REDUCTION OF CO$_2$-TO-GRAPHITE CONVERSION TIME OF ORGANIC MATERIALS FOR ^{14}C AMS

METTE S. THOMSEN and STEINAR GULLIKSEN

Radiological Dating Laboratory, The Norwegian Institute of Technology, N-7034 Trondheim Norway

ABSTRACT. Graphite is the most common type of target for ^{14}C accelerator mass spectrometry (AMS). It is readily produced by catalytic reduction of CO$_2$, but the presence of a small amount of impurities (*e.g.*, sulfur compounds) may retard the reaction. We have tested some techniques to find a method that reduces the impurity content of CO$_2$ produced by combustion of organic material. We found that using water during combustion reduces the average time for graphite conversion of CO$_2$ from organic matter from >3 h to *ca.* 2 h. This is the time for graphite production from CO$_2$ obtained by acid hydrolysis of calcite. Measurements of known-age and background samples show that this combustion method neither changes the isotopic ratios nor introduces any additional background.

INTRODUCTION

Graphite is the most common type of sputtering target used in ^{14}C accelerator mass spectrometry (AMS). We produce graphite by the catalytic reduction of CO$_2$ by hydrogen over an iron-group metal powder (Vogel *et al.* 1984). At the Radiological Dating Laboratory (T) in Trondheim, we are now preparing graphite targets that are dated at the Uppsala Tandem Accelerator Laboratory (Ua). With our apparatus for CO$_2$-to-graphite conversion, we found a constant reaction time of two hours for CO$_2$ produced by acid hydrolysis of carbonate samples. However, CO$_2$ obtained by combustion of organic samples showed large variations in reaction time (up to more than seven hours), and for some samples conversion did not succeed.

Organic material contains sulfur and nitrogen compounds, which form gaseous impurities during combustion. The effect of these impurities on graphite formation has been studied for more than three decades (Podgurski 1954; Olsson & Turkdogan 1974). Reduction of CO$_2$ to graphite takes place in several steps, which include dissociation of the carbonaceous gas on the surface of the catalyst and formation of a metal carbide. Graphite is then precipitated from the carbide. This precipitation is inhibited by several non-metallic compounds (Klemantaski 1952; Podgurski 1954), as they combine chemically with the metal surface, and thereby block the nucleation of graphite. Podgurski (1954) showed that absorption of a monolayer of sulfide on the catalyst surface was sufficient to cause retardation of the graphite precipitation.

Thus, large variations in reaction time for organic samples should be avoided if CO$_2$ is purified prior to reduction. In gas counting laboratories, purification of CO$_2$ to remove electronegative elements is a standard procedure (*e.g.*, Freundlich & Rutloh 1972), because more than about 1 ppm of impurities in CO$_2$ will impede counting (de Vries 1955/6).

We have tested various methods of CO$_2$ purification and find that the most efficient is using water during combustion. ^{14}C and δ^{13}C measurements on samples with known isotopic content agree with the expected values, and no additional ^{14}C background is introduced during combustion when water is used.

METHODS

During our standard combustion procedure, the sample is mixed with *ca.* 0.5 g CuO powder in a quartz dish placed in a quartz tube. The tube is connected to the CO$_2$ preparation line (Fig. 1) and heated to ~900°C with a gas torch. The CO$_2$ is dried by a cold trap at −78°C and transferred to

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the graphitization apparatus. For the measurements presented here, we used a modified version (G. Possnert, personal communication) of the forced-circulation apparatus described by Hut, Östlund and van der Borg (1986). In the apparatus, the graphite sample is produced directly onto a copper disk which fits into the sample wheel of the ion source. The catalyst is a 99.9% pure, −325 mesh iron powder, and the oven temperature is 625°C. Prior to admission of CO_2, the sample holder and ~1 mg Fe is heated at 700°C in vacuum for 10 min. We found that this step generally reduced the reaction time of CO_2 from calcite samples *ca.* 30 min. The pressure of $CO_2 + H_2$ *vs.* time (initial pressure 100 to 500 mb; H_2 to CO_2 ratio ~4) is monitored continuously by solid state pressure transducers and an x-t recorder. The reaction time is defined as the time interval from when the oven is switched on until the pressure in the apparatus is constant.
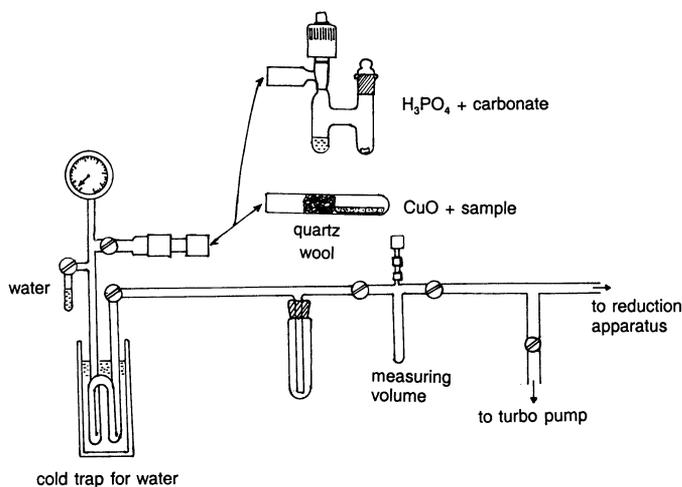

Fig. 1. The CO_2 preparation line

The following procedures were tested in the attempt to find a simple method to obtain a CO_2 reduction time independent of the origin of the sample gas: 1) Combustion with Ag wool was carried out by placing it between the sample dish and the quartz wool in the combustion tube. In this position, it reached a temperature of 400–500°C during combustion. 2) The action of silver during CO_2 reduction was also tested by placing some Ag wool beside the copper holder with the iron catalyst. 3) Repeated sublimation of CO_2 at −78°C followed by condensation at −196°C was an attempt to obtain a purification by using differences between the vapor pressure of CO_2 and some possible contaminating compounds (de Vries 1955/6). 4) The effect of water for removal of impurities at room temperature was tested by mixing CO_2 with saturated water vapor. After 30 min, the CO_2 was dried by a cold trap at −78°C and transferred to the reduction apparatus.

We also tested the presence of water during the combustion. First, we pretreated the CO_2 preparation line, including the combustion tube, with *ca.* 25 mbar water vapor as a "cleansing" agent (Vogel, Nelson & Southon 1989). Next, *ca.* 5 mg distilled water was condensed in the cold finger of the combustion line. During the following thawing of the water by a hot-water bath, the pressure increased to *ca.* 30 mbar and fine drops of water developed on the glass walls. The sample was then heated with a gas torch (T ~900°C) for 5–10 min, until the pressure remained constant for some minutes. After cooling of the gas, the water was condensed at −78°C, and the CO_2, now ready for reduction, was transferred to the measuring volume.

RESULTS AND DISCUSSION

Table 1 shows that many of the procedures we tested had no significant effect on the reduction

time of CO_2 from the selected sample. Gurfinkel (1987) reported that she used silver wire in the combustion tube to remove sulfur and halogen compounds during the combustion of AMS samples. Although we did observe a shorter reduction time (4 h) for the sample when silver wool was present during combustion, only 64% of the CO_2 had been reduced when the pressure stopped decreasing. We further tested this method by transferring a CO_2 sample to a separate oven containing copper and silver at 450°C. However, we observed no improvement of the reaction time after a 12-h treatment of the CO_2 in this oven.

TABLE 1. Procedures applied to ~1 mg C aliquots of a sample for which the reduction time of CO_2 from a standard combustion was 4 times longer than for CO_2 from carbonate samples

Combustion procedure	Treatment after combustion	Reaction time
Standard	None	8 h
Standard	CO_2 reduction with Ag wool	7 h 30 min
With Ag wool	None	Pressure constant after 4 h but 36% of CO_2 did not react
Standard	Sublimation (–78°C) and condensation (–196°C) of CO_2 several times	>8 h
Standard	$CO_2(g)$ mixed with $H_2O(g)$ + $H_2O(l)$ at 25°C for 30 min	>8 h
With $H_2O(g)$ + $H_2O(l)$	None	2 h 30 min

The only procedure gaining a complete reduction of CO_2 within a shorter time was the addition of water during combustion. Combustion with water has been done for several years in conventional ^{14}C laboratories that use the bomb combustion technique (Barker, Burleigh & Meeks 1969). More than 99.9% of the sulfur and nitrogen contaminants are removed in the bomb (Dörr, Kromer & Münnich 1989) by precipitation as nitric and sulfuric acid on the wall of the reaction vessel. A corresponding effect is obtained in the simple combustion line for AMS-sized samples described above.

We found, in contrast to the pronounced effect of adding water during combustion, that treatment of CO_2 gas with water vapor at room temperature did not improve the reduction time. This suggests that the elevated temperature – and kinetic energy of the molecules – enhance the probability for collisions yielding reactions between gaseous impurities and the water molecules.

We have oxidized a large number of organic samples submitted for dating by the new method. Table 2 shows the average reduction times for CO_2 from combustion of various types of organic samples. For comparison, the average value for reduction of 22 samples of CO_2 produced by acid hydrolysis of calcite and mollusk shells is also shown. The average reduction time for charcoal samples did not change by adding water during combustion. Further, this value (2 h) agrees with the average value for carbonate samples. For the other types of organic material, the average reaction time was reduced from >3 h to *ca.* 2 h. This indicates that the method is efficient enough to produce CO_2 by combustion of organic material that is as pure as CO_2 obtained by acid hydrolysis of carbonate samples.

To see if the reaction time, in general, could be reduced to less than two hours, we also tested another design of apparatus for CO_2-to-graphite conversion. This was a modified version of the one developed by Lowe and Judd (1987) based on a small volume and a higher start pressure of the CO_2 + H_2 mixture. We used an initial pressure of *ca.* 1500 mbar and a H_2 to CO_2 ratio of about 4. With this design, we were able to obtain complete reduction (estimated from the pressure de-

TABLE 2. Average CO$_2$-to-graphite conversion times for carbon dioxide from combustion of various types of organic samples

Sample material	Standard combustion		Combustion with water	
	Reaction time (min)*	#	Reaction time (min)*	#
Charcoal	115 ± 10	4	120 ± 8	5
Plant macrofossils, wood	177 ± 18**	6	126 ± 10	10
Bone gelatin	240	1	135 ± 8	10
Humic acid	188 ± 16	8	127 ± 11	5
Carbonate			120 ± 8	22

*The errors quoted are one standard error
**The reaction times of two samples of plant macrofossils (430 min and 460 min) are not included

crease) of CO$_2$ samples in the range, 200 μg to 2 mg C, in less than 1 h. However, at present, we prefer the apparatus with forced circulation because the ion-source current of samples produced in this apparatus is, on average, about a factor of two higher. The lower ion current of samples graphitized in the smaller-volume apparatus is probably due to formation of graphite filaments with a different structure during the very fast CO$_2$ reduction (Vogel, Southon & Nelson 1987).

We have measured ^{14}C and δ^{13}C of humic acid used in Stage 2 of the International Collaborative Study (ICS) (Scott *et al.* 1989). We obtained a δ^{13}C value on CO$_2$ from combustion with water, on a conventional mass spectrometer, of −28.4‰, whereas the ICS median value is −28.6‰ (E. M. Scott, personal communication). Eight targets of the humic acid were measured at the Uppsala Tandem Accelerator Laboratory and the weighted average was 3407 ± 20 BP (one standard error), in good agreement with the average ICS value of 3390 BP. Further, we measured the IAEA ^{14}C Quality Assurance Sample C3 to 129.9 ± 1.2 pMC (TUa-110; 1 σ), whereas the consensus value is 129.41 ± 0.06 pMC (Rozanski *et al.* 1992).

We determined the ^{14}C background of organic samples produced by this combustion technique by measuring wood, assumed to be of interglacial age, and gelatin from an arctic whale bone (T >80 ka). Table 3 shows the weighted averages of the measured ^{14}C concentrations. Also shown are the ^{14}C concentrations for samples of calcite (Icelandic double spar) and industrial CO$_2$, produced by combustion of natural gas (Beukens 1990). These results indicate that no additional contamination is introduced during combustion with water. Sample TUa-204, which has about a factor of two higher ^{14}C concentration than TUa-76 and TUa-121, has been stored in a non-air-tight plastic bag in the laboratory for about 25 years and may have been contaminated during storage (Gulliksen & Thomsen 1992).

TABLE 3. Weighted Average ^{14}C Concentrations of ~1 mg C Background Samples

Sample material	TUa* no.	pMC	Apparent age (BP)
Interglacial wood (Åstbrua, Norway)	-76	0.16 ± 0.03	51,800
Whale bone (Beaufort Sea, Alaska)	-121	0.18 ± 0.03	50,800
Interglacial wood (Hensmoen, Norway)	-204	0.38 ± 0.02**	44,800
CO$_2$ from natural gas	-200	0.17 ± 0.03	51,200
Double spar (Iceland)	-201	0.18 ± 0.03**	50,800

*A composite of T − Radiological Dating Laboratory, Trondheim and Ua − Uppsala Tandem Accelerator Laboratory
**The standard error of five ^{14}C measurements; other errors quoted are based on counting statistics of two measurements

Apart from reducing the CO_2-to-graphite conversion time by removal of impurities from CO_2 before reduction, this combustion technique may have another advantage. Vogel, Southon and Nelson (1987) found that the bulk isotopic fractionation of the graphite targets was a strong function of the reaction rate. If the CO_2 contains many impurities, a specific isotopic fractionation may be introduced to the sample if the transformation of metal carbide into graphite is incomplete.

CONCLUSIONS

By combustion of organic matter with water, we have avoided introducing impurities known to retard CO_2-to-graphite conversion. In this way, we have reduced the average reaction time of CO_2 from various organic materials to two hours, which also is the time for calcite samples. The measured ^{14}C concentrations of background samples indicate that this technique introduced no additional combustion background.

ACKNOWLEDGMENTS

REFERENCES

Barker, H., Burleigh, R. and Meeks, N. 1969 New method for the combustion of samples for radiocarbon dating. *Nature* 221: 49–50.

Beukens, R. P. 1990 High-precision intercomparison at IsoTrace. *In* Scott, E. M., Long, A. and Kra, R. S., eds., Proceedings of the International Workshop on Intercomparison of ^{14}C Laboratories. *Radiocarbon* 32 (3): 335–339.

de Vries, H. 1955/6 Purification of CO_2 for use in a proportional counter for ^{14}C age measurements. *Applied Science and Research* B5: 387–400.

Dörr, H., Kromer, B. and Münnich, K. O. 1989 Fast ^{14}C sample preparation of organic material. *In* Long, A. and Kra, R. S., eds., Proceedings of the 13th International ^{14}C Conference. *Radiocarbon* 31(3): 264–268.

Freundlich, J. C. and Rutloh, M. 1972 Radiocarbon dating by carbon dioxide method: Influence and removal of known impurities. *In* Rafter, T. A. and Grant-Taylor, T., eds., *Proceedings of the 8th International ^{14}C Conference*. Wellington, Royal Society of New Zealand 1: B25–B35.

Gulliksen, S. and Thomsen, M. S. 1992 Examination of background contamination levels for gas counting and AMS target preparation in Trondheim. *Radiocarbon*, this issue.

Gurfinkel, D. M. 1987 An assessment of laboratory contamination at the IsoTrace Radiocarbon Facility. *Radiocarbon* 29(3): 335–346.

Hut, G., Östlund, H. G. and Borg, K. van der 1986 Fast and complete CO_2-to-graphite conversion for ^{14}C accelerator mass spectrometry. *In* Stuiver, M. and Kra, R. S., eds., Proceedings of the 12th International ^{14}C Conference. *Radiocarbon* 28(2A): 186–190.

Klemantaski, S. 1952 Action of inhibitors of carbon deposition in iron ore reduction. *Journal of the Iron and Steel Institute, London* 171: 176–182.

Lowe, D. C. and Judd, W. J. 1987 Graphite target preparation for radiocarbon dating by accelerator mass spectrometry. *Nuclear Instruments and Methods* B28: 113–116.

Olsson, R. G. and Turkdogan, E. T. 1974 Catalytic effect of iron on decomposition of carbon monoxide: II. Effect of additions of H_2, H_2O, CO_2, SO_2 and H_2S. *Metallurgical Transactions* 5: 21–26.

Podgurski, H. H. 1954 Stabilization of metal carbides by nonmetallic elements. *Annals of the New York Academy of Sciences* 58: 959–970.

Rozanski, K., Stichler, W., Gonfiantini, R., Scott, E. M., Beukens, R. P., Kromer, B. and van der Plicht, J. 1992 The IAEA ^{14}C Intercomparison Exercise 1990. *Radiocarbon*, this issue.

Scott, E. M., Aitchison, T. C., Harkness, D. D., Baxter, M. S. and Cook, G. T. 1989 An interim progress report on Stages 1 and 2 of the International Collaborative Program. *In* Long, A. and Kra, R. S., eds., Proceedings of the 13th International ^{14}C Conference. *Radiocarbon* 31(3): 414–421.

Vogel, J. S., Nelson, D. E. and Southon, J. R. 1989 Accuracy and precision in dating microgram carbon samples. *Radiocarbon* 31(2): 145–149.

Vogel, J. S., Southon, J. R., Nelson, D. E. and Brown, T. A. 1984 Performance of catalytically condensed carbon for use in accelerator mass spectrometry. *In* Wölfli, W., Polach, H. A. and Andersen, H. H., eds., Proceedings of the 3rd International Symposium on Accelerator Mass Spectrometry. *Nuclear Instruments and Methods* B5: 289–293.

Vogel, J. S., Southon, J. R. and Nelson, D. E. 1987 Catalyst and binder effects in the use of filamentous graphite for AMS. *In* Gove, H. E., Litherland, A. E. and Elmore, D., eds., Proceedings of the 4th International Symposium on AMS. *Nuclear Instruments and Methods* B29: 50–56.