ULTRA SMALL-MASS GRAPHITIZATION BY SEALED TUBE ZINC REDUCTION METHOD FOR AMS ^{14}C MEASUREMENTS

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ABSTRACT. A modified sealed tube Zn reduction method based on Khosh et al. (2010) has been developed to graphitize ultra small-mass samples ranging from 4–15 µg carbon (C) for accelerator mass spectrometry (AMS) radiocarbon measurements. In this method, the reagent TiH_2 is removed from the previous method while the amounts of Zn and Fe powder remain the same. The volume of the sealed reactor is further reduced by ~40% to ~0.75 cm^3 and the graphitization temperature is lowered to 450 °C. Graphite targets produced by this method generally yield $^{12}C^{+1}$ currents of about 0.5 µA per 1 µg C, similar to the small mass (15–100 µg C) sealed tube Zn reduction method previously reported by Khosh et al. (2010) when measured on the same AMS system at KCCAMS, University of California, Irvine. Change of Fe powder to Sigma-Aldrich (400-mesh) has yielded further improved backgrounds over Fe powder of Alfa Aesar (325-mesh). Modern C background from combustion and graphitization is estimated to be 0.2–0.8 µg C, and dead-C background to be 0.1–0.4 µg C. The accuracy and precision of ultra small-mass samples prepared by this method are size and ^{14}C content dependent, but is usually ±4–5% for the smallest sample size of ~4–5 µg C with modern ^{14}C content. AMS on-line δ^{13}C measurement that allows for correction of both graphitization and machine-induced isotopic fractionation is the key for applying the sealed tube Zn reduction method to ultra small-mass sample graphitization.

INTRODUCTION

Ultra small-mass (<25 µg C) radiocarbon analysis by accelerator mass spectrometry (AMS) has gained higher demand in recent years because of the increasing needs of compound specific radiocarbon dating (CSRD), and for biological dating of specific cells in specific organs, such as in brains, hearts, etc. The amount of materials from these samples is usually in the µg C range, often <25 µg C after multiple chemical extraction steps that often involve chromatographic separations. Although ultra-small CO_2 gas samples can be successfully measured by CO_2 gas ion source AMS, such as the work by Fahrni et al. (2010), graphitization of ultra small-mass samples still poses some advantages because solid graphite targets can usually last longer in a solid ion source. Longer measurement time would allow lower statistical counting error and thus result in higher measurement precision, as long as the backgrounds associated with graphitization can be controlled and quantified. Several methods using H_2 reduction have shown to be able to successfully graphitize ultra small-mass samples (Hua et al. 2004; Santos et al. 2007a; Yokoyama et al. 2010), particularly impressive is the method (H_2 reduction on Fe catalyst) reported by Santos et al. (2007a) that can graphitize and measure samples as small as 2 µg C. Salehpour et al. (2008) reported a Zn reduction method modified from Ognibene et al. (2003) that could graphitize a few tens of micrograms of C from biological samples.

The work presented here is a continuation of the low-cost and high-throughput sealed tube Zn reduction method developed by Xu et al. (2007) and Khosh et al. (2010). The first paper described graphitization of samples larger than 0.1 mg C for high-precision ^{14}C AMS measurement, and the second paper demonstrated that sample sizes ranging from 15 to 100 µg C could also be successfully graphitized and measured at the Keck Carbon Cycle AMS facility (KCCAMS) at the University of California, Irvine. We have recently carried out more tests in order to push the sample size limit to

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<15 µg C by removing the reagent TiH_2, further reduction of the reactor volume, and lowering graphitization temperature. The test results, the new procedure, background, precision, and accuracy associated with the modified method will be reported and evaluated herein.

METHODS

Experiments

The reagents used in the sealed tube Zn reduction method by Xu et al. (2007) and Khosh et al. (2010) are Zn and TiH_2 powders, with Fe as catalyst. As illustrated in Xu et al. (2007), the chemical reactions responsible for the graphite formation are both H_2 and Zn reductions of CO_2; where H_2 originates when TiH_2 reaches temperatures over 440 °C, and Zn in the meantime, reduces H_2O back to H_2 to keep the CO_2 reduction reaction going to near completion. However, a small fraction of CH_4 could form in the presence of excess H_2 (McNichol et al. 1992; Verkouteren et al. 1997). This is not much of a problem for regular-size samples of 1 mg C because the fraction is usually <5% and any mass-dependent isotope fractionation associated with the incomplete graphitization can be fully corrected by the simultaneous on-line AMS $\delta^{13}C$. However, CH_4 formation could become a significant problem for ultra small-mass samples with <15 µg C. We have observed that <10 µg C samples failed to graphitize following the setup by Khosh et al. (2010), although it can successfully graphitize samples of 100 to 15 µg C size after modifying the original method by reducing the reactor tube volume and reagents proportionally to accompany the small sample size. Graphitization can be realized without H_2 or TiH_2, but with Zn alone at a slower rate (Slota et al. 1987). We tested the method by removing TiH_2 to see if it would help ultra small-mass samples reach a more complete graphitization by avoiding the formation of CH_4. Since it is difficult to evaluate the graphitization yield by measuring C% of such a small mass graphite, we decided to check the relative graphitization completeness (or graphite quality) by looking at its beam currents ($^{12}C^{+1}$) measured in the high-energy end of the AMS. Higher beam currents would indicate better or more complete graphitization assuming other conditions, such as target pressing and ion source, are more or less the same.

Figure 1 shows that when a sample size is >15 µg C, graphite formed with TiH_2 present generally has higher currents than the ones without (Figure 1A). When a sample size is ~15 µg C (Figure 1B), the graphite with TiH_2 starts with higher currents but decreases quickly to about the same as those without TiH_2 after the first 3 cycles of measurements in AMS. However, this indicates clearly that graphite formed without TiH_2 present gives out much higher and more stable currents when sample size is <15 µg C (Figure 1C). Based on this experimental result, TiH_2 is removed for graphitization of samples <15 µg C in our new ultra small-mass graphitization procedure.

Procedure

A reactor tube consists of a 6-mm-outside-diameter (OD) Pyrex® tube with Zn powder carefully placed on the bottom of the tube, and a 3.7-mm-OD glass tube, containing the Fe catalyst, resting on an indentation above the Zn powder. Its preparation is basically the same as described in Khosh et al. (2010) in terms of tube sizes and the amounts of Zn and Fe powders used, except that TiH_2 is no longer needed for ultra small-mass (<15 µg C) graphitization (Table 1). All Pyrex tubes are prebaked at 550 °C before reagents are added, and all assembled reactor tubes are baked at 300 °C for 1 hr before use in order to lower modern C contamination from ambient CO_2 adsorbing to the reagents and tube surfaces (Khosh et al. 2010). The unused reactor tubes can be stored next to a dish filled with a 1N NaOH solution inside an airtight cabinet for about 2 weeks, and can be rebaked at 300 °C for 1 hr if they have been stored for more than 2 weeks.

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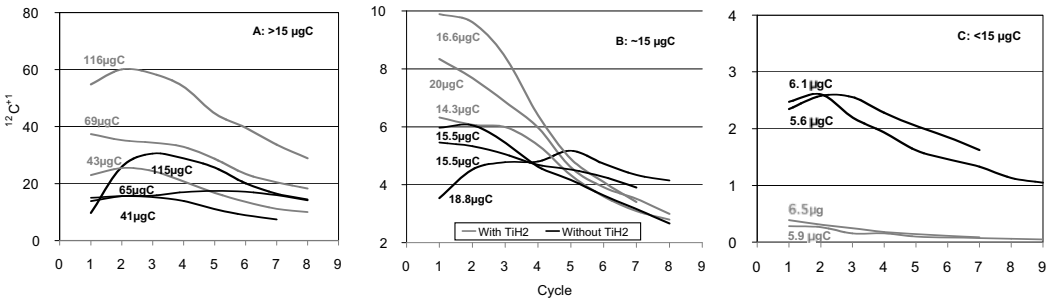


Figure 1 Beam current ($^{12}C^{+1}$ current at high energy) changes vs. measuring cycle on AMS for graphite samples of different sizes. Each cycle is 2.5 min or 50,000 counts when less than 2.5 min. Gray lines are the graphite targets formed with the reagent TiH_2 and black lines are the ones without. A, B, and C represent cases for sample sizes >15, ~15, and <15 µg C, respectively.

CO_2 from a sample or standard combusted in a quartz tube with CuO is cryogenically purified on a vacuum line (see detailed descriptions in Xu et al. 2007 and Khosh et al. 2010). Extracted CO_2 is quantified by a Silicon Microstructures pressure transducer (SM5812, capable of measuring 0–5 psi with a detection limit of ~0.1 µg C) in a known-volume reservoir. The transducer is calibrated (and recalibrated often) by several aliquots of CO_2 produced by combustion of accurately weighed out known C% material, such as acetanilide. After the yield is determined, CO_2 is frozen into a reactor tube using liquid nitrogen and sealed off by a torch. In the method for 15–100 µg C samples by Khosh et al. (2010), the reactor tube was sealed off to a length of ~100 mm, or a volume of 1.3 cm^3. In the modified method, the reactor tube is sealed off shorter, to ~60 mm long, or a volume of ~0.75 cm^3.

Sealed reactor tubes are set upright in an aluminum block and placed inside a muffle furnace to graphitize at 450 °C for 7 hr. The temperature is reduced from the regular-size sample graphitization settings of 500 °C for 3 hr plus 550 °C for 4 hr. This follows the graphitization temperature setting for ultra small-mass samples reported by Santos et al. (2007a) where they showed that lower temperature helped to increase graphitization yields.

Table 1 Dimensions of reaction tubes used for the graphitization of ultra small-mass (5–15 µg C) samples. Numbers in parentheses are tube sizes after sealing. Amounts of zinc (Aldrich, #324930) and iron catalyst (400-mesh, Sigma-Aldrich, #05406) used in the graphitization process are listed in the last 2 columns. The reagent zinc is placed in the bottom of the outer tube and catalyst iron is placed in small borosilicate tube that sits inside on a dimple made ~1 cm from the base of the reaction tube.

	OD (mm)	ID (mm)	Height (mm)	Volume (cm^3)	Zn (mg)	Fe (mg)
Outer tube	6	4	152 (60)	1.91 (0.75)	9.8–11.4	
Inside tube	3.7	3	25	0.18		4–5

Performance of Graphite in Ion Source

High ionization efficiency in the ion source followed by high beam currents after the accelerator is a prerequisite for getting high-performance measurements on ultra-small samples. The AMS system at KCCAMS where our ultra small-mass graphite samples are measured is a NEC 0.5MV 1.5SDH-1 machine that uses a modified NEC MC-SNIC ion source (Southon and Santos 2007). It is capable of generating high beam currents of ~80–100 µA $^{12}C^{+1}$ for regular-size samples of ~1 mg C, and

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about 1 µA/1 µg C for samples ranging between 2–10 µg C for graphite produced by the H_2 reduction method (Santos et al. 2007a). As expected, currents produced by ultra small-mass samples are strongly mass dependent. Maximum $^{12}C^{+1}$ currents of ~0.5 µA/1 µg C were obtained for 5–15 µg C samples prepared with this method (Figure 2), which is similar to the current (µA)/size (µg C) observed for 15–100 µg C samples reported by Khosh et al. (2010). The lower beam current per sample size compared to that of the H_2 reduction method may be resulting from a lower graphitization yield by the sealed tube Zn reduction method.

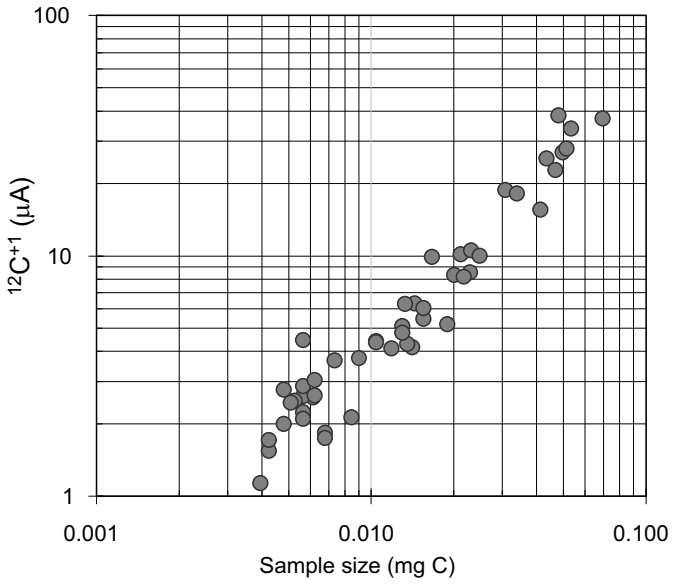


Figure 2 Plot of the maximum $^{12}C^{+1}$ beam current versus sample size

Mass-Dependent C Isotope Fractionation Correction

Proper on-line AMS $\delta^{13}C$ measurement is another prerequisite for getting reasonably good precision and accuracy for ^{14}C measurements on small and ultra small-mass samples. Regardless of sample size, all AMS ^{14}C measurements made at KCCAMS are currently corrected using AMS $\delta^{13}C$ values. For ultra-small samples, this is more critical because they tend to fractionate much more than regular-size samples inside the machine. A drift of as much as 20‰ from that of the original material has been observed based on the AMS $\delta^{13}C$ measurements (Santos et al. 2007a). Also, the ranges and patterns of AMS $\delta^{13}C$ drifting with sample size and running time can be highly variable from target to target, and from wheel to wheel. In addition, mass-dependent fractionation also occurs during the graphitization process when using the sealed tube Zn reduction method, as described by Xu et al. (2007). Therefore, simultaneous on-line AMS $\delta^{13}C$ measurement that allows for correction of both isotopic fractionation processes during graphitization and inside the AMS machine is a key step in the measurement.

RESULTS AND DISCUSSION

Background

For background corrections and normalizing AMS ^{14}C measurements of small to ultra small-mass samples, we adopt the standard and blank setup in a wheel from the non-matching method described

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by Santos et al. (2007a). In this method, the modern C background is estimated and corrected based on a set of ^{14}C-free material, such as coal, covering the size range of the ultra-small samples, and the dead-C background is corrected based on a set of similar-sized modern standard, such as OX-I (Khosh et al. 2010). Results from our test wheels show that the modern C background is ~0.2–0.8 µg C (Figure 3) and dead-C background is ~0.1–0.4 µg C. Accurate CO_2 size quantification is important since all background corrections are size dependent.

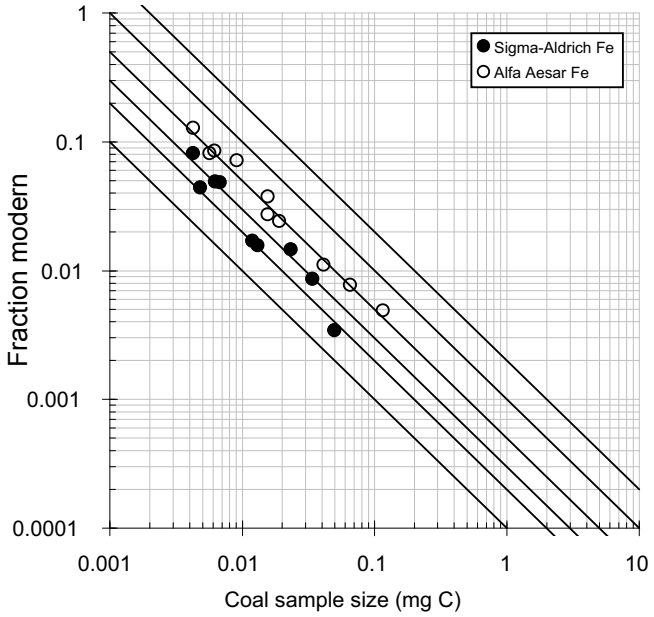


Figure 3 Modern C background estimates. 400-mesh Fe powder from Sigma-Aldrich (solid circles) has yielded further improved backgrounds over 325-mesh Fe powder from Alfa Aesar (open circles) used previously. Solid lines represent 0.1, 0.2, 0.3, 0.5, 1.0, and 2.0 µg of modern C contamination.

Reducing the modern C background component remains a challenge to make this method useful for older samples. Baking assembled reaction tubes at 300 °C for 1 hr before use was found to produce the best results by Khosh et al. (2010). We have kept this cleaning procedure for our ultra small-mass samples, and we prefer to do the baking right before graphitization to minimize ambient CO_2 adsorption onto the surfaces of reagents and the glass tube walls. We have also examined the modern C backgrounds of the 400-mesh Fe powder from Sigma-Aldrich. The test results show that the finer Fe catalyst from Sigma-Aldrich indeed has lower modern C blank than the Alfa Aesar 325-mesh Fe that is used for our regular-size sample graphitization (Figure 3), and this is consistent with what Santos et al. (2007b) reported. However, Sigma-Aldrich 400-mesh Fe was found to have a tendency to sinter during H_2-reduced graphitization, and thus is not used with our regular-size samples. On the other hand, ultra small-mass graphite produced by sealed tube Zn reduction appears to be more chunky and harder than regular-sized Zn-reduced graphite. The chunky characteristics of small-sample graphite is the result of not enough CO_2 to form fluffy filamentous graphite, and instead small patches of Fe_3C are formed. This is illustrated in a scanning electron microscope (SEM) image of a small-sample graphite with 0.011 mg C, reported by Santos et al. (2007c, Figure 5). The use of Sigma-Aldrich 400-mesh Fe in this study does not seem to have made the ultra small-mass graphite harder to press into the target holders. The less sintering may be due to the fact that graphitizing tem-

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perature is reduced from 550 to 450 °C in this modified method. Therefore, Sigma-Aldrich 400-mesh Fe has been substituted for the Alfa Aesar 325-mesh Fe in our ultra small-mass sample graphitization procedure.

It should be noted that the backgrounds discussed here only include those from combustion, graphitization, target press, and machine-induced. Backgrounds associated with prior sample processes, such as chemical and physical separations, are not discussed here, but they can be much higher and should be investigated carefully and accounted for properly in background corrections and in the final error calculations.

Precision and Accuracy

To test the accuracy and precision of this modified method, ultra small-mass samples of primary and secondary standards (OX-I, OX-II, ANU sucrose, and TIRI Wood B) spanning a 5–15 µg C range were measured and normalized to regular-size (1 mg C) OX-I standards using the non-matching method described by Santos et al. (2007a). Figure 4 shows the results of the 4 small-mass standards after all corrections have been applied. Final results of all 4 small-mass samples are consistent with the corresponding sample consensus values, indicating that both modern-carbon and dead-C backgrounds for this method are correctable.

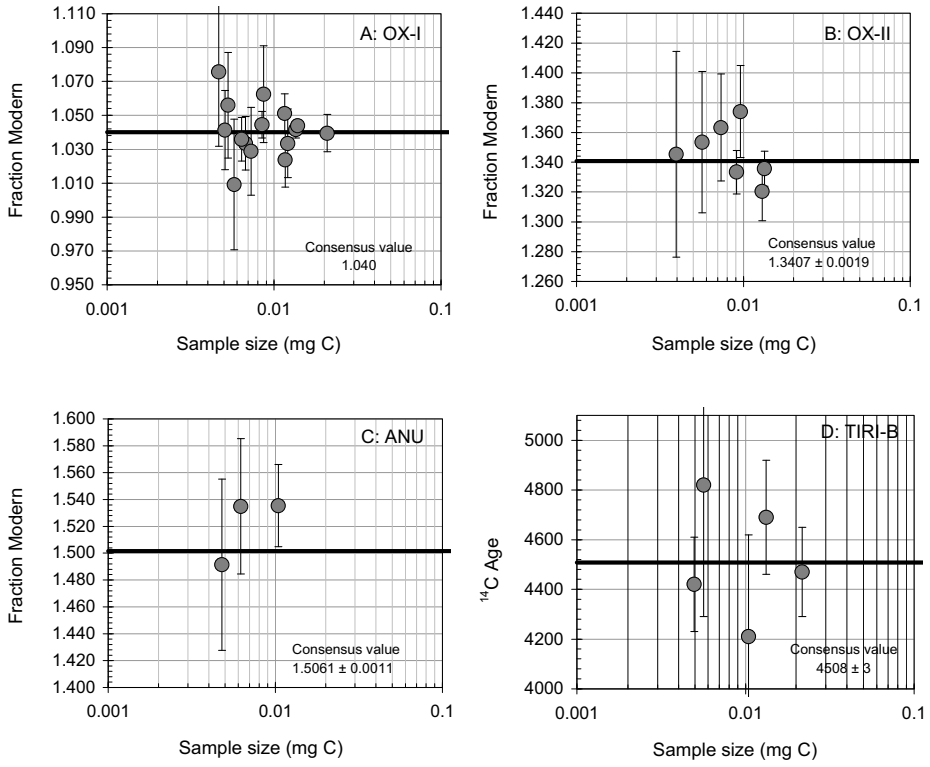


Figure 4 Fraction modern results for OX-I (A), OX-II (B), and ANU (C) samples, and ^{14}C age results for TIRI-B (D) samples ranging from 0.005–0.020 mg C, measured from multiple wheels by AMS at KCCAMS. Solid lines represent the consensus values of the standards. Error bars are ±1σ. Results have been normalized to independent sets of six 1-mg C OX-I standards in each wheel. All results have been corrected for both machine- and graphitization-induced isotopic fractionation using the simultaneous on-line AMS $\delta^{13}C$ measurements.

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The accuracy and precision of ultra small-mass samples prepared by this method are size and ^{14}C content dependent, but is usually ±4–5% for modern samples of size ~4–5 µg C, based on the limited number of duplicate measurements of primary and secondary standards. The analytical errors (see error bars in Figure 4) heavily depend on the sizes and uncertainties of both the modern and dead-C components.

An Example of Ultra Small-Mass ^{14}C Measurement

Quartz filter blank evaluation is important, although difficult, for particulate organic carbon (POC) ^{14}C measurements since quartz filters are often combusted together with the POC collected on them. Researchers have noticed that the magnitude and variability of the extraneous C found in processed quartz filters subjected to similar POC collection and handling procedures can be large. As a result, the filter blank has become one the biggest obstacles in preventing high-precision measurements of POC ^{14}C AMS, when the amount of expected POC is small, such as in ice cores (Steier et al. 2006).

We examined the size and effect of storage time on Whatman quartz filter blanks (2.2 µm pore size, 32 mm diameter). Filters were precleaned by baking at either 500 °C or 900 °C for 2 hr. (No difference was found between these 2 baking temperatures in terms of size of the blank.) Filters were stored for different amounts of time: 0, 7, or 30 days. Then, 2 prebaked filters were loaded in a prebaked 9-mm-OD quartz tube with CuO, evacuated, sealed, and combusted at 900 °C for 3 hr. CO_2 was cryogenically purified and graphitized if the amount was >4 µg C, using this sealed tube ultra small-sample method.

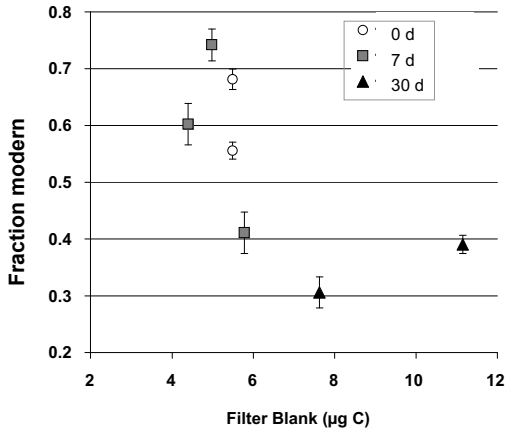


Figure 5 Plot of FM of Whatman quartz filters vs. filter blank size (µg C) at different lengths of storage time ranging from 0 day (open circles), 7 days (gray squares), and 30 days (black triangles).

Figure 5 shows that there is no significant difference in quartz filter blank size between 0 and 7 days of storage time. The filter blank ranges from 4.4 to 5.8 µg C for two 32-mm-diameter Whatman filters, or 0.18–0.24 µg C/cm^2 of filter area. Despite the relatively constant blank size, the variation of ^{14}C content of the blank is surprisingly large, from 0.41 to 0.74 Fm. Although we do not know why the ^{14}C range is so big, the sources of the filter blank seem to be from a mixture of modern CO_2 and old volatile organic C (VOC) in the lab ambient air. Blank size increased to 7.6–11.1 µg C (or 0.32–0.46 µg C/cm^2) after 30 days of storage in prebaked glass jars. In the meantime, ^{14}C of the blank

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decreased to 0.31–0.39 Fm, which may indicate a higher fraction of VOC adsorption onto the filters with longer storage time. These results show that the much higher processed filter blanks observed before (as high as 17 µg C/cm^2, Steier et al. 2006; 6 µg C/cm^2, personal communication with Fenwei Zeng) probably did not come from the filter itself or due to prebaking or regular storage in air (if <30 days), but most likely due to processes during sample collection and handling. In addition, the large variation in filter blank ^{14}C would make the filter blank correction on POC ^{14}C measurements more challenging. Nevertheless, the results have proven that the modified sealed tube Zn reduction method can be successfully applied to ultra-small samples, such as to evaluate quartz filter blanks.

CONCLUSIONS

Removing the reagent TiH_2, reducing the sealed reactor volume to ~0.75 cm^3, and lowering the graphitization temperature to 450 °C have helped to successfully extend the sample size range to 4–15 µg C using the sealed tube Zn reduction graphitization method developed by Xu et al. (2007) and modified by Khosh et al. (2010) when measured on the AMS system at KCCAMS. Table 2 summarizes the differences and improvements of the sealed tube graphitization method from 2007 and 2010 to current work. Both modern and dead-C backgrounds from combustion and graphitization are compatible to those from the ultra small-mass H_2 reduction method by Santos et al. (2007a). Although the H_2 reduction method can graphitize smaller sample sizes (2 µg C), the low cost, high throughput, and ease in storage of graphite after formation still make this method useful for many applications where the ^{14}C content variation is large in samples and thus do not require ultra high precision. Also, we should bear in mind that in many cases backgrounds associated with sample pretreatments, such as those in specific compound separations, are often much larger than the backgrounds from combustion/graphitization and thus become the limiting factors in determining the usefulness of ultra small-sample ^{14}C data rather than the graphitization process itself (Santos et al. 2010).

Table 2 Differences and improvements of sealed tube Zn reduction graphitization method from 2007 and 2010 to current work.

Paper	Sample size (mg C)	Reaction tube (outer/inside)	Reagents	Modern C background (^{14}C yr)
Xu et al. (2007)	0.1–1.2	9 mm OD/6 mm OD	Zn, TiH_2, and Fe	~50,000 for 1 mg C
Khosh et al. (2010)	0.015–0.1	6 mm OD/3.7 mm OD	Downsized Zn and TiH_2 with same amount of Fe	Up to 58,000 for 1 mg C; Modern C as low as 0.3 µg C
This work	0.004–0.015	Shorter 6 mm OD/ 3.7 mm OD	Downsized Zn, no TiH_2, same amount of Fe	Modern C as low as 0.2 µg C

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