 4 times higher ion beam current intensity for ultra-small samples by optimization of graphite position in the target holder with the new ionizer geometry. CO₂ gas graphitized in the newly developed vacuum line is pressed to a depth of 1.5 mm from the front of the target holder. This is much deeper than the previous position at 0.35 mm depth. We measured ¹²C⁴⁺ beam currents generated by small standards and ion beam currents (15–30 μA) from the targets in optimized position, lasting 20 min for 0.01 mg C and 65 min for 0.10 mg C. We observed that the measured ¹⁴C/¹²C ratios are unaffected by the difference of ion beam currents ranging from 5 to 30 μA, enabling measurement of ultra-small samples with high precision. Examination of the background samples revealed 1.1 μg of modern and 1 μg of dead carbon contaminations during target graphite preparation. We make corrections for the contamination from both the modern and background components. Reduction of the contamination is necessary for conducting more accurate measurement.

INTRODUCTION

Radiocarbon dating has been widely used for archaeology, geology, and oceanography (Stuiver and Polach 1977; Yokoyama et al. 2008). With the advancements in accelerator mass spectrometry (AMS) small amounts of sample (~1 mg C) can be routinely dated (Yokoyama et al. 2007). Methods are currently being developed to measure ¹⁴C content in very small (1–10 μg C) samples for recently developed compound-specific radiocarbon dating (CSRD) as well as for *in situ*-produced ¹⁴C in rocks (e.g. Lifton et al. 2001; Ohkouchi et al. 2003; Naysmith et al. 2004; Yokoyama et al. 2004). A promising application of CSRD is to date sediments from the Southern Ocean where there exists a paucity of organic carbon. Samples are processed through several steps of organic chemistry using gas chromatography. However, collecting 1 mg of C requires burdensome laboratory steps. This has been a major obstacle preventing CSRD from becoming a ubiquitous method as only a limited number of laboratories have successfully established systems to measure very small samples (e.g. Southon and Santos 2007; Santos et al. 2007). Nevertheless, various efforts have been made in laboratories to accurately measure small samples (e.g. von Reden et al. 1998; Graven et al. 2007; Santos et al. 2007; Shah and Pearson 2007; Smith et al. 2007; Southon and Santos 2007; Kjeldsen et al. 2008) including promising gas ion sources (Ruff et al. 2007). We therefore have developed an experimental protocol together with the installation of new MC-SNIC ion sources to the accelerator mass spectrometry (AMS) systems at the University of Tokyo.

METHOD

Sample Preparation

Our previous graphitization system was designed at the University of Tokyo for a graphite size of ~1 mg C (Yokoyama et al. 2007). Between 1–1.5 mg of iron catalyst, depending on the sample size,

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to make the iron to graphite ratio nearly 1:1, is used to reduce sample CO₂ under hydrogen atmosphere at 630 °C for 6–10 hr. In 2008, a newly designed metal line was installed that reduced the internal volume dramatically (Figure 1), as much as 45% from 8.0 to 4.5 mL in the reaction vessels where iron catalysts are placed. This led to an increase of partial pressure of gases in the vessel, thus improving the efficiency of the reaction. The size of catalysts and duration of reduction steps follow Santos et al. (2007), who use large iron catalysts (4–4.5 mg) and lower temperature (450 °C) during graphitization. Iron catalysts are prereduced under hydrogen atmosphere at 450 °C for >1 hr to reduce the surface of the iron catalyst. The line was kept under vacuum with a ribbon heater (85 °C) after sample treatments to remove any gasses absorbed during experiments. Samples used for the experiments are standard materials provided from IAEA and NIST, which were weighed and processed to produce graphite targets.

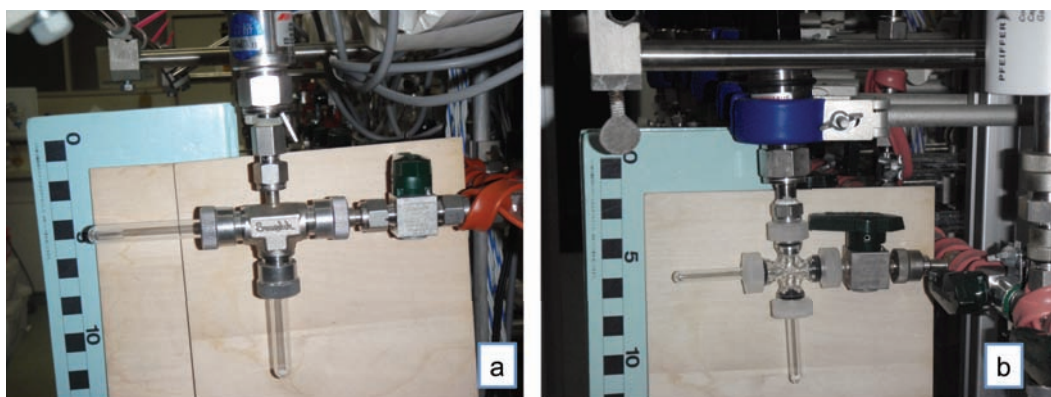


Figure 1 Photos showing the old (a) and new (b) graphitization reaction vessels with respective internal volumes of 8.0 and 4.5 mL. The previous reaction apparatus was built mainly using stainless steel tubing and Swagelok valves attached with glass tubes of 9 mm outer diameter (Yokoyama et al. 2007), whereas the new apparatus employed 1/4" Swagelok valves attached with 6-mm OD glass tubes. To reduce internal volume further, specially designed glass cross-fittings were made. The scale bar behind each apparatus is in cm.

The accelerator mass spectrometry (AMS) system at the University of Tokyo is a 5UD tandem Pelletron (Matsuzaki et al. 2007). To this system, we installed a new cesium sputtering ion source, MC-SNICS, which dramatically increased ionization efficiency (cf. Southon and Santos 2007). MC-SNICS consists of spherical ionizer, Cs diffuser, and immersion lens. Since the new ion source can produce a high-intensity Cs⁺ beam, we sought the optimum geometric conditions for the beam to reach the target graphite in the cathode cone.

RESULTS AND DISCUSSIONS

Seeking the Optimized Position of the Graphite in a Cathode Cone

¹⁴C measurements by AMS require sufficient beam intensities and the long duration of a stable beam to measure small amount of samples. Ionization efficiency of samples in a cathode cone depends on the position of the graphite because it is expected that the confinement of plasma created by the Cs⁺ beam entering the cathode cone has an impact on the effective negative ionization of sample (Figure 2). We processed the graphite and pressed at 0.35 mm from the edge of the cathode for 0.1 mg and 0.01 mg of IAEA-C6 to observe the effect on the strength of the beam current (Figure 3). The result shows that 0.01 mg of graphite produced only half the intensity. We then tried to find the best position of the graphite in the cathode cone (Figure 2) and found that the deeper the graphite, the longer

and stronger the produced stable beam current (Figure 4). For cathodes with 0.1 mg graphite, both 1.5- and 2.0-mm depth position measurements lasted sufficiently long (i.e. >50 min), whereas <0.5 mm deep could not withstand 15 min. In this experiment, ionization efficiencies for 1.5- and 0.35-mm cases were 10% and 0.7%, respectively. Similar behavior was found for smaller samples. For 0.01 mg of graphite, the 1.5-mm-depth produced a ~30% stronger beam current that lasted >20 min (Figure 5). The relationship between sample depth in the target holder and ionization efficiency is summarized in Figure 6. Pressing the graphite in deeper in the cathodes dramatically improved ionization efficiency by >4 fold, which is observed for different graphite sizes.

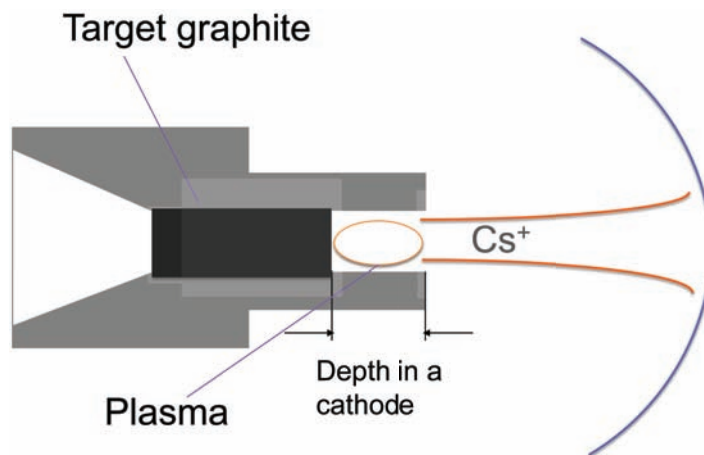


Figure 2 Schematic diagram of cesium spattering of the newly installed MC-SNICS

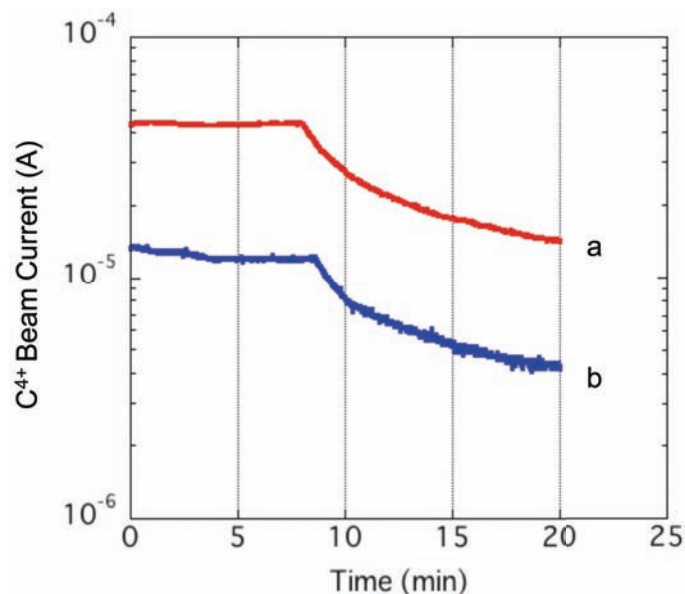


Figure 3 Diagram showing the size-dependent C^{4+} beam intensities and durations for the samples hold at the “conventional” depth in the cathode cone (0.35 mm) for 0.1 mg (a) and 0.01 mg (b) of graphite.

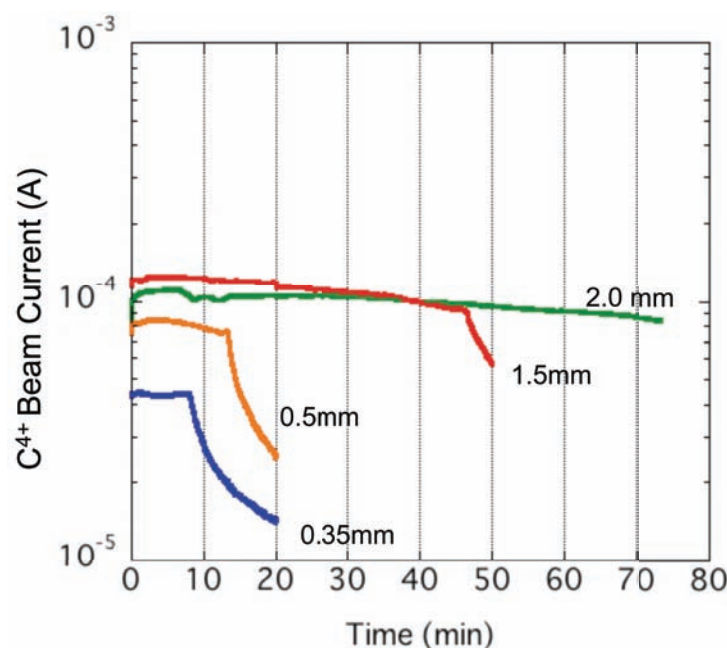


Figure 4 Experimental results showing increased performance in producing strong and stable beam currents using the same amount of graphite target (0.1 mg C of ANU) but for different positions of the samples in the cathode cones.

Negative ions are generated during sputtering by Cs^+ ions incident on the target surface. A fraction of the fragments of target material, including atoms and molecules, pick up electrons and are negatively ionized. In the present experiments, a longer tube length in front of the target surface has led to an increase in ionization efficiency.

The new type of MC-SNICS ion source has a spherical ionizer that concentrates Cs^+ ions onto the target. The Cs^+ ions are concentrated in a confined tube-like space where positive voltages generated by space-charge effects lead to efficient extraction of negative ions from the target (J Southon, personal communication, 2008). Another possible explanation relates to the deep positioning of the target surface, whereby the cylindrical inner surface area is increased. In this case, the area of neutral Cs layer, which contributes to the negative ions, increases so that the probability that a sputtered fragment interacts with neutral Cs is enhanced. Middleton (1983, 1989) already noted that predrilling of the target surface greatly enhanced negative ion generation, yet this was not explicitly interpreted. The exact nature of processes at the surface of the target are not well known at this stage. Therefore, systematically designed experiments with variable cathode geometries are desirable to better define the process occurring at the sample surface related to space-charge effects, surface effects, or a combination of both.

Evaluation of Degrees of Modern Carbon Contamination During the Experiments

As smaller samples are used, the degree of contamination is a major concern for ^{14}C measurements. We first tested several cases to see the threshold of the “minimum” beam current using NIST standard material (modern standard, 134.066 pMC; Stuiver 1983). Following our finding of the optimal position for graphite in the target, all samples were placed at 1.5 mm depth in the cathode holder. A graphite size of 100 μg C is set as the standard sample size and examined for 3 cases to evaluate the

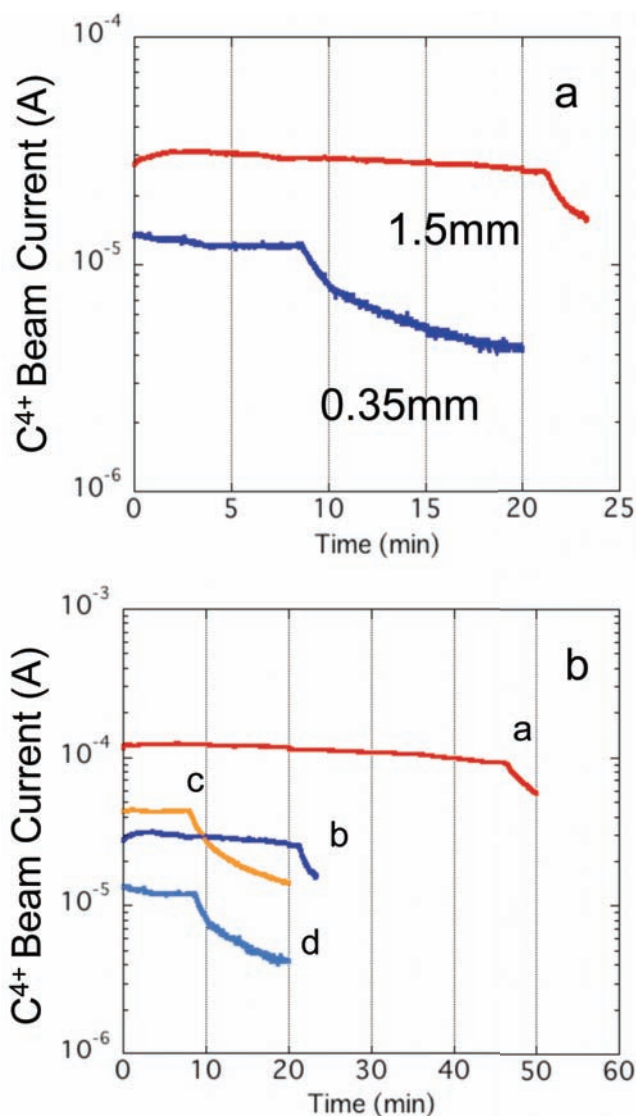


Figure 5 (a) Graphite targets containing small amounts of C (0.01 mg C ANU) when placed at 1.5 mm depth in the cathode cone produce much stabler, stronger beam currents. (b) Summary of optimization conditions for 100 μg C (a, c) and 10 μg C (b, d) graphite measurements. Beam intensity for 1.5 mm position in a cathode cone (a, b) produce 10-fold higher beam intensity and more than twice as long beam output duration compared with the cases for 0.35 mm (c, d).

effect of contamination during the combustion process, ranging from 0.1 to 10 mg C equivalent NIST. Graphite targets that were larger than 100 μg produced more than 7 μA of beam current and showed stable and accurate $^{14}\text{C}/^{12}\text{C}$ ratios (Figure 7). However, when the beam current lower than 5 μA , as is the case for 30 μg of graphite, the ratio fluctuated greatly.

We also tested the contamination effect for ^{14}C -dead samples. Approximately 1 mg of graphite was produced from the oxalic acid (Wako Chemical Co.) and measured by AMS. The results showed

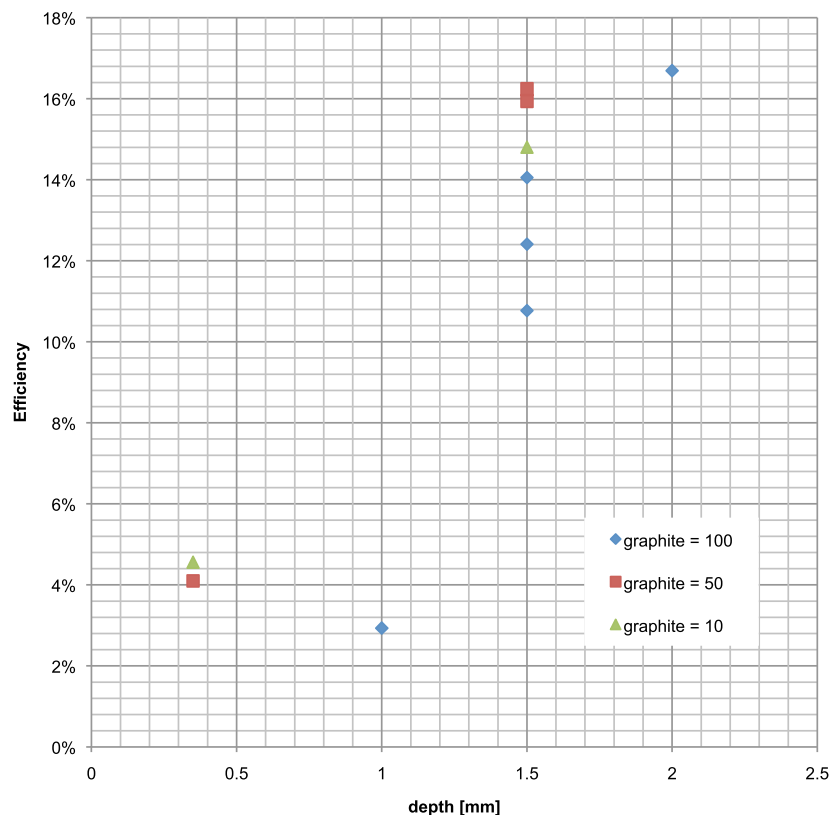


Figure 6 Ionization efficiency by position of target graphite in the cathode cone. A ~4-fold better ionization efficiency was obtained for graphite targets containing 10, 50, and 100 $\mu\text{g C}$.

that the oxalic acid is ^{14}C -free (0.17 ± 0.04 pMC); hence, it is suitable for using it to monitor levels of modern carbon contamination for sample combustion sizes ranging from 0.1 to 10 mg C equivalent oxalic acid. The ratio of ^{14}C against stable ^{12}C is constant for the combustion size of oxalic acid, yet the $^{14}\text{C}/^{12}\text{C}$ increased as the combusted sample sizes decreased. This suggests that the degree of modern carbon contamination is constant; therefore, the effect from it is in proportion to the sample sizes. It would thus be possible to calibrate the secondary carbon contaminations (cf. Santos et al. 2007).

^{14}C -free oxalic acid was used to estimate secondary contaminations for different sizes of graphite (Figure 8). For larger samples, longer sealed glass tubes were used to convert into CO_2 . The gas was then introduced to the vacuum line to split into 100 $\mu\text{g C}$ equivalent values. We evaluated the degrees of contamination during the experimental steps and made corrections according to the method described by Santos et al. (2007). Corrections can bring the results to the recommended values for both modern and background samples (Figure 9). However, for the background sample, results from before and after correction are identical for the 30 $\mu\text{g C}$ samples, though the absolute value of pMC shifted higher than expected (Figure 9). The source of this uncertainty should be resolved by further analyses since the results does not seem to be created by contamination arising from preparation. The results demonstrate that the contamination correction is efficient and provides expected values. We assess carbon contamination for 1 ± 0.2 and 1 ± 1 μg for modern and ^{14}C -free

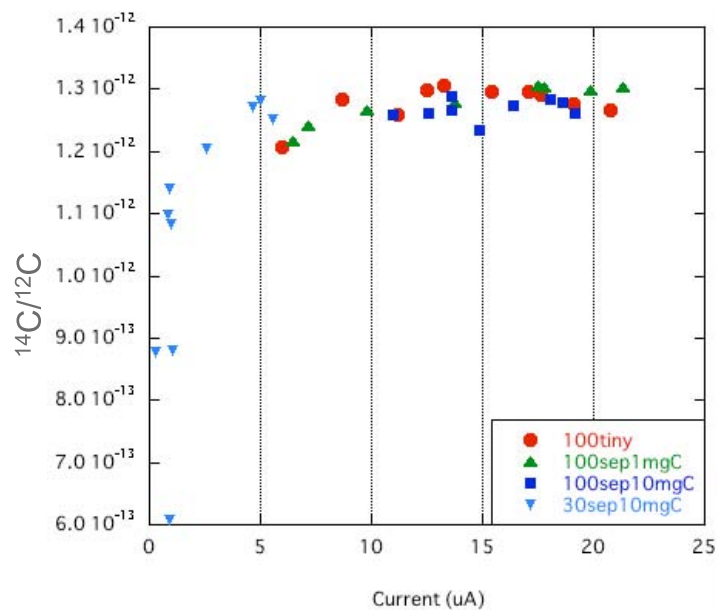


Figure 7 Contamination evaluations during graphitization steps for 100 and 30 μg C of modern carbon standard (NIST), which was split in differently. Individual samples are labeled as “XsepYmg” where X indicates actual size of graphite samples in μg being split from larger quantities of CO_2 gas of Y mg C equivalent. For “Ztiny,” the original gas size and final graphite size is 1:1 and the amount of graphite samples used was “Z μg C.”

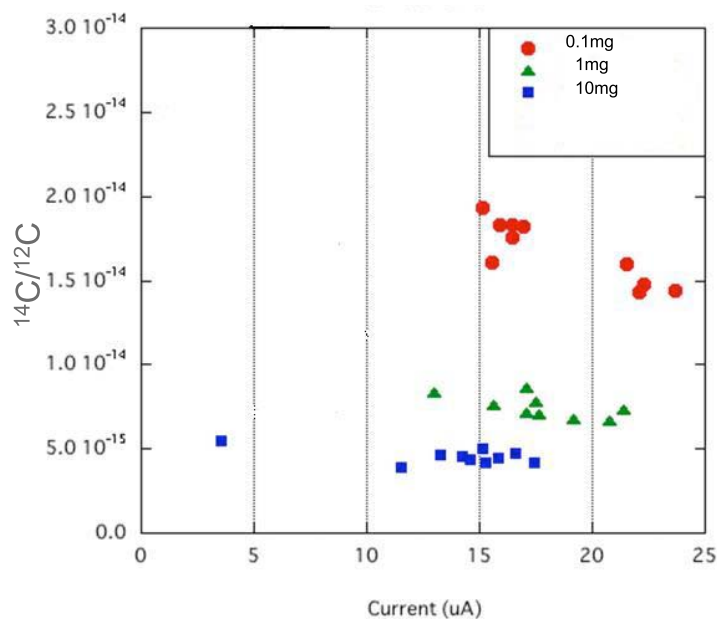


Figure 8 Contamination evaluations during graphitization steps for 100 μg C ^{14}C -free oxalic acid, which was split in differently. A longer tube was used for producing more CO_2 gas (i.e. 10 mg C equivalent). The gas was then transferred to the vacuum line and separated as 100 μg C quantities. As graphite samples decreased, ^{14}C ratios increased proportionally.

contamination, respectively. Further reduction of contamination during preparation will be required since the current values are 2–5 times larger than for other laboratories (e.g. Santos et al. 2007).

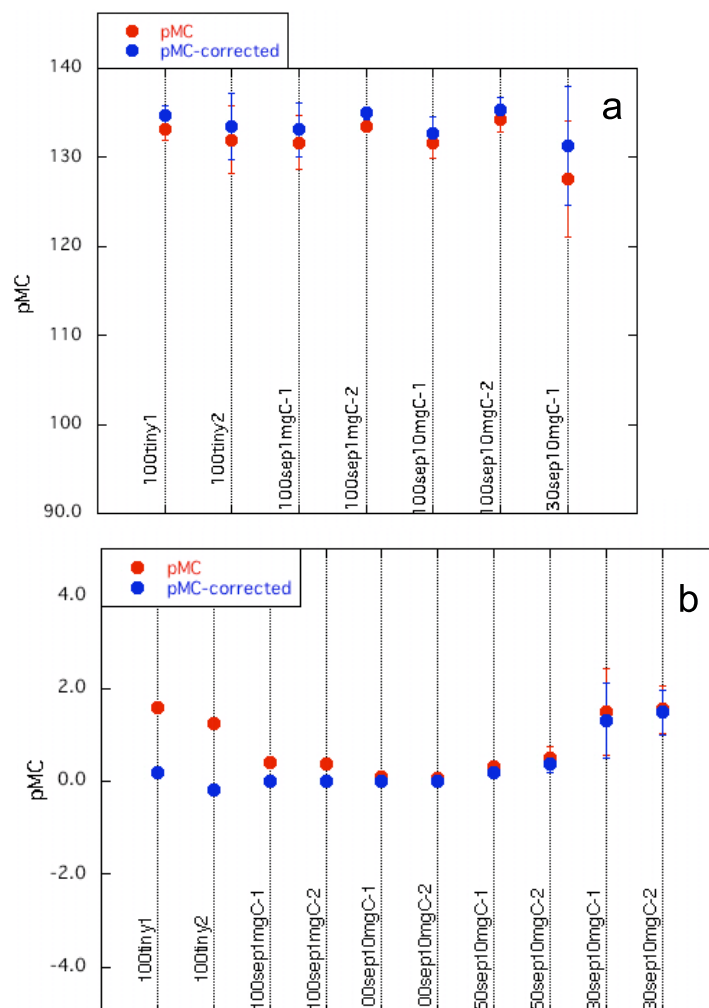


Figure 9 Applicability of contamination correction proposed by Santos et al. (2007). Results for the NIST (modern standard) and ¹⁴C-dead oxalic acid laboratory standard (background standard) were respectively drawn in panel a and b. Individual samples are labeled as “XsepYmg” where X indicates actual size of graphite samples in μg being split from larger quantities of CO_2 gas of Y mg C equivalent. In case of “Ztiny,” the original gas size and final graphite size is 1:1 and the amount of graphite samples used was “Z μg C.”

CONCLUSIONS

We succeeded measuring small (<1 mg C) graphite samples due to the recently implemented following modifications: installation of the new MC-SNICS ion source; building the new, small-volume graphitization line; and optimizing the position of the graphite in the cathode cone.

A newly installed small-volume vacuum line efficiently graphitizes sample CO_2 with low background due to the smaller internal surface areas. The position of the graphite in the cathode cone is particularly important for producing strong, long-lasting beam currents. The optimized position of the graphite target in the cathode cone is much deeper than previously used, i.e. 1.5–2.0 mm below the edge of the cone. We were also able to assess the degree of secondary contamination during the experimental processes by showing that only 1 μg of modern and “dead” carbon contaminants are introduced.

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