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ELSEVIER

## Enrichment of sub-milligram size carbon samples

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### Abstract

We have developed a carbon isotope enrichment system for use in conjunction with the Groningen Accelerator Mass Spectrometer. Using thermal diffusion of CO, we obtained an enrichment factor of about 3 for  $^{13}\text{C}$  for half-gram carbon in 5 days. This means we expect for  $^{14}\text{C}$  an enrichment factor of 6, corresponding to an extension of the radiocarbon time scale by 15000 years.

### 1. Introduction

Most of the advantages of Accelerator Mass Spectrometry (AMS), as reductions in sample size and in counting time, are well established. However, the advantage of extending the  $^{14}\text{C}$  time scale beyond limits typically achieved by decay counting [1] has not yet occurred.

One potential approach to extend the age range is by increasing  $^{14}\text{C}$  content of the sample by a known factor using enrichment. The  $^{14}\text{C}$  measurement of enriched samples decreases the influence of contamination during sample handling such as graphitization because of the high count rate. In addition, the enrichment of carbon to suitable size for AMS measurement is effective for old samples. A 1 mg AMS size sample enriched contains more than 260 atoms because a 500 mg sample of carbon 100 ka old still contains about  $1.3 \times 10^5$   $^{14}\text{C}$  atoms.

We have developed a thermal diffusion isotope enrichment system for use with the Groningen AMS [2,3]. Our goal is to increase the  $^{14}\text{C}$  count rate for very old samples. We report here the preliminary results of carbon isotope enrichment as well as a description of the system.

### 2. Apparatus and operation condition

Enrichment of carbon isotopes for extending the  $^{14}\text{C}$  time scale beyond 50 ka BP has been developed in the past for conventional counting [4–7]. We enriched samples in the form of CO by means of thermal diffusion which was also applied in the past for conventional dating. Compared with conventional dating, the system size can be scaled down considerably for AMS because the amount of enriched sample is much smaller.

The AMS enrichment system consists of a single thermal diffusion column with a top reservoir of 510 ml (Fig. 1). A 0.2 mm diameter Platinum–Iridium (80–20%) wire with five spacers for centering is suspended in the 6 mm diameter Pyrex inner tube. The effective length of the wire and column is 3 m. The wall of the Pyrex tube is cooled on the outside by water flowing up between the wall and a second concentric Pyrex tube of 30 mm diameter. The column construction is similar to that published in Ref. [6]. The power consumption is about 200 W (28.1  $\Omega$ ), resulting in a wire temperature of about 900 K. The cold wall temperature is about 25°C.

The graphitization of the enriched CO was carried out at the reactor connected directly to the bottom of enrichment column (see Fig. 1). The enriched CO was expanded into the small expansion volume (2.65 ml) and hydrogen of 10% excess of CO was mixed into the quartz reactor tube containing 5 mg of iron powder. A heater was placed around catalysis and then heated at  $630 \pm 10^\circ\text{C}$ . A cold trap of ethanol and dry ice was used to freeze out water produced during the reaction. The pressure change during the graphitization was monitored by a pressure transducer. A typical reaction time was 6 h.

The AMS  $^{14}\text{C}$  measurements were performed with the high-throughput AMS installed at the Centre for Isotope Research in Groningen, The Netherlands [3]. The measurements of the  $^{13}\text{C}/^{12}\text{C}$  ratio to determine the enrichment factor were carried out by both conventional stable isotope ratio mass spectrometry (after combustion of produced graphite from enriched CO) and the AMS.

### 3. Determination of the enrichment factor

The optimal operational conditions such as the pressure in enrichment column should be determined by the construction of enrichment system. There is a serious discrep-

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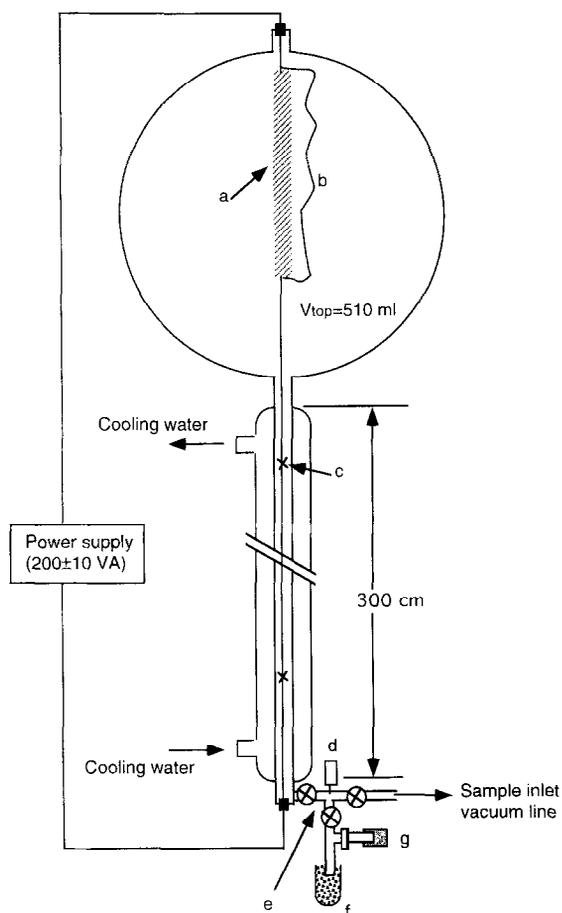


Fig. 1. Small-scale AMS thermal diffusion enrichment system for Groningen AMS  $^{14}\text{C}$  measurement: (a) steel spring, (b) flexible copper wire, (c) Pt-Ir (80–20%) 0.2 mm diameter wire spacers for centering, (d) pressure transducer, (e) expansion volume of 2.65 ml for taking enriched  $\text{CO}$ , (f) dry ice and ethanol trap for removing water produced during the graphitization, (g) small oven for graphitization.

ancy between theoretically calculated and observed enrichments [5] and the precise effects of different configurations, especially for the high pressure during the enrichment, are unknown [6]. In order to determine the optimal condition for our enrichment system, we enriched  $\text{CO}$  from a commercially obtained cylinder at the different pressures of 976, 1462 and 1950 mb, corresponding to 0.36, 0.50 and 0.67 g carbon, respectively.

In Fig. 2, we show the enrichment factor ( $q^{13}$ ) as a function of this pressure. The  $q^{13}$  is defined as [7],

$$q^{13} = R_{\text{enriched}}/R_{\text{sample}}, \quad (1)$$

where  $R$  is  $^{13}\text{C}/^{12}\text{C}$  ratio. The enrichment appears to approach equilibrium during the first three days. Enrichment as a function of time is not sensitive to pressure. However, the optimal enrichment depends on pressure,

which in turn depends on sample size. In our system, we expect a maximum enrichment factor of about 3 for  $^{13}\text{C}$  and 6 for  $^{14}\text{C}$  in about 3 days. The optimal operation pressure is 1500 mb, corresponding to 0.5 g carbon. Fig. 3 shows the enrichment factor  $q^{13}$ , measured by both conventional stable isotope mass spectrometry and AMS. These enrichment factors show excellent agreement in the range of a factor of 1–3. Based on the theoretical consideration [5–7], the enrichment depends on the ratio of the total sample mass to the mass of enriched samples collected. Decreasing the mass of enriched samples tends to increase the enrichment factor of sample. Because of AMS, however we do not need additional sampling for determining the enrichment factor of the sample.

The enrichment measurements are performed for  $^{14}\text{C}$  background materials. The  $^{13}\text{C}$  measurements of these backgrounds are shown in Fig. 3. The  $^{14}\text{C}$  enrichment factor  $q^{14}$  has not yet been obtained; we will test the enrichment system with samples with a known  $^{14}\text{C}$ -age (not background).

#### 4. Conclusion and prospects

We have built an enrichment system for AMS-size samples, based on thermal diffusion. We have measured them for the stable carbon isotope enrichment factor for  $^{13}\text{C}$ , both by AMS and conventional stable isotope mass spectrometry. At present we obtained an enrichment factor of 3 for  $^{13}\text{C}$ . We should be able to obtain a  $^{14}\text{C}$  enrichment factor of 6.

We expect that the isotope enrichment/AMS combination technique becomes a useful approach for the extension of the radiocarbon time scale as well as for reduction of

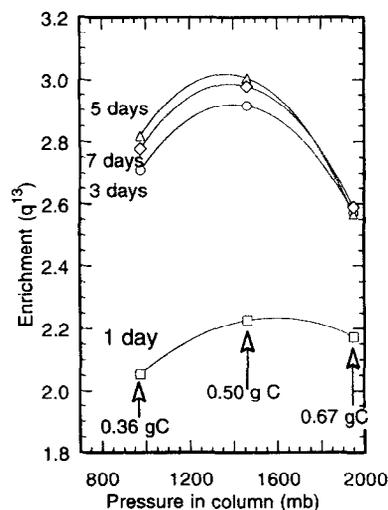


Fig. 2. Enrichment factor for  $^{13}\text{C}$  as a function of pressure in column, and time.

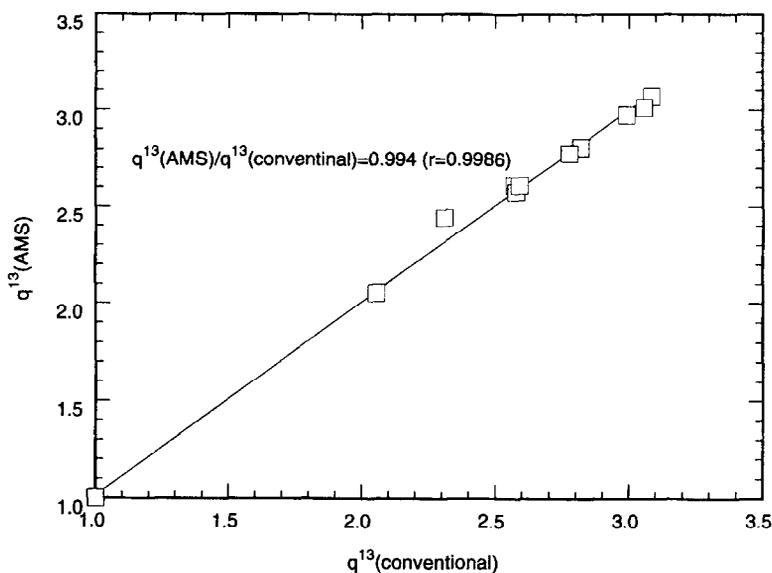


Fig. 3. Enrichment factors for  $^{13}\text{C}$  measured by conventional stable isotope mass spectrometry and AMS.

AMS counting time of (very) old samples. This requires further progress of isotope enrichment technique developed thus far, in particular, the reduction of contamination levels during the graphitization. This work is in progress and we intend to give a full account in the near future [8].

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