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BAG OF TRICKS: A SET OF TECHNIQUES AND OTHER RESOURCES TO HELP ^{14}C LABORATORY SETUP, SAMPLE PROCESSING, AND BEYOND

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ABSTRACT. Over the last few decades, radiocarbon laboratories have used different procedures for measuring a broad range of carbonaceous materials. To produce reliable results, the processes employed for sample processing, graphite target production, and spectrometer measurement must be rigorous, well tested, and reproducible. Most of the procedures have been developed, improved, and published as part of the laboratories' quality control and research programs, and can be frequently found in the literature. Nevertheless, there are suites of laboratory techniques (or "small useful skills"), products, and other resources that either have never been described in publications, or have been somewhat hidden in much larger scientific articles and reports. We feel that with the rapid rise of newer laboratories and facilities, a set of resourceful suggestions might come in handy. Here we gathered these skill sets that can be used in all aspects of ^{14}C sample processing, with the intention to simplify and expedite procedures, from glass-tube making to graphitization and measurements. We also included some miscellaneous items to help in laboratory setup.

KEYWORDS: "small useful skills," sample processing, graphite target production, spectrometer measurement.

INTRODUCTION

Radiocarbon dating is a widely used technique in archaeology, paleoclimate, and paleodiet reconstructions, environment studies, and forensics. Since its advent, a myriad of methods devoted to produce samples as graphite or carbon dioxide (CO_2) targets from various carbonaceous materials have been developed. However, the revolution continues as new measurement techniques allow for the reduction of the sample size from grams to milligrams, and eventually to submilligram samples. As the list of applications and carbonaceous samples for ^{14}C dating continues to increase, there is a clear need to expedite the sample processing, while maintaining quality, precision, and accuracy.

Although some of the current ^{14}C sample procedures are fairly straightforward, existing labs may use different techniques, instruments, and tools, as well as consumables from a variety of vendors. Less-experienced facilities, which are on the rise, sometimes have difficulty in choosing between procedures for simpler and less expensive setups, as recommendations cannot be easily found. Here, we compiled laboratory techniques, mostly focused on small useful skills, items, and other resources that have been either never published or somewhat hidden in much larger scientific reports. The idea emerged from our multiple interactions with students, users, and newer laboratories. Emphases will be on (a) the conventional methodological techniques for processing samples from natural carbonaceous materials, (b) the practical aspects to help laboratory setups, and (c) consumables and miscellaneous items. Vendors, background information, and references to publications will be provided (if available).

This compilation is intended to help ^{14}C users of all levels. However, it is not intended to define if a procedure is right or wrong, as assorted laboratory techniques, different equipment setups, and intrinsic sample heterogeneity may also come into play. Moreover, not all ideas and items may be directly adaptable at first, but may serve as examples for extra tests and improvements. Further, we would like to invite the community to participate in this effort with further ideas and suggestions. With your help, maybe one day the "bag of tricks" can become the "whole nine yards" or, at least close to it.

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METHODS

Most ^{14}C facilities employ laboratory procedures that include physical and chemical treatments, sealed-tube combustion of organics, leaching and hydrolysis of carbonates, extraction and/or ultrafiltration of collagen from tooth and bone samples, and extraction of $^{14}\text{CO}_2$ from air collected in canisters/traps or bubbled from water samples. More specialized treatments may require the use of filters, Soxhlet, gas chromatography mass spectrometry (GC-MS), high-performance liquid chromatography (HPLC), or other types of special instruments. The goal of these processes is to clean (isolate a particular fraction) and convert the carbonaceous “raw” materials into CO_2 or solid graphite targets to be loaded into the ion sources for accelerator mass spectrometry (AMS) measurement. Since identifying scenarios in which practical procedures to facilitate, expedite, or even improve measurement results may be inappropriate for other facilities and laboratories, we can at least confidently recommend the following.

CONVENTIONAL METHODOLOGICAL TECHNIQUES

Sample Storage and Handling

It is important to advise submitters and students how to better collect and pack samples, so that possible field and laboratory contamination can be avoided (Gillespie and Hedges 1984; Gupta and Polach 1985; Hedges 1992). Most facilities offer a checklist to assist submitters, which normally includes the following recommendations: (a) keep samples stored dry or frozen; (b) pack and clearly label each sample individually (preferably using Al foil and zipper bags); (c) if using vials, secure the lids; and most importantly, (d) never handle samples in or in close proximity to labs where tracer ^{14}C might have been used. We go further and suggest that newer facilities access the history of the samples before accepting them for processing. Contamination by ^{14}C tracer is a very serious problem, possibly leading to facility downtimes (Zhou et al. 2012), or even equipment losses (Jull et al. 1990). Useful tips to avoid or recover from ^{14}C tracer incidents can be found in Buchholz et al. (2000) and Zermeño et al. (2004). However, the following might also apply:

- Avoid direct contact of samples, tools, glassware, chemicals, and etc. with the bare top surface of benches and hood areas. Place them in plastic trays (heavy duty and clear polypropylene trays), and cover the heavily used areas with heavy-duty aluminum foil. If contamination or suspicion of contamination occurs, both trays and foil can be easily replaced at a minimum cost.
- Separate tools and chemicals to be used in each lab or area, and avoid sharing them.
- Borrowed or shared instruments should be used wisely by ascertaining their history and users frequently.
- Dispose of used gloves when moving from one procedure to another, or between lab spaces.
- Clean laboratory spaces yourself as much as possible, since hired cleaners working in multiple labs or buildings can carry contamination from one space to another through the cleaning tools (baskets, brooms, mops, etc.).
- To conduct a swiping procedure choose small quartz (QZ) filters, such as 25 mm \times 0.4 μm , from SKC-West (Item #: 225-1825; skcwest.com), as after prebaking the filters at 900°C, they become brittle and larger filters tend to be harder to handle.

Pretreatments of Carbonaceous Materials

To produce graphite samples from carbonaceous raw materials, one should try to remove any contamination that is not associated with the sample itself. Besides being inherently impossible (Santos et al. 2010), this can be extremely complex and highly variable, as identifying and then

extracting sample-specific carbon from unknown contaminants can be methodological or sample dependent (Turney et al. 2001), especially when dealing with degraded raw materials (Bird et al. 1999a,b; Boaretto 2009; Ascough et al. 2011a,b; Bird and Ascough 2012), or mixed carbon pools (e.g. Trumbore and Zheng 1996; Plante et al. 2013). Therefore, some types of samples may require specific chemical and instrumental extractions, which will not be detailed here (for further information, check Taylor and Bar-Yosef 2014 and Trumbore et al. 2016).

Standard sample pretreatments include physical and/or chemical steps to remove any unwanted material before conversion to CO₂ (by combustion or acid hydrolysis), and have been extensively covered in the literature (especially in the proceedings of the International Radio-carbon and Accelerator Mass Spectrometry Conferences). However, recommendations are given as to the following steps.

Organic Fractions

Carbon buried in soils and sediments may have several fractions (total organic carbon, soil organic matter, humin or refractory carbon, humic and fulvic acids) and/or biomarkers of different ages. One must choose the carbon fraction of interest to be dated, and then select the appropriate physical and chemical procedure to isolate it. Many examples can be found in the literature (e.g. Ingalls and Pearson 2005; Rosenheim et al. 2008; Shah et al. 2008; Boaretto 2009; Druffel et al. 2010; Bird and Ascough 2012; Birkholz et al. 2013; Martin et al. 2013; Taylor and Bar-Yosef 2014; Trumbore et al. 2016 and references therein).

- Most organic samples (e.g. charcoal, wood, macrofossils, etc.) can undergo an acid/base/acid (ABA) treatment, including some protein samples (feathers, animal and human hair) if the alkaline washes are diluted and performed at room temperature. However, the typical procedure involves a series of warm acid and alkaline washes, and rinsing with deionized water. Santos and Ormsby (2013) made a compilation of several ABA treatments to evaluate their weaknesses and strengths, and found that most of them are suitable even when ¹⁴C ages are close to the ¹⁴C limit (>50 ka BP).
- Organic samples that are difficult to clean may require a more aggressive treatment, such as wet oxidation (also termed ABOX, e.g. acid, base, oxidation treatment) with or without the stepped-combustion procedure (Bird et al. 1999a; Santos et al. 2001; Brock and Higham 2009; Haesaerts et al. 2013), stepped-combustion alone (McGeehin et al. 2004), or hydrolysis (Ascough et al. 2010). Regardless of the chemical strategy adopted, note that those harsh digestions may require several milligrams of organic material (more than usual); therefore, the risks of the procedure should be evaluated carefully (Higham et al. 2009; Santos and Ormsby 2013).
- ABA pretreatments (as well as holocellulose extractions, Southon and Magana 2010) can be carried out in large batches when using 13 × 100 mm disposable borosilicate glass tubes coupled with heat blocks up to ~200°C maximum. Samples needing heating can be securely placed in these heat blocks on bench tops, with culture tubes covered by ventilated plastic caps (Kim-Kap disposable closures, natural, 13 mm for plain-end glass culture tubes). To expedite the procedure and reduce centrifuge usage between chemical supernatant removals, one can try disposable fine-tip pipettes (Thermo Scientific; Samco; 5.0 mL Extended Fine Tip Transfer Pipets).
- After the last acidification, rinse the sample well to get rid of most of the salt to prevent it from etching the combustion tube. Use double-tube combustion (e.g. an open 6-mm inside of a 9-mm-OD QZ tube) if salt cannot be rinsed off, such as dissolved organic carbon

(DOC) samples from freeze-dry down or any other materials that contain salts and tend to erode the QZ tube during combustion.

- Bone, dentine, and enamel require special extraction procedures prior to combustion as well as quality control assessment by the C:N atomic ratio, and the % carbon and % nitrogen using an elemental analyzer coupled with an isotope ratio mass spectrometer (EA-IRMS) have been extensively discussed elsewhere (DeNiro 1985; Stafford et al. 1987; Ajie et al. 1990, 1992; Stafford et al. 1990; Hedges and van Klinken 1992; Brown et al. 1988; Burky et al. 1998; van Klinken 1999; Taylor et al. 2001; George et al. 2005; Brock et al. 2007, 2013; Boaretto 2009). Nevertheless, two simple initial tests can indicate the state of preservation of bone and teeth samples:
 - (a) *Does the sample feel hard under contact with implements and tools?* The strength of a bone is derived from the presence of the collagen that binds the crystalline component together. Soft samples may give low gelatin extraction yields and highly fractionated results.
 - (b) *Does the sample smell burnt when ground by an instrument (such as a Dremel coupled with diamond points)?* Good-quality bone or tooth material, when in contact with a high-speed burr or cutter, often smells, indicating the presence of proteinaceous material (Santos et al. 2006; Beaumont et al. 2010).
- It would be helpful to know whether a bone sample would yield sufficient collagen for any kind of isotopic analysis and warrant additional sample preparation such as ultrafiltration by Millipore Centriprep filters (Brown et al. 1988; Beaumont et al. 2010). After a bone sample has undergone demineralization and hydrolyzation, it is possible to ascertain whether a sample may contain enough collagen to require further preparation. Introducing air using a clean pipette into the gelatin solution should create bubbles of gelatin. If the bubbles do not readily pop, it signifies long strands of collagen present; if bubbles pop immediately or none form, this would signify broken or shorter chains of collagen that may or may not survive ultrafiltration (Hector M de La Torre, University of Alberta, Edmonton, Canada, personal communication).

Removal of Secondary Carbonates

- X-ray diffraction (XRD) and scanning electron microscope (SEM) imaging may help to identify secondary calcite precipitates, and therefore determine sample quality prior to dating (Grothe et al. 2016 and references therein).
- To remove secondary carbonates (Chappell and Polach 1972) from shells, corals, speleothem, and foram samples, a leach in diluted HCl may be applied. The strength of the leaching procedure can vary (e.g. 10%, 30%, or 50%) depending on sample appearance under the microscope and/or the amount of material available (Santos et al. 2004). These acid-etching treatments are based on the assumption that secondary carbonates are preferentially soluble than the original calcite. For an alternative method, check Douka et al. (2010).
- We use 3-mL glass silica-coated Vacutainer blood collection vials (Becton-Dickinson) for direct leaching and hydrolysis of carbonates. The main advantages of using these vials are their reduced costs and less acid waste, as used vials filled with a small amount of acid can be disposed directly into a waste basket (Santos et al. 2004). The drawback is that this brand is no longer manufactured by Becton-Dickinson. An alternative product is the 3-mL non-silicone-coated

glass tube from Monoject (Kendall). However, one must be aware that the red rubber septum is a bit different from the made by Becton-Dickinson; therefore, from our experience, the operator must be extra careful when puncturing the septum to avoid leakage.

- If you are planning on letting acidification hydrolysis to linger for several hours when using blood vial types such as Vacutainers (Yokoyama et al. 2007), consider buying the uncoated glass vials, as it is unclear whether the graphitization reaction could be jeopardized by the breaking down of the rubber or silica coating under the hot acid vapor. Further tests on this subject are needed.
- Acid fumigation method for getting rid of carbonates from soils or sediments may not work for ^{14}C analysis when the carbonate content is high, especially with dolomite [$\text{CaMg}(\text{CO}_3)_2$] in your sample. Even though the method may work for $\delta^{13}\text{C}$, ^{14}C is much more sensitive to dead C contamination (Elisabet Nadeu, Campus Universitario de Espinardo, Murcia, Spain, personal communication). Also, if the acid fumigation method is to be employed, the fumigation time should not exceed 24 hr to minimize blank carbon incorporation (Komada et al. 2008).

Glassware and Reagents

Preparation, baking, and storage of glassware, glass tubes, and reagents are part of the preparation steps necessary during sample processing.

A) Cutting and making tubes for combustion of organics is relatively simple. The tubes can be produced from high-temperature fused silica (such as QZ or Vycor) tubing.

- Vycor by Corning is a borosilicate type of glass with 96% of silica and a temperature limit of 1200°C. It is generally cheaper than pure quartz. However, early evaluations in its quality/background indicate that they may introduce a higher blank (Vogel et al. 1987). We have not noticed this phenomenon in recent years.
- To evenly score glass tubes, consider using glass tubing cutters (such as Griffin-Type Cutters Z150770-1EA from Sigma-Aldrich) rather than four-edged glass scoring knives. Glass tubing cutters cut tubing up to 1-1/2 in. (38 mm) in diameter.
- It is also easier and more efficient to make two tubes at once by flaming off a tube in the middle of the desired length, constantly rotating the tube until a thick wall at the tip is formed. The opening should be slightly polished for better performance, and to avoid the sharp edges cutting the O-rings in the vacuum line attachments.
- Glass or QZ tube “wormholes” (bubbles in glass that are formed when the glass is overheated) can be avoided by adjusting the flame to a slightly lower temperature. Sometimes wormholes can be visible under a microscope, or felt when blowing air into the tube. Avoid using these defective tubes to prevent sample loss.

B) Some laboratories apply specific cleaning procedures for their glassware using soap, lab-grade detergent, or even diluted acid rinses. In fact, most glassware can be sterilized by just subjecting it to baking close to the melting point and letting it cool down slowly, followed by storage in clean areas (such as wet cabinets). The combination of cleaning with detergent and baking are not recommended. Alkalis (used in soap-making) at elevated temperatures will etch glass (refer to glassware vendors for details), and may unintentionally affect the background, when residues are allowed to bond with the glass tubes.

- Borosilicate glasses (such as Pyrex, Duran, Kimex, or Simax) can easily stand baking at 500–550°C, whereas fused quartz and Vycor can be baked at >950°C.
- The term “wet cabinet” refers to a desiccator acrylic cabinet from Fisher brand with vented shelves. A neoprene gasket and door latches keep it well sealed. By adding a small plastic tray with 10–20 mL 1N NaOH solution on the bottom of the cabinet, one can trap the atmospheric CO₂ inside the cabinet, while helping to reduce the static from the baked glassware. The alkaline solution should be replaced frequently (every 15 days or so). These air-tight cabinets with NaOH trays (solution is poured directly on the polypropylene tray) are also very useful for storing graphite until measurement can be performed. However, be aware that filament graphite does change slowly with time (see details in Beverly et al. 2010).
- If one can afford to purchase larger Pyrex and/or quartz dressing jars (with loose lids made of metal or quartz), smaller glassware items can be baked directly inside them. Remove jars still warm from the furnace and store immediately into the wet cabinets. This procedure is effective and keeps the glassware sterilized longer, and is far less time consuming. Thus, it simplifies the overall transferring, baking, and restoring of smaller prebaked glassware items.
- QZ tubes for combustion can also be stored inside a wet cabinet without losing their sterility if they are tightly wrapped in clean aluminum foil until use, or if baked together with reagents inside them, in a standing position.

C) Dealing with reagents

- We chose to use rods/wire of cupric oxide (CuO) from Fisher. For surface cleaning, we bake a small quantity of material at 900°C for 3 hr in a small ceramic crucible, and transfer it to a prebaked glass vial while it is warm for storage. We repeat the procedure at least every 15 days. However, before baking make sure to remove the very fine powder with a metal sieve #200. By removing the fine powder, less CuO becomes attached to the inner wall of the QZ tube during loading, and therefore does not interfere with the torch sealing procedure.
- To remove sulfur and/or other undesirable gases after combustion that may poison graphitization (such as Cl), a small amount of prebaked silver (Ag, as powder, sheets, or wire) can be added into the QZ tubes. We prefer to use annealed Ag wire (1.0 mm × 0.04 in. diameter, 99.9% metal basis from Alfa Aesar), which is easy to cut into small pieces, and prebake in its own storage glass vial at 500°C until it is ready to be used. If desired, those can be baked together with CuO directly into the QZ tubes at 900°C before combustion of organics. Silver cups (used in EA-IRMS) may also be used during combustion of those “problematic” organics. Although we have not attempted the procedure ourselves, colleagues at the Australia National University reported good success. We suggest to preferably prebake the cups at 300–400°C before using them, and to test the procedure using a ¹⁴C-free blank material to account for any possible exogenous C added by the addition of the silver cups.
- For the sealed-tube Zn reduction method (Xu et al. 2007), prebaking the assembled reaction tubes with all reagents (Zn, TiH₂ in the bottom of a 9-mm-OD Pyrex tube, and catalyst Fe inside a 6-mm-OD culture tube sitting above Zn/TiH₂) at 300°C in air has shown to be an efficient way to reduce graphitization background (Khosh et al. 2010).

CO₂ PRODUCTION FROM CARBONACEOUS SAMPLES

CO₂ production can be achieved via combustion of the organic materials or acidification of carbonates. It is important to take the precaution of purifying the undesirable gases that may potentially poison the reduction step (e.g. graphitization).

Combustion of Organics

- As an extra effort to minimize blanks, we normally combust samples within 6-mm-OD QZ tubes. Larger surface areas, even if they are prebaked, are still prone to pick up more exogenous carbon.
- To produce enough CO₂ for 1 mg C of graphite, weigh ~60 mg of CuO directly into the QZ tube with the help of a spatula. This amount of CuO is stoichiometrically much higher than the amount necessary to convert 1 mg of OC into CO₂ (Santos et al. 2010). Larger amounts of CuO may introduce larger backgrounds, as the prebaking procedure cannot remove all C embedded in CuO rods (Vandeputte et al. 1998).
- When dealing with static and loading of very small pretreated samples (such as charcoal), try make use of a funnel made of a weighing paper, so that the sample can be loaded directly into the prebaked QZ tubes. An Al foil wrapped around the quartz tube is also helpful to lower the static, while weighing samples using a balance.
- To better deal with static issues in general, an antistatic gun (Zerostat 3 Antistatic Gun) may be used. It is available online from several suppliers.
- To expedite reagent loading into combustion tubes, we use small spoon-shaped medical devices, such as Chalazion curettes. These are metallic spoons sold online by several suppliers in several shapes and sizes. Once one's consistency in using the spoons is calibrated and verified, the reproducibility of the reagent weight by using the small spoon alone (without actually using the balance) is relatively good.
- When samples are known to be naturally loaded with sulfur, several pieces of annealed Ag wire may be used so that S is kept as AgS (see case study in Santos et al. 2001).
- When dealing with powdery samples, QZ wool may be used. Once samples and reagents have been loaded, place a small ball (~5–6 mm wide) in the very top of the QZ tube, then proceed with slow evacuation, and sealing with a torch at ~2–3 cm under the QZ wool plug. Although QZ wool may be baked >900°C before use, its large surface area and strong absorptive properties cannot prevent CO₂ and volatile organic carbons (VOCs) from air to be trapped back into it as soon as it cools off. Thus, it is not recommended to leave the QZ wool inside the combustion tubes. A cheaper and less brittle material option is glass wool. However, the glass wool sterilization must be done at <550°C to avoid melting it.
- When weighing fine particulate and powdery material (such as sediments or wood powder), burn the neck of the QZ tube just after the sample has been loaded and before attaching it to the vacuum line for evacuation. This simple procedure can combust off the organic matter left from weighing samples, preventing SiC to be formed and easing the sealing of the QZ tube under vacuum (Southon and Magana 2010).
- Once samples are loaded, and combustion tubes are evacuated and sealed, lay down the QZ tubes horizontally and spread out the inside material to lower the risk of sample and reagents eroding the tube from inside, or exploding inside a muffle furnace.
- To isolate the combustion tubes in a muffle furnace and prevent a chain-reaction disaster (if one tube avertedly explodes), ~25.5-mm-OD (~1-in.) Sillimanite mullite tubes with open ends can be used. They are suitable for operating in temperatures up to 1700°C. Alumina ceramic tubes are a cheaper alternative, and can be found at the required length from some online vendors.
- Some labs prefer to identify sample tubes by their particular position within the muffle furnace after combustion (e.g. Marzaioli et al. 2008). On the other hand, combusted

samples can also be identified directly by their IDs written onto the QZ tubes by using a high-temperature marker that can withstand up to $\sim 1100^{\circ}\text{C}$. Once QZ tubes are combusted at $850\text{--}900^{\circ}\text{C}$, the marker ink tends to fade to a lighter shade, but is still visible to the naked eye. Markers are available from different manufacturers; however, we have had good experience with the Dykem High Temperature Tip Marker (sold online by several vendors).

Hydrolysis of Carbonates

For carbonate samples, CO_2 can be produced by in-vacuum acid hydrolysis. To ensure that evacuation of the carbonate vessel occurs before acid reaction, a two-arm flask may be used. However, we choose to perform the in-vacuum acid hydrolysis directly in a 3-mL blood collection vial by piercing the rubber septum with a needle syringe (Hamilton Series 1000 5-mL Luer-Lock syringe #1005):

- Put a small drop of water around the needle after punching for a better seal during evacuation of a vial, and wipe off the water before pulling the vial off the needle that is attached to a vacuum line to prevent water getting into the line through the needle.
- For injecting ~ 0.8 mL of 85% phosphoric acid through the septum of an evacuated vial, put a drop of phosphoric acid on top of the rubber septum first to prevent air leaking in.
- Heat may enhance the acid hydrolysis reaction, expediting the CO_2 production in the vial headspace. However, do not exceed the reaction time duration unnecessarily, as the heated acid vapor may break down the rubber or inner coating of vials (see also the *Removal of Secondary Carbonates* section for further details).
- Prior to CO_2 extraction, a needle attached to the graphitization vacuum line is partially inserted into the septum of the tube, so that the dead volume between the loading portion of the line and needle tip can be evacuated (Santos et al. 2004).
- Quantitative extraction of DIC from natural waters by using CO_2 -free gas bubbling through the water for ^{14}C analysis by AMS has long been used by many laboratories (McNichol et al. 1992; Kwong et al. 2004). Recently, a rapid method utilizing a headspace-extraction approach has been developed by Gao et al. (2014). A syringe is used to remove the CO_2 from the headspace after acidification and the CO_2 is then injected into a vacuum line for purification and graphitization. The main advantage of this method is that water is isolated from the vacuum line, thus speeding up the process significantly. The small fractionation introduced by the headspace extraction can be completely corrected for by using the online AMS $\delta^{13}\text{C}$.

CO_2 Extraction from Canisters and Molecular Sieve Traps

- U-shape traps with small glass beads in them can significantly increase the trapping efficiency of CO_2 in liquid nitrogen. Also, the use of flow controlling devices is highly recommended for extracting CO_2 from atmospheric samples.
- Releasing CO_2 sampled by the molecular sieve trap is usually done by heating the trap to $500\text{--}600^{\circ}\text{C}$. Pumping down the trap first before heating can reduce tailing of CO_2 release. Avoiding water entering during sampling and avoiding overheating during extraction can prolong the life of molecular sieves.
- Capillary or flow-rate control devices attached to the inlet of an air canister can be used for taking a time-integrated air sample.

- Canisters, capillary tubes, and flow controlling devices can be purchased from Alltech or Fisher.

REDUCTION OF CO₂ TO GRAPHITE

In most cases, a ~100% graphitization yield can be achieved with the right combination of graphitization reaction volume, reaction temperature, and time; effective water removal by cryogenic or chemical sorption for the H₂ reduction method (Vogel et al. 1984; Santos et al. 2004); as well as the right combination of reagents (Zn process method) (Vogel 1992; Xu et al. 2007):

- Pyrex tubes can replace quartz during the graphitization reduction without deterioration of the background level. Pyrex is cheaper than quartz and less prone to lithium contamination (which can be a concern for those spectrometers running at charge states 2+ or 4+; Loyd et al. 1991; Santos et al. 2007c). Reaction temperatures must be carefully adjusted to ~550°C (Santos et al. 2004) when using Pyrex to avoid softening, bulging, or misshaping the tubes, as this temperature is already very close to its melting point.
- There are a few ways to determine graphitization yield. One common and direct way is to monitor the pressure (CO₂ + H₂) reduction during graphitization. Residual gas analysis after graphitization (McNichol et al. 1992; Liebl et al. 2010 and references therein) and carbon stable isotope signatures of filamentous graphite produced from known reference materials (Santos et al. 2007a; Macario et al. 2015) are two other examples. However, if the graphitization reaction yield cannot be verified by the aforementioned techniques, an alternative step to evaluate reaction efficiency can be conducted by comparing the weights of the catalyst preloaded and filamentous graphite after reaction. A well-calibrated balance will be required for that.
- To effectively remove water from the graphitization reaction (which is essential for fast and complete graphitization), a water trap (also termed cold finger), which is part of the graphitization reactor, will be necessary. Typical water traps are obtained by touching or emerging a section of the graphitization reactor into an isopropanol–dry-ice mixture (slush) or Peltier chillers (Smith et al. 2007). To avoid dealing with isopropanol–dry-ice mixtures or expensive chiller setups, we suggest to use a standard-grade anhydrous magnesium perchlorate [Mg(ClO₄)₂] to remove water (Santos et al. 2004).
- Recently, we have been purchasing Mg(ClO₄)₂ from Sigma-Aldrich (222283, 500 g). However, the key is to purchase a product that looks coarse-grained and is from a well-sealed jar. Make sure to keep the unused chemical as dry as possible by tightly closing the jar and limiting its exposure time to the air after it is opened.
- For loading Mg(ClO₄)₂ into reactors, we use a small “baked” strainer (using a heat gun for few minutes) to avoid the powder, and quickly scoop it from the strainer and load it into the tubes, then immediately attach the loaded tubes to the reactor and evacuate them.
- Sulfur species (e.g. SO_x) obtained during combustion of some organics can prevent the graphite synthesis to occur (Santos et al. 2001; Kwong et al. 2004). If CO₂ separation from SO₂ is required before transferring CO₂ to the graphitization reactor, an open n-pentane bath immersed in liquid nitrogen may be helpful. Note that the procedure is dangerous; therefore, a risk assessment should be conducted before attempting it. Details on this procedure can be found in Johnson and Komada (2011) and also check Mizutani and Oana (1973) and Kusakabe (2005).

- If the SO₂/CO₂ mixture has been inadvertently transferred to the graphitization reactor and an attempt to proceed with the graphitization reaction has started, the reaction would likely linger until a premature ending, as SO_x species interfere with the iron carbide formation phase and consequently the filamentous graphite growth (Santos et al. 2007b). Occasionally, tapping the iron powder tube helps to break down the sintered iron. By resurfacing some of the catalyst and resetting the reaction temperature, the reaction may continue as expected (Kwong et al. 2004).
- Reducing the volume of the graphitization reactor and lowering the graphitization temperature can help to produce ~100% graphite of ultra-small samples with ≥1 μg C (H₂ reduction, Santos et al. 2007a,b, 2010) and up to 4 μg C (Zn reduction, Xu et al. 2013).
- When shipping graphite to be measured by an independent AMS facility, consider the following: (a) if the graphite is already pressed into target holders, use a plastic EA sample tray (Costech, #080016 Sample Trays) for holding and separating the pressed targets; and (b) if the graphite is loose, use Al foil as envelopes for holding the powder for shipping. Al foil is better than plastic or glass vials, as it lowers the static effects and avoids graphite losses during pressing.
- Beware that the rubber caps or stoppers used to keep the graphite stored in their original glass vials, such as the ones sold by Sigma-Aldrich #Z565776, contain fossil-fuel synthetic byproducts. Occasionally, this type of cap can shred, contaminating the filamentous graphite. If graphite is required to be stored for a maximum of a month or so, choose the Sigma-Aldrich #Z127434 white rubber septa, 13-mm-ID tubing instead. For more details, refer to Beverly et al. (2010).
- A common element in graphite production is the filament graphite catalyst, which can directly affect the graphitization reaction time, graphite structure, and homogeneity as well as ion-beam intensity and sputtering time. Santos et al. (2007c) have shown that some off-the-shelf catalysts are suitable to produce filamentous graphite for ¹⁴C applications, after thorough evaluations of available catalysts (e.g. iron and cobalt powders) were performed. However, beware the following:
 - (a) Industrial-scale production of catalyst powder prevents catalytic features to be reproduced, leading to differences even within the same lot numbers of a particular brand (Santos et al. 2007c). Be prepared to bulk purchase your preferred catalyst, or to conduct continuous reevaluations of them.
 - (b) Embedded carbon catalytic impurities also affect background levels (Santos et al. 2007c; Fallon et al. 2012), and can be more problematic at submilligram-level graphitization. Thus, further examinations are required (Santos et al. 2007b), regardless of whether the catalyst is surface pretreated/reduced by H₂ or O₂.
 - (c) For those facilities running charge state distributions 2+ or 4+, lithium contamination can be also avoided by careful evaluation of the catalyst batches. Some catalysts, even from the same vendor, may vary in lithium content (Santos et al. 2007c).

REFERENCE MATERIALS

Frequent measurements of standards and blanks (¹⁴C-free materials) are important in quality assessment (Switsur 1990). This should include all stages of sample production (e.g. pretreatments and extraction procedures, CO₂ production, graphitization, and target handling) and for AMS analysis as well (Santos et al. 2010). Over the years, the ¹⁴C community has conducted

several interlaboratory comparisons (such as TIRI, FIRI, VIRI, and SIRI), which have led to a set of consensus values of these standard materials to evaluate laboratory precision and accuracy, as well as to help obtaining realistic estimates of uncertainty (Scott 2003; Scott et al. 2010 and references therein). The standard materials for the aforementioned interlaboratory comparisons were selected mainly to evaluate conventional procedures, such as chemical pretreatment of organics, collagen extraction from bones, and combustion and hydrolysis of carbonaceous samples. However, they can also be adapted into some more exotic applications, e.g. compound-specific C isolation (Ingalls et al. 2006, 2010; Shah and Pearson 2007; Druffel et al. 2010; Santos et al. 2010; Martin et al. 2013) or thermal treatments (Fernandez et al. 2014). For evaluating the accuracy and precision of source apportionment of fossil and nonfossil airborne particulates, refer to Currie et al. (2002), Steier et al. (2006), Szidat et al. (2013), and references therein, and Mouteva et al. (2015).

A number of reference materials with different properties and ^{14}C signatures are commercially available from the following:

- a) The International Atomic Energy Agency (IAEA) - <http://www.iaea.org/programmes/aqcs/> (Rozanski 1991; Hogg et al. 1995; Le Clercq et al. 1998);
- b) National Institute of Standards and Technology (NIST) - <https://www-s.nist.gov/srmors/detail.cfm> (including oxalic acid OX2, 4990C; Stuiver 1983);
- c) Useful reference materials from University of Zurich (<http://www.geo.uzh.ch/en/units/physische-geographie-boden-biogeographie/services/black-carbon-reference-materials/charcoals/>); and
- d) Argonne Premium Coal Samples (<http://web.anl.gov/PCS/>).

AMS ANALYSIS, DATA REDUCTION, CORRECTIONS, AND DATA REPORTING

Most of the current data acquisition systems and software analysis packages are supplied by the vendor with the AMS system. However, it is important to have a general understanding of how these analyses are performed, and how background corrections for different sample types can be satisfactorily accomplished, so that the results passed on to the users are reliable.

- To attain high precision, some users have adopted the online $\delta^{13}\text{C}$ values obtained by the AMS for isotopic fractionation corrections. Nevertheless, the methodology should be considered to all of those measuring submilligram samples (Santos et al. 2007a,b), and for those producing graphite by the procedure termed the Zn process (Vogel 1992; Ognibene et al. 2003; Xu et al. 2007) as machine isotope fractionation effects and/or fractionation during graphitization tend to be larger.
- Make sure to use the correct units of $\delta^{13}\text{C}$ when applying $\delta^{13}\text{C}$ for the mass-dependent fractionation correction. In the equations of Stuiver and Polach (1977) and Reimer et al. (2004), the $\delta^{13}\text{C}$ does not need to be multiplied by 0.001. Confusion has been seen in newer AMS facilities on this point. Cross-checking the data reduction process with an established laboratory is recommended.
- Some facilities choose to design their own analysis software packages, adapting them to the characteristics of their specific spectrometers (Tumey et al. 2004; Wacker et al. 2010; Steinhof 2013; Castro et al. 2015).

- For offline analyses of data produced by AMS systems from National Electrostatics Corporation (0.5MV 1.5SDH-1 Pelletron, NEC), we suggest to combine the stripchart module in NEC's *abc* analysis code and the *Fudger* AMS analysis software (Ognibene and Vogel 2005). The stripchart allows identifying anomalous measurements for later removal. The *Fudger* software deciphers the raw data from the measurements, and allows isotopic fractionation correction loop-by-loop, including normalization by primary standards. These steps can be performed simultaneously with the removal of the identified anomalous runs shown by the *abc* analysis code. The blank subtraction can be done later in an Excel spreadsheet (Santos et al. 2007b).
- Recently, Dr. Ognibene (Lawrence Livermore National Laboratory) has adapted *Fudger* to handle the raw spreadsheet data for the single-stage AMS system (SSAMS), also produced by NEC. Care should be taken when adapting a new version. Thorough testing and comparison with the proven version is recommended.
- When reporting data, be sure to adhere to the conventional notations; see Stuiver and Polach (1977) and Reimer et al. (2004) for details.
- Several potential sources of exogenous carbon background in ^{14}C -AMS processing and measurements using catalytically condensed graphitic carbon targets have been described previously by Vogel et al. (1987) and Kimer et al. (1995). Most of these evaluations focus on the contamination by modern carbon. Santos et al. (2007a,b, 2010) demonstrated that the residual amount of dead exogenous carbon is also apparent when graphite targets are lower than $<0.050\text{ mg C}$ by measuring a suite of small HOxI (oxalic acid I with $\text{FmC} = 1.0398$; Stuiver and Polach 1977; Currie and Polach 1980) targets. Special chemical pretreatments, and the use of instruments such as those used in compound-specific analyses, may introduce a much larger dead carbon contaminant. Thus, a larger suite of reference materials to evaluate all steps of the sample processing may be required (see examples in Ingalls et al. 2006, 2010; Shah and Pearson 2007; Druffel et al. 2010; Santos et al. 2010; Martin et al. 2013; Fernandez et al. 2014; Mouteva et al. 2015).
- To obtain more representative blanks, one must choose the appropriate ^{14}C -free materials (e.g. carbonates and organics) and sample sizes to closely match the actual unknown samples (check *Reference Materials* section for suitable materials). Also, try to subject the reference materials to most (if not all) of the sample preparation processes, so that a proper procedural blank can be evaluated.
- When dealing with ultra-small samples, matching size blanks are imperative so that proper background corrections for both modern and dead carbon can be applied (Santos et al. 2007a,b, 2010; Shah et al. 2008; Shah Walter et al. 2015). Note that to estimate the blank size, one has to measure several reference materials of different sizes and isotopic signatures. Once an apparent isotopic composition different from that of the reference material emerges, and it is corrected by subtracting it, the magnitude of the blank itself can be then inferred. To facilitate, we split the blank in two end-members, e.g. modern carbon (MC) and dead carbon (DC) (Brown and Southon 1997; Santos et al. 2007a,b, 2010). The uncertainty associated with the blanks can also be estimated from the spread of the blank ^{14}C results.
- All graphite targets measured should receive a unique identification (UID) number linked to the facility's database, whether prepared in-house or received from outside submitters. Insist that these UID numbers are listed when results are published. An UID number is important to recover sample information when needed.

LAB SETUPS

The requirements for a conventional ^{14}C dating laboratory in site setup will largely depend on the type and expected quantity of samples to be processed. It may be wise to choose instruments (and procedures) that are easy to handle by all users.

Vacuum Lines

- To protect vacuum lines from undesirable powder, rather than install larger inline strainers that can also restrain the vacuum speed, try inline metal filters. Lay down porous discs ($2\ \mu\text{m}$ porosity \times 1/2" OD frits from Supelco; item# 58255) in strategic places in the vacuum line, to prevent sample particles (when evacuating combustion tubes) or CuO powder (when releasing CO_2 in a graphitization bellows/cracker) from getting into the vacuum line. The strainer fits loosely between the O-ring and the 1/2" Ultra-Torr metal body. To better hold it in place, try to use it with a fat O-ring. The strainer needs to be cleaned (by blowing it with air) or replaced from time to time. The frequency of cleaning or replacement will depend on the vacuum line usage.
- If possible, consider building a vacuum line that is relatively simple and short/small in overall volume, to reduce pump-down time duration to reach the vacuum desired. Also, avoid long and relatively "skinny" tubing to avoid limiting the ultimate pressure. Eliminate unnecessary sections and valves to lower the chance of leakage. When in operation, limit the volumes exposed to ambient air pressure by isolating portions of the vacuum line, and thus speeding up the pumping.
- Beware that certain types of valves have a small dead volume that could trap gases, such as Ball valves from Swagelok. Opening and closing the valve a few times helps to get rid of the unwanted trapped gases.
- When dealing with extraction of CO_2 in air or other samples with high non-condensable gases, use U-traps with glass bead inserts to slow down pumping speed and increase sample extraction yield.
- Use an LN_2 trap between an oil mechanical pump and the remaining vacuum line to prevent oil vapor from back-flowing into the line. An LN_2 trap between the turbopump and the line can also speed up pumping, especially for samples that contain lots of water.

FUTURE DIRECTIONS

We hope the tips and tricks presented here are helpful to users, especially for new labs in the community. However, it is highly advisable to validate these techniques at your own laboratory, or modify them to adapt to your specific situations. In addition, we intend to encourage vigorous discussions on the methods used for ^{14}C dating and C cycle studies. Please contact us if you have helpful tips to share and we will try to incorporate them in the next report.

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