AMS sample handling in Groningen

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Abstract

The Groningen AMS target laboratory has a capacity of producing 2000 targets annually. Samples are combusted by a CN analyser/mass spectrometer combination. A 25-fold graphitization setup is employed. We emphasize a combination of automation and quality. Backgrounds of better than 45 ka are routinely achieved. Test measurements on contamination, backgrounds and fractionation are reported.

1. Introduction

As is the case with the Groningen conventional laboratory, the AMS laboratory handles about 1000 samples annually. The Groningen AMS system has now been operational for two years, during which time about 4000 targets were produced; half of these are standards, backgrounds and targets for various test programs, the other half were targets for “real samples”. These samples consisted of water (DIC, Dissolved Inorganic Carbon) from ground water and the ocean, marine and fresh-water carbonates, atmospheric CO2, organic deposits such as peat, soils and macrofossils, and the complete spectrum of archaeological datable materials such as wood, charcoal and fossil bone. In addition, many samples arrived in the laboratory in the form of breakseals (CO2 sealed in glass containers) ready for graphitization. Furthermore, special target preparation systems are made for PhD projects such as ocean DOC (Dissolved Organic Carbon), Particulate/Dissolved Inorganic/Organic Carbon in sediments and pollen concentrates. On these special projects we report elsewhere at this conference [1,2]. For a description and performance of the Groningen AMS system we refer to [3]. A diagram indicating the different sample materials handled by the AMS-sample laboratory is shown in Fig. 1.

2. Sample treatment

Analogous to the conventional 14C laboratory which also has a capacity of about 1000 samples per year, we realised a separate preparation laboratory. The organic samples are chemically pretreated to remove contamination, before they are combusted to CO2. The form and the intensity of the pretreatment depends on the type, quality and quantity of the sample. The usual method is Acid-Alkali-Acid (AAA) for the peat and other organic deposits, charcoal and wood, Longin for bone and phosphoric acid for carbonates. For a complete description we refer to literature [4,5] with the obvious note that the amount of material for AMS is scaled down considerably.

For inorganic samples bi-carbonate from water is converted to CO2. CO2 from air samples is trapped cryogenically. Breakseals are broken on one of the laboratory’s mass spectrometers, enabling direct measurements of stable isotopic ratios (13C, 18O); the samples then are trapped cryogenically and transferred to the graphitization setup.

The organic samples are combusted in an automatic CN-analyser, of which we employ two: Europa Scientific

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Fig. 1. Diagram indicating the various sample materials handled by the Groningen AMS laboratory in the first two years of operation. The total number of samples is about 2000.
20/20-roboprep CN combination and Fisons/Carlo Erba Optima/NA 1500 combination. Both consist of a Cr$_2$O$_3$ flash combustion tube, Ag and CuO purification furnaces and a Cu reduction tube, a water trap and a gas chromatographic column to separate N$_2$ and CO$_2$. Each CN-analysers is coupled on-line to a stable isotope mass spectrometer enabling high-precision $^{13}$C and $^{18}$O determinations. The CO$_2$ is trapped cryogenically for graphitization later on. At present this is done manually; an automatic system is under construction.

3. Target production

The (purified) CO$_2$ as produced by the CN-analysers, breaks seals, the water laboratory or the conventional $^{14}$C laboratory (test measurements, standards and conventional samples which appear too small) is cryo-trapped in small glass vessels. These are transferred to the graphitization room. For graphite production, we employ the method of reduction under an excess of hydrogen gas, using iron powder as a catalyst [6]: CO$_2$ + 2H$_2$ \rightarrow (Fe) \rightarrow H$_2$O + C. Our excess of the H$_2$ gas is a factor of 2.5 times the amount of CO$_2$. The Fe-powder we use is < 325 mesh and > 99.5% pure. Before the actual reduction, we flush with H$_2$ in order to remove any unwanted CO$_2$. The CO$_2$ is transferred to a variable volume to adjust the amount of gas. The H$_2$O is trapped in a cold finger, which is cooled to $-18^\circ$C by a Peltier element. The temperature of the reduction oven is kept at 600°C. During the reduction reaction, the pressure is monitored on computer screens. In general the reaction takes 200 min. We employ one 10-fold and one 15-fold graphitisation system, with volumes ranging from 3 to 8 ml. With this setup we can handle samples from 150 $\mu$g C and up.

The final step is the transfer of the graphite powder to the target holder which fits in the caroussel of the AMS ion source. This is done in a laminar crossflow installation in a semi-clean room. The graphite is pressed into the target holder with a force of 2.5 Nm, either by hand (one by one) or by an automatic system. The automatic press is shown in Fig. 2. It consists of a wheel which can be loaded with 24 targets. First, the graphite powder is poured into the target through a funnel. Next, steel pins are loaded; the graphite is pressed from the back between these steel pins and a stainless steel foil, covering the front surface of the target. The force applied transfers the graphite powder to a solid with a flat and shiny surface (after removal of the foil); the force applied also joins the steel pin into the (aluminum) target holder.

The pressing force for the hand-press is applied by a torque-wrench; for the automatic system this is done with stepping motors; all loaded targets are pressed sequentially. The force applied on the target is measured by a pressure transducer in order to improve reproducibility of the pressing procedure; in the past we have experienced some difficulties with the hand-press in this respect.

We employ two types of targets. The standard ones have a 2 mm diameter graphite surface, and is sputtered at 8 positions during measurement [3]. For small samples (< 0.7 mg C), however, targets with a 1 mm diameter graphite surface are used. These small targets are also sputtered at 8 positions, albeit in a smaller radius. Both 1 and 2 mm targets can be pressed with the manual and automatic target press.

For logistic reasons, we assign a Groningen number (GrA) to each fabricated target, thus including standard, background and various test targets. Following the pressing procedure, the targets are stored in specially designed memory effect graphitisation

![Fig. 2. The new automatic graphite target press.](image-url)

Fig. 2. Results from a memory-effect test of the graphite system: $^{14}$C/C ratio (versus sample number) for anthracite. In-between each anthracite, a sucrose (IAEA-C6) sample was graphitised.
4. Experimental results

In the first two years of operation of the Groningen AMS system, the target laboratory has produced about 4000 graphite targets. For overall performance of the Groningen AMS we refer to [3]; for scientific results obtained thus far we refer to [2].

Here we report on specific tests concerning contamination effects in the laboratory, several background materials, the graphite system, and fractionation during graphite production.

Contamination has been tested by graphitising CO₂ from anthracite and sucrose in an alternating way. This "sandwich test" mimics the worst possible case. The results for the 5 anthracite samples are shown in Fig. 3, clearly indicating a small memory effect due to the sucrose. The memory effect is roughly a factor of 2 for this procedure. The sucrose measurements (performed in between the anthracites) are omitted in the figure.

Backgrounds of the target preparation laboratory have been investigated extensively. Various background materials and sample handling systems were tested, with the results shown in Fig. 4. The lowest background has been obtained from a graphite rod, which could be mounted in a target holder and was not exposed to any handling in the sample laboratory. The $^{14}\text{C}/C$ ratio (per gram of carbon)

![Graph showing background measurements](image)

Fig. 4. Results for background measurements for materials indicated; $^{14}\text{C}$ (expressed in $^{14}\text{C}/C$ ratios), top and $^{13}\text{C}$ (in $^{13}\delta$), bottom.

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for this background is $5 \times 10^{-17}$, corresponding to an age of about 65 ka. In addition, graphite powder was tested; the only sample handling was pressing in a target holder. In this case the background level is $1-2 \times 10^{-16}$. Rommenhöller is a fossil CO$_2$ gas which had to be graphitized and pressed; the background level is $10^{-16}$. For anthracite we distinguish two batches. One is anthracite combusted by the conventional laboratory and used as background for the proportional gas counters; this high purity CO$_2$ is trapped and transferred to the graphitization setup. AMS measurement yields backgrounds of $3 \times 10^{-16}$. The second batch is anthracite, combusted by the CN-analyser as used for most organic AMS samples; this background anthracite is higher by a factor of $2 \times (6 \times 10^{-16})$.

Finally, we tested the backgrounds for two systems in use for CO$_2$ production from inorganic samples: marble and water, which was bubbled through with Rommenhöller-CO$_2$. These backgrounds were $8 \times 10^{-16}$ and $3-4 \times 10^{-16}$, respectively. Representative background measurements are shown in Fig. 4; the top part of Fig. 4 shows the background in $^{14}$C/C ratio, the bottom part shows the AMS-$^{13}$C values for the same targets.

Fractionation during CO$_2$-graphite conversion has been studied in detail. In principle, fractionation is not critical for $^{14}$C age determination, since the $^{14}$C signal is fractionation-corrected. However, if one uses the mass spectrometer to determine the $^{13}$C ratio of the CO$_2$ gas prior to graphitisation, the fractionation during the graphitisation process is not corrected for. A safer way is to use the $^{13}$C measurement of the accelerator itself. Nevertheless, one would like to be able to rely on the $^{13}$C determination, so one gets an extra check parameter on the accelerator’s performance: the $^{13}$C comparison. We have repeated the graphitisation reaction several times with the same CO$_2$ under identical conditions. The main (reversible) reactions are: CO$_2$ + H$_2$ $\leftrightarrow$ H$_2$O + CO and CO + H$_2$ $\leftrightarrow$ H$_2$O + C.

Since the water vapour is continuously removed, the equilibrium of both reactions is almost completely on the right side of the reaction. In addition methane can be produced: C + 2H$_2$ $\leftrightarrow$ CH$_4$; this is, however, an undesirable complication [7].

We analysed our graphitisation reactors in the following way: at a time varying between 1 and 100 min, the reaction is stopped. The rest gas mixture, consisting of H$_2$, CO$_2$, CO and possibly CH$_4$, is then transferred to a circulation system that separates the gases in the following way: all CO$_2$ is captured in a liquid air cold trap by circulating during = 10 min, until there is no more pressure change. Then, the trap is isolated, and the rest gas is directed through a hot CuO oven ($T = 400^\circ$C). This oven oxidizes CO (and H$_2$), but not (much of) the CH$_4$. The formed H$_2$O and CO$_2$ are trapped in a dry ice and liquid air trap, respectively.

The two “sorts” of CO$_2$, the original one, and the one oxidized from CO, are isotopically analysed on the SIRA-9 IRMS (as far as the amounts allow). Also the formed graphite is combusted and $^{13}$C-analysed. Some of the graphite, however, is $^{14}$C-analysed in the AMS. Also, all amounts of gas are measured. The isotope measurements are shown in Fig. 5, plotted as a function of the relative amount of CO$_2$ left at any time. The $^{13}$C of the CO$_2$ and C, as well as the $^{13}$C of C can be fitted with Rayleigh curves:

$$\delta = (N/N_0)^{a} + \delta_0 \quad \text{for the } ^{13}\text{C of CO}_2,$$

$$\delta = (1 + \delta_0) \times (1 - (N/N_0)^{a-1})/(1 - N/N_0) - 1$$

for $^{13}$C of C.

These fits yield the following fractionation factors for the reactions involved: $^{13}\epsilon = -6.6 \pm 0.2%_0$ for CO$_2$ + H$_2$ $\rightarrow$ H$_2$O + CO, and for CO + H$_2$ $\rightarrow$ H$_2$O + C: $^{13}\epsilon = -39 \pm 3%_0$ and $^{13}\epsilon = -81 \pm 14%_0$. The fraction ratio $^{14}\epsilon/^{13}\epsilon$ of process 2 is $2.1 \pm 0.4$ which is according to what one would expect.

Finally, it appears that the $^{13}$C value for the formed graphite is equal to the $^{13}$C of the original CO$_2$ gas by better than 0.5%o. Still, further investigations are necessary, revealing directly the amount of CH$_4$. Clearly, this amount should be minimised.

5. Conclusions

In Groningen, we have setup an AMS sample handling system with a present capacity of 2000 samples annually, next to and partly intertwined with the conventional $^{14}$C laboratory (1000 samples/year) and stable isotope facility (15000 samples/year).

We have achieved background levels for $^{14}$C/C at best of $10^{-16}$, depending on materials and setup used. In the near future, we will employ an automatic graphite target press (24 samples) and an automatic cryogenic trapping system, coupled to the CN analyser (combustion system). This device will operate fully automatic under processor control, greatly enhancing efficiency. An automatic carbonate system will be considered as well.
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References


