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^{14}C AMS measurement of CO_2 samples with the high throughput HVE gas interface system

G Scognamiglio[1], M Klein[1], A Stolz[2], R Walet[1] and D Mous[1]

[1]High Voltage Engineering Europa B.V., 3812 RR Amersfoort, Netherlands and [2]Institute of Nuclear Physics, University of Cologne, 50937 Cologne, Germany

Corresponding author: G Scognamiglio; Email: info@highvolteng.com

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Abstract

The newly designed HVE gas interface enables the AMS measurement of carbon samples in CO_2 form. The CO_2, e.g. resulting from the sample combustion in an elemental analyzer, is adsorbed in a zeolite trap and subsequently transferred to a motor-driven syringe. Once diluted with He, the gas mixture is transferred into the ion source of the AMS system. A carbon ion beam is formed in the ion source and mass-analyzed by the AMS system, resulting in $^{13}C/^{12}C$ and $^{14}C/^{12}C$ isotopic ratios. The HVE gas interface features two traps and two syringes to maximize the sample throughput, which results in more than 10 samples per hour. The first performance results of CO_2 gas sample AMS measurements that were performed with the HVE gas interface in combination with the HVE 210 kV AMS system are presented in this paper. The measurements show that the gas interface contribution to the $^{14}C/^{12}C$ background is in the 10^{-15} level and to the precision is at or below 1%.

1. Introduction

The graphitization process, required for the preparation of solid carbon samples for ^{14}C AMS, has two disadvantages: it is laborious and contaminates the samples, compromising the measurement background and precision at masses below 150 µgC. Avoiding graphitization, the AMS analysis of CO_2 samples is attractive for biomedical applications with high sample throughput and for the dating of small sample masses. The AMS measurement of CO_2 samples requires a gas handling device that transfers the CO_2 from the gas source to the AMS system with a specific flow and timing, and an ion source capable of producing a C^- beam from CO_2 (Bronk Ramsey and Hedges 1994; Wacker et al 2013).

The HVE AMS ion sources support the operation with gas samples and are used with gas interfaces independently developed by several laboratories (Braione et al 2015; Duijn et al 2014; Klein et al 2023; Stolz et al 2017, 2019, 2020). Recently, HVE designed and manufactured its own gas interface and performed the first tests to determine its contributions to the AMS measurement in terms of background, precision, and efficiency.

2. The gas interface system

The HVE gas interface system is based on the design developed at the University of Cologne (Stolz et al 2017, 2019, Stolz 2020). It connects the AMS system to different peripherals (Figure 1), accepting gas from lecture bottles, typically containing a blank or standard gas for calibration purposes, and other devices. The external gas source used for the tests is an elemental analyzer (EA), whose operation is controlled by the gas interface software. The EA combusts solid or liquid samples and separates in time

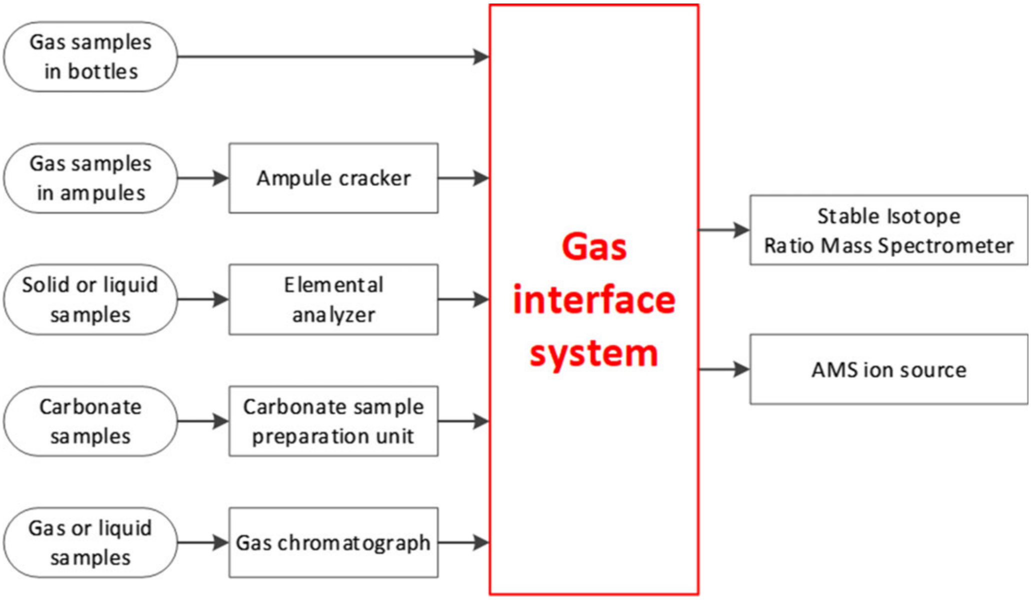

Figure 1. *The gas interface system connects the AMS machine with different peripherals.*

the gases resulting from the combustion, which reach the EA exit port in a He stream. A thermal conductivity detector generates a signal for each combustion product and allows the identification of the CO_2 peak, enabling the transfer to the gas interface system. The mixture of CO_2 and He passes through a zeolite trap at room temperature, which adsorbs the CO_2 only, while the He is directed to waste. By heating the trap to 500ºC, the CO_2 is released from the zeolite and transferred to a motor-driven syringe. CO_2 from lecture bottles, instead, flows directly to the syringe. CO_2 in the syringe is then diluted with He to the desired mixing ratio. The syringe drives the mixture of CO_2 and He via a capillary to the AMS ion source with a controlled gas flow rate. Between processing two samples, the gas interface system runs a cleaning procedure, consisting of purging the trap, syringe, and capillaries with He. The trap is heated to 500ºC during purging and set back to room temperature before accepting the next sample.

The gas interface system features two syringes and two zeolite traps, which are used in parallel to minimize the dead time required for purging, as shown in Figure 2. The resulting sample throughput of more than 10 samples per hour is limited only by the combustion time needed by the EA.

3. Test setup

The described measurements are performed using the test setup shown in Figure 3. The HVE gas interface system is coupled to a ThermoFisher FlashSmart EA and a HVE 210 kV ^{14}C–dedicated AMS machine, whose overall performance is described in (Klein et al 2019; Scognamiglio et al 2021).

The CO_2 from the gas interface is injected into the AMS ion source head through a capillary with a flow rate of about 1.5 µgC/min following the results at CologneAMS (Stolz et al 2017). The ion source is a hybrid SO-110C Cs sputter ion source, which accepts both solid and CO_2 samples (Klein and Mous 2017). The CO_2 is guided onto the Ti insert mounted at the tip of the gas target piece and is adsorbed on the Ti surface from where it is sputtered, as shown in Figure 4. To minimize cross-talk effects between one sample and the next, the target piece is replaced and the capillary between the gas interface and the AMS is flushed with He.

The samples used for the tests have known $^{14}C/^{12}C$ isotopic ratios and are listed in Table 1.

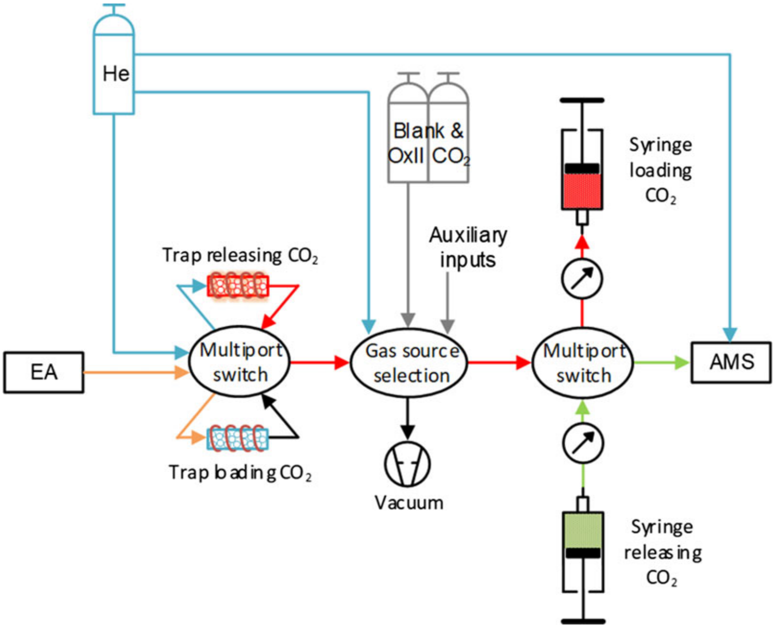

Figure 2. *Schematics of the HVE gas interface. Having two zeolite traps and two syringes allows parallel operation and fast sample throughput. Switching valves direct the* CO_2 *to the desired trap or syringe. While one trap is collecting* CO_2 *from the EA combustion (yellow arrows), the other trap releases the* CO_2 *to the syringe (red arrows). Similarly, when one syringe is loaded (red arrows), the other injects* CO_2 *into the AMS ion source (green arrows). He can flow through the trap to collect the residual* CO_2*, to the syringe to dilute pure* CO_2 *or to the AMS ion source to purge the transfer capillary while pre-sputtering the targets (blue arrows).*

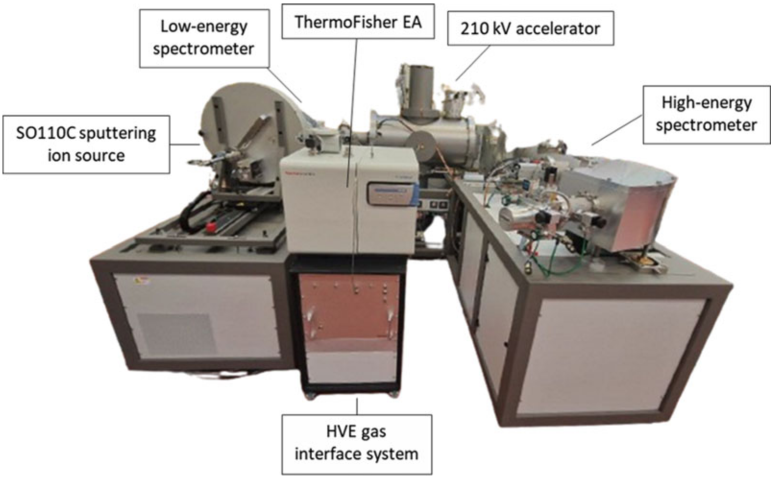

Figure 3. *The test setup used for the measurements, with the HVE gas interface accepting* CO_2 *samples from a ThermoFisher FlashSmart EA and transferring* CO_2 *to the HVE 210 kV AMS machine.*

Blank and OxII CO_2 are admitted to the interface from gas bottles. These samples go directly from the bottle to the syringe. Solid samples supplied by the IAEA with $^{14}C/^{12}C$ isotopic ratios ranging between $3 \cdot 10^{-15}$ and $1.5 \cdot 10^{-12}$ are combusted in the EA. To make sure that the desired number of ^{14}C

Table 1. *Samples used for the tests*

Name	Supplier	Material	Nominal $^{14}C/^{12}C$ ratio
Blank	Linde PLC (2024)	Gas, CO_2 blank (100% CO_2)	$< 5 \cdot 10^{-15}$ (Stolz 2020)
OxII	Isotoptech Zrt. (2024)	Gas, OxII and He mixture (5% CO_2, 95% He)	$1.57 \cdot 10^{-12}$
IAEA-C-3	IAEA (2024)	Solid, cellulose	$1.5206 \cdot 10^{-12} \pm 0.05\%$
IAEA-C-4	IAEA (2024)	Solid, wood	$2.35–5.17 \cdot 10^{-15}$
IAEA-C-7	IAEA (2024)	Solid, oxalic acid	$5.820 \cdot 10^{-13} \pm 0.2\%$
IAEA-C-8	IAEA (2024)	Solid, oxalic acid	$1.77 \cdot 10^{-13} \pm 1.1\%$

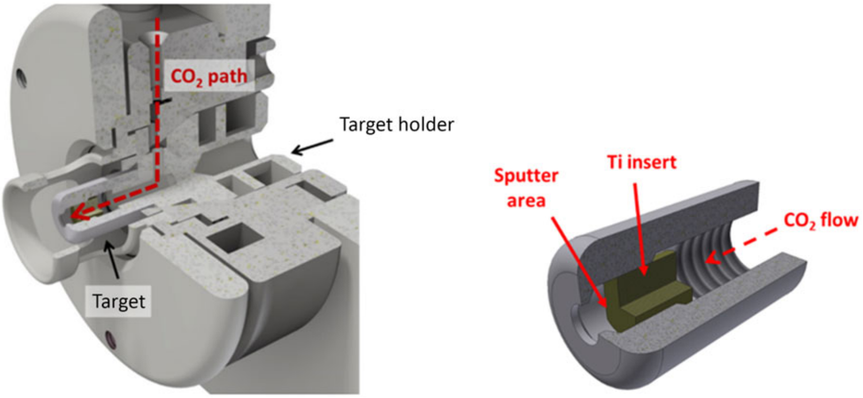

Figure 4. *Left: The sample CO_2 reaches the source head via the target holder and is guided onto a Ti insert placed in the target piece. Right: Section of a gas target piece.*

counts is reached and that the AMS analysis doesn't stop due to lack of sample material, a high sample mass is used for combustion (> 200 µgC per sample) and the excess is discarded at the end of the AMS analysis.

All non-prediluted samples are mixed with He in the syringe to obtain a final sample with a CO_2 content of about 5% for optimal source efficiency.

4. Measurement results and discussion

The experiments with CO_2 samples have been done to characterize the interface contribution to the efficiency, precision, and background of the AMS measurements. The measurement time has been 15 minutes for OxII samples and 20 minutes for blank samples.

4.1. Source output

During the tests, the ion source is operated with a target voltage of 10 kV, an extraction voltage of 30 kV and a Cs reservoir temperature of 110ºC to obtain $^{12}C^-$ currents of a few µA. Figure 5 shows the typical $^{12}C^-$ beam current during the AMS measurement of the OxII reference gas.

Before admitting the sample CO_2 into the ion source and starting an AMS analysis, a new target piece with Ti insert is loaded and pre-sputtered, while pure He is injected into the ion source. Environmental CO_2 that is adsorbed on the surface of the Ti insert generates a small pulse of $^{12}C^-$ output current, that quickly drops to a background current of about 50 nA. When this low current is stabilized, the target is considered to be cleaned by sputtering.

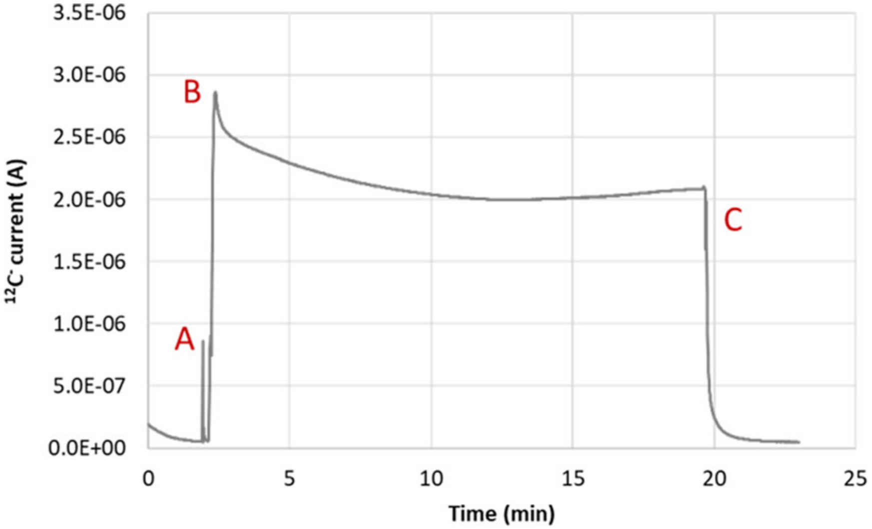

Figure 5. *12 C^- beam current of an OxII bottle gas sample measured in the Faraday cup at the accelerator entrance. The plot shows a peak in the current due to the target insertion (A), the admission of sample CO_2 into the ion source (B) and the purging of the feed capillary with He (C).*

Upon the CO_2 injection into the ion source at a flow rate of 1.5 µgC/min, the $^{12}C^-$ beam current rises within seconds to a value between 2 and 2.5 µA, corresponding to an ion source efficiency of about 1%. At the end of the AMS measurement, the gas feed system is purged with He, and the target piece is replaced.

Higher currents are expected to be obtained with a higher Cs reservoir temperature. Furthermore, in a study realized by CologneAMS on their SO110B ion source, it has been shown that the Cs beam is focused on the Ti insert on a small spot of less than 1 mm in diameter and that the ion source efficiency can increase to 3% by enlarging the sputtering area (Stolz et al 2017). This was achieved by changing the target piece's shape and the ion source geometry. Further investigations are required to confirm that similar changes beneficial to the sputtering efficiency can be applied to the SO110C.

4.2. Background

The $^{14}C/^{12}C$ background ratio is measured as $2.3 \cdot 10^{-14} \pm 10\%$ from the blank gas bottle and $2.8 \cdot 10^{-14} \pm 9\%$ from the IAEA-C-4 wood, with the measurement error determined by the counting statistics. The small discrepancy can be explained by the use of the EA and the trap for the IAEA-C-4 samples, which are not used for gas bottle samples. The contribution of the AMS machine is in the mid 10^{-16} level for solid samples and therefore insignificant for gas measurements.

The measured background is about 2 PMC, which is consistent with the background current being about 2% of the $^{12}C^-$ measured current (see Section 4.1). This indicates that contamination of the target piece represents the main contribution to the gas sample background and that the gas interface contribution is therefore in the 10^{-15} level. Improving the pre-sputtering procedure, e.g. extending its duration, is expected to provide a reduction of the measured $^{14}C/^{12}C$ background to the 10^{-15} level, as measured at CologneAMS (Stolz et al 2019).

4.3. Precision and linearity

The precision was determined by measuring 10 targets that were fed with OxII gas samples from the bottle and 10 targets that were fed with IAEA-C-3 samples combusted in the EA in two different batches. The results are plotted in Figure 6 and listed in Table 2.

Table 2. *AMS results of two batches of reference samples. Each batch measured 10 samples of the same kind, whose values are shown in Figure 6*

	OxII (bottle)	IAEA-C-3 (EA)
Average measured $^{14}C/^{12}C$	$1.35 \cdot 10^{-12}$	$1.28 \cdot 10^{-12}$
Measured ratio/nominal ratio	86%	84%
$^{14}C/^{12}C$ average statistical error	1.35%	1.32%
$^{14}C/^{12}C$ standard deviation	1.85%	1.80%
$^{13}C/^{12}C$ standard deviation	0.23%	0.40%

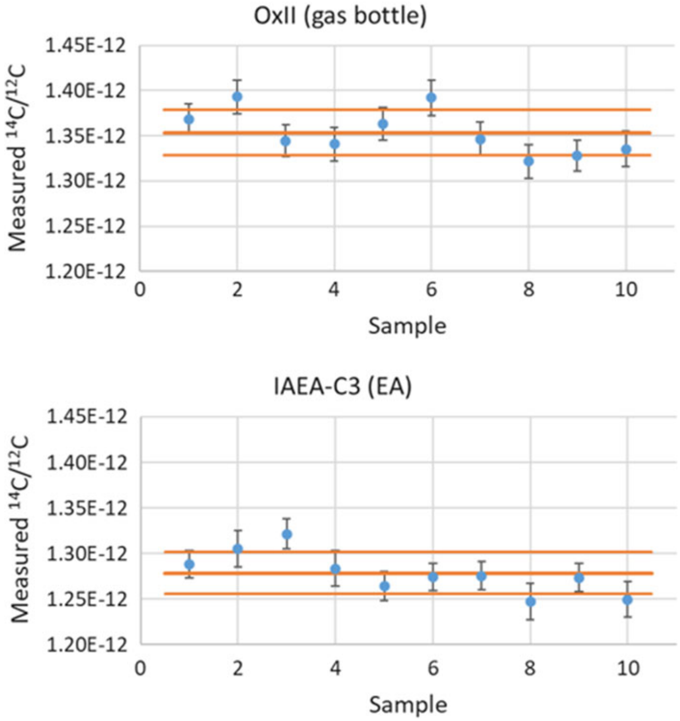

Figure 6. *Results of the AMS measurement of 10 OxII and 10 IAEA-C3 standards. Each data point is reported with the statistical error. The orange lines indicate the calculated average value ± its standard deviation. The normalization factor, defined as the ratio between the nominal and the measured ratio, is about 1.18.*

Since the $^{13}C/^{12}C$ ratio is not influenced by the counting statistics, it is a good indication of the AMS machine's stability and achievable precision. The $^{13}C/^{12}C$ ratios of the combusted samples and gas bottle samples have a standard deviation of 0.4% and 0.23%, respectively. Since the AMS system precision measured for solid samples is 0.2%, the gas interface contribution to the $^{13}C/^{12}C$ ratio error of bottle samples is minor. The EA and the traps are instead the main contribution when combusted samples are measured.

Concerning the $^{14}C/^{12}C$ precision, a statistical error of 1.3% and a standard deviation of 1.8% are measured for both batches. The main contribution to the $^{14}C/^{12}C$ achievable precision is therefore the counting statistics in this case. Further investigations with a higher number of counts are required to determine the contribution of the gas interface to the $^{14}C/^{12}C$ precision. However, the measured $^{13}C/^{12}C$ precision suggests that a $^{14}C/^{12}C$ precision at or below 1% is achievable.

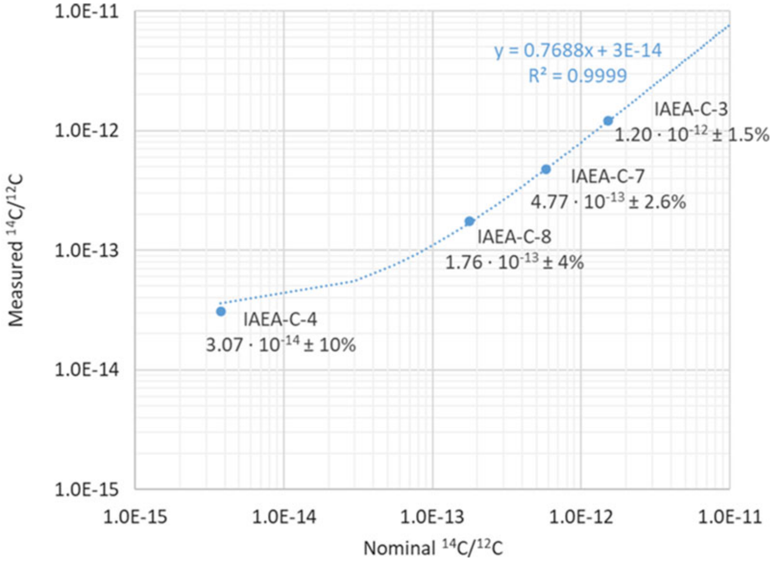

Figure 7. *Measured (non-normalized) $^{14}C/^{12}C$ ratio of different IAEA samples as a function of their nominal value.*

IAEA standards with different $^{14}C/^{12}C$ isotopic ratios are used to determine the linearity of the measurement with the setup based on EA, gas interface and AMS system. The measured ratios are displayed in Figure 7. Since the analysis time is the same for all target pieces, the uncertainties are larger for samples with a lower ^{14}C content and consequently poorer counting statistics. The slope of the linear fit suggests an average measured/nominal ratio of 77%, which is lower than the typically measured 85% (Table 2). The differences are explained by the applied AMS system settings (especially the einzel lens), which were not adjusted for gas measurements after preceding solid sample tests using 30-fold higher beam currents.

5. Conclusions and outlook

A gas interface between an EA and an AMS system has been developed by HVE in collaboration with the University of Cologne. The prototype has been manufactured and coupled to the HVE 210 kV AMS system for preliminary functional and performance tests.

The ion source settings have been kept moderate resulting in a $^{12}C^-$ current of 2–3 μA. The measured background level in the low 10^{-14} is consistent with the 50 nA current measured without CO_2 admission and is related to contamination of the target pieces. Consequently, the background contribution from the gas interface system is in the 10^{-15} regime. The $^{14}C/^{12}C$ precision measurement was limited to 2% by counting statistics. However, a gas interface contribution at or below 1% is anticipated, since the measured $^{13}C/^{12}C$ precision is below 0.5%.

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