

PRODUCTION OF  $C^-$  DIRECTLY FROM  $CO_2$  USING THE ANIS  
SPUTTER SOURCE

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ABSTRACT. Micro-ampere beams of  $C^-$  have been produced with the Aarhus negative-ion source, operated on  $CO_2$  gas. The efficiency of the source and memory effects have been measured, using  $^{13}C$ -enriched  $CO_2$ , in order to evaluate the applicability of the source to  $^{14}C$  dating by accelerator mass spectroscopy.

INTRODUCTION

Although primarily intended for solids, the Aarhus negative-ion source (ANIS) may be operated on gas feeds as its negative-ion production is based on a Penning-type discharge (Andersen and Tykesson, 1975; Tykesson, Andersen, and Heinemeier, 1976). We describe here an investigation of the production of  $C^-$  from gaseous samples, intended to evaluate the applicability of the source to  $^{14}C$  dating by tandem-accelerator mass spectrometry. For a recent review of this technique, see Hedges (1981).

While most conventional  $^{14}C$  dating is done by radioactivity counting on  $CO_2$  samples, all successful accelerator dating up till now has relied on  $C^-$  production from solid graphite or carbonaceous samples used as sputter targets in various designs of the Middleton type of ion source. The preparation of  $CO_2$  samples is a thoroughly understood process, while the further conversion into solid samples is associated with varying isotope fractionation, as discussed in detail by Hedges (1981). Several contributions to this conference report that fractionation in the sputtering and ion-extraction process is sensitive to the shape and position of the solid sample in the ion source, thus introducing severe irreproducibility in the measured isotopic ratios. Handling of solid microsamples, sufficiently small to fully exploit the high efficiency of the accelerator method, is difficult and introduces a risk of contamination with modern carbon. Thus, the use of solid samples for radioactivity counting ('the carbon black method') was abandoned during the early history of  $^{14}C$  dating because of problems with contamination. Although the advantages thus are obvious, very few attempts to use gaseous samples for the accelerator method have been made. Middleton (1978) finds low  $C^-$  output from his source when jetting  $CO_2$  onto a titanium

sputter cone and also finds that the exit aperture of a duo-plasmatron gets blocked by carbon deposits when operated on  $\text{CO}_2$ . Shea et al (1980) conclude that the Dawton-type carbon-ion source with gas charge exchange is unsuitable for dating due to memory effects. Thus, we investigated the performance of the ANIS source in terms of (i)  $\text{C}^-$  beam intensity, (ii) ionization efficiency, (iii) memory effects, and (iv) background of  $\text{C}^-$  beam originating from residual gas and the source, itself, rather than from the gas feed. All measurements described in the following were made on our ion-source test bench.

#### EXPERIMENTAL PROCEDURE

The ANIS source is shown schematically in figure 1. A Penning discharge is maintained on a mixture of  $\text{CO}_2$  gas and cesium vapour in the stainless-steel discharge chamber, which is heated to ca  $500^\circ\text{C}$  by the two filaments, which also provide

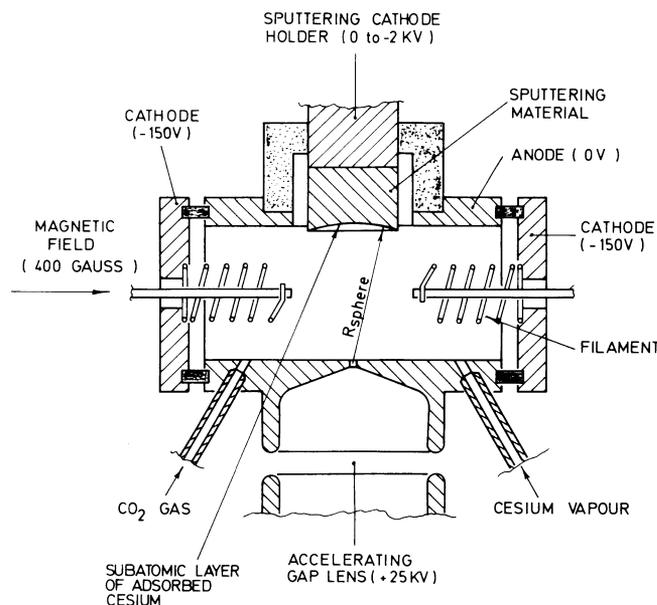


Fig 1. Schematic drawing of the ANIS source

the electrons for the discharge. Positive ions from the plasma impinge on the sputter cathode at an energy corresponding to the sputtering voltage of ca  $-1.5\text{keV}$ . The cesium-enhanced negative sputtered ions are accelerated across the plasma sheath at the spherically concave cathode surface and thus directed

towards the outlet aperture. Apart from beams corresponding to the cathode material, micro-ampere beams of C<sup>-</sup> and O<sup>-</sup> are produced from carbon and oxygen implanted in the cathode by bombardment with positive plasma ions such as C<sup>+</sup>, CO<sup>+</sup>, CO<sub>2</sub><sup>+</sup>, and O<sup>+</sup>. Thus, with the high sputter currents (10mA) typical of this operation, rapid sputtering of the cathode will bring the implanted ions near the surface, where they are sputtered off, with only a short delay. Adsorption of CO and CO<sub>2</sub> may also contribute to the process.

A simple way of evaluating the carbon memory effects down to a level of ~0.5% consists of recording the <sup>13</sup>C/<sup>12</sup>C beam-intensity ratio while alternating between gas feeding of natural CO<sub>2</sub> and <sup>13</sup>C-enriched CO<sub>2</sub>. The gas-flow rate to the source is measured by monitoring the pressure difference ΔP across a known molecular-flow resistance with an electronic membrane differential manometer. The pressure signal is also used for feed-back regulation of the flow rate through two remote-control needle valves, one for each gas supply. Changing gas sample simply involves switching the control signal from one valve to the other. When both valves are closed, ΔP decreases exponentially with a time constant of 30 sec, which also governs the partial pressure in the gas feed of the previous gas sample after sample changes. Thus, the gas-control system not only allows an accurate determination of the ionization efficiency but also ensures a rapid change of isotopic composition of the sample gas without changing the total CO<sub>2</sub> flow rate or any other ion-source parameter. For memory measurements, this method is more reliable than, eg, closing off the gas supply and watching the decrease in C<sup>-</sup> intensity, which may be affected by a change in ionization efficiency, with changing operating conditions. Likewise, the processes responsible for the liberation of the carbon deposited in various parts of the source may depend on the CO<sub>2</sub> supply.

After sample change from enriched to natural CO<sub>2</sub>, the beam intensity I<sub>13</sub> at mass 13 relative to the mass-12 intensity I<sub>12</sub> reflects the fraction of the total C<sup>-</sup> output which remains as a 'memory' of the previous sample. Taking into consideration mass-13 background and enrichment ε (normally 90%), we define the memory fraction

$$F = \frac{I_{13} - (I_{13}/I_{12})_0 \cdot I_{12}}{I_{12} + I_{13}} \frac{1}{\varepsilon}, \quad (1)$$

where (I<sub>13</sub>/I<sub>12</sub>)<sub>0</sub> is the ratio of the mass-13 to -12 beams for a natural CO<sub>2</sub> sample. It is usually ca 2%, due to the natural 1.1% abundance of <sup>13</sup>C as well as a component of <sup>12</sup>CH<sup>-</sup>. Ideally, F should vary from 100% before to zero after sample change.

In order to ensure reliable results, unaffected by a possible background of  $^{12}\text{C}^-$ , the ionization efficiency was normally determined from the  $^{13}\text{C}^-$  intensity and the measured flow rate of 90% enriched  $^{13}\text{CO}_2$ . The ionization efficiency is defined as the number of  $\text{C}^-$  ions per second in the source output divided by the number of carbon atoms per second in the gas flowing to the source. Beam intensities were measured in a suppressed Faraday cup after magnetic analysis at 20keV. No correction was made for transmission losses, eg, in the two gridded lenses between the source and the magnet.

## RESULTS

In this study we have used sputter cathodes made of copper since this material proved superior to other sputter materials such as magnesium, titanium, yttrium, gold, and tantalum. Typical  $\text{C}^-$  currents observed for a copper cathode were 2 to 4  $\mu\text{A}$  and up to 7  $\mu\text{A}$  on a few occasions. These values were found for  $\text{CO}_2$  flow rates of ca  $5 \times 10^{-4}$  torr  $\text{l s}^{-1}$  (0.03  $\text{cm}^3/\text{min}$ ), where the ionization efficiency defined above attained 0.15%. A typical mass spectrum (fig 2) shows that the  $\text{C}^-$  production is accompanied by strong beams of  $\text{O}^-$ ,  $\text{C}_2^-$ , and  $\text{Cu}^-$ . The high inten-

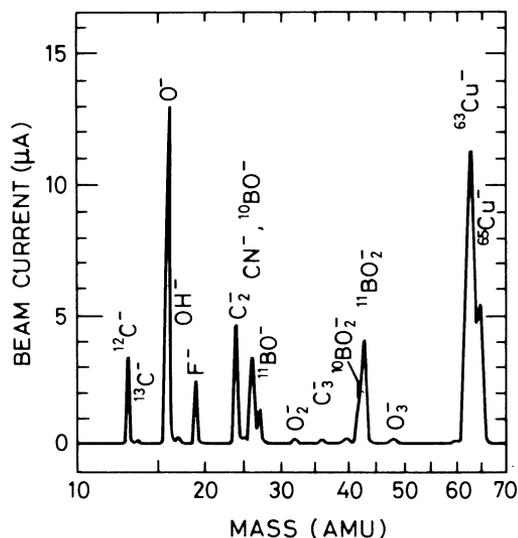


Fig 2. Output of the negative ion beams from the source using natural  $\text{CO}_2$  gas and a copper sputter cathode. The ions are magnetically analyzed at 20keV energy.

sity of  $\text{C}_2^-$  cannot be exploited for dating purposes since injection of  $^{14}\text{C}^{12}\text{C}^-$  into a tandem at a mass setting of 26

would not allow  $^{14}C$  to be separated from  $^{14}N$ , abundantly accelerated as  $^{12}C^{14}N^-$  at the same mass setting. The ratio of the mass-13 to -12 beams varies from 1.5 to 2.5%, depending on source parameters, and can be kept fairly constant at ca 2% if these parameters are not changed.

Sputter cathodes of yttrium and magnesium were tried because their work functions are lower than that of copper (3.1, 3.7, and 4.5eV, respectively) and therefore might be expected to increase the negative-ion production in the carbon sputtering process. However, very low yields,  $0.2\mu A C^-$ , were found for yttrium, probably because of the imperfect shape of the sputter cathode, which was made of foils. The magnesium tests were stopped because of extremely unstable source operation, probably due to evaporation of the cathode material when heated by the positive-ion bombardment from the plasma. Up to  $10\mu A C^-$  was recorded for a tantalum cathode (work function 4.2eV), but the output was not well correlated to the gas-flow rate, which may be consequential to the severe memory effects for tantalum, discussed below. A cathode of gold was tested despite its high work function of 5.3eV because low memory effects might be expected if chemical processes and/or gas adsorption on the cathode surface were responsible for these effects. However, the  $C^-$  output was only  $0.25\mu A$  and the efficiency as low as 0.009%; memory effects are quite similar to those of copper.

A few attempts were made to feed the source on  $CH_4$  gas in connection with cathodes of copper and tantalum. The increases in  $C^-$  beams were only minor, whereas the mass-13 to -12 ratio increased to ca 30%, due to  $^{12}CH^-$ . Only with a hot cathode made of thermally insulated tantalum foil did the ratio drop to 2%. In all cases, the correlation between gas-flow rate and  $C^-$  was poor; no further attempts were made.

The decay of the memory fraction measured as described above was recorded as a function of the time elapsed after switching from enriched to natural sample. This was done for several different values of 'exposure' time,  $T$ , in which the source had been operated on the enriched sample. Cathodes of copper, gold, and tantalum were used. The memory decay could not be described as a simple exponential or even as a sum of two exponentials. Rather, the decay curve follows a power law  $F \propto t^{-x}$  at first and then approaches a single exponential, as shown in figure 3. The power dependence indicates a continuous distribution of time constants as known from, eg, activation analysis and thermoluminescence. The components of long time constants contribute more heavily, the longer the exposure time. Thus, as illustrated in figure 4, the value of the exponent,  $x$ , in the power decay decreases with increasing

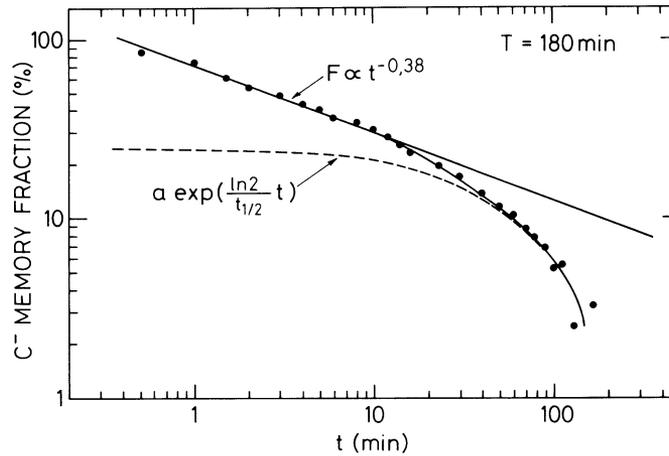


Fig 3. Double logarithmic plot of the memory fraction  $F$  (Eq (1)) as a function of time after change from 90% enriched  $^{13}\text{C}\text{O}_2$  to natural  $\text{CO}_2$ . A power-law dependence has been fitted to the first part of the curve and an exponential ( $t_{1/2} = 48$  min) to the last part. A copper cathode was used, and the exposure time was 180 min.

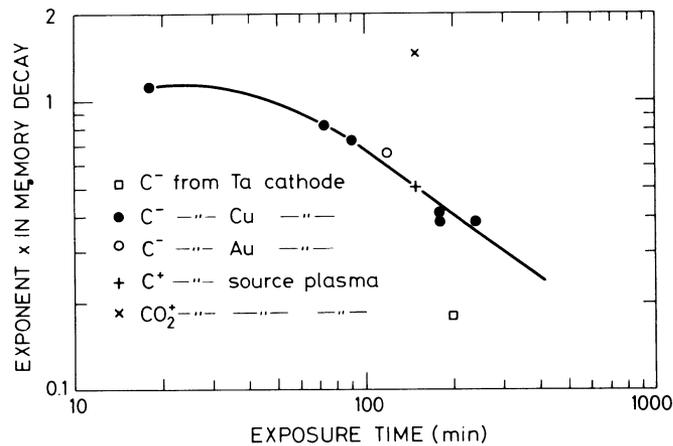


Fig 4. The exponent  $x$  in the power-law decay,  $F \propto t^{-x}$ , plotted as a function of exposure time for different sputter materials. Also shown are values for positive beams, extracted from the source at reversed potential (see text).

exposure time, indicating that memory effects grow with exposure time. The memory effects must be governed by a competition between, on the one hand, processes depositing carbon in the source such as  $C^-$  sputtered from the cathode being implanted around the source outlet, positive ions from the plasma being implanted in the end-plate cathodes, and adsorption of C and CO diffusing to the discharge-chamber walls, and, on the other hand, processes liberating carbon chemically or by sputtering or desorption. High deposition rates in certain parts of the source do not necessarily lead to severe memory effects since liberation rates may be correspondingly high. This seems to be the case for the copper sputter cathode, itself. Thus, changing the exposed cathode to an unexposed one (which can be done in ca 5 minutes) simultaneously with sample change did not alter the memory effects as compared to the normal procedure when the same cathode is used throughout. Probably the long-lived memory components come from the more 'remote' parts of the source, where deposition and liberation rates are low. It should be added that the copper cathode was originally chosen because it sputters readily so that carbon-implanted layers are rapidly removed from the cathode, and a layer of copper builds up on the inside of the anode cylinder, continuously 'burying' the carbon deposits, thereby reducing memory effects.

If the source is allowed to 'clean up' for 5 to 10 hours by running on cesium vapour alone, then F attains 100% within the measuring uncertainty of 2% when 90% enriched  $CO_2$  is introduced. This is an indication that essentially all the  $C^-$  beam originates from the gas feed rather than from the vacuum system or the source, itself. Under the same conditions, the  $C^-$  beam increases by a factor of 500-1000 both absolute and relative to the  $Cu^-$  beam when  $CO_2$  is introduced, supporting the above conclusion.

Results are summed up in figure 5, which shows the delay in reaching 2% memory level as a function of exposure time. Note the high value for the tantalum cathode, probably due to the porous nature of commercial tantalum. For copper and gold, the delay is of the order of the exposure time. Rapid changing between a sample to be  $^{14}C$  dated and a known standard would not be practical with the ANIS source in its present design unless their compositions are matched to some extent.

Included in figure 5 are delay values for beams of  $C^+$ ,  $CO^+$ , and  $CO_2^+$ , extracted from the source at a reversed potential of +20kV in intensities of 3, 12, and 0.5  $\mu A$ , respectively. The delay time for  $CO_2^+$  is remarkably low, a factor of ten lower than for  $C^+$  and  $C^-$  at similar exposure times, and only

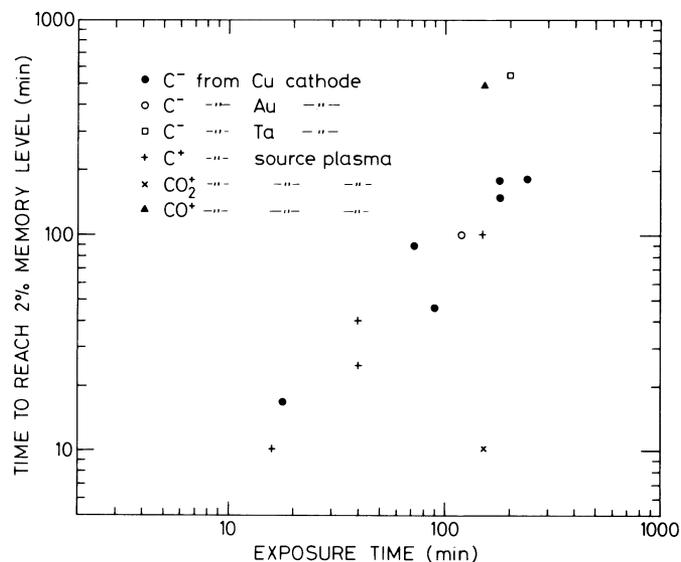


Fig 5. Time taken to reach 2% memory level after sample change, plotted as a function of exposure time.

a factor of three higher than the pumping time. This is a confirmation that adsorption of  $\text{CO}_2$  in the gas-supply system or in the source, itself, is not responsible for the observed  $\text{C}^-$  memory effects. The observation also suggests that memory-free  $\text{C}^-$  beams could be produced by break-up and charge exchange in a metal vapour of  $\text{CO}_2^+$  beams, extracted from a positive source. This idea was tested on a  $12\mu\text{A}$   $\text{CO}_2^+$  beam extracted at 20kV from an RF source with 2% efficiency. The memory effects were essentially determined by the pumping time. By collision in sodium vapour, the  $^{12}\text{CO}_2^+$  beam was converted into 5.5keV  $^{12}\text{C}^-$  with an efficiency of 4.4%. According to the charge-exchange data (Heinemeier and Hvelplund, 1978), the expected fraction of negative carbon ions at this final energy is 35%, provided the vapour-target thickness is sufficient to breakup all the molecules and bring the carbon ions into charge-state equilibrium. The low yield observed appears to be due to the difficulty of breaking up the  $\text{CO}_2^+$  molecule as well as beam scattering reducing the transmission. The test should be repeated at higher beam energy, where both effects would be less severe.

#### CONCLUSION

The intensity and efficiency of  $\text{C}^-$  ions produced in the ANIS source from  $\text{CO}_2$  gas is well below the values,  $40\mu\text{A}$   $\text{C}^-$  beam at  $\sim 10\%$  efficiency, routinely achieved by sources operating

on solid-carbon samples (Hedges, 1981). Background beams of  $C^-$  from the ANIS source itself seem to be similar to the  $\sim 1\%$  values found by Hedges, Wand, and White (1980). Memory effects in the ANIS source are clearly more severe than for the Middleton type, although we are not aware of detailed studies for these sources. Berthier et al (1981) have used a carbon sputter cathode to produce a  $C^-$  beam from an ANIS source and find that  $^{14}C$  memory drops to less than 1% after change to a copper cathode. Improved memory properties could possibly be achieved by reducing the surface area of the discharge chamber and by briefly running an intense discharge of an inert gas between successive  $CO_2$  samples. We plan to try such measures along with further investigations of the alternative solution of  $C^-$  production by charge exchange. A comparison of the ANIS source with other gaseous sources indicates that it is superior in performance parameters relevant to the production of  $C^-$  beams for dating purposes.

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