



Gaseous radiocarbon measurements of small samples

M. Ruff^{a,b}, S. Szidat^{a,*}, H.W. Gäggeler^{a,b}, M. Suter^c, H.-A. Synal^c, L. Wacker^c

^a *Laboratory for Radio and Environmental Chemistry, University of Bern, Switzerland*

^b *Paul Scherrer Institute, Villigen, Switzerland*

^c *Laboratory for Ion Beam Physics, ETH Zurich, Switzerland*

ARTICLE INFO

Article history:

Available online 9 October 2009

Keywords:

AMS
¹⁴C
 Gas ion source
 Small samples
 MICADAS
 Blank

ABSTRACT

Radiocarbon dating by means of accelerator mass spectrometry (AMS) is a well-established method for samples containing carbon in the milligram range. However, the measurement of small samples containing less than 50 µg carbon often fails. It is difficult to graphitise these samples and the preparation is prone to contamination. To avoid graphitisation, a solution can be the direct measurement of carbon dioxide. The MICADAS, the smallest accelerator for radiocarbon dating in Zurich, is equipped with a hybrid Cs sputter ion source. It allows the measurement of both, graphite targets and gaseous CO₂ samples, without any rebuilding.

This work presents experiences dealing with small samples containing 1–40 µg carbon. 500 unknown samples of different environmental research fields have been measured yet. Most of the samples were measured with the gas ion source. These data are compared with earlier measurements of small graphite samples. The performance of the two different techniques is discussed and main contributions to the blank determined. An analysis of blank and standard data measured within years allowed a quantification of the contamination, which was found to be of the order of 55 ng and 750 ng carbon (50 pMC) for the gaseous and the graphite samples, respectively. For quality control, a number of certified standards were measured using the gas ion source to demonstrate reliability of the data.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Within the last few years, interest in radiocarbon measurements of samples containing less than 50 µg carbon increased. These samples are difficult to handle because of a possible contamination during sample pre-treatment [1] or a difficult preparation in conventional graphitisation facilities [2]. There are two strategies for solving those problems: one is the construction of mini-graphitisation systems, reported by the Keck Laboratory in Irvine [3] or the VERA Laboratory in Vienna [4]. They succeeded in graphitising and measuring samples with carbon contents smaller than 10 µg. Another solution for dealing with small samples is the gaseous measurement subsequent to the sample combustion. After first tests by Middleton 1984 [5], the Oxford AMS Laboratory built up a first system for measuring gaseous samples using a special constructed Cs sputter ion source [6]. Later, the Erlangen AMS Laboratory [7], ETH-PSI Zurich [8] and the SUERC in Glasgow [9] followed. While both, Middleton and Bronk Ramsey, worked with self-constructed gas ion sources, the Erlangen AMS group used a

NEC MC-SNICS Cs sputter ion source modified by NEC (National Electrostatics Corporation). Nowadays, commercial versions of hybrid Cs sputter ion sources are available and most laboratories investing within the last years in new machines, got equipped with ion sources capable to handle gases.

The Zurich ETH-PSI AMS group has been working successfully with a self-constructed hybrid Cs sputter ion source for more than three years. The source installed at the smallest accelerator, the MICADAS [10], can easily be switched from solid to gaseous mode by just opening a high vacuum valve placed directly underneath the source box. The valve is on source potential and connected to the gas inlet system by a 2 m fused silica capillary (ID: 60 µm). It serves as an insulator of the 40 kV source potential and reduces the pressure of the gas entering the ion source to about five orders of magnitude, to keep the vacuum inside the source box stable while feeding the source with gas.

A first gas inlet system was built based on a combination of an ampoule cracker and a gastight syringe for sample storage and mixture with the helium carrier gas [8]. The syringe can be adjusted to the amount of carbon dioxide of the sample. The gas mixture of helium and carbon dioxide is pressed into the ion source with a constant flow of 36 µl/min (STP) using a stepping motor. During the last 2 years we were able to measure more than 500 unknown gaseous samples containing 1–60 µg carbon.

* Corresponding author. Address: Department for Chemistry and Biochemistry, University of Bern, Freiestrasse 3, 3012 Bern, Switzerland. Tel.: +41 31 631 43 08.
 E-mail address: soenke.szidat@iac.unibe.ch (S. Szidat).

The following work presents our experiences we gained within the last few years working with the gas ion source. Quality and limitations of measurements are discussed as well as detailed dispute is given on the measured blank value. The collected standard and blank data are compared to earlier results with low amounts of graphite samples (8–80 μg carbon), which were measured with the 600 kV ETH/PSI small tandem accelerator (Tandy) [11].

2. Operation and performance

2.1. Sample preparation

Most unknown, standard and blank samples were prepared at the radiochemistry laboratory of the University of Bern. All samples were enclosed in common glass tubes with 4 mm diameter and 6–10 cm length. The borosilicate glass tubes were pre-treated by heating them up to 500 °C and a 3 min evacuation. The samples were prepared in a combustion system called THEODORE described in [12]. The strictly used NIST Ox-I standards were directly filled up from a gas bottle. The blank samples were taken from a common carbon dioxide gas bottle (CARBAGAS, Switzerland, 99.9% purity). The sizes of the used standards and blanks were widely spread over the whole range of sample sizes between 1 and 40 μg carbon. The measured reference materials IAEA C5–C8 were prepared as following: each material was combusted two times at 650 °C, for which three to five ampoules of different sample sizes were filled. The amount of combusted reference material was $\geq 500 \mu\text{g}$.

Solid targets were prepared as described in [2]. Briefly, the sample carbon dioxide was sealed into silica glass ampoules together with manganese and cobalt as catalyst for the graphitisation procedure. The sample ampoules were heated in an oven over 5 days at 630 °C.

2.2. Gas inlet system

The gas inlet system is described in [8]. Briefly, the interface consists of a cracker unit and a gastight syringe. By bending the cracker tube (100 mm stainless steel tube, ID 4.5 mm) in order to destroy the scored glass ampoule, the sample CO_2 is released into the evacuated cracker. After flushing the CO_2 to the gastight syringe (new: 1.3 cm^3 , borosilicate glass, HAMILTON, Reno, USA), the sample gas is mixed with helium as carrier gas. A constant mixture of 5% CO_2 in He is pressed into the ion source using a stepping motor to move the plunger. The volume of the syringe is adjusted to different sample sizes by starting the plunger from different positions. The flow into the ion source is 36 $\mu\text{l}/\text{min}$ (STP) or 1 μg carbon per minute. Two mini pressure sensors, located at the syringe and the ampoule cracker, have been exchanged with more robust and reliable models (KELLER AG, Winterthur, Switzerland).

As the cracker unit and the syringe work independently, the ampoule cracker can be refilled and prepared (about 3 min plus 2 min for flushing) for the next sample in parallel to the running measurement. Thus, no time is lost for the ampoule change and the AMS machine time is dominated by the measurement. In earlier measurements we used to clean the glass ampoules with acetone and water before placing them in the ampoule cracker. But as measurements without performing this cleaning procedure resulted in same blank values, cleaning of the ampoules was stopped. They are just wiped with a lint-free tissue before loading the cracker and handled with gloves.

2.3. Gas target

The gas ion source contains 20 new titanium gas targets per magazine. The magazine can easily be changed during the running

measurement because the outside of the source box and the sample changer are on ground potential. The targets are prepared in house and contain a holder and an aluminium cap with the titanium insert. A detailed description of the target is given in [8]. We clean the targets as following:

- Acetone bath for a few minutes.
- Flushing several times with pure water.
- Main cleaning step: ultrasonic bath in 1% Aclean solution (Chemetal AG, Dintikon, Switzerland) for about 20 min. The cleaning solution based on a boric acid buffer is free of carbon and has potential to dissolve inorganic as well as organic residues on the surface of the titanium targets and the aluminium caps.
- Flushing intensively with pure water.
- For drying: storage of the cleaned targets for 4 h at 130 °C.

However, there is still a surface contamination left on the targets, which is reduced by a pre-sputtering in the ion source of about 2–5 min in a pure He stream. A typical background current of a target is 15–30 nA source current (LE) resulting in 1.5 ^{14}C counts per minute.

2.4. AMS measurements

The gaseous ^{14}C measurements of carbon dioxide were carried out at the MICADAS with 195 kV terminal voltage [10]. This AMS machine has now been running for more than 4 years and is routinely used for radiocarbon analysis of gaseous as well as solid samples. The hybrid gas ion source is typically fed with a 5% CO_2 in helium mixture [8]. Under these conditions the source produces 3–5 μA C^- currents with an ionisation efficiency of typically 3–5% (overall ^{14}C efficiency from cracker to detector: 1.2–1.5%). For a typical 20 μg Ox-I sample, >8500 ^{14}C counts (uncertainty: 1.1%) are achieved in the detector (for 3 μA $^{12}\text{C}^-$ current). CO_2 enters the source with a flow rate of 1 μg carbon per minute. Thus, a sample of 20 μg carbon takes 20 min measurement time and additional 2–5 min for the pre-sputtering process.

In general, we collect data for the ^{12}C and ^{13}C currents and the ^{14}C counts over 20 s and calculate isotopic ratios and currents for these intervals. At the beginning of a typical gas measurement, the current rises very poorly within the first 40 s, often from 30 nA to only 300 nA, because the capillary leading to the gas target is filled with pure helium gas that has to be flushed out by the sample mixture. After that, the current rapidly increases to about 90% of the maximum current within the next minute [8].

The sputtering processes on the target itself are not fully understood, but it is assumed that first a kind of graphitisation occurs, which is getting faster in time because of an autocatalysis. Then the currents rise slightly till the end of the measurement. When the syringe stops, it takes typically one 20 s cycle until the current drops down. The decrease of the current is slower than its increase, meaning that a deposit of carbon on the surface or even an implantation into the titanium occurs [6]. The current drop is slower the more carbon dioxide is measured. For very small samples $<5 \mu\text{g}$ it is possible to reach the background level of the target again after a few minutes post sputtering.

The solid ^{14}C measurements of graphite were done using the ETH/PSI Tandy accelerator, a compact 500 kV pelletron AMS system [11]. The machine is equipped with a MC-SNICS Cs sputter ion source. Processed graphite of 8–80 μg were pressed into the NEC aluminium standard target holder. The graphite was mixed with the cobalt catalyst. Currents (LE) of 0.6–6 μA were achieved from the small graphite targets.

Download English Version:

<https://daneshyari.com/en/article/1683568>

Download Persian Version:

<https://daneshyari.com/article/1683568>

[Daneshyari.com](https://daneshyari.com)