FAST AND COMPLETE CO_2-TO-GRAPHITE CONVERSION FOR ^{14}C ACCELERATOR MASS SPECTROMETRY

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ABSTRACT. With Fe powder as a catalyst, CO_2 is completely converted to graphite within 90 minutes. The reaction proceeds at 650°C with an excess of H_2. The reaction rate is enlarged by forced circulation and by keeping the water vapor pressure very low. The graphite samples obtained, consisting of 5mg of carbon, almost immediately produce stable $^{12}C^-$ currents of the order of 20–30μA in the sputter source of a Van de Graaff accelerator. The currents can be maintained for at least 10 hours and are comparable to those from commercial graphite. No memory effects in the preparation system have been observed.

INTRODUCTION

The sample is first converted to CO_2 for conventional ^{14}C dating. Decay counting is then often performed directly on this CO_2 or after a subsequent conversion on CH_4, C_2H_6, C_2H_2 or C_6H_6.

Until now ^{14}C measurements by accelerator mass spectrometry (AMS) require that the sample be transformed into elemental carbon or graphite in order to produce intense, stable ion beams with a negligible memory effect in the ion source. So far, graphite preparation techniques reported are rather elaborate or time consuming, like piston cylinder graphitization (Bonani *et al*, 1984) and catalytic heating (Lowe, 1984) or produce only thin layers of graphite by cracking of carbon monoxide (Grootes *et al*, 1980), acetylene (Beukens & Lee, 1981) or of carbon dioxide (Andrée *et al*, 1984).

The direct use of carbon dioxide in an ion source would be the most favorable procedure. However, in our first attempt to use a sputter source for CO_2, as reported by Middleton (1984), we observed a rather large memory effect.

Our method is based on the well-known catalytic action of Fe powder on CO_2 to yield elemental carbon. Due to its industrial importance, the CO_2–CO–C system has been extensively investigated (Rutherford, 1966; Rutherford & Liner, 1970; Turkdogan & Vinters, 1974; Olsson & Turkdogan, 1974).

Vogel *et al* (1984) were the first to deploy this catalytic reaction for AMS sample preparation. In their system, the possibly present iron oxide in the iron catalyst is first reduced by H_2 for one hour. Subsequently, CO_2 and H_2 must reach the Fe catalyst by diffusion to produce elemental carbon and water vapor. This is a very slow process.

In our procedure, we apply a method for AMS target preparation similar to the one originally used by Rutherford and Liner (1970) for the preparation of elemental ^{13}C and $K^{13}CN$ from $^{13}CO_2$. Compared to Vogel *et al* (1984) we omit the iron reduction step preceding the conversion and reduce the reaction time from 8 to 12 hours to < 1.5 hours due to forced circulation of the gases.

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EXPERIMENTAL PROCEDURE

The reduction system is outlined in Figure 1. The tubing is made of pyrex with an inner diameter of 4mm. Inside the oven the tube is made of quartz with an inner diameter of 12mm. The different elements are coupled by Rotulex spherical joints with viton O-rings. The total volume is ca 50cm³. The pressure in the system is monitored using a Philips KP100A monolithic pressure sensor. The gas is circulated at ca 50cm³/min by a small vane type pump. This pump is a modified version of what is known as the "Schiegl" pump. It consists of a stainless steel housing and rotor. The rotor is supported by two bearings and contains a permanent magnet. Two vanes can move freely radially by centrifugal force and are made of nylotron which absorbs almost no water. The top of the pump is covered by a glass plate and sealed with a large viton O-ring. The pump is driven by an external magnetic stirrer motor with variable speed.

The catalyst, 99.9% pure iron powder, −325 mesh is contained in a well, 3mm in diameter and 2mm deep, in a copper disk, 7.5mm in diameter and 5mm thick. The copper disk fits directly into the revolving head of the ion source of the Utrecht tandem accelerator.

The disk is placed on a quartz holder attached to a quartz rod. The use of quartz became essential in avoiding a large heat flux from the disk. A pyrex tube containing a stainless steel grid prevents carbon particles to circulate and cause cross-contamination. A typical run is illustrated by a pressure *vs* time curve in Figure 2.

Ca 10ml STP of CO₂ is condensed into the cold trap by liquid N₂ and
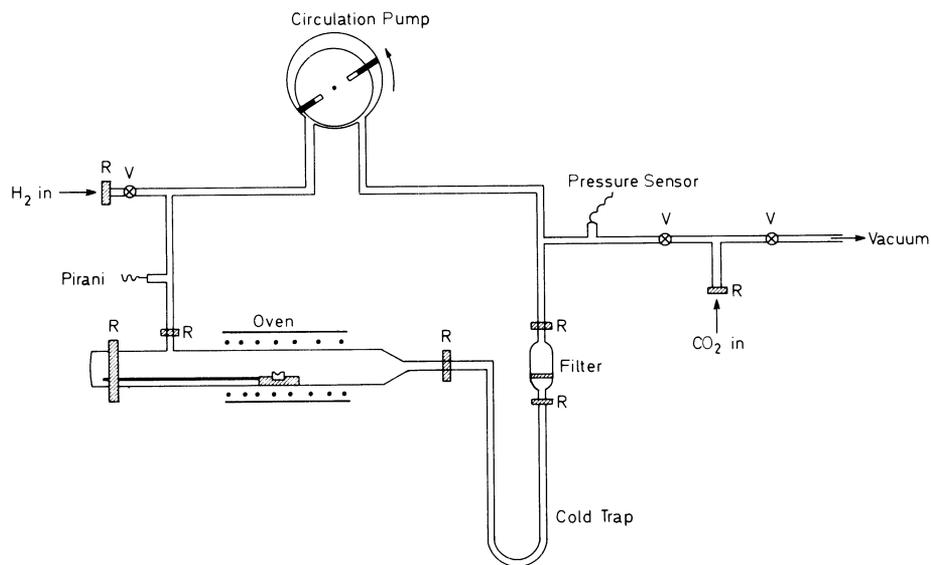

Fig 1. Outline of the reduction system. Tubing is pyrex with ID=4mm; tubing inside oven is quartz with ID=12mm. R: Rotulex spherical joints with viton O-rings, V: valves. Vacuum is obtained by a two-stage rotary pump.
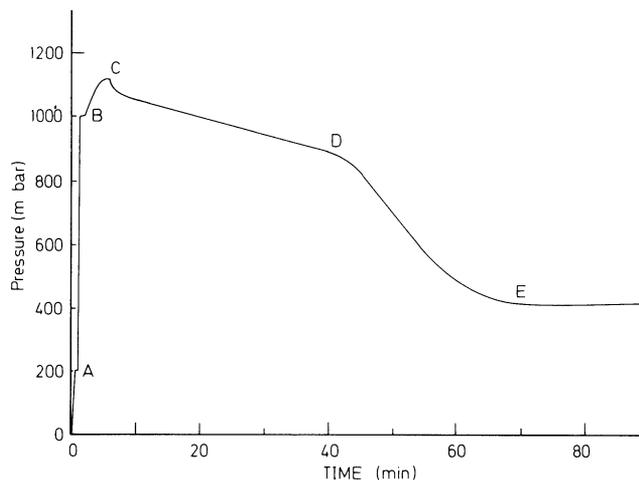
Fig 2. Typical example of pressure in reduction system *vs* time during a run. The CO_2 pressure is 200mbar, H_2 pressure is 800mbar, and the reduction was made at 650°C. Note that the oven is switched on at B and thus, at 650°C, the residual H_2 pressure should be well above 400mbar.

afterwards expanded in the reduction system to ca 200mbar (A, Fig 2). The trap temperature is now raised to −80°C by a dry-ice acetone mixture and 800mbar of H_2 is let in (B). The temperature of the oven is then raised to 650°C. The reaction starts at 500°C (between B and C) presumably with the reduction of CO_2 to CO. This reaction is rather slow (C-D) until the pressure has decreased by ca 200mbar, *ie*, as if all CO_2 had been reduced to CO. At this time (D), the process continues by the reduction of CO to C.

The reaction rate increases and then becomes about constant until tailing off slightly below the pressure expected from the excess of H_2 at this temperature (E). This is attributed to H_2 consumption for reducing a small amount of iron oxide in the original iron. The pressure drop immediately after C is probably also due to the reduction of iron oxide.

A similar experiment with CO instead of CO_2 yielded a pressure *vs* time curve starting at D in Figure 2. This supports the notion that the reduction to CO essentially precedes the final reduction to elemental carbon.

We also performed the reduction with iron powder in a quartz boat. The overall reaction time was shorter than using the copper disk, due to the larger available iron surface. However, copper is preferred since less handling of the carbon is required afterwards; the elemental carbon "grows" on top of the iron powder and is later simply pressed into the well.

The samples were measured in the inverted sputter source of the Utrecht tandem Van de Graaff accelerator facility (Van der Borg *et al*, 1984).

RESULTS AND DISCUSSION

To date, 34 reduction runs were made under various experimental conditions. Most experiments were done in the weight range of 4.0 to 5.5

mg, using between 15 and 20mg of iron. The yields were determined by weighing and always indicated, within weighing error, complete reduction of CO_2 to carbon deposited on the iron particles. Further, we were never able to freeze out any remaining CO_2, not even when the reaction had been initially stopped at pressures well above the value of excess H_2 (pressure between D and E in Fig 2). This also supports the idea of complete reduction.

From the complete reduction we conclude that no detectable amount of CH_4 is produced during the warming phase (*cf* Vogel *et al*, 1984). This may be due to the short time necessary for warming up—in general, in <2 minutes the final reaction temperature has been reached.

Table 1 presents data for reductions with copper disk and quartz disk support. These results indicate that:
— the reduction temperature should be at least 650°C
— the excess H_2 is only of importance to the reduction time and not to the value of the $^{12}C^-$ ion current
— the amount of iron powder is not very critical.

X-ray diffraction spectra showed that the elemental carbon made at 600°C is amorphous, whereas the carbon prepared at 650°C and 700°C is polycrystalline graphite.

In order to get an idea of the minimum amount of sample that can be prepared in this system, we decreased the CO_2 pressure. We found that complete conversion is obtained at 650°C, 400mbar excess of H_2 and with ca 15mg of iron, also for smaller sample sizes.

The conversion time, however, increases with decreasing sample size: 75 minutes for 5mg, 135 minutes for 2.5mg, and 160 minutes for 1.25mg of carbon (original CO_2 pressures of ca 200, 100, and 50mbar, respectively).

Although samples smaller than 5mg can be handled with this system, we believe that they should be prepared in a system with a smaller volume. The amount of iron should then be decreased so that the graphite is not diluted too much by iron. A reasonable conversion time is still to be expected. On the other hand, for most applications, the requirement of 10ml of CO_2 at STP can easily be met.

Background measurements on ^{14}C in commercial graphite in the

TABLE 1

$^{12}C^-$ currents obtained from elemental carbon targets (I_s) compared to the $^{12}C^-$ currents from commercial graphite (I_g)

Disk no.	T (°C)	Fe (mg)	C (mg)	Excess H₂ (mbar)	Reaction time (min)	I_g (µA)	I_s (µA)	I_s/I_g (%)
2-16	600	19.6	4.8	200	100	29.5	6	20.3
2-17	600	19.5	4.9	400	45	29.5	13.5	45.8
2-18	650	18.9	4.1	200	75	29.5	29.5	100
2-19	650	19.0	5.2	400	75	23.5	23.5	100
2-10	700	16.8	5.0	200	65	23.5	21	89.4
3-1	700	15.3	5.0	400	80	28	28	100

Utrecht tandem accelerator yield an age limit of 44,000 yr. Background samples prepared with this method yield an age limit of 44,000 yr as well.

Some samples were used for duration tests of the $^{12}C^-$ current. They all yielded stable currents that decreased gradually by ca 20% until they broke down after 10 to 15 hours.

The compressed samples turned out to be very tight, and could be mailed without damage.

ACKNOWLEDGMENTS

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