

USE OF THE CO₂ SOURCE IN RADIOCARBON DATING BY AMS

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ABSTRACT. Since Middleton showed the potential for a sputter source working from CO₂, we have been building a source which can automatically change samples. The source produces a maximum beam of 25 μA of C⁻, with typical operation between 10 and 20 μA. Although beam generation from the source is very reliable, the mechanics of sample changing have given considerable problems. The changing of samples also involves considerable care in gas handling, and a computer control system has been written which ensures the correct sequence of the 16 operations required for sample change.

INTRODUCTION

Although the potential advantages of an ion source generating C⁻ from CO₂ gas have been recognized for a long time, serious problems were also encountered at an early stage. Heinemeier and Andersen (1983) showed that cross-contamination and memory effects were unacceptably large in a discharge-type source. An approach based on sputtering which successfully produced 20 μA C⁻ was described by Middleton (1984). This design made automatic sample changing almost impossible; nor was it established if memory effects would be too severe.

We have taken Middleton's basic concept, engineered it for sample changing and automatic computer-controlled operation, measured its performance parameters, and developed it to the point where it can be used with advantage for ¹⁴C dating. The basic design and most of the measurements relating to ion beam formation have been reported previously (Bronk & Hedges, 1987). The main purpose of this paper is to give a more practical account. We hope this will enable designers of AMS systems to assess the requirements and usefulness of the source as a practical proposition in ¹⁴C dating.

Potential Advantages

The source has not yet been adequately used to claim that its inherent advantages have been realized, but the principle of the CO₂ source has the following implications:

- simplification of the target preparation chemistry
- simplification in analyzing the source of laboratory contamination in chemical pretreatment
- easier handling and more efficient consumption of sub-milligram samples
- more reproducible target geometry, so potentially more reproducible beam behavior
- more reproducible current, and control of current through gas-flow
- measurement of the AMS system background possible (before admitting sample).

The source gives very much greater current with graphite targets (by a factor of 5–10). It is also of potential value for other ion beams generated from solid targets, eg, BeO⁻, where sufficient beam intensity is hard to attain.

Potential Disadvantages and Difficulties

- cross-contamination between samples, because of the impossibility of spatially confining the target gas
- susceptibility to residual gas contamination in the source from other sources than targets. The gas source is, in fact, an extremely sensitive residual gas analyzer for carbon
- susceptibility to residual (solid) carbon contamination on targets
- mechanical complexity of sample-changing mechanism
- sample changing requires fairly complex control system
- possible problems in CO₂ handling, eg, isotopic fractionation and gas adsorption.

The experience of our design has been that it is possible to reduce the first three effects to well within acceptable levels. We have not yet entirely eliminated problems arising from system reliability, and have not yet been able to observe CO₂ handling problems.

PHYSICAL DESCRIPTION

Figure 1 shows details of the sputtering chamber. C⁻ is generated from CO₂ at the surface of a titanium pellet enclosed in a disposable aluminium holder. A sputtering beam of Cs⁺ of 5 keV energy and ca 1mA is focused to 0.5mm diam at the target by the field geometry and space charge. This is produced from a coil of 3mm diam Ta tube, heated with an internal, ohmic heater, which thermally ionizes the ambient concentration of Cs in the chamber. The ionizer maintains the chamber at an overall temperature of 300–400°C, and the Cs concentration is adjusted by controlling the temperature of a Cs reservoir (usually maintained at up to 200°C). The target holder must be cooled to maintain a sufficient Cs concentration at the sputtering surface so that the work function is kept low for efficient ionization. In our design, this is done by pressing the chamber on the Al target holder against a stainless-steel plate which is cooled with an air pipe. (Originally, we used paraffin coolant, but were unable to eliminate carbon contamination leaking from unions.) To extract the negative ion beam, the target is maintained at ca – 24 kV with respect to ground.

This arrangement is based on Middleton's original design, with minor modifications to the extraction geometry. However, the mechanical arrangement (including cooling, thermal gradients and electrical insulation) is quite different. During intermittent use for a total of several hundred hours, the source has reliably generated an intense Cs beam although sometimes several hours of heating are required. Sparking is infrequent, the ionizer appears to perform consistently without the need for cleaning, and small displacements do not alter the Cs⁺ beam focus position. However, operation can be halted by the formation and movement of Al flakes from the target which are liable to short out applied voltages.

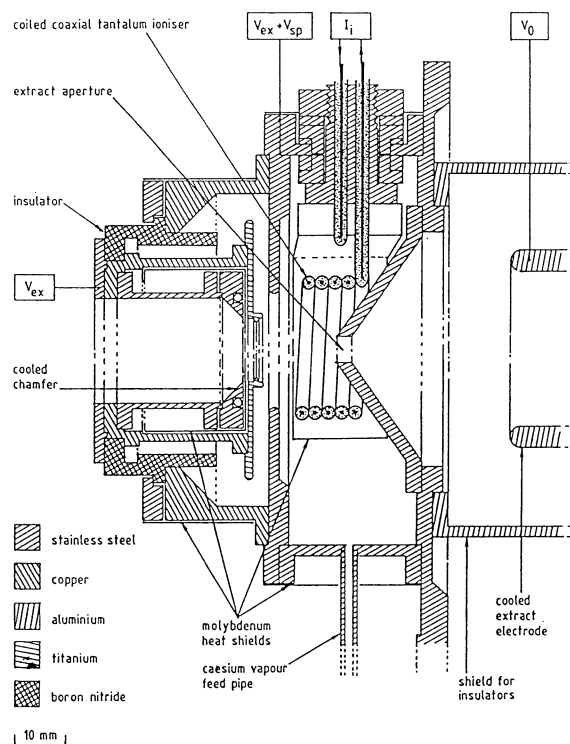


Fig 1. Details of ionizer chamber of CO_2 source

The principle of the sample-changing arrangement which takes 12 targets has been described elsewhere (Bronk & Hedges, 1987). We have found it very useful to interpose a gate valve between the source and the sample-changing mechanism. Although failures in sample changing are now rare (perhaps one in several hundred), we have not had sufficient intensive running to regard the reliability of sample changing as entirely satisfactory.

The design of the disposable target must satisfy several criteria: ease and economy of manufacture, reproducibility of performance and low background. The present arrangement is shown in Figure 2. A 2mm diam Ti pellet is slightly squashed from a circular cross-section, to allow gas to pass,

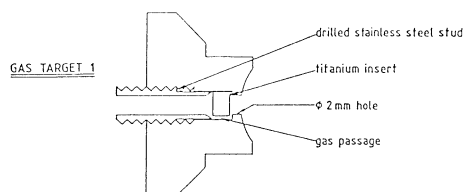


Fig 2. Disposable target for CO_2 sputter source

and pressed against a 1.6mm diam retaining Al lip. The Cs⁺ beam erodes a crater to a depth of 1mm in ca 5 hr.

Gas handling. The flow of gas to the target is regulated with a metering valve, adjusted according to the input gas pressure. Because any one sample will be admitted on several occasions, sample loss is minimized by re-freezing the CO₂ in liquid-nitrogen-cooled traps. These can be heated to release the gas in ca 20 sec. Figure 3 shows the schematic of the gas handling system, and Figure 4, the trap. Note that the gas handling must be remotely controlled, since it must be maintained at the same potential as the target (cathode).

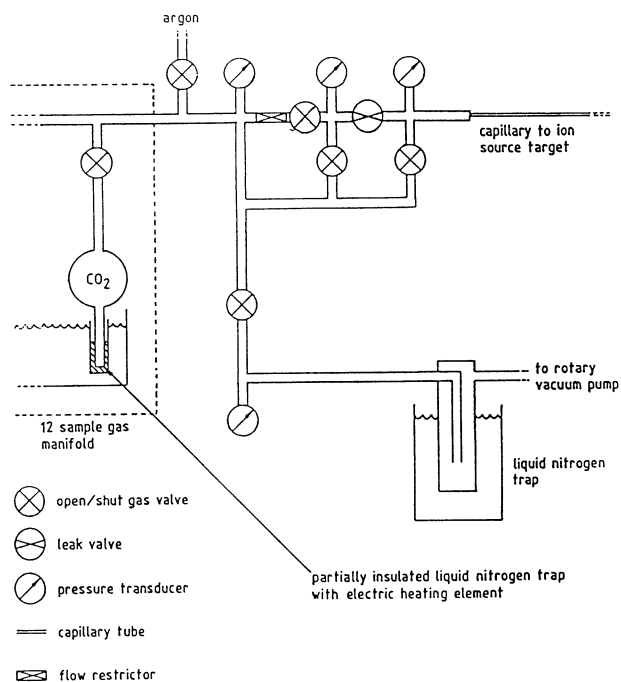
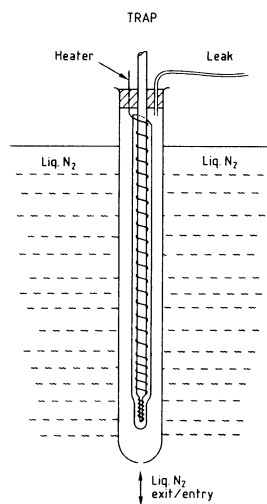


Fig 3. Schematic of gas handling system

Control system. Serial optical links pass signals to and from a controlling computer (an Amstrad PCW8512 running a program compiled in Modula-2) which is at ground potential. Some 50 channels are necessary for control and monitoring of the ion source and gas handling rig. Spark protection is necessarily incorporated into the interfacing hardware but the problems of spark damage have not been entirely eliminated.

Fig 4. CO₂ trap design

BEAM PERFORMANCE

Current and efficiency. C⁻ beam current increases roughly linearly with CO₂ flow rate, reaching a plateau and gradually falling from a maximum of 20 μA and a flow rate of ca 0.25 atmos.cc/hr. When linear, the O⁻ current is about twice the C⁻ current, but saturation is reached at flow rates greater than 3 atmos.cc/hr. CO₂ deliberately contaminated with 2–5% of SO₂, H₂O and NO₂ gives similar beam currents to pure CO₂. The effective conversion of CO₂ to C⁻ (ie, the proportion of carbon atoms passing through the capillary that can be measured as C⁻ ions after the injection magnet) is roughly constant at a value of 8–10%, falling as the plateau is reached.

Emittance. Figure 5 compares the emittance of the CO₂ source (used with graphite) with that measured for the reflected sputter source normally used in the AMS system. The two curves are very similar in magnitude. However, the error bars on the curve indicate the standard deviation of a large number of measurements made on different but similar targets in each case. The CO₂ source exhibits about half the variation of the back-reflected source. We believe this is due to the greater reproducibility of the target geometry.

Background. Before admitting CO₂, cleaned targets produce C⁻ beams of initially several microamps, due to surface contamination. With careful attention to system vacuum, this current reduces to 50–100 nA, that is 0.2–0.5% of the CO₂ current, after sputtering for 15 min. Subsequent reintroduction of a target produces a similar beam, after sputtering for 5 min. Once CO₂ has been admitted, carbon is implanted in the target and the current drops to ca 4 μA on switching the gas off. This falls very slowly with a time constant of ca 10 min. In steady operation, therefore, ca 20% of the beam is derived from implanted carbon.

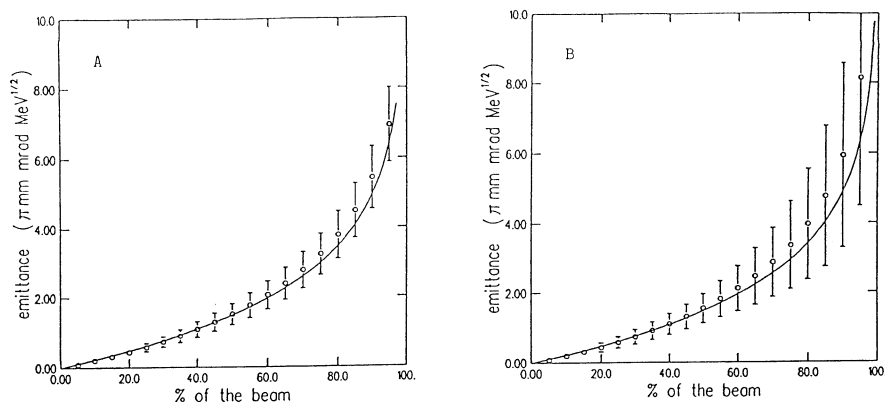


Fig 5. Comparison of emittance plots from the CO₂ source (A) and the back-reflected source (B). Error bars reflected variance of results from a series of measurements for different targets.

There appear to be two sources of background current; from residual gas (which has a high CH⁻ content), and from carbon which is perhaps derived from the ionizer (eg, by secondary electron impact). There is a higher background if a graphite target is used followed by a clean gas target with no gas flowing through it. This is because most of the carbon is sputtered as neutral atoms and clusters whereas for CO₂, it is likely that the fraction sputtered to neutral carbon is quite low, since most of the admitted gas is unlikely to be sputtered at all. The background is not affected by “cleaning” the source (using usual uhv procedures – *ie*, acid, distilled water and methanol washes followed by baking).

Cross-contamination and memory effects. The existence of a significant background argues for a potential source of cross-contamination. We have investigated this by using CO₂ enriched to 90% with ¹³C. After running for 30 min, the increase in ¹³C⁻ from the following target was measured (with and without CO₂ admitted) and corresponded to a cross-contamination of <0.05% of the total current (Bronk & Hedges, 1987). This is a very encouraging result.

Sensitivity of beam direction. During the brief interval in which the source was tested on the main AMS system, it became apparent that the extracted beam was strongly steered (30mrad) off axis, (probably) by a 0.2–0.4mm misalignment of the target axis. Although this misalignment has been corrected, the sensitivity of steering to alignment is of concern, since the present design of the source requires tolerance for thermal expansion. We have been investigating modifications of the field about the target which will produce an immersion lens the image of which is less sensitive to the source position.

OPERATION

One of the most significant factors in operation is the length of sputtering time required to clean the targets. This is 15–20 min initially, and a fur-

ther 2–3 min for every recall of the target. If each target is measured for a total of 60 min (0.3% statistics on a modern target), in 4 sessions of 15 min, the total time for 12 targets is just under 24 hr. This would produce 8–10 dates. There would be an advantage in productivity to having more than 12 targets in the sample changer, and in having an additional facility to clean up waiting targets. It is clearly necessary for the system to work under automatic control.

Sample changing requires a number of concerted actions: switch off extract voltage, withdraw target, trap remainder of the CO₂ sample, move sample wheel to new position, insert new target, ensure adequate vacuum in gas line, heat CO₂ trap, transfer aliquot of gas and adjust bleed valve to give suitable flow rate, switch on extract voltage. The reliability of the system controlling these actions is likely to be the determining factor in the overall system reliability.

Operation of the source on the AMS system was too brief to obtain much useful information. For example, background level and cross-contamination measurement of ¹⁴C, vital for ¹⁴C dating, were not made. We have observed that on introducing a target, the carbon beam content is initially high in ¹⁴C (50% modern or greater), but that the ¹⁴C/¹³C ratio falls with a time constant of 1–2 min. The other important measurement of performance would be the reproducibility of isotopic ratio measurement within and between targets. On limited data, the reproducibility of ¹³C/¹²C on one target was substantially improved over that typically obtained from the back-reflected source. Further, changing the gas flow rate to give a threefold change in beam current caused a change only of the order of 0.5% in the ratio. Equally the between-target reproducibility appears to be substantially more constant (*ie*, a variance of <0.5%). It should be noted however that these are only preliminary measurement.

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