STATUS REPORT OF THE NEW AMS ^{14}C SAMPLE PREPARATION LAB OF THE HERTELENDI LABORATORY OF ENVIRONMENTAL STUDIES (DEBRECEN, HUNGARY)

M Molnár[1,2] • R Janovics[1,3] • I Major[1,3] • J Orsovszki[3] • R Gönczi[1] • M Veres[3] • A G Leonard[4] • S M Castle[4] • T E Lange[4] • L Wacker[5] • I Hajdas[5] • A J T Jull[1,4]

ABSTRACT. We document chemical laboratory procedures and results on international comparison samples at the Hertelendi Laboratory of Environmental Studies, Debrecen, Hungary. We also show results using the new MICADAS system and compare these results to internationally recognized standards and blank materials. The newly developed sample preparation system in HEKAL can handle samples as 1) organic material, 2) cellulose fraction of plant, 3) bones, 4) carbonate and shell, and 5) dissolved inorganic carbon of groundwater. The results of radiocarbon measurements on intercomparison samples confirm the reliability of the sample preparation system at HEKAL Lab and also the good performance of the MICADAS ^{14}C system. The blank levels for each type of sample of 1 mg C carbon content are well reproducible, ~0.3–0.5 pMC.

INTRODUCTION

An important feature in the establishment of a new accelerator mass spectrometry (AMS) laboratory is the documentation of processes used, and also to demonstrate the reliability of measurements by comparison to internationally recognized standards. We discuss here the new chemistry laboratories associated with the EnvironMICADAS specialized accelerator mass spectrometry system (ETH Zürich) in Debrecen, Hungary. We introduce the entire series of AMS ^{14}C sample preparation techniques that are applied at the new AMS laboratory. These include chemical preparation processes developed at ETH Zürich and Arizona, or adaptations from them. All of the AMS ^{14}C measurements presented below were made using the new AMS installation in Debrecen (Molnár et al. 2013).

SAMPLE PREPARATION METHODS

Organic Materials

Most organic materials, such as charcoal and plant fragments, are treated using the standard acid-base-acid (ABA) method, following standard protocols (e.g. Jull et al. 2006). In our laboratories, we treat samples with a sequence of 1N HCl, distilled water, 1M NaOH, distilled water, and then 1N HCl. After the final acid wash, the sample is washed again with distilled water to neutral pH (4–5) and then dried. The sample is then ready for combustion. We have also adopted a Soxhlet extraction protocol similar to that applied by Hajdas et al. (2004) for textiles and art samples. In this case, the samples are extracted in a sequence of solvents: hexane, ethanol, and methanol, followed by a distilled water wash. The samples are dried before combustion.

Cellulose Extraction

The main constituents of plant materials (primarily wood) are cellulose (40–60%), lignin (16–33%), hemicellulose, resins and waxes (5–10%). For ^{14}C age determinations of wood, the most stable constituent is recommended. The most stable compound from plant material is α-cellulose; therefore,

[1]Institute of Nuclear Research of the Hungarian Academy of Sciences (ATOMKI), Debrecen, Hungary.
[2]Corresponding author. Email: molnar.mihaly@atomki.mta.hu.
[3]Isotoptech Zrt, Debrecen, Hungary.
[4]NSF Arizona AMS Laboratory, University of Arizona, Tucson, Arizona, USA
[5]Laboratory of Ion Beam Physics, ETHZ, Zürich, Switzerland.

Proceedings of the 21st International Radiocarbon Conference edited by A J T Jull & C Hatté
RADIOCARBON, Vol 55, Nr 2–3, 2013, p 665–676

the separation and utilization of this cellulose content is the most suitable for a ^{14}C age determination. Lignin and hemicellulose contain carbon that is more easily exchangeable, hence it is not suitable for age determination (Nemeč et al. 2010).

Our cellulose extraction method is adapted from procedures at the ETH Zürich laboratory in Switzerland. In this method, the conventional acid-base-acid (ABA) procedure was modified (BABAB) by adding an additional bleaching step. There are 2 main differences between the revised method and the original method. The BABAB procedure uses an alkaline step at the beginning of the process to remove alcohols, phenols, and compounds with carboxyl groups (Nemeč et al. 2010). This method is widely applied in the paper manufacturing industry. The other difference is that there is an additional alkaline bleaching step at the end of the pretreatment. The extracted material is washed to a weakly acidic pH at the end of the process and carefully dried.

Bones

Bone is one of the most complex sample materials for ^{14}C dating. After burial, its physical state and chemical composition can be affected by many environmental processes. On the surface of bones, old carbon may be deposited in the form of inorganic carbonates that are derived from soil and groundwater (Olson and Broecker 1961). In addition, the preservation of the organic component (collagen) in the bone is affected by temperature, humidity, pH changes, and microbial activity (van Klinken 1999). The organic fraction of the bone is also influenced by interactions with humic substances penetrating into the porous material of the bone, where they may become adsorbed or interact with the intrinsic degradation processes occurring in the bone, known as Maillard processes (van Klinken and Hedges 1995). Depending on local environmental and soil characteristics, these factors may increase or decrease the apparent ^{14}C age of bone collagen (Stafford et al. 1988; Tripp et al. 2006).

At the Hertelendi Laboratory of Environmental Studies, we have extensive experience in the preparation and ^{14}C measurement of bone samples. Initially, we prepared samples for gas proportional counting (GPC), but due to the low concentration of organic material in bone, the GPC measurement required high initial sample amounts (~50 g). In the case of our AMS bone preparation technique, after ultrasonication in distilled water, drying, surface cleaning, and grinding, the sample is sieved to get the appropriate sized sample fraction (0.5–1 mm) out of which 500–1000 mg may be measured, depending on the preservation state of the bone.

We have developed continuous-flow bone sample preparation equipment (Figure 1) similar to the method used at the Oxford Radiocarbon Accelerator Unit (ORAU). In our unit, Omnifit® columns (C in Figure 1) are used as flow cells to automate the ABA cleaning system (Bronk Ramsey et al. 2004). From 3 types of reagents (S in Figure 1), each one is injected via a 4-way valve and inert plastic tubing to an Ismatech® IPC 12 channel peristaltic pump (P in Figure 1) to ensure a constant flow rate. Reagents are selectively pumped to the reaction cells containing small-grained bone samples, with a sequence of 0.5M HCl and 0.1M NaOH solution, interspersed with flushing with distilled water. At the end of the process, the reagents together with the contaminants are collected using a collection bottle (R in Figure 1) for each cell. During the 16-hr-long process, reagents follow a well-defined sequence that is controlled by a computer program and a special electronic driver device (E in Figure 1).

The cleaned sample is inserted into a test tube containing 5 mL, pH 3 aqueous solution, and it is placed into a heating block at 75 °C for 24 hr. Dissolved collagen/gelatin is filtered via a 0.45-μm

glass fiber filter (Whatman® AUTOVIAL 5) into a clean vial, and after freezing, it is freeze-dried, which takes about 1–2 days (Figure 2).

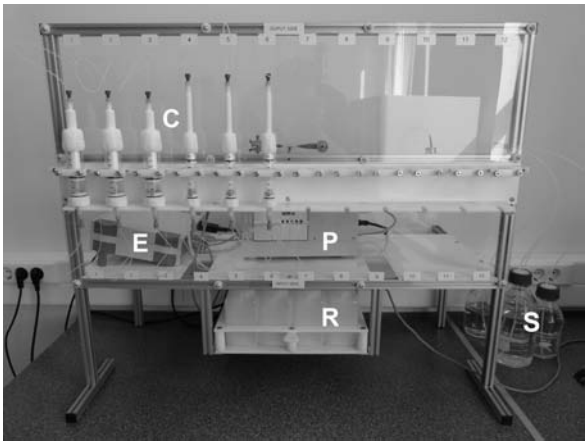

Figure 1 Automated continuous-flow bone ABA cleaning system, made by ATOMKI (O: Omnifit flow cells; E: electronic driver unit; P: peristaltic pump; R: used solvent collection bottles; S: fresh solvents).

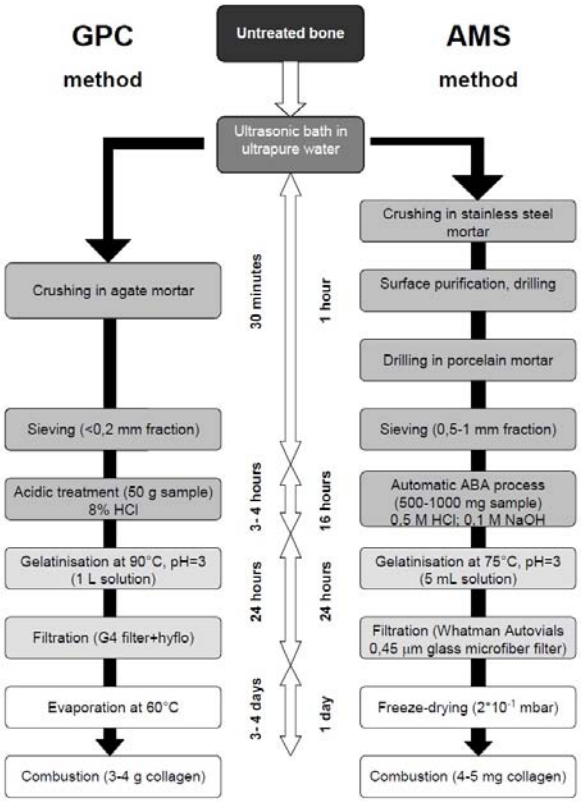

Figure 2 Comparison of GPC and AMS bone preparation protocols in HEKAL.

Carbonate and Shell

The acid treatment of snails, shells, and other carbonaceous depositions occurs in a vacuum-tight 2-finger glass flask with a valve (Figure 3). We place the sample into one of the fingers, with phosphoric acid in the other. After evacuating the flask, the acid can be poured onto the sample in the other finger. The CO_2 produced from the carbonate in the sample can be introduced into our on-line combustion/CO_2 purification system.

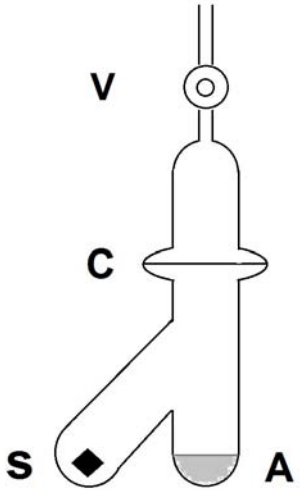

Figure 3 Glass carbonate sample prep setup at HEKAL (S: solid phase carbonaceous sample; A: phosphoric acid; C: glass and O-ring (Viton) vacuum-tight connection; V: Kontes glass valve).

Dissolved Inorganic Carbon (DIC) of Groundwater

Two water sample preparation methods were developed and tested in HEKAL. The first method is for water samples with low dissolved carbonate content (LDC method) where up to 500 mL of water sample is needed to obtain enough (>0.5 mg) carbon for graphitization. The second method is for water samples with high dissolved carbonate content (static HDC method) where a maximum of 20 mL water is enough to obtain the necessary amount (>0.5 mg) of carbon for graphitization.

In the LDC method, water samples (up to 500 mL) are transferred to a 1000-mL round-bottom flask using a funnel just before the bulb is closed. Immediately after the water is transferred, a large dry-ice trap is connected to the top. The entire volume is pumped out quickly with the vacuum system of our in-line combustion/CO_2 purification system. Then the bulb is closed and a small amount (5 mL) of 85% phosphoric acid can be injected using a needle and septum arrangement (Figure 4). After 15 min reaction time while the water is intensively stirred by a magnetic stirrer, the CO_2 produced from the water sample can be introduced directly into our on-line combustion/CO_2 purification system.

The preparation of the relatively high dissolved inorganic carbon (static HDC method) samples is performed by a novel method combining the advantages of the preparation of carbonate and water samples. The setup is basically similar to that used for carbonate samples, but instead of the second sample holder finger, a silicone septum fitting is used (Figure 5). The internal volume is about 70 mL. The reaction cell has been previously evacuated already containing 3 mL of 85% phosphoric acid, and 10–20 mL water sample is introduced later into the evacuated and closed reaction cell by a disposable sterile medical plastic syringe via the septum. The water and acid mixture at the bottom of the reaction cell is heated to 75 °C in a heating block for at least 1 hr to increase the rate of reac-

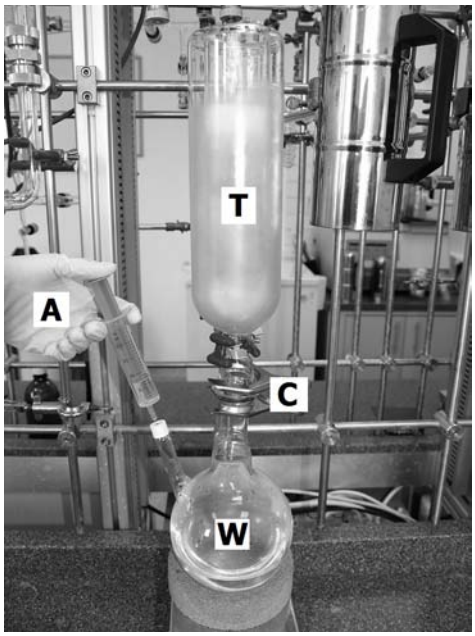

Figure 4 LDC water preparation setup, adapted from the University of Arizona design (Burr et al. 2001; Leonard et al., these proceedings) (W: water sample in the 1000-mL flask; A: phosphoric acid injection through a septa-sealed cup; C: glass and O-ring (Viton) vacuum-tight connection; T: large dry-ice trap).

tion and get better CO_2 extraction yield. Instead of phosphoric acid, we can also use the same setup with a variety of oxidizing acids (like chromic acid, etc.) to liberate different organic compounds also. The CO_2 produced off-line from the water sample can be also introduced into our in-line combustion/CO_2 purification system.

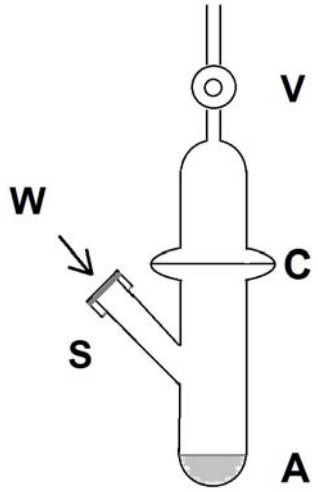

Figure 5 HDC water preparation setup developed by HEKAL (W: water sample injection by a sterile plastic syringe; S: septa silicon-sealed cup; A: phosphoric acid; C: glass and O-ring (Viton) vacuum-tight connection; V: Kontes glass valve).

In-Line Combustion and CO_2 Purification Line

For combustion of samples, we used a system similar to that at the University of Arizona (Jull et al. 2006). Samples can be combusted in the presence of CuO or oxygen gas. The carbon dioxide is cryogenically separated from water at –78 °C, passed over Cu/Ag to reduce nitrogen oxides and remove halogens, and trapped in a known volume at liquid nitrogen temperature. The gas pressure

is measured in a known volume, to calculate the yield. The gas is transferred to a sealed tube for graphitization. The system uses Na-borosilicate glass tubes by Pyrex® and glass valves by Kontes® with Viton® seals. The glass valves are lubricated with Apiezon® vacuum grease, which has a vapor pressure of 10^{-9} mbar. The parts are attached by stainless Ultra-Torr fittings by Swagelok®. The final pressure of the system is 3×10^{-5} mbar ensured by an SH-110 dry scroll vacuum pump and a Navigator 301 turbomolecular pump by Varian. Between the system and the turbomolecular pump, there is a cryogenic trap that uses liquid nitrogen (Figure 6/10). For measurement of the vacuum, an Edwards WRG vacuum gauge is used. The combustion of the samples takes place in quartz tubes (Figure 6/1a).

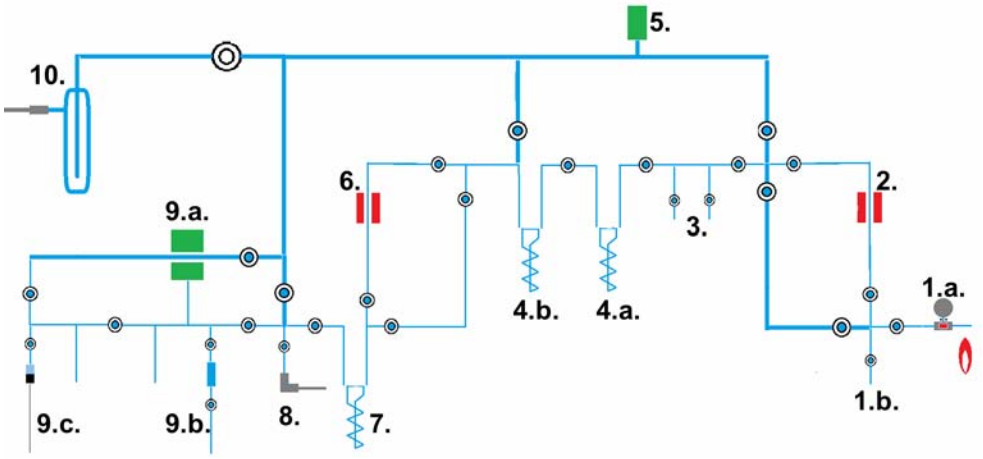

Figure 6 Scheme and main parts of the on-line combustion and CO_2 purification line, adopted from UA (1a/b: combustion cell, with manometer and oxygen gas inlet; 2: afterburning furnace; 3: off-line-produced CO_2 sample inlet valves; 4. a/b cold/freezing traps; 5: WRG Edwards pressure gauge; 6: cleaning furnace with Cu/Ag; 7: cold trap; 8: precleaned CO_2 sample inlet (like OxII gas or blank CO_2 gas); 9a: known volume with pressure sensor; 9b/c: cleaned CO_2 sample storage vessel/tube; 10: high-vacuum pumping with lN_2 trap. All the round symbols are Kotes glass valves.

In the case of a CuO combustion, the temperature necessary for the oxidation is produced by a gas torch at 1100 °C. A Watlow® tube oven with a precision temperature controller is used for heating during stepped combustions. In this case, oxygen is introduced from a high-purity Linde O_2 gas supply, fed into the reaction field (Figure 6/1b). To check the combustion process, a vacuum-tight stainless steel Swagelok manometer is used. The gas is passed through a tube at a 1000 °C filled by quartz pearls (Figure 6/2), which ensures complete conversion to CO_2 (after burning in the furnace). The quartz oven is followed by 2 spiral cold traps with a functional length of ~500 mm each. The first trap (Figure 6/4a) is cooled by a mixture of isopropyl-alcohol and dry ice to –78 °C, and removes the water vapor from the combustion process. The next cold trap (Figure 6/4b) is frozen by liquid nitrogen to –196 °C and is used to freeze out the CO_2 generated and to pump away waste gases. Gases frozen out at –196 °C pass through a catalyst oven (Figure 6/6) at 500 °C filled with elemental copper and silver to eliminate sulfur, nitrogen oxides, and halogens. After cleaning in the furnace, there is a second –78 °C trap to remove the water vapor generated in the course of the reduction. The determination of the quantity of the CO_2 gas is made in a calibrated volume using an MKS Baratron pressure gauge (Figure 6/9a). The calibrated volume can be split into 2 equal parts. One half of the sample gets graphitized (Figure 6/9b) while the other half gets reserved in a sealed glass tube (Figure 6/9c).

Graphitization and AMS Measurement

All the graphite targets were prepared by a sealed tube graphitization method in HEKAL (detailed information in Rinyu et al. 2013). Amounts of the reagents and catalyst used were kept constant, independent of sample size (typically between 0.2 and 1.5 mg of C), using 10 mg titanium-hydride (Alfa Aesar, #012857), 60 mg zinc (Aldrich, #324930), and 4.5 mg iron powder (Aldrich, #20,930-9). During the pretreatment process, the reagents and iron catalyst are weighed into the reaction tubes, which are then kept at 300 °C for 1 hr. After the transfer of the CO_2 gas and sealing of the reaction tubes, the graphitization process consists of 2 steps: 1) 3 hr at 500 °C to release the hydrogen and reduce the iron powder, and 2) 5 hr at 550 °C regular graphitization process.

All of the ^{14}C measurements reported below were performed by our EnvironMICADAS AMS at Hertelendi Laboratory in Debrecen (Molnár et al. 2013). Measurement time and conditions were set to collect at least 200,000 net counts for every single target in case of a modern sample. The overall measurement uncertainty for a modern sample is <3‰, including normalization, background subtraction, and counting statistics.

RESULTS ON INTERCOMPARISON SAMPLES

Wood and Other Organic Samples

For testing the various organic sample preparation procedures at HEKAL, we have used international ^{14}C reference materials with known ^{14}C activity. IAEA-C4 reference wood samples (very old, no ^{14}C) were prepared using different amounts of sample. In this way, we can investigate the contamination level and its effect of sample size on the measurements. The blank results obtained (Figure 7) showed consistent results down to the 0.5 mg carbon content, the blank in the HEKAL Lab does not vary significantly for samples of this size. For smaller-sized samples (<0.5 mg C), we prepared blanks of similar size with the unknown samples to evaluate the proper blank correction.

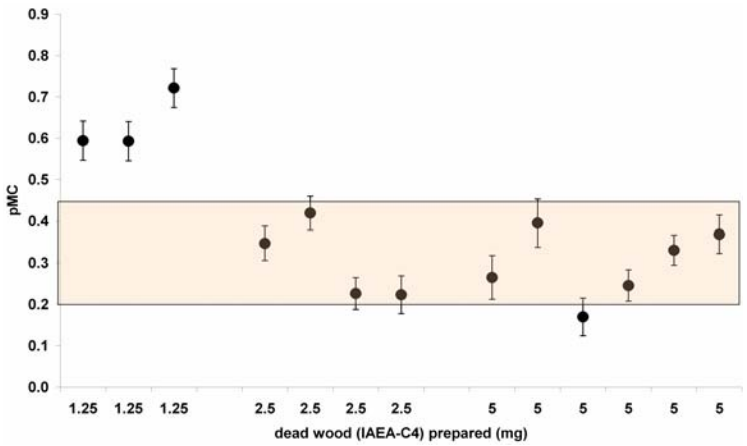

Figure 7 Sample-size dependence of processed blank using IAEA-C4 wood international ^{14}C reference material. Carbon content of the IAEA C-4 sample is ~40%.

To investigate reproducibility in the sample preparation process, the known activity ^{14}C reference organic material from IAEA (C5 wood, 23.05 ± 0.02 pMC) was prepared using different sample sizes. The results obtained (Figure 8) showed excellent agreement with the reference value in all cases, regardless of size.

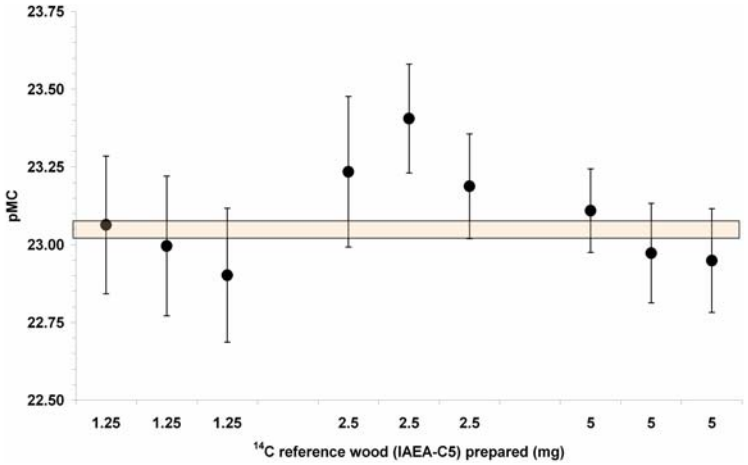

Figure 8 Sample-size dependence of ^{14}C results of processed IAEA-C5 wood. Carbon content of the IAEA C-5 wood sample is ~40%.

Bone/Collagen Samples

To assess bone- and collagen-extraction procedures at HEKAL, we studied known-age bone samples that had been previously analyzed at the NSF ^{14}C AMS Facility, Tucson, Arizona, USA (Stafford et al. 1991), although using different sample preparation techniques. To measure the ^{14}C contamination during the AMS analyses, an old (10 kyr BP) bone sample from the Dent Mammoth (Stafford et al. 1991) was prepared, 0.5 g of each. The results obtained in the Debrecen laboratory (DeA- codes in Figure 9) showed excellent agreement with the earlier published NSF results (AA-code in Figure 9). This confirms that the ^{14}C contamination level at our laboratory is not significant for bone samples of ~0.5 g or more.

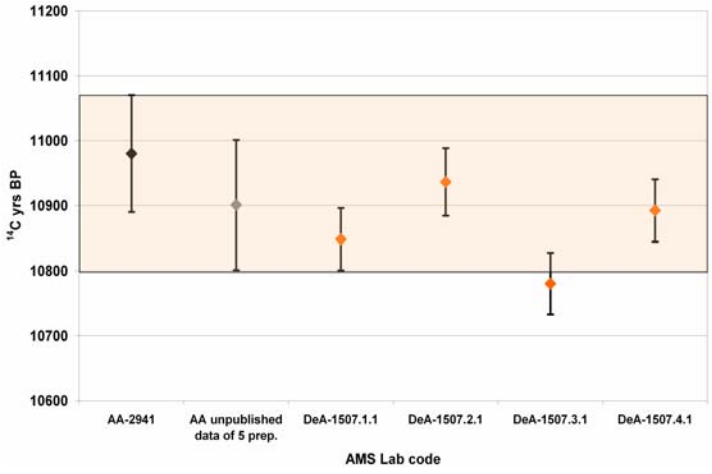

Figure 9 Comparison of NSF (AA-) and HEKAL (DeA-) results for the same old mammoth bone (Dent Mammoth Bone).

To investigate the sample preparation reproducibility and possible extra contamination effect by an optional ultrafiltration process, a known-age bone sample, previously dated by GPC at HEKAL,

was prepared several times for AMS ^{14}C analyses (0.5 g bone for each preparation). The results obtained (Figure 10) showed very good reproducibility and excellent agreement with the classical GPC measured value in the case of ultrafiltration.

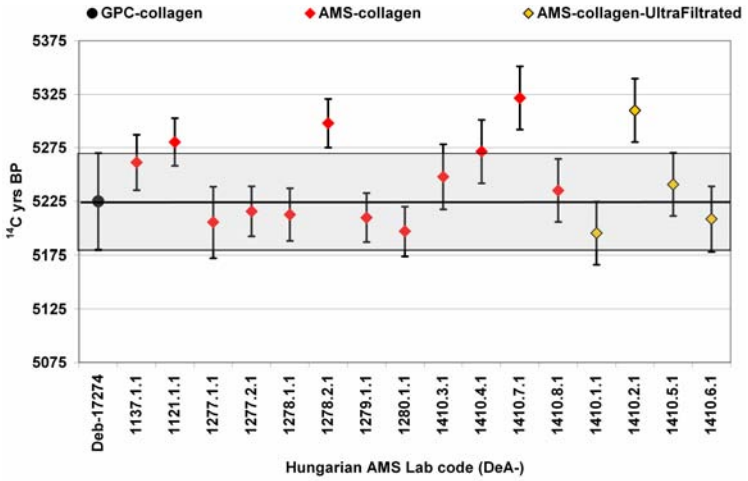

Figure 10 Repeatability and ultrafiltration test using a GPC-dated bone sample of HEKAL

Carbonate Samples

We analyzed IAEA reference materials with known ^{14}C activity to establish our blank for carbonate samples. To measure possible ^{14}C contamination during AMS analyses, IAEA-C1 reference carbonate samples were prepared using different amounts of the sample. The blank results obtained (Figure 11) showed that the ^{14}C contamination level in the HEKAL Lab is not significant for samples down to 1 mg carbon. For smaller-sized samples (<1 mg C), it is necessary to prepare parallel blank samples together with those of unknown activity samples to obtain the appropriate blank correction. We also analyzed the ^{14}C reference IAEA carbonate material C2 travertine (41.14 ± 0.03 pMC) to establish sample reproducibility. These results (Figure 11) are in excellent agreement with the reference value for 3 repeated sample preparations.

Water Samples

As a ^{14}C reference groundwater sample was not available, we prepared reference materials with a known ^{14}C concentration for water samples by adding Milli-Q®, deionized water to IAEA C-2 (pMC: 41.14 ± 0.03%) and C-1 (blank) standards. In this process, we dissolved 20 mg of C2 reference carbonates in water acidified with phosphoric acid. The dissolved inorganic carbon (DIC) was then prepared following the normal procedure used for groundwater samples.

As a comparison of the possible sample preparation, a ^{14}C blank between the 2 different methods (LDC and static HDC) IAEA-C1 reference carbonate samples were prepared (20 mg C1 carbonate per sample). The blank results obtained (Figure 12) showed that ^{14}C blank levels for the LDC approach are higher than those of the HDC method, but still acceptable for normal AMS analyses, with proper blank correction. In case of the LDC blank preparation, we have added a few hundred cm^3 of Milli-Q water above the IAEA C-1 blank carbonate to simulate the real conditions for water sample preparation. This may be responsible for the elevated blank levels, if the Milli-Q water contained a tiny amount of DIC carbon. To compare the methods, we measured IAEA C2 travertine

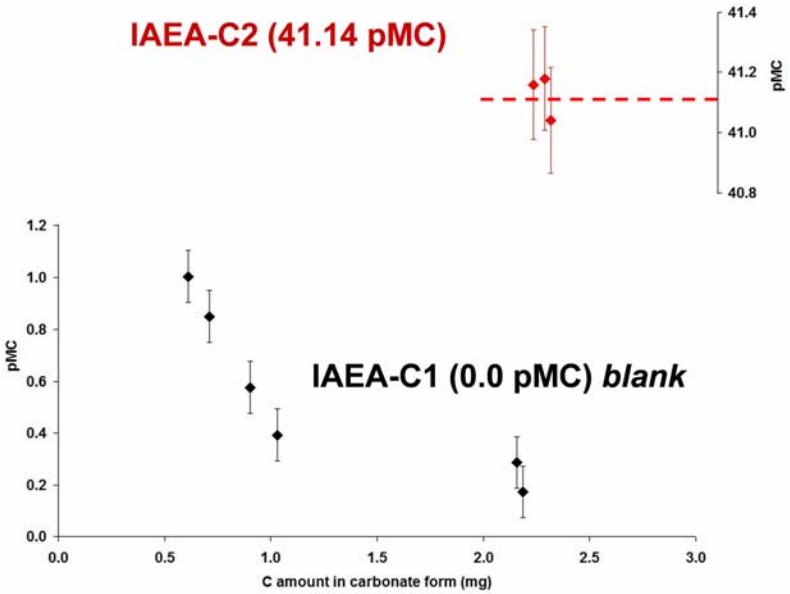

Figure 11 ^{14}C results obtained for blank (IAEA-C1) and a known activity (IAEA-C2) reference carbonate material.

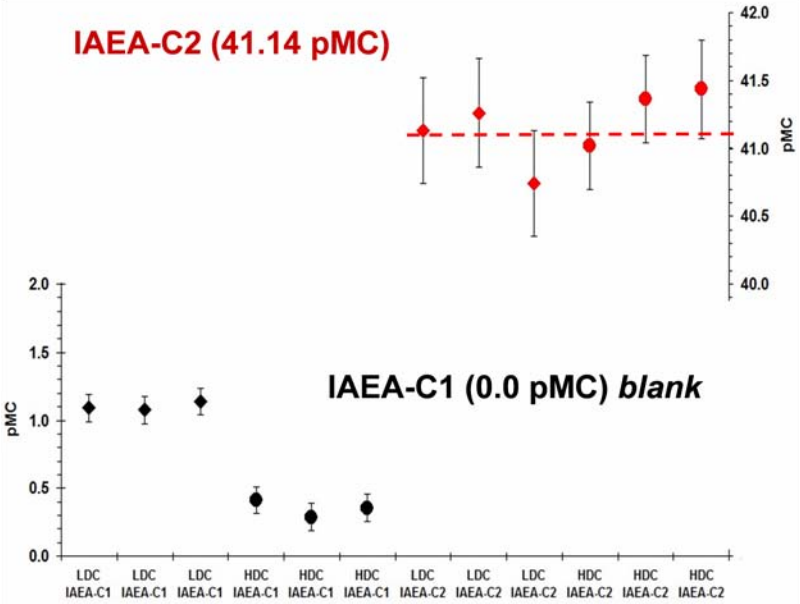

Figure 12 ^{14}C results obtained for blank (IAEA-C1) and a known activity (IAEA-C2) reference carbonate material using the low dissolved carbonate (LDC) and high dissolved carbonate (HDC) water sample preparation methods described in the text.

using both methods. The results obtained (Figure 12) showed excellent agreement with the reference value for both (LDC and HDC) methods.

SUMMARY

In 2011, improved technological methods and equipment were added to the pre-existing ^{14}C counting facility in Hungary, based on AMS using a small MICADAS system. The advantage of the new method is that it requires much smaller sample quantities (0.01–100 mg) than counter methods (1–100 g), which significantly expands the scope of possible applications and research fields. In addition, the AMS technique can provide 10 times higher throughput of samples, when compared to our previous method.

In this project, a further improved AMS technique dedicated to ^{14}C studies was developed in connection with environmental research. We anticipate the new equipment to have many applications to environmental samples as our AMS is equipped with a gas inlet system to handle CO_2 samples. This unique EnvironMICADAS developed for environmental studies is a first in eastern Europe and one of very few in the world where on-line gas handling can be accomplished.

The newly developed sample preparation system in HEKAL can handle the samples as 1) organic material, 2) cellulose fraction of plant, 3) bones, 4) carbonate and shell, and 5) dissolved inorganic carbon of groundwater. The results of ^{14}C measurements of intercomparison samples provide evidence of the reliability of the sample preparation system at HEKAL Lab and also the good performance of the MICADAS ^{14}C system. The blank level for each type of samples in case of 1 mg C carbon content is well reproducible around 0.3–0.5 pMC.

ACKNOWLEDGMENTS

Special thanks to the engineers and technical staff of ETHZ and HEKAL for their great job during the development and installation of the EnvironMICADAS, its gas interface, and the HEKAL sample preparation laboratory. These infrastructure developments were financed by Isotoptech Zrt (Debrecen, Hungary) and the Hungarian Academy of Sciences and were performed in part under the New Hungary Development Plan under Project No. GOP-2.1.1-09/A-2009-2008 and GOP-1.3.1-09/A-2009-0032. The research was also supported by the Hungarian Government, managed by the National Development Agency, and financed by the Research and Technology Innovation Fund (ref code: OTKA MB08-A 81515).

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