

PROGRESS IN RADIOCARBON TARGET PREPARATION AT THE ANTARES AMS CENTRE

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ABSTRACT. We present routine methods of target preparation for radiocarbon analysis at the ANTARES Accelerator Mass Spectrometry (AMS) Centre, as well as recent developments which have decreased our procedural blank level and improved our ability to process small samples containing less than 200 µg of carbon. Routine methods of ¹⁴C sample preparation include sample pretreatment, CO₂ extraction (combustion, hydrolysis and water stripping) and conversion to graphite (graphitization). A new method of cleaning glassware and reagents used in sample processing, by baking them under a stream of oxygen, is described. The results show significant improvements in our procedural blanks. In addition, a new graphitization system dedicated to small samples, using H₂/Fe reduction of CO₂, has been commissioned. The technical details of this system, the graphite yield and the level of fractionation of the targets are discussed.

INTRODUCTION

The radiocarbon target preparation laboratory at the ANTARES Accelerator Mass Spectrometry (AMS) Centre prepares ~1000 samples per annum for research projects in archaeology, Quaternary sciences, oceanography and global climate change (Lawson et al. 2000; Tuniz et al. 1997). The laboratory deals with a great variety of sample types such as wood, charcoal, bone, textile and beeswax (archaeology); sediment, peat, shell, coral and foraminifera (Quaternary sciences); seawater (oceanography); and tree rings and CO₂ from ice cores (global climate change). With the increasing demand for dating by AMS, especially for dating small samples, new methods and equipment have been developed to improve procedural blanks and to expand the capability of the laboratory in handling small samples containing less than 200 µgC (throughout this document we use symbols µgC and mgC as the shortened forms of µg and mg of carbon, respectively). In this paper, routine methods of target preparation and recent developments at the radiocarbon laboratory of the ANTARES AMS Centre are described.

ROUTINE METHODS OF TARGET PREPARATION

Sample Pretreatment

Samples are physically and chemically pretreated to remove contamination before they are converted to CO₂. The method and the intensity of the pretreatment depend on the type, quality, quantity, likely age and surrounding environment of the sample. Physical treatments consist of cleaning, sorting, grinding or milling, and sieving. Chemical treatments include the standard A-A-A (acid-alkali-acid) for charcoal, wood, sediment and peat; alpha-cellulose extraction from wood and tree ring (Hua et al. 2000); collagen extraction from bone (Brown et al. 1988; Law and Hedges 1989; Longin 1971); and pollen separation from sediment (Gillespie 1991; Regnell 1992; van der Kaars 1997).

CO₂ Extraction

Pretreated organic samples are converted to CO₂ by combustion using the sealed-tube technique (Vandeputte et al. 1996). Vycor[®] silica tubes (6 mm OD × 190 mm) and CuO wire (technical grade) used in the combustion are pre-cleaned at 900 °C in air for at least 3 hr. The pretreated sample (several to tens of milligrams depending on sample type) together with silver wire (99.9% pure) and pre-

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cleaned CuO (0.5–1 g), are placed in a pre-cleaned combustion tube. The sample tube is attached to a vacuum line, evacuated and flame sealed. Sealed-tubes are then placed in a muffle furnace and heated to 900 °C for 5 hr for the combustion of samples. After slow cooling (at least 4 hr), the sample tubes are re-attached to a vacuum line and cracked under vacuum by using a tube cracker. After removing water vapor by using a dry ice/ethanol trap (–78 °C), the sample CO₂ is cryogenically transferred to a known-volume using LN₂, and the frozen sample is opened to vacuum for 20 seconds to remove incondensable gases. The yield of pure CO₂ is then measured manometrically with a capacitive pressure transducer.

Pretreated carbonate samples such as shells, corals and foraminifera are hydrolyzed to CO₂ using a modified method of Hoefs (1987). In this method, the carbonate sample (10–20 mg) and H₃PO₄ (85%, ~2 mL) are placed at the bottom and in the side arm of a glass reaction vessel, respectively. The reaction vessel is attached to a vacuum line, evacuated and tap-sealed. The phosphoric acid is tipped over the sample and the reaction is maintained at 60 °C overnight. The following day, the sealed reaction vessels are re-attached to a vacuum line. As the required vacuum is reached, the reaction vessel's tap is opened to transfer sample CO₂ to the line. After removal of water (using a dry ice/ethanol trap) and incondensable gases, the sample CO₂ is cryogenically transferred to a standard volume for determination of CO₂ yield.

Dissolved inorganic carbon from water samples is stripped out as CO₂ gas using a method described by McNicholl and Jones (1991). Water samples are stored at 3–4 °C prior to processing. To prevent ingress of atmospheric CO₂, the water sample (200–500 mL) is transferred to the sparging unit, under nitrogen. Inorganic carbon from groundwater and seawater is extracted by sparging the acidified water with He gas for 15 minutes. The gas is recirculated, passing through two dry ice/ethanol traps to remove water, and a LN₂ trap to condense the CO₂. After removal of the He and other incondensable gasses, the yield of CO₂ is determined by transferring to a standard volume and measuring the pressure.

The sample CO₂ extracted from combustion, hydrolysis and water stripping steps are finally stored in glass vials sealed with Viton O-ring stopcocks, ready for graphitization.

Graphitization

Graphite targets are prepared in single tubes by the reduction of carbon dioxide using zinc (400 °C) and iron catalyst (600 °C) in the presence of small amount of hydrogen (Jacobsen et al. 1997). Approximately 400–600 mg of Zn powder (>99.5% pure) and about 1 mg of –325 mesh Fe powder (99.9% pure) are used for each graphitization reaction. Pyrex[®] glass tubes (6 mm OD × 150 mm) used in the reaction are pre-cleaned at 600 °C in air for at least 3 hr. There are 8 graphitization units for routine sample processing. The volume of each unit, including a capacitive pressure transducer (Leybold[®] DI 2000), is ~13 mL. The gas pressure of each graphitization reaction is monitored by a PC. A typical reaction lasts 6–10 hr. On the completion of the graphitization reaction, the graphite iron mixture is pressed into an aluminium cathode (either by front or rear loading) for ¹⁴C analysis using the ANTARES facility (Lawson et al. 2000).

IMPROVEMENT IN PROCEDURAL BLANKS

A new method of cleaning glassware and chemicals used in the sample processing has been recently developed. Vycor[®] tubes and CuO (for combustion), and Pyrex[®] tubes (for graphitization) are pre-cleaned in a large tube furnace (75 mm ID × 400 mm) at 600 °C for 2 hr under a stream of pure oxygen (1 L/min), instead of in air as described in the previous section. To evaluate the effectiveness of

this method in reducing contamination, two series of blanks ranging from 20 to 2000 μgC were prepared, using reagents and apparatus pre-cleaned by the new method (silver wire was not pretreated), and measured by AMS. We used spectroscopic grade powdered graphite (Lot No. 40V) from Union Carbide Corporation and bottled CO_2 (research grade, gas code 160) from BOC Pty Ltd as blank materials for combustion and graphitization, respectively.

An improvement in our procedural blanks is found for both processes. For procedural blanks, we find that there is a fixed amount of contamination (assumed to be modern level of 100 pMC) incorporated during sample processing. For combustion, contamination is significantly reduced from 1.92 ± 0.04 to $0.26 \pm 0.02 \mu\text{g}$ of modern carbon (Figure 1). Meanwhile for graphitization, contamination is slightly reduced from 0.18 ± 0.03 to $0.14 \pm 0.02 \mu\text{g}$ of modern carbon (Figure 2). These results indicate that the new cleaning method is more effective in the removal of trace amounts of carbon on the glassware and CuO reagent used in sample processing.

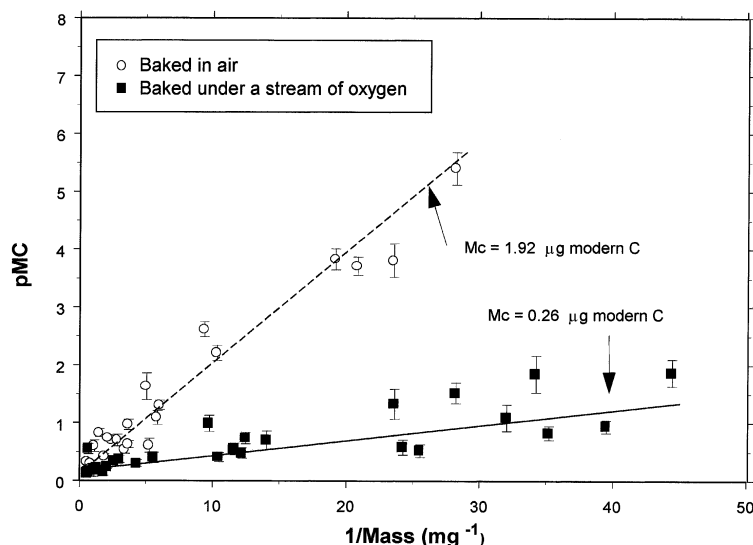


Figure 1 pMC versus inverse sample carbon mass for combustion blanks. Spectroscopic grade powdered graphite from Union Carbide Corporation was used as blank material. Contamination is significantly reduced to $0.26 \mu\text{g}$ of modern carbon.

The contamination incurred during processing of organic samples is currently $0.26 \pm 0.02 \mu\text{g}$ of modern carbon, of which $0.14 \pm 0.02 \mu\text{g}$ derives from graphitization. This reduced contamination has extended our limit for radiocarbon dating to $\sim 50,000$ years for organic samples containing 1 mgC . The accelerator background corresponding to $\geq 55,000$ years, determined by measuring unprocessed spectroscopic grade graphite, is a small contribution to our background limits (Lawson et al. 2000).

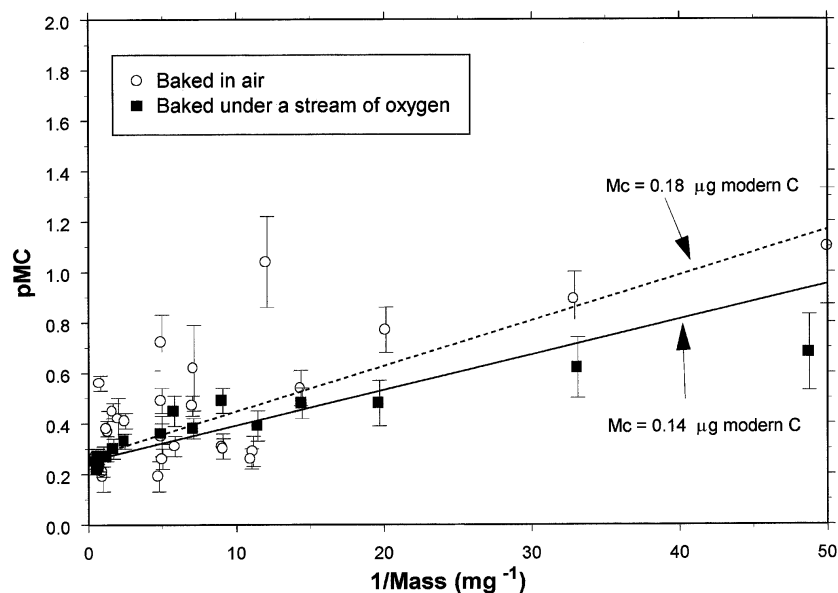


Figure 2 pMC versus inverse sample carbon mass for graphitization blanks. Bottled CO₂ gas from BOC Pty Ltd was used as blank material. Contamination is slightly reduced to 0.14 μg of modern carbon.

GRAPHITIZATION OF SMALL SAMPLES

Description of the New Graphitization System

A new graphitization system dedicated to small samples containing less than 200 μgC has been recently commissioned. Carbon dioxide is reduced to graphite over iron catalyst (600 °C) in the presence of excess H₂ (Vogel et al. 1984). The new graphitization system (Figure 3a) consists of 10 individual units: 6 for the left manifold and 4 for the right one. The set-up of a single reaction unit is shown in Figures 3b and 3c. A fixed amount of ~1 mg iron powder (–325 mesh, 99.9% pure) is loaded into a Pyrex[®] glass tube (6 mm OD × 65 mm). The tube is attached to one end of a union cross (modified from a Cajon[®] Ultra-Torr union tee). The top end of the union cross is connected to a small-volume pressure transducer (Micro Switch 142PC30A, Honeywell Corporation) to monitor reaction progress. The lower end of the union cross is connected to a cold finger (Pyrex[®] glass tube of 6 mm OD × 47 mm), where a two-stage Peltier cell (–39 °C) is positioned during the reaction to condense water vapor, a by-product from the reduction reaction. An Embell[®] stopcock is attached to the other end of the union cross to separate the reaction unit from the manifold. The volume of the reaction unit including the pressure transducer is ~3.5 mL. The overall assembly of these reaction units is illustrated in Figure 3c. The H₂:CO₂ ratio used in the reaction is 2.5–3:1, with a typical reaction lasting 4–8 hr. Relevant parameters of the graphitization reactions, such as temperature of the tube furnaces, temperature of the Peltier cells and the reaction gas pressure, are displayed on a control box and monitored by a PC (see Figure 3a).

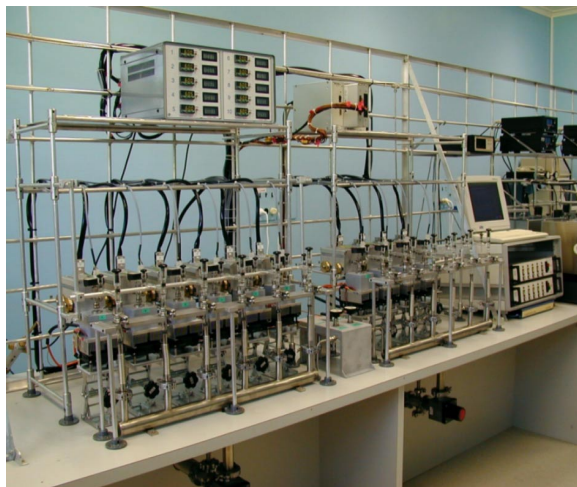


Figure 3a The new graphitization system dedicated to small samples



Figure 3b A single reaction unit of the new graphitization system

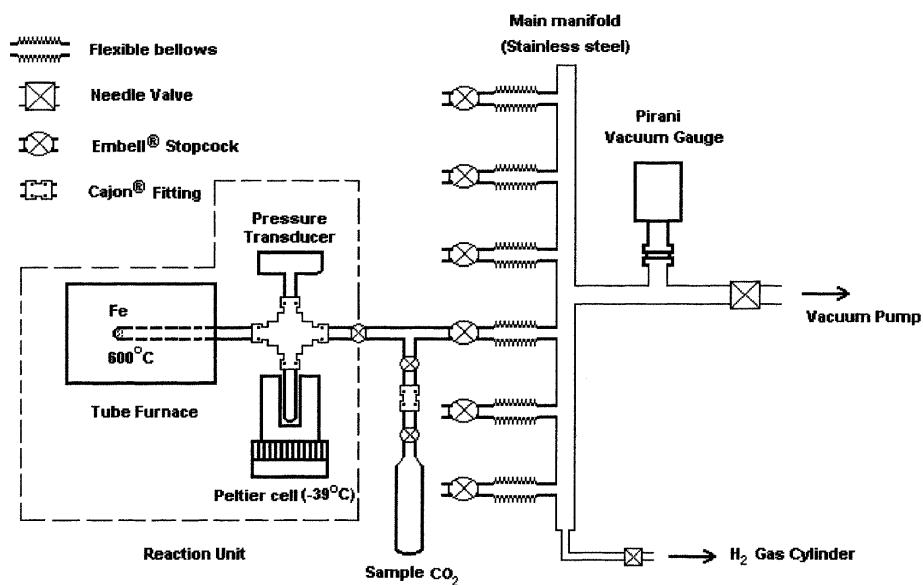


Figure 3c Schematic diagram of a single reaction unit and the overall assembly of the new graphitization system

Fractionation for Small Samples

To investigate the fractionation effects, which may occur during graphitization and the AMS measurement of small samples, ~60 small oxalic acid (HOxI) samples ranging from 13 to 250 μgC were prepared in the new graphitization system, and characterized by $\delta^{13}\text{C}$ and ^{14}C analyses.

Approximately 30 graphite targets prepared from HOxI was used for determining $^{13}\text{C}/^{12}\text{C}$ ratios using the Micromass Prism III Elemental Analyser/Isotope Ratio Mass Spectrometer (EA/IRMS) at the University of Wollongong. We define the graphite yield (or the efficiency of a graphitization reaction) as follows:

$$\text{Graphite yield} = \frac{\text{Initial pressure} - \text{Final pressure}}{3 \times \text{CO}_2 \text{ pressure}} \times 100\%$$

where the Initial and Final pressure (of a reaction) are due to both H_2 and CO_2 . The numerator of the above formula is pressure difference for an actual reaction and the denominator represents theoretical pressure difference for a 100% reaction.

Graphite yield and $\delta^{13}\text{C}$ values for small HOxI of different masses are shown in Figure 4. In both cases a clear mass-dependent trend is observed for samples $\leq 50 \mu\text{gC}$. This strongly suggests that for such samples, the deviations observed in $\delta^{13}\text{C}$ values are a result of isotopic fractionation due to incomplete graphitization reactions, as indicated by the graphite yield. A maximum isotopic fractionation of 14‰ for samples of 21 μgC is found. For samples of 50–100 μgC , the graphite yield shows a slight mass-dependence. However, such small decreases in the graphite yield do not cause significant isotopic fractionation in $\delta^{13}\text{C}$. No isotopic fractionation is observed for samples $\geq 100 \mu\text{gC}$.

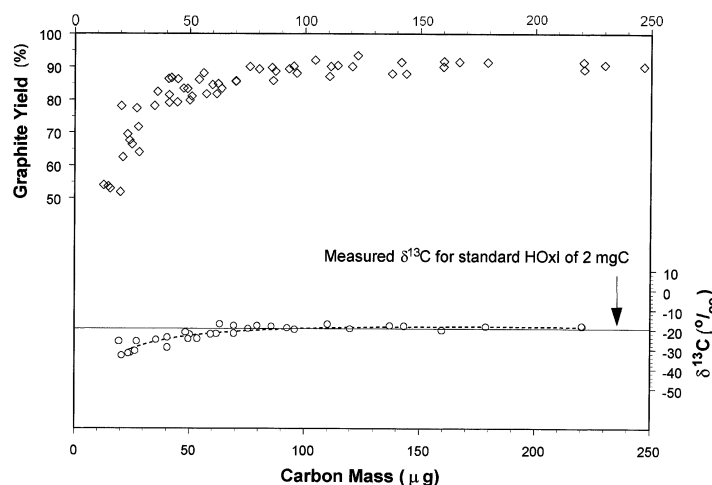


Figure 4 Graphite yield and $\delta^{13}\text{C}$ of small HOxI vs sample carbon mass. The dashed line represents the fitting curve for $\delta^{13}\text{C}$ data obtained from EA/IRMS.

The remainder of graphite targets prepared were submitted for AMS measurement using the ANTARES facility (Lawson et al. 2000). At the ANTARES AMS Centre, ^{14}C content of a sample is determined by comparing the measured $^{14}\text{C}/^{13}\text{C}$ ratio of this sample with that of standard materials such as HOxI and ANU sucrose (Hotchkis et al. 1996; Smith et al. 1994). To correct for the fractionation, which occurs during graphitization, the $^{14}\text{C}/^{12}\text{C}$ ratios of small HOxI samples were calculated

from uncorrected $^{14}\text{C}/^{12}\text{C}$ ratios (derived from measured $^{14}\text{C}/^{13}\text{C}$ ratios) and $\delta^{13}\text{C}$ values (estimated from measured $\delta^{13}\text{C}$ data by using the fitting curve shown in Figure 4). As mentioned above the carbon contamination of the procedural blanks is assumed to be of 100 pMC, very close to the level of HOxI samples, therefore the chemical blank correction is negligible and it was not applied for these small HOxIs presented here.

Figure 5 shows the $^{14}\text{C}/^{12}\text{C}$ ratios of small HOxI normalized to the corresponding values of standard HOxI (containing 2 mgC) as a function of sample mass. No significant deviation is found for samples $\geq 50 \mu\text{gC}$, except for one data point at $104 \mu\text{gC}$ where the deviation is $\sim 2\%$. A mass-dependent trend is found for samples $\leq 50 \mu\text{gC}$. A maximum deviation of less than 4% for samples of $15 \mu\text{gC}$ is observed.

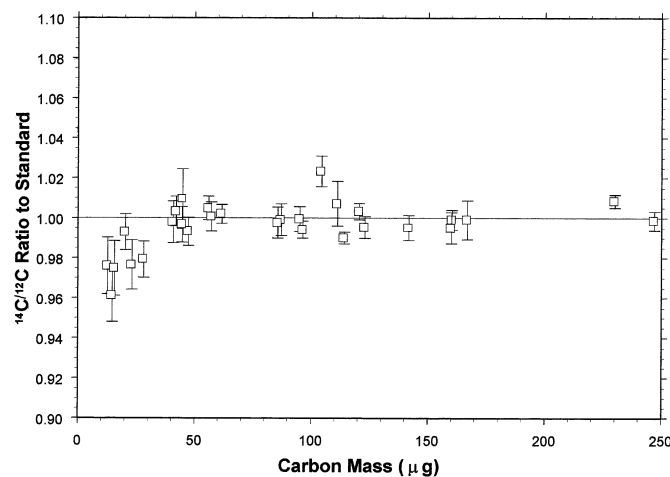


Figure 5 $^{14}\text{C}/^{12}\text{C}$ ratios of graphite prepared from HOxI of various masses. The isotopic ratios were corrected for $\delta^{13}\text{C}$ and normalized to the corresponding value of standard HOxI of 2 mgC. No procedural blank correction was applied.

This mass-dependent trend for these samples may be due to: 1) mass fractionation occurring in the ion source of the tandem accelerator (Nadeau et al. 1987), 2) the effect of contamination of less than 100 pMC (modern level) for procedural blanks (Brown and Southon 1997), or 3) a combination of the above effects (Alderliesten et al. 1998). Further investigation of this phenomenon is being carried out.

CONCLUSION

By using a more rigorous method for cleaning reagents and glassware used in sample processing—baking them under a stream of pure oxygen instead of in air—we have significantly reduced contamination for organic samples. Our sample processing limit for radiocarbon dating is now $\sim 50,000$ years for organic samples containing 1 mgC.

The new graphitization system dedicated to small samples is routinely used. The experimental results showed: 1) the system is able to handle samples as small as 13 µgC, 2) there was a high graphite yield and no significant isotopic fractionation for samples containing ≥50 µgC, and 3) for samples ranging 13–50 µgC, a clear mass-dependent trend in the graphite yield, $^{13}\text{C}/^{12}\text{C}$ and $^{14}\text{C}/^{12}\text{C}$ was observed. However, this is not a problem for AMS analysis of such small samples if the samples are measured against HOxI standards of similar sizes.

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REFERENCES

- Alderliesten C, van der Borg K, de Jong AFM. 1998. Contamination and fractionation effects in AMS-measured $^{14}\text{C}/^{12}\text{C}$ and $^{13}\text{C}/^{12}\text{C}$ ratios of small samples. *Radiocarbon* 40(1):215–21.
- Brown TA, Southon JR. 1997. Corrections for contamination backgrounds in AMS ^{14}C measurements. *Nuclear Instruments and Methods in Physics Research B*123:208–13.
- Brown TA, Nelson DE, Vogel JS, Southon JR. 1988. Improved collagen extraction by modified Longin method. *Radiocarbon* 30(2):171–7.
- Gillespie R. 1991. Charcoal dating—oxidation is necessary for complete humic removal. *Radiocarbon* 33(2): 199.
- Hoefs J. *Stable Isotope Geochemistry*. Third Edition, Springer-Verlag, Berlin, 1987.
- Hotchkis MAC, Fink D, Hua Q, Jacobsen GE, Lawson EM, Smith AA, Tuniz C. 1996. High-precision radiocarbon measurements at the ANTARES AMS Centre. *Nuclear Instruments and Methods in Physics Research B*113:457–60.
- Hua Q, Barbetti M, Jacobsen GE, Zoppi U, Lawson EM. 2000. Bomb radiocarbon in annual tree rings from Thailand and Australia. *Nuclear Instruments and Methods in Physics Research B*172:359–65.
- Jacobsen GE, Hua Q, Tarshishi J, Fink D, Hotchkis MAC, Lawson EM, Smith AM, Tuniz C. 1997. AMS radiocarbon analysis of microsamples. In: Handbook of the Sixth Australasian Archaeometry Conference, 10–13 February 1997, Sydney, Australia. p. 36.
- Law IA, Hedges REM. 1989. A semi-automated bone pretreatment system and the pretreatment of older and contaminated samples. *Radiocarbon* 31(3):247–53.
- Lawson EM, Elliott G, Fallon J, Fink D, Hotchkis MAC, Hua Q, Jacobsen GE, Lee P, Smith AM, Tuniz C, Zoppi U. 2000. AMS at ANTARES — the first 10 years. *Nuclear Instruments and Methods in Physics Research B*172: 95–9.
- Longin R. 1971. New method of collagen extraction for radiocarbon dating. *Nature* 230:241–2.
- McNicholl AP, Jones GA. 1991. Measuring ^{14}C in seawater ΣCO_2 by Accelerator Mass Spectrometry, WHP Operations and Methods. In: Joyce T, Corry C, Stalcup M, editors. 1991. *WOCE operations manual*. Part 3.1.2, Requirements for WHP data reporting. Woods Hole, Massachusetts: WHPO Publication. 90-1:71 p.
- Nadeau MJ, Kieser WE, Beukens, RP, Litherland AE. 1987. Quantum mechanical effects on sputter source isotope fractionation. *Nuclear Instruments and Methods in Physics Research B*29:83–6.
- Regnell J. 1992. Preparing pollen concentrates for AMS Dating—a methodological study from a hard-water lake in southern Sweden. *Boreas* 21:373–7.
- Smith AM, Fink D, Hotchkis MAC, Jacobsen GE, Lawson EM, Shying M, Tuniz C, Watt GC, Fallon J, Ellis PJ. 1994. Equipment and methodology for high precision, high throughput ^{14}C AMS analyses at ANTARES. *Nuclear Instruments and Methods in Physics Research B*92:122–8.
- Tuniz C, Fink D, Hotchkis MAC, Jacobsen GE, Lawson EM, Smith AM, Hua Q. 1997. Research and measurement program at the ANTARES AMS facility. *Nuclear Instruments and Methods in Physics Research B*123:73–8.
- van der Kaars W. 1997. Modification of the standard palynological procedure (personal communication).
- Vandeputte K, Moens L, Dams R. 1996. Improved sealed-tube combustion of organic samples to CO_2 for stable isotopic analysis, radiocarbon dating and percent carbon determinations. *Analytical Letters* 29(15): 2761–73.
- Vogel JS, Southon JR, Nelson DE, Brown TA. 1984. Performance of catalytically condensed carbon for use in Accelerator Mass Spectrometry. *Nuclear Instruments and Methods in Physics Research B*5:289–93