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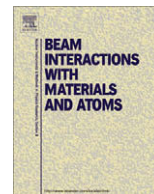
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Small-mass graphite preparation by sealed tube zinc reduction method for AMS ^{14}C measurements

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ABSTRACT

Previous work has demonstrated that the sealed tube Zn reduction method for converting CO_2 to graphite for AMS ^{14}C measurements produces targets that can be measured with high precision and low background for samples of about 1 mg C down to approximately 0.1 mg C at the Keck Carbon Cycle AMS facility at the University of California, Irvine (KCCAMS). Now a modified method has been developed to prepare small-mass samples ranging from 0.015 to 0.1 mg C. In this modified method, the volume of the sealed reactor tube is reduced to $\sim 1.9\text{ cm}^3$, and the amounts of Zn and TiH_2 reagents are reduced proportionally. The amount of Fe catalyst used remains the same to ensure a long lasting current in the AMS. Small-mass samples prepared by this method generally yield $^{12}\text{C}^{+1}$ currents of about $0.5\ \mu\text{A}$ per $1\ \mu\text{g C}$. An in situ simultaneous AMS $\delta^{13}\text{C}$ measurement allows for correction of both graphitization and machine-induced isotopic fractionation, and is a prerequisite for high precision and accurate measurements using the Zn reducing method. Corrections for modern-carbon and dead-carbon background components are applied to samples based on small-mass samples of a ^{14}C free material and of a modern standard covering the sample size range. It was discovered during additional investigation into lowering the modern-carbon background component that baking assembled reactor tubes at $300\ ^\circ\text{C}$ for 1 h prior to use resulted in significantly lower modern-carbon background values. The accuracy and precision of small-mass samples prepared by this method are size dependent, but is usually $\pm 10\text{--}15\%$ for the smallest samples (0.015–0.02 mg C), based on duplicate measurements of primary and secondary standards.

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1. Introduction

Currently there is a growing demand to process small-mass samples ($<0.1\text{ mg C}$) for AMS ^{14}C measurements. The ability to perform AMS ^{14}C measurements on small-mass samples is useful for performing compound specific studies on samples isolated by preparative capillary gas chromatography, and for studies where only microgram quantities of sample are available. Several methods have already been described for the production of graphite from small-mass samples for AMS ^{14}C measurements using the H_2 reduction method [1–3]. The ability to process small-mass samples for AMS ^{14}C measurements using the sealed tube Zn reduction method offers a comparatively low cost, rapid production alternative.

2. Methods

2.1. Reactor tube preparation

The reactor tubes used to prepare small-mass samples are 152 mm long, 6 mm outside diameter Pyrex (borosilicate) tubes that are sealed at one end with a small indentation approximately 2 cm from the bottom. Tubes are pre-cleaned by baking at $500\ ^\circ\text{C}$ for 3 h, and then at $550\ ^\circ\text{C}$ for 4 h. After tubes have been baked, 9.8–11.4 mg of Zn (Aldrich, #324930) and 3.3–4.9 mg of TiH_2 (Alfa Aesar, #12857) are placed into the bottom of each reactor tube. Then 4–5 mg of Fe catalyst (Alfa Aesar, 350 mesh, #39813) is weighed separately into pre-cleaned (baked at $500\ ^\circ\text{C}$ for 3 h, and then at $550\ ^\circ\text{C}$ for 4 h) 25 mm long, 3.7 mm outside diameter Pyrex vials (Scientific Instrument Services Inc.). This amount of Fe catalyst has been shown to produce a long lasting current in the ion-source at KCCAMS for 0.004–0.1 mg C samples prepared using the H_2 reduction method [1]. The small 3.7 mm outside diameter tube with the Fe catalyst is gently inserted into the 6 mm outside diameter reactor tube and is suspended above the Zn and TiH_2 reagents by the small indentation near the bottom of the reactor tube. After reactor tubes are assembled, they are placed upright

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in a furnace and baked at 300 °C for 1 h. Tubes are allowed to cool before they are placed inside an airtight cabinet with a 1 N NaOH solution to prevent ambient CO₂ from adsorbing to the reagent and Fe catalyst surfaces, and reactor tube walls. Tubes are stored for a period of up to 2 weeks in the cabinet and are used when needed.

2.2. Combustion of small-mass samples

In order to produce small-mass samples of standards and blanks covering a 0.015–0.1 mg C size range, amounts of reference material equivalent to the carbon sample size can be weighed out and combusted individually, or CO₂ gas from larger combusted samples can be split to produce a number of smaller samples. The latter is more easily accomplished because of the difficulties in accurately weighing and quantitatively transferring microgram quantities of material to combustion tubes. Previous studies have reported no difference in results between either of these two methods [1,2]. All test samples reported here were produced by splitting CO₂ gas from combusted 1–4 mg C samples.

2.3. CO₂ extraction and sample preparation

CO₂ from a combusted sample is cryogenically purified and quantified using a simple vacuum line set-up that consists of a mechanical pump and a liquid nitrogen trap between the pump and the line as described by Xu et al. [4]. Purified CO₂ is quantified by measuring the CO₂ pressure in a known-volume reservoir using a Silicon Microstructures pressure transducer (SM5812) capable of measuring 0–5 psi. A measured amount of carbon (as CO₂) is frozen into a reactor tube using a liquid nitrogen filled dewar, and the reactor tube is then sealed using a torch (length of reactor tube after sealing is ~100 mm).

Sealed reactor tubes are set upright in an aluminum heating block and placed inside a furnace and heated at 500 °C for 3 h, and then at 550 °C for 4 h. Filamentous graphite forms at the surface of the Fe powder catalyst. After graphitization, samples are stored in the sealed reactor tubes until immediately prior to pressing into sample holders for AMS ¹⁴C analysis. This helps to prevent adsorption of ambient CO₂ onto the graphite-sample surface. An in depth examination of the graphitization process using the sealed tube Zn reduction method is presented by Xu et al. [4].

3. Results and discussion

3.1. Performance of graphite in ion source

When measured at KCCAMS, which uses a modified NEC MC-SNIC ion-source [5,6], small-mass samples produce currents that are strongly mass dependent. Maximum ¹²C⁺¹ currents of about 0.5 μA per 1 μg C of sample were obtained for 0.015–0.1 mg C samples prepared with this method (Fig. 1). Over time, ¹²C⁺¹ currents decrease for small-mass samples with larger decreases seen in smaller sized samples (Fig. 2). This decrease in ¹²C⁺¹ current is observed in similarly sized samples produced using the H₂ reduction method [1].

3.2. δ¹³C correction

As described by Xu et al., mass-dependent fractionation of carbon isotopes does occur during the graphitization process when using the sealed tube Zn reduction method [4]. Machine-induced isotopic fractionation also occurs for small-mass samples. Santos et al. report that AMS δ¹³C measurements of small and ultra small-mass samples differed as much as 20‰ from that of the ori-

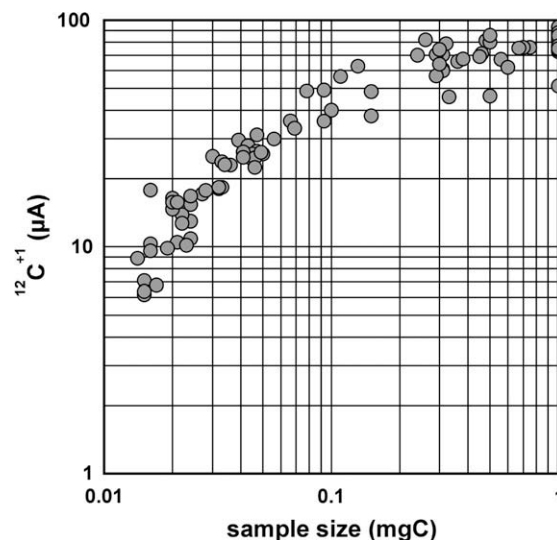


Fig. 1. Plot of the maximum ¹²C⁺¹ current versus sample size, for samples produced using the sealed tube Zn reduction method. Samples larger than 0.130 mg C were produced using the method presented by Xu et al. [4].

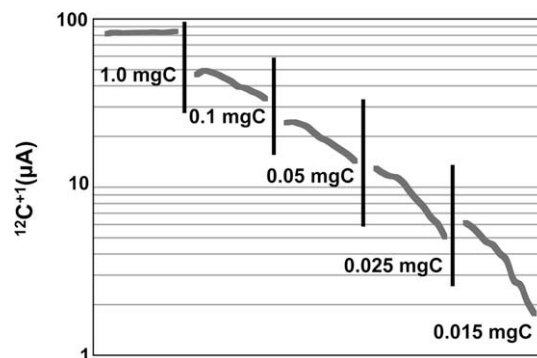


Fig. 2. Plot of ¹²C⁺¹ currents from OX-1 samples of different sizes between 0.015 and 1 mg C. Eleven individual measurements were made on each sample target with a maximum of approximately 50,000 counts for the largest samples. Samples were time limited to 150 s resulting in a minimum of about 2000 counts for the smallest sample.

ginal material with an overall trend towards lighter values [1]. In situ simultaneous AMS δ¹³C measurement allows for correction of both isotopic fractionation processes, which helps to reduce scatter and improve accuracy of the AMS ¹⁴C measurements significantly. Regardless of sample size, all AMS ¹⁴C measurements made at KCCAMS are currently corrected using AMS δ¹³C values.

3.3. Background corrections

Using the non-matching method described by Santos et al. for normalizing AMS ¹⁴C measurements of small-mass samples, corrections for two background components are applied; a modern-carbon correction and a dead-carbon correction [1]. It is thought that modern-carbon is introduced during sample preparation and handling, and that dead-carbon is present in the Fe graphitization catalyst. The modern-carbon background is corrected based on small-mass samples of a ¹⁴C free material, such as coal, covering the size range of the samples, and the dead-carbon background is corrected based on small-mass samples of a modern standard, such as OX-1. For our samples, the dead-carbon background component varied between 0.15 and 0.30 μg C, and modern-carbon background component values of about 0.3 μg C were obtained.

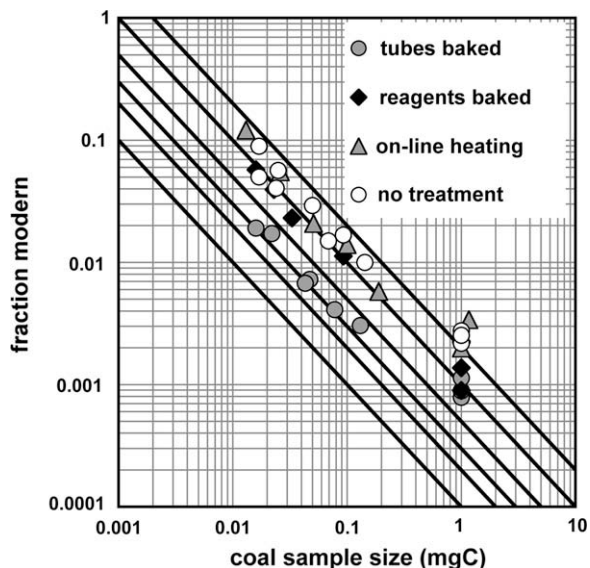


Fig. 3. Fraction modern values of 0.015–1 mg C ¹⁴C free coal samples prepared using different pre-treatment strategies aimed at reducing the modern-carbon background component. From left to right, the solid lines represent the effect of 0.1, 0.2, 0.3, 0.5, 1.0, and 2.0 µg of modern-carbon present in the total sample size.

3.4. Modern-carbon background improvements

Background control is a key step for successful small-mass AMS ¹⁴C measurements. In an effort to try to reduce the modern-carbon background in our processed samples, several strategies of pre-treating reagents and assembled reactor tubes were attempted. Fig. 3 summarizes the modern-carbon background values obtained from a ¹⁴C free coal prepared using the different pre-treatment strategies.

The first attempt involved placing assembled reactor tubes under vacuum and applying gentle heating with a torch. Pre-treatment of the Zn and TiH₂ reagents by separately baking ~2 g of each reagent in vacuum-sealed Pyrex tubes (9 mm OD × 120 mm length) at 360 °C for 3 h was also attempted [7]. Neither of these treatments gave significantly improved results, with treated and control samples yielding comparatively equivalent modern-carbon background component values between 0.9 and 1.5 µg C.

Baking assembled reactor tubes at 300 °C in open air for 1 h prior to use produced the best results with values of 0.3 µg C being observed [7]. This indicates that most of the modern-carbon background component is from adsorbed ambient CO₂ on the surface of the reagents, catalyst, and or reactor tube walls, and not from contaminating carbon inside the lattice of the Zn reagent, which would require heating to a temperature above the melting point of Zn (419.58 °C) to eliminate. For the same reason, keeping pre-cleaned

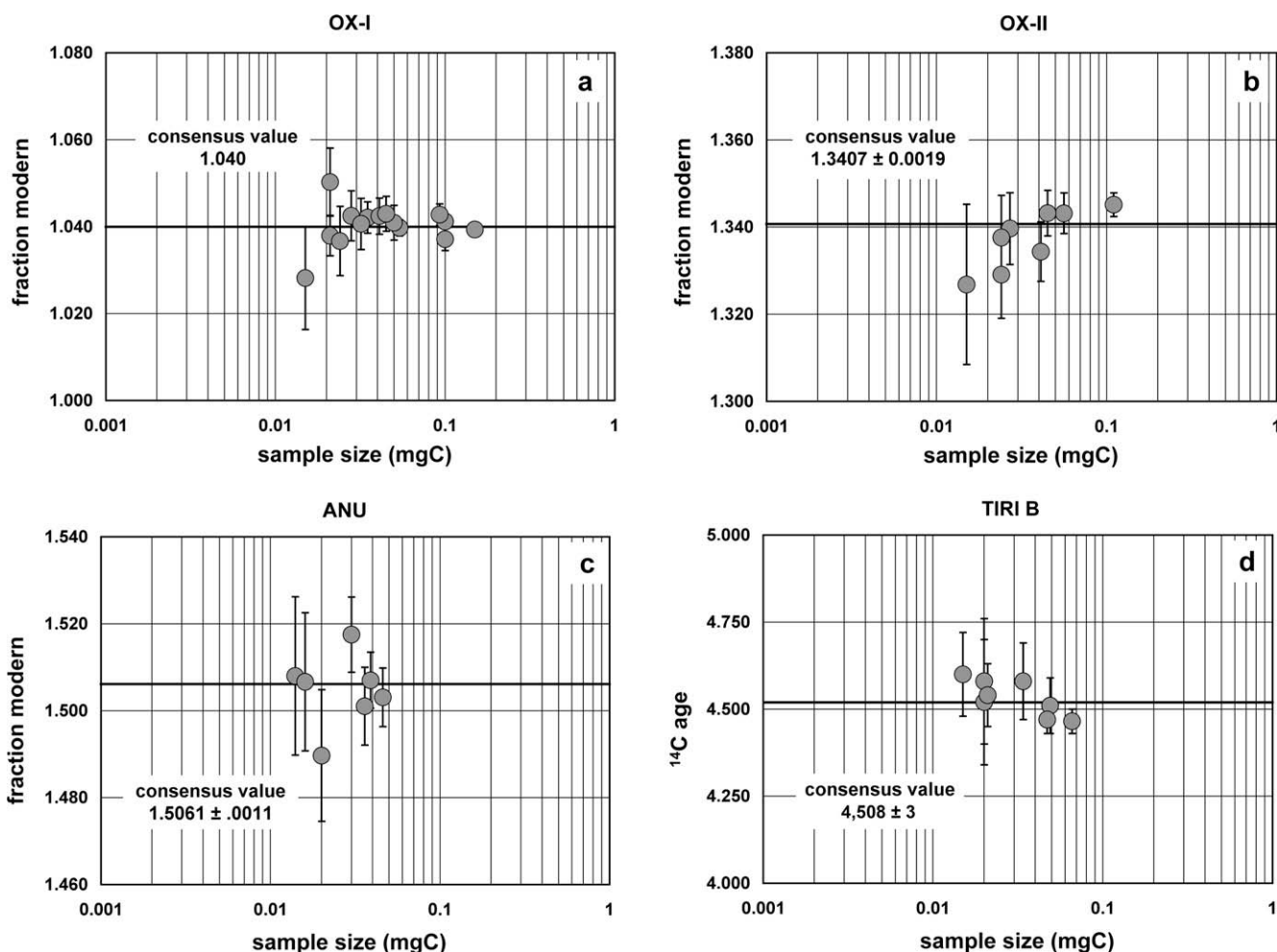


Fig. 4. Fraction modern results of OX-I (a), OX-II (b), and ANU (c) samples, and ¹⁴C age results of TIRI B (d) samples from multiple AMS ¹⁴C measurements. Results have been normalized to independent sets of six normalizing 1 mg C OX-I standards using the non-matching method described by Santos et al. All results have been corrected for both machine and graphitization induced isotopic fractionation using in situ simultaneous AMS δ¹³C measurements. Corrections for both modern and dead-carbon background components were adopted from that of Santos et al., as are error bars [3]. Solid lines represent corresponding sample consensus value [8–11].

reactor tubes in an airtight cabinet can prevent CO₂ adsorption and extends the time between baking and use of the reactor tubes to 2 weeks. If tubes are not all used after the 2 weeks period, baking at 300 °C is again applied to ensure a lowered background. The 300 °C heating of the Fe catalyst did not seem to alter the physical characteristics of the resulting graphite (only slightly less fluffy), or its performance in the ion source.

3.5. Small-mass sample results

To test the accuracy and precision of this modified method, small-mass samples of primary and secondary standards (OX-I, OX-II, ANU sucrose, and TIRI B) spanning a 0.015–0.1 mg 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. [1]. Fig. 4 shows the results of the four small-mass samples after all corrections have been applied. Final results of all four small-mass samples are consistent with the corresponding sample consensus value indicating that both modern-carbon and dead-carbon backgrounds for this method are correctable.

The precision of small-mass samples prepared using this method is size dependent. For samples in the 0.015–0.02 mg C range, results of ± 10 – 15% were obtained, while analysis of 0.02–0.05 mg C samples were about ± 5 – 9% , and samples of 0.05–0.1 mg C were ± 2 – 4% .

3.6. Summary

This modified sealed tube Zn reduction method has been shown to reliably produce graphite for AMS ¹⁴C analysis that can be measured with satisfying accuracy and precision for 0.015–0.1 mg C samples. The maximum current and integrated current values from small-mass samples prepared using the sealed tube Zn reduction method are comparable to those of similarly sized samples prepared using the H₂ reduction method. Additionally, the dead-carbon background component values from our samples are comparable to those reported by Santos et al., and our modern-carbon background component values are only slightly higher (0.3 μg C and 0.2 μg C, respectively). Currently, the size of samples that can be processed (down to 0.002 mg C) using the H₂ reduction method is smaller than can currently be achieved using this modified sealed tube Zn reduction method [1].

Similar to the original method, this modified sealed tube Zn reduction method for the processing of small-mass samples provides a comparatively inexpensive and easy alternative to the H₂ reduction method. The sealed tube Zn reduction method also has a higher sample production rate, and graphite from processed samples can be stored for a longer period of time. This method can provide benefits to many disciplines seeking to measure the ¹⁴C content of small-mass samples using AMS.

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