DEVELOPMENTS IN SAMPLE COMBUSTION TO CARBON DIOXIDE, AND IN THE OXFORD AMS CARBON DIOXIDE ION SOURCE SYSTEM

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ABSTRACT. We describe the operation of a commercial system as modified for preparation of CO_2 for the CO_2 source. AMS samples are automatically combusted in a CHN analyzer, and stable isotope measurements are made on line. We describe the performance of this equipment, with reference to yield, sample contamination, memory effect, accuracy of isotope measurement, convenience and cost. We discuss the current status of dating using the CO_2 source. This is the only source in operation at Oxford, and has been in routine dating since September 1989. We assess the practicalities of operation, including the latest measurements on background, memory, sample-size requirements and operating schedules. We also describe modifications to the sputter beam optics and to the gas handling systems.

INTRODUCTION

We describe here two technical advances in the conversion of a sample for AMS dating from its pretreated state to a beam of C^-. These are: 1) the use of an automated CHN analyzer interfaced with a stable isotope ratio mass spectrometer to combust the sample to CO_2; and 2) the subsequent generation of C^- from the CO_2. Whereas the two techniques could be directly interfaced, with the output from the CHN analyzer being fed directly to the ion source, it is logistically more convenient to store prepared CO_2 in sealed ampoules until scheduled for AMS analysis. The CO_2 source has been described previously (Bronk & Hedges 1987, 1989, 1990), so that here we present an update based on running experience since September 1989.

AUTOMATED SAMPLE COMBUSTION

The system used is commercially available (Europa Scientific, Crewe, England), requiring only the building of a sample collection facility. It is shown schematically in Figure 1.

Principle of Operation

Samples can be introduced as solid, liquid or gas. The solid sample is enclosed in a high-purity tin capsule which, after purging from atmospheric gases, is dropped into an oven at 1000°C, through which a flow of helium passes (1 ml atm sec^{-1}). A pulse of high-purity oxygen is timed to coincide with the sample drop, and reaction with the capsule raises the temperature temporarily to about 1600°C. The sample is volatilized and oxidized both by the O_2 gas, and by the solid bed of Cr_2O_3. Materials other than Sn may be used, and additional oxidants (*e.g.*, V_2O_5) can be added to the sample for materials that are difficult to combust. However, using the method given above, we find yields from graphite are as good as from easily volatile materials. The combustion products are carried through an oven containing Cu at 800°C, in which nitrogen oxides are reduced to nitrogen and any excess O_2 is reduced to CuO, then through a bed containing magnesium perchlorate (to remove water). Components of the gases are separated by passing through a gas chromatographic column, so that a pulse of N_2 emerges about three minutes before the CO_2 pulse. About 1% of the effluent gas flow is split off and injected into a dedicated mass spectrometer that can be electronically switched to measure ion currents first at masses 27, 28 and 29, (for N_2), and subsequently, at masses 44, 45 and 46 (for CO_2). The remainder of the gas is switched to flow through a liquid nitrogen trap during the period when CO_2 is present (*i.e.*, for *ca.* 30–40 sec, with a delay of *ca.* 6 min after the dropping of the sample). The trapped CO_2 is subsequently transferred to a glass ampoule, which is manually flame-sealed.
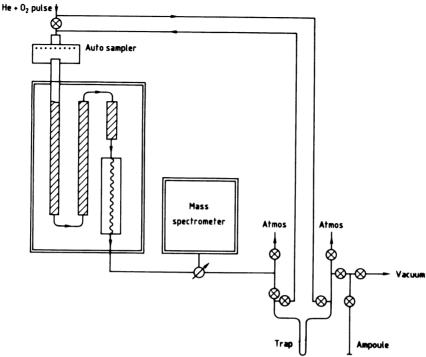
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Fig. 1. Schematic of the CHN analyzer interfaced to the stable isotope mass spectrometer and CO_2 sample collection system.

Operational Details

We aim for a standard quantity of 1–2 mg C. Most materials being combusted contain 10–60% carbon, and are easily enclosed in cylindrical tin containers, 8 mm × 5 mm in diameter. However, sediments containing 1–2% carbon pose difficulties, in that the maximum quantity that can be burned as one sample is about 40 mg. Liquid samples tend to escape from the container through capillarity, but can be immobilized by absorbing onto "chromosorb" (low carbon diatomite). Gas samples are injected as in gas chromatography. Typically, about 20 samples are run as a batch, which will include several standards. (We use granules of nylon, which is 'dead', contains suitable levels of C and N, and is easily handled). Batch operation, together with gas chromatographic and mass spectrometric data processing, is controlled by computer, takes about 2.5 h. A second computer controls the valve switching and trap temperatures for gas transfer for sample (CO_2) collection. Although the system is automated, we use only one point for CO_2 trapping to the ampoule, and the intermittent replacing and sealing of ampoules requires human intervention.

Performance

The system has worked remarkably reliably, the maintenance required being mostly changes of bed contents in the different ovens (about every 500 combustions).

Background Levels. A residual carbon level can be measured by combusting empty tin containers, *etc.* From this, the background C level is shown to be 1.2 ± 0.4 μg C. This level is proportional to the mass (area) of tin used, and depends upon prior careful cleaning. (We use cyclohexane, acetone, very dilute HCl, acetone and drying at 110°C. We have recently used Al foil, baked at 500°C, but find similar carbon levels.

The level of carbon from the O_2 pulse is only *ca.* 0.1 of this. The gas is 99.995% pure, and passed through "Carbosorb." The level of carbon contribution from the 99.9995% helium is negligible. Note that one very great advantage of this system is that levels of carbon impurities can be more or less continually monitored. Nitrogen backgrounds can easily arise through leaks in the system (despite its operation at slightly over atmospheric pressure). In general, the smallest reliable nitrogen signal is about 2 μg. The smallest sample that we have handled is about 50 μg, but with care, the system could reproducibly handle 10 μg.

¹⁴C Age of the Background. Collection of the background component from combusting 30 samples of cleaned tin gave an apparent age of *ca.* 6 ka. This seems to be typical of such measurements, but has no obvious interpretation. It does provide a measure of the background to be expected in ¹⁴C dating. The AMS measurement of the mass-dependent background on combusted samples is about twice this value (*i.e., ca.* 0.15 pMC on a 1-mg sample), and further measurements are planned to reduce this inconsistency.

Memory and Cross-Contamination. Provided combustion is "complete," cross-contamination is less than 0.5%, and is easily observed since the carbon signal can be continually monitored. It is a simple matter to alternate blanks with samples where such a level of cross-contamination is a problem. As far as we are aware, there is no general "memory" effect – results from newly changed combustion tubes, *etc.*, are no different, in terms of stable carbon or radiocarbon results, from those from unused tubes. Other combustion impurities potentially can be released from previous runs (*e.g.*, SO_2), although we have not observed any evidence for this.

Stable Isotope Measurements. The system is primarily intended for preparing AMS samples, and measuring $\delta^{13}C$ values for fractionation corrections. Of course, it could separately be used for stable isotope measurements on C and N, and for C/N ratios. The manufacturer's specification is for a precision (one standard deviation, 1 σ) of 0.2–0.3‰ on carbon and 0.5‰ on nitrogen, based on replication of similar samples. Such precision is much lower than for a dual inlet, pure CO_2 system, and is largely due to the variation of ion-source performance, as the partial pressure of sample gas changes in an atmosphere of He. Thus, the precision can be reduced if the sample quantity varies, and the effect of this depends upon the specific tuning of the instrument. However, with careful use, we can rely upon a precision of 0.5‰ for carbon. (Our experience with nitrogen is, so far, too limited to give data. The main problem, according to the manufacturers, lies in keeping the blank nitrogen suitably low.)

Advantages

Advantages are listed as follows:

- Major reduction in personnel time required to combust samples
- Stable isotope measurements and C/N ratios obtained without extra effort
- Combustion process is highly reproducible
- Product is purified by GC and yield is accurately measured
- Continuous and sensitive monitoring of combustion system for changes in background carbon level, and/or in combustion performance.

Although the equipment was commissioned to interface with the CO_2 source, it should be equally useful in preparing and purifying gas for subsequent reduction to graphite. Carbonates can be pyrolyzed to CO_2, but this will usually include the combustion of non-carbonate impurities. Therefore, with carbonates, we inject the gaseous product from acidification, thereby purifying the gas as well as obtaining a $\delta^{13}C$ ratio.

THE CO₂ SOURCE

Principle of Operation

A high-intensity Cs sputter beam, of the same basic design as that used in the current generation of AMS ion sources (*e.g.*, GIC Model 846) generates C^- from CO_2 as the gas flows over a Ti surface (Middleton 1983). In comparison to graphite, the resultant beam of C^- is reduced by about a factor of 10, but the efficiency of ion production is similar. Because graphite is produced around the sputter area, each sample ("target") must have its own (disposable) sputter environment, in much the same way as for solid samples. Figure 2 illustrates the basic principles, together with the disposable sputter head. Details of the design are to be found in the references cited.

In addition to the sputtering arrangements and changeable target heads, a CO_2 source requires a gas delivery system. Our present system handles 12 gas samples (soon to be upgraded to 18), and delivers 4 aliquots from each sample during the course of a complete dating run. The automated handling of sample gases is one of the more complex and demanding requirements for achieving satisfactory reliability. Further details are given below.
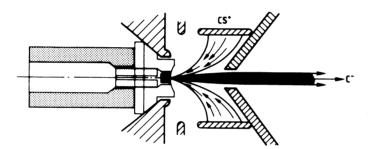

Fig. 2. Simplified scale drawing of sputtering chamber in the source, showing where the C^- is generated. Shown "docked" into the source is the target "shuttle," with its disposable Al head and Ti sputter area. The gas feed is not shown.

Performance

Beam Current. We operate at 10 μA C^-. This value can be stabilized by controlling the gas flow, although normally, a given constant gas flow produces a given current. Some 20 μA can be achieved with the source on a test bench, but so far, successful matching of the source to the accelerator system has been achieved at the price of loss of current. The reasons for this are not entirely clear. The test bench configuration differed in a number of ways, including the sputter surface design (which is not suitable for mass production), and extraction electrode geometry. The design for the AMS system was optimized for transmission through the accelerator, rather than for maximum beam production. Clearly, in terms of sample throughput, a higher current would be desirable. We have noted previously that the high levels of O^- associated with the C^- beam give rise to noticeable space charge effects before the beams are separated in the injection magnet.

Background Beam. This is probably the aspect of the source performance most in need of improvement. The background beam, measured before gas is admitted to the sputtering surface, depends upon the cleaning of the target surface. We now use solvents, followed by a bake-out in air at 400°C, followed by sputtering in the source. We have noticed that some reusable components need very careful cleaning, presumably from deposited and subsequently carboxylated Cs, if they are not to produce a highly temperature-dependent background beam. A significant improvement has been achieved by replacing the original ionizer design (in which a helical coil is enclosed in a chamber) with a hemispherical ionizer, which is more directly pumped.

Under routine conditions, the background beam current is 0.5 ± 0.3% of the sample beam, with a ^{14}C age of 50 ± 20 pMC. The hemispherical ionizer configuration changes this to 0.4 ± 0.15%, with the same ^{14}C age. Thus, the ionizer does not reduce the background greatly, but does reduce the variation very significantly, and also reduces the length of time to "clean up" to this value from 10 min per target to 3 min per target. Although it is impossible to measure the background current when running with gas, we note that no change is observed on admitting O_2, and that a correction based on the background before admitting gas accounts for 85 ± 15% of the background observed in dating "background" samples. We note that the background subtraction, from the figures given here (hemispherical ionizer) is 0.25 ± 0.1 pMC, and this represents a limit to the age that can presently be determined (*ca.* 50 ka). We do not know the origin of this residual level of background. The possibility of a small additional component introduced as contamination during gas handling cannot yet be ruled out.

Cross-Contamination and Memory. We emphasize here that these effects, contrary to prejudice, are very minor on the CO_2 sputter source. They are easily measured, and results have already been reported. The following parameters characterize the source under routine conditions:

Sample-to-sample contamination: 0.2% from gas handling
0.2% with a time constant of 3 min from ion-source memory effects.

There is no long-term memory effect. The background (see above) is independent of source cleaning.

Efficiency and Sample Size. The efficiency under routine operating conditions (10 μA) is *ca.* 5%, although we believe the maximum possible, with reduced beam current, is over 10%. The efficiency, defined as the ratio of C^- ions produced to CO_2 molecules consumed, is easily evaluated since the consumption of CO_2 is easily measured. At 10 μA, the consumption is 100 μg or 0.2 ml atm h^{-1}. We have not used the source for measuring samples smaller than *ca.* 100 μg, and, although several samples in the 100–300 μg range have been dated, the present gas handling system is not designed to deal efficiently with samples under 1000 μg. A design to accomplish this is described later.

Reproducibility and Accuracy. The operation of the source is highly reproducible, and is much more satisfactory in this respect than previous sources we have used. It has been our hope that this would be matched by a corresponding improvement in isotopic ratio reproducibility, but this is not yet consistently apparent (*e.g.*, from stable isotope data). Of course, such a measurement depends upon the details of transmission through the entire AMS system. (The reproducibility of stable isotope measurement from target to target is about 0.5%, although it is the number of "outliers" that are in greatest need of improvement.)

Operational Details

We run the system on a 24-h cycle, typically measuring 14 samples (including 3 standards and 1 or 2 backgrounds or known-age samples). Each sample is measured for about 1 h. Thus, the total measurement time is about 16 h. An additional 2 h are required for target cleaning, 3 h for background estimation and 1 h for alignment and system checks. Sample changing and pumpdown account for the remainder (2 h).

Most of the data collection is performed overnight without operator supervision, and this places a premium on system reliability. (A single date requires a total of about 200 successful computer-controlled electromechanical changes in the ion source.)

In order to prevent the buildup of sputtered material that may internally short the source, fairly frequent cleaning (about every 150 samples) is needed, although new designs should obviate this. The mechanics of sample changing are now satisfactorily reliable. The gas handling system is being redesigned, partly to improve reliability.

Current and Future Improvements

Hemispherical Ionizer. This system (Middleton, Klein & Fink 1989) gives a better-focused sputtering beam, and also allows for better pumping in the sputtering region. A prototype has been tested, and gives more reproducible backgrounds with similar or higher beam currents, and will require less maintenance.

Gas Handling. A new design is in prototype form, in which the samples are handled at ground potential. The sample is mixed with He up to about atmospheric pressure, and an aliquot of this mixture transferred by He flow to a cold trap at the source potential. (This is similar to the system used to transfer CO_2 from the combustion system to a glass ampoule, as outlined above.) The trapped CO_2 is then transferred to a bellows assembly, from which it is squeezed to the source at constant flow rate. This system is potentially much more reliable, and has the advantage that small samples can be fully exploited since dead volumes can be kept small.

SUMMARY

The CO_2 source has been in routine operation since September 1989. It has turned out to have the advantages originally predicted for it, although we do not consider the beam current and background to be fully satisfactory, and believe they can be improved further. The reliability under routine operation is now satisfactory. However, a second generation version should be capable of improved reliability and easier maintenance. The source and the automated combustion system together make a powerful combination, particularly for routine work and for small samples.

ACKNOWLEDGMENTS

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