

**MEASUREMENT OF  $^{14}\text{C}$  DIRECTLY FROM  $\text{CO}_2$  USING A  
TANDETRON ACCELERATOR MASS SPECTROMETER FACILITY**

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**ABSTRACT.** Tests have been carried out on the measurement of  $^{14}\text{C}$  directly from  $\text{CO}_2$ , using a source designed by Middleton, and a Tandetron accelerator mass spectrometer system. These tests were very promising from the point of view of minimum quantity of carbon necessary ( $<50\mu\text{g}$ ), but suffered from a background (apparently *not* memory effect) giving an equivalent age of  $\sim 25,000$  years. As a demonstration of the technique, a single thread from the mummy wrapping of the Egyptian king Ramses II was dated.

INTRODUCTION

It has been realized since the beginning of  $^{14}\text{C}$  measurements by accelerator mass spectrometry (AMS) that a source operating with  $\text{CO}_2$  gas would offer many advantages, including ease of sample preparation, potential for using smaller (sub-milligram) samples, more reproducible sample conditions, and less potential for sample contamination. However, initial attempts to operate some negative ion sources in such a mode suggested that cross-contamination between samples might be a severe problem (Shea, 1980; Heinemeier & Anderson, 1983). At the last AMS symposium in Zurich, Middleton (1984) described operation of an ion source of his design with  $\text{CO}_2$ , which appeared quite promising in this respect. At our Tandetron AMS facility, we use a commercial (General Ionex model 860) version of Middleton's source for  $^{10}\text{Be}$  and  $^{26}\text{Al}$  measurements (described in another paper at this meeting). It therefore appeared interesting to try operation of this source with  $\text{CO}_2$  on the Tandetron.

EXPERIMENTAL

The cooled cathode holder of the source was first modified according to the description of Middleton (1984; *pers commun*). Two types of Ti cathodes were tried. The first consisted of solid (but not particularly pure) metal; the second was made from 99.9% pure Ti powder, pressed into a 5mm depression in a Cu cathode, similar to that shown in Middleton (1984, Fig 4). Although based on a quite limited number of tests, no significant differences were observed between the two types of cathode. Most of the experiments described here were carried out with the solid metal cathodes.

A schematic diagram of the gas inlet system, which floats at the 20KV operating potential of the source, is shown in Figure 1. The flow rate to the source could be optimized while operating by adjusting the leak valve (V2) with an insulated plastic rod. A broad maximum in the  $\text{C}^-$  current was observed for flow rates of  $\sim 0.03\text{--}0.15\text{cm}^3$  (STP)/hour ( $\sim 15\text{--}75\mu\text{g}$  carbon/hr). The lower value is about an order of magnitude smaller than the flow rate cited by Middleton (1984), for a pressed Ti cathode. Unfortunately, our optimum  $\text{C}^-$  currents, of  $\sim 2\mu\text{A}$ , were also more than an order of mag-

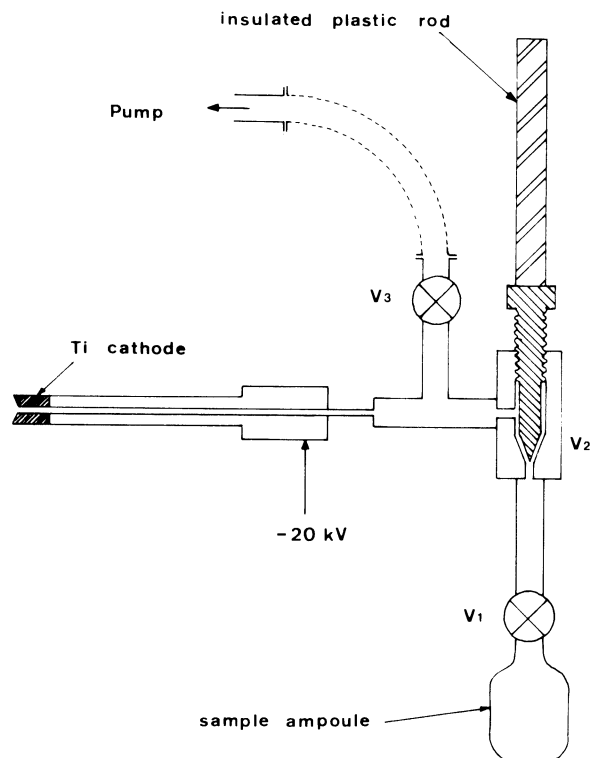


Fig 1. Schematic diagram of gas inlet system for operation of source with  $\text{CO}_2$ . Pump is disconnected from V3 during measurements.

nitude smaller than those observed by Middleton. The current was very stable, however, and even with the rather large dead space in our gas system it was quite easy to operate for more than an hour with a  $\text{CO}_2$  sample of  $50\mu\text{g}$ .

The Tandetron was operated at a nominal terminal voltage of 2MV. At the time of these experiments, the Tandetron was giving rather variable  $^{14}\text{C}/^{12}\text{C}$  ratios using solid samples (since improved significantly). It was, therefore, decided to carry out these tests using only the  $^{14}\text{C}/^{13}\text{C}$  ratio. Measurements consisted in cycling between  $^{13}\text{C}$  (10 sec) and  $^{14}\text{C}$  (100 sec), until the desired number of  $^{14}\text{C}$  counts was obtained. Measurements were made with  $\text{CO}_2$  prepared from standard oxalic acid, and commercial  $\text{CO}_2$  which had been shown to have an equivalent age  $> 45,000$  yr. The  $^{14}\text{C}$  count rate for an oxalic acid standard and  $1\mu\text{A}$  of  $\text{C}^-$  was  $\sim 1.5\text{cps}$ .

To change samples, we first closed the leak valve (V2), removed voltage from the source, and then, after having condensed the sample between V1 and V2 into the sample ampul if desired, closed the valve on the sample ampul V1. A new sample ampul was then put in place and, with V2 open, the whole gas inlet system was pumped out through V3. Tests were made in which the Ti cathode was or was not changed. V2 was then closed and V1

opened. The source was then put at potential and V2 adjusted for optimum  $\text{C}^-$  current.

#### TEST RESULTS

We summarize below the results of various tests:

1) *Reproducibility*—During a two week period the standard deviation of the absolute  $^{14}\text{C}/^{13}\text{C}$  ratio of the oxalic acid standard was  $\sim 2.5\%$  which was only marginally larger than the statistics of the number of events counted in a given measurement. Since high precision was not a main objective of this work, no attempt was made to make longer runs.

2) *Minimum sample size*—As mentioned above, our gas inlet system was far from optimized, particularly with regard to dead space. Despite this, it proved quite easy to make measurements on contemporary samples containing as little as  $50\mu\text{g}$  of carbon. With an improved gas handling system, we believe that this could be quite readily reduced to  $20\mu\text{g}$  or less.

3) *Memory effect*—In view of earlier results, we made several attempts to check cross-contamination between samples. However, within the limits imposed by the observed (non-sample-associated) background discussed below, we found no difference between dead  $\text{CO}_2$  run directly after an oxalic acid standard, or after several hours of operation with dead  $\text{CO}_2$  (this result also seemed independent of whether we changed the Ti cathode or not).

4) *Background*—A  $^{14}\text{C}$  count rate of  $\sim 5\%$  that of the oxalic acid standard was observed either when operating with the dead  $\text{CO}_2$ , or when operating without gas (with V2 closed). With the dead  $\text{CO}_2$  the  $^{14}\text{C}/^{13}\text{C}$  corresponded to an age of  $\sim 25,000$  yr, while without gas the equivalent age varied between 1000–3000 yr. Since, as mentioned above, this count rate appeared to be independent of the preceding sample, or whether the Ti cathode was changed, we do not believe it can be attributed to a memory effect. Following the report of Gillespie and Hedges (1984), we recently submitted a sample of the source turbo-pump oil to be  $^{14}\text{C}$  analyzed by decay counting. The result was an equivalent age of  $\sim 7000$  yr. Although the vapor pressure of this oil should not normally give a significant contribution to the hydrocarbons in the source, it seems at least possible that at some time backstreaming of this oil might have contaminated the source. Another possibility is contamination in the Ti cathodes, although the fact that the metal and pressed powder gave similar backgrounds is then a surprising coincidence. Further tests to discover the source of this background are obviously warranted.

#### RAMSES II

As a demonstration of the feasibility of dating  $\text{CO}_2$  by the procedure described above, we decided to test the technique by dating a thread from the mummy wrapping of the Egyptian king Ramses II. A larger quantity of the same material had been previously dated by decay counting. The sample (representing  $\sim 1\text{mg}$  of carbon) was combusted in a quartz tube. The  $\text{CO}_2$  was cleaned by passing over hot  $\text{CuO}$ , and washed through a  $\text{KMnO}_4$  solution. An aliquot representing  $\sim 250\mu\text{g}$  of carbon was condensed in a glass sample ampul which could be attached to the ion source, as shown in Figure

1. The sample was measured on the Tandetron directly after a measurement of the oxalic acid standard. Subsequently, a run under as nearly identical conditions as possible was made using the dead CO<sub>2</sub>. The correction for background was made assuming it was the same for the oxalic acid and Ramses II as for the CO<sub>2</sub>. The resulting age for the mummy wrapping is 2900 ± 250 BP, where in addition to statistics, we have included an uncertainty equal to 50% of the background correction. This result is in acceptable agreement with that found by decay counting, of 3130 ± 60 BP (G Delibrias, pers commun). In both cases the ages are calculated with a half-life of 5730 years, and non-calibrated.

#### DISCUSSION AND CONCLUSIONS

The experiments reported here were performed over a period of only three weeks. Thus, they are preliminary and incomplete. Nevertheless, they demonstrate considerable promise. In particular, the technique described appears to offer considerable potential for measuring smaller quantities of carbon than are presently measurable with solid sources. Indeed, one of the principal objectives of this work was to investigate the possibility of directly dating the CO<sub>2</sub> occluded in Antarctic ice cores. Considerable variations have been found for <sup>10</sup>Be concentrations in these ice cores (Raisbeck *et al*, 1981, Yiou *et al*, 1985). In order to estimate what part, if any, of this variation is due to production variations, it is necessary to have an independent method of dating the cores (Raisbeck & Yiou, 1980). Assuming that the background problem discussed above can be eliminated, the present technique would appear to offer the most promising method of <sup>14</sup>C dating the extremely small quantity of CO<sub>2</sub> (~15 μg carbon/kg ice) found in such ice.

#### ACKNOWLEDGMENTS

We thank D Deboffe for constructing the gas inlet system, H Cachier for combusting the Ramses II sample, and G Delibrias for providing the oxalic acid and blank CO<sub>2</sub> samples, allowing us to quote the unpublished measurement of the Ramses II mummy wrapping, and for measuring the <sup>14</sup>CO<sub>2</sub> from the turbopump oil.

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