DIRECT COUPLING OF AN ELEMENTAL ANALYZER AND A HYBRID ION SOURCE FOR AMS MEASUREMENTS

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ABSTRACT. The requests to measure many samples, and samples with very low carbon masses, make it necessary to develop new techniques in sample handling to accelerate sample preparation and to eliminate carbon contamination. Our 40 MC-SNICS was recently modified to a hybrid ion source. To run the hybrid ion source with a gas parameter, settings were studied and a gas handling system for the direct coupling of an elemental analyzer and a gas ion source was developed.

INTRODUCTION

The Erlangen group uses the accelerator mass spectrometry (AMS) technique for radiocarbon dating. The ratio of ^{14}C to ^{12}C is determined from graphite targets with an ion-sputter source (40 MC-SNICS). Restricting the use of solid targets is the demand for samples of carbon masses of at least 100 μg. Another disadvantage is the time-consuming and labor-intensive step of the graphitization. Motivated by projects in sectors of environmental science, where only small samples are provided (e.g. ~10 μg after a collection time of 1 yr), and life science, where many samples have to be measured, the ion source was modified by National Electrostatic Corporation (NEC) to a hybrid ion source. With this kind of ion source, it is possible to measure graphite samples as well as CO_2 samples. Due to the direct use of CO_2, the usual graphitization and formation of solid sputter targets is not necessary. Because of the higher efficiency of gas ion sources (Bronk Ramsey and Hedges 1997) and less contamination with carbon due to the minimized preparation line, it should be possible to measure samples with carbon masses down to 1 μg. The difficulty is the handling of these small samples. In Erlangen, an elemental analyzer is used for the combustion of samples. The development of a gas handling system for a direct coupling of the elemental analyzer and the hybrid ion source for online measurements is explained in the following.

DEVELOPMENT OF A SYSTEM TO FEED GAS INTO THE HYBRID ION SOURCE

The first aim was to reach a maximum efficiency of produced carbon ions from the CO_2 samples. To determine and investigate carbon ion affecting parameters systematically, a gas-feeding system was designed. As shown in Figure 1, helium (carrier gas for CO_2) is sent to a 3-way valve which leads the gas into the ion source or into a separate vacuum system for flushing the gas-feeding system. The low flow (0.1 standard mL per minute—sccm) is pre-adjusted by the pressure of the helium and the geometry (length, inner diameter) of the glass capillary. Possible flow variations from temperature or pressure variations are regulated by a mass-flow controller. The glass capillary enables the easy tuning of He and CO_2 pressure and switching of the CO_2 valve at ground potential during operation of the ion source at high voltage. The 3-way valve at the high potential of the ion source is switched by a pneumatic actuator. CO_2 is metered (in the range of percentage) in a micro-volume Y-connector into the helium flow through a second glass capillary by the pressure difference between the CO_2 and the helium. The response time of the gas-feeding system due to switching of valves and changing of CO_2 pressure is given in the Table 1. The fast response times were reached by using short transportation ways and very low dead volume connections.

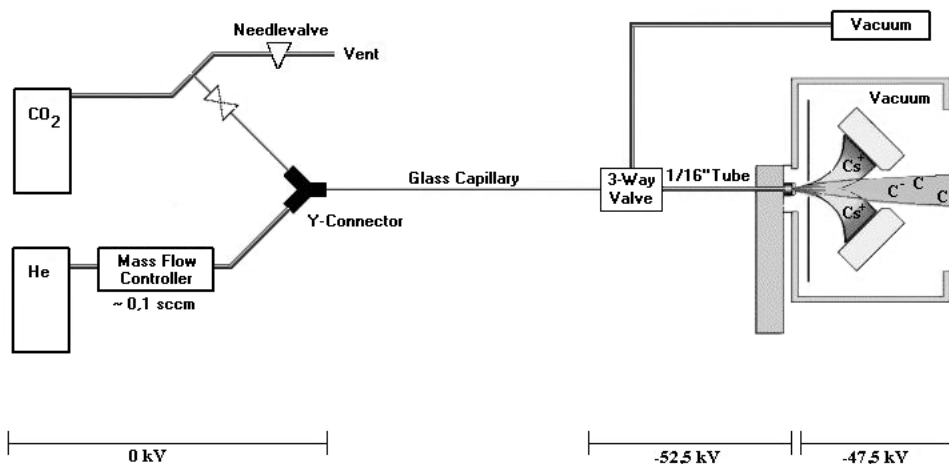[1]Corresponding author. Email: Thomas.Uhl@physik.uni-erlangen.de.

Figure 1 The gas-feeding system

Table 1 Response time of the gas-feeding system.

Operation	Time
Switching of 3-way valve	~10 s
Opening CO_2 valve	~20 s
CO_2 pressure changes	~20 s
Decreasing of $^{12}C^-$ current to offset current after closing CO_2 valve	~5 min
Decreasing of $^{12}C^-$ current to offset current after reducing CO_2 pressure beneath He pressure	~40 s

STUDY OF CATHODE SURFACES FOR GAS SAMPLES

After installation of the gas-feeding system, the geometry of the cathodes for the production of negative carbon ions was optimized. Two different cathode types are offered by NEC, one with a "flat" surface and a second with a "crater" surface (Figure 2). These cathodes differ from the cathodes for solid samples by a using titanium insert in the cathode holder. They are fixed in a cathode wheel where the gas tube is pressed on the backside of the cathode. The CO_2-He mixture is fed directly through the gas tube to the cathode where it passes the titanium insert. The titanium reduces the CO_2 to carbon and oxygen, and carbon ions are produced by cesium sputtering. The maximum obtainable $^{12}C^-$ current for a pre-set cesium offer, the derived efficiency (ratio of the produced carbon ions to the CO_2 molecules introduced into the ion source), and the background current from unused cathodes are given in Table 2. The background current does not depend whether another gas target nearby was used before or not.

Table 2 Investigations of cathode surfaces.

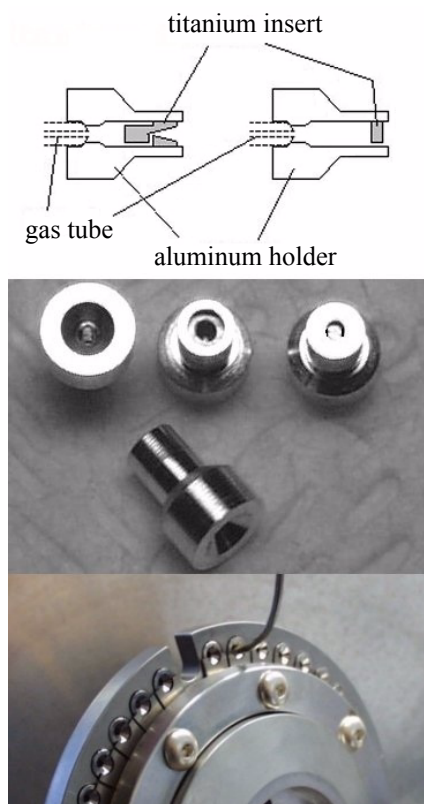| Cathode	Maximum $^{12}C^-$ current (µA)	Maximum efficiency	Background $^{12}C^-$ current (nA)
Flat	3.5	~0.9	14
Crater	4.2	~3.4	100

titanium insert

gas tube

aluminum holder

Figure 2 Comparison of 2 different styles of cathodes

Figure 3 shows a $^{12}C^-$ background-current plot of direct-sputtered gas cathodes over time. As a result of Figure 3, there must be a cleaning (sputtering) process of the titanium surface of about 2 to 3 min before using CO_2 samples.
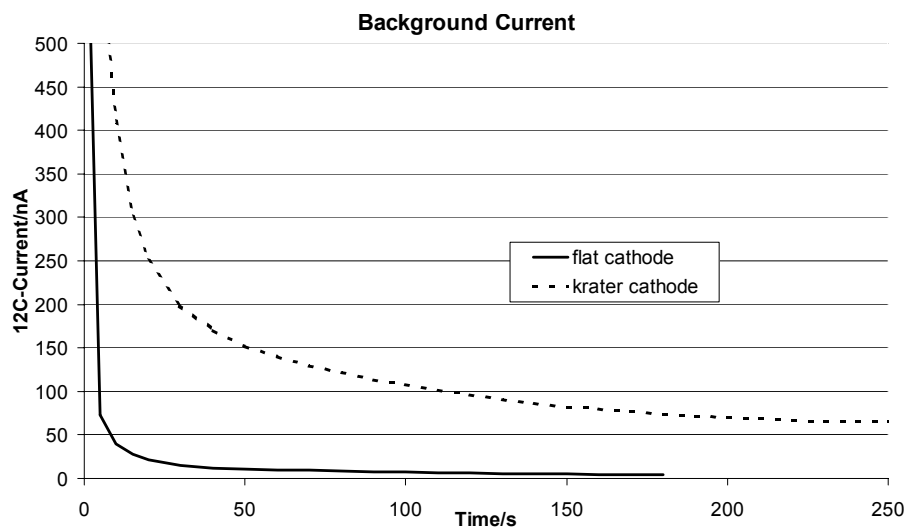

Figure 3 Background $^{12}C^-$ current over time

DETERMINATION OF OPTIMUM PARAMETER SETTINGS FOR THE GAS ION SOURCE

Due to the much higher efficiency, only the "crater" cathodes were taken for subsequent investigations. The following critical parameters for the production of the negative carbon ions have been tested: He flow, Cs oven temperature, electric power of the ionizer, and CO_2 flow (see Figure 4a–d).
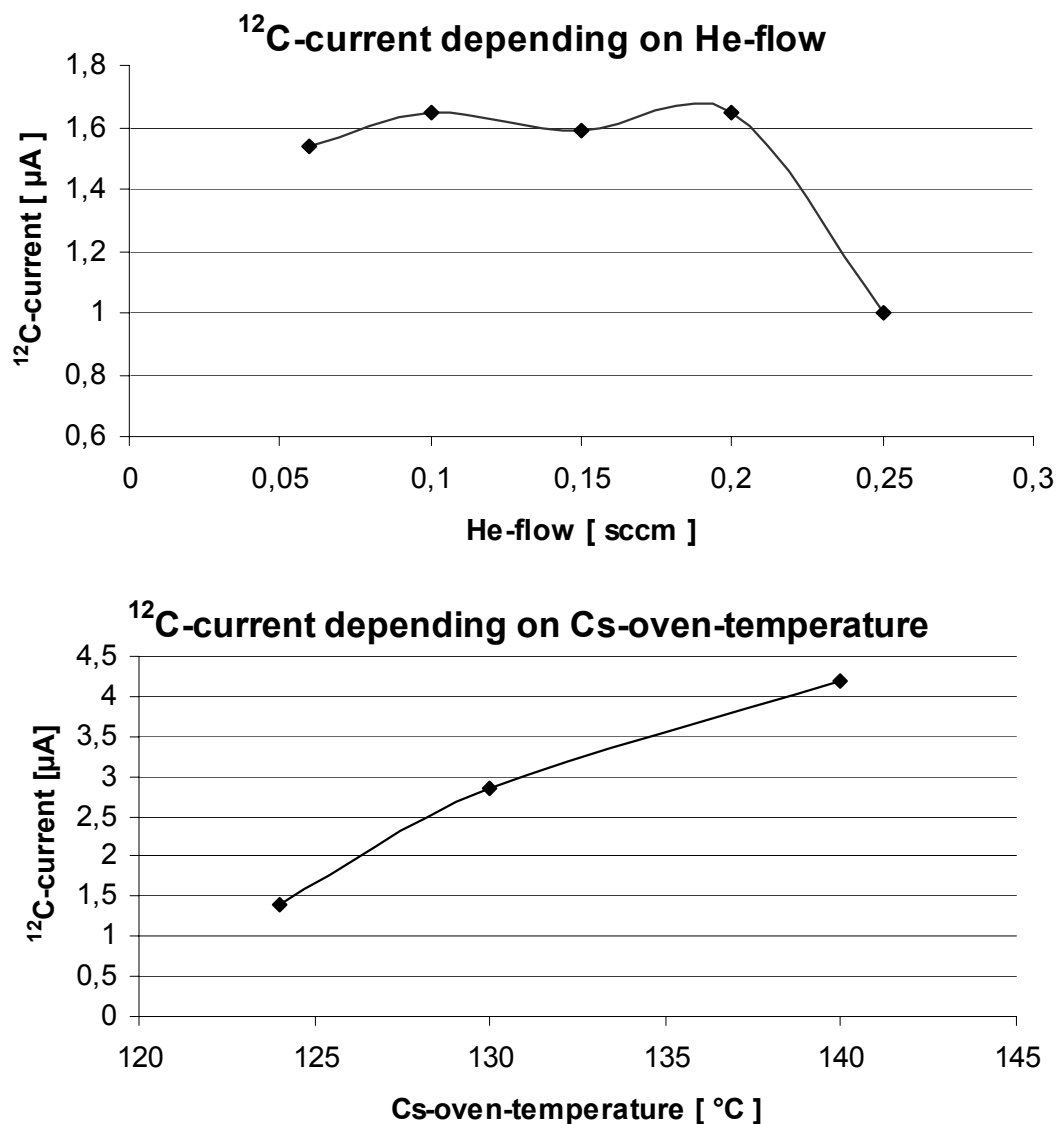

Figure 4 (a–b) Plots of $^{12}C^-$ current versus He flow and Cs oven temperature, respectively.

^{12}C-current depending on electric power of ionizer

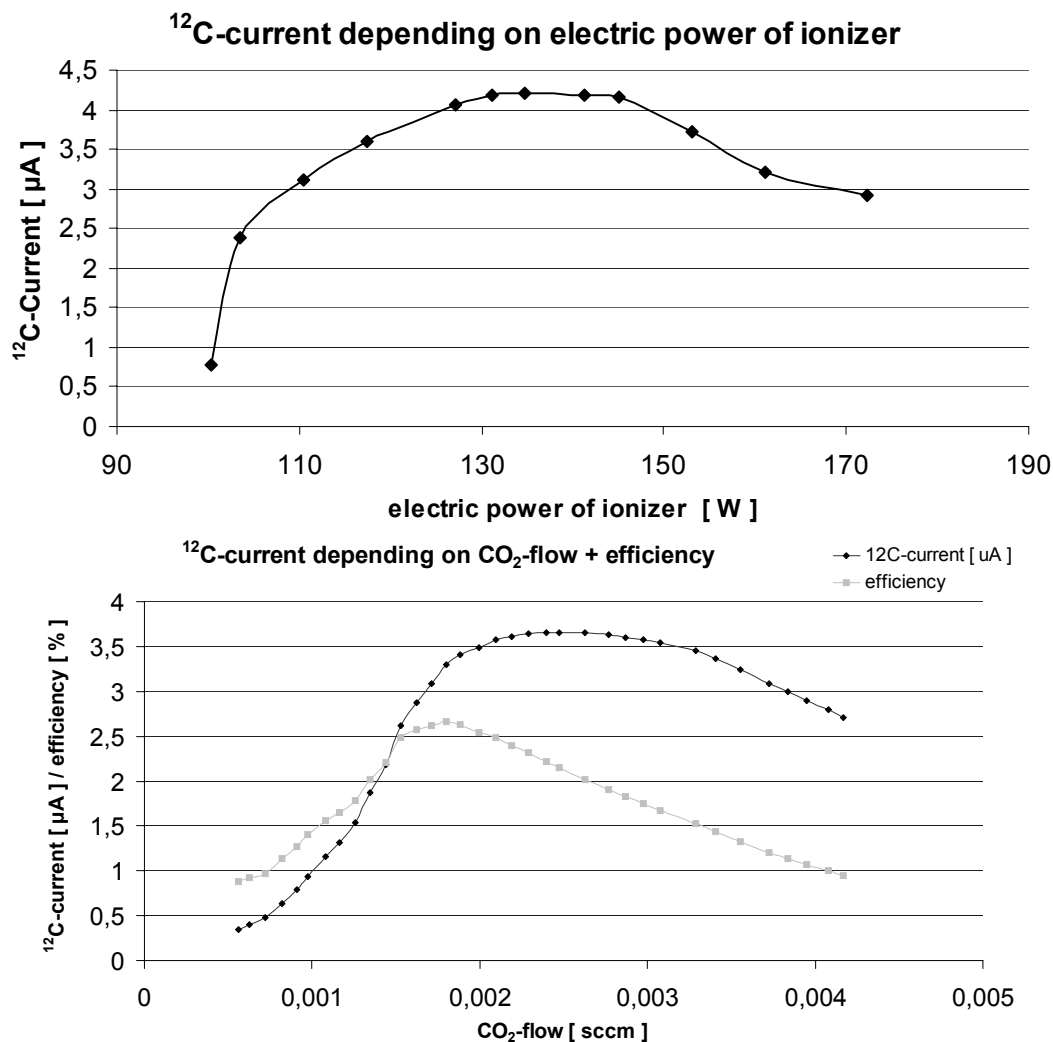## ^{12}C-current depending on CO_2-flow + efficiency

Figure 4(c–d) Plots of ^{12}C$^-$ current and electric power of ionizer and CO_2 flow and efficiency, respectively.

The conclusion from Figure 4a–d is:

- He flow should not exceed 0.2 sccm;
- The higher the Cs oven temperature, the higher the ^{12}C$^-$ current; we did not exceed the 140 °C because it is our aim to reach a maximum efficiency with a minimum use of Cs in order to reduce the contamination of the ion source with Cs;
- The optimum electric power of the ionizer is ~140 W;
- Maximum efficiency is reached at a CO_2 flow of ~0.002 sccm (0.001 sccm = 0.53 μg [carbon/min]).

Figure 5 shows a plot of the long-term sputtering of a cathode with a constant CO_2 flow. It shows a continuous increasing of the ^{12}C$^-$ current for 20 min, until it remains at a constant level. Closing of the 3-way valve causes a drop of the current only to 50% of maximum (so every cathode can only be used for 1 gas sample). The current rises back to the previous value after opening the valve again.

long term ^{12}C-current
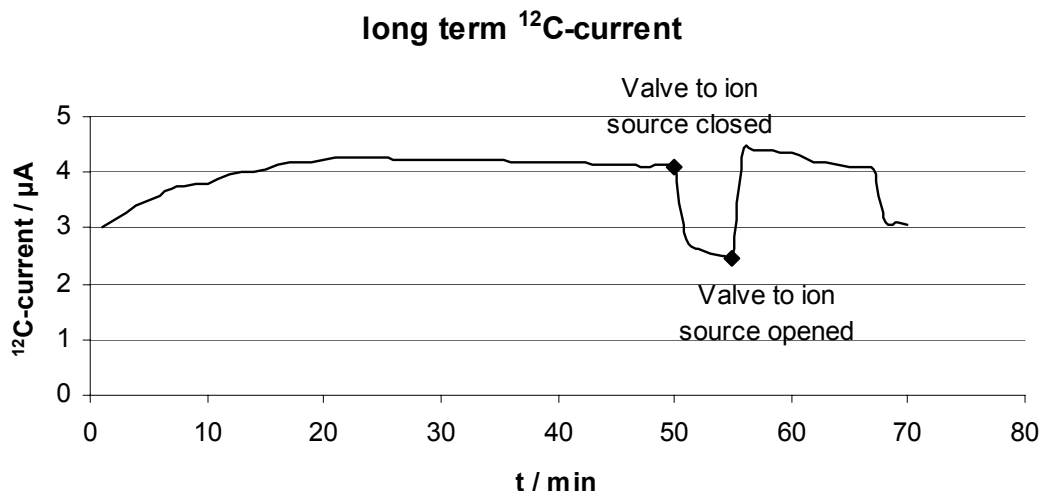
Figure 5 Long-term ^{12}C$^-$ current plot

DEVELOPMENT OF A TECHNIQUE TO HANDLE CO$_2$ SAMPLES: 'CRYOGENIC STORAGE AND RELEASE'

The standard method used in Erlangen for the formation of solid targets is to combust carbonaceous samples with an elemental analyzer (EA), to collect the CO$_2$ cryogenically, to graphitize it, and to press it into the cathode holder.

A direct coupling of the EA and the hybrid ion source skips the last 2 steps. Therefore, a method had to be developed to link the EA and the ion source that resolves 2 problems:

1. As learned from Figure 4a, the maximum helium flow is 0.2 sccm, but the EA provides a helium flow of 100 sccm.
2. CO$_2$ from the EA is only provided for ~40 s. For the optimum CO$_2$ flow of 0.002 sccm and a sample size of 10 µg, a constant flow should last at least 10 min.

The idea to solve these problems (similar to the method described in Bronk Ramsey et al. 2004) was to store the CO$_2$ that comes from the EA cryogenically and then to release it subsequently into helium with a flow rate of 0.1 sccm. Figure 6a–b demonstrates the principle of the "cryogenic storage and release" technique. In Figure 6a, the valves V1 and V2 are open so that the CO$_2$ coming from the EA with the high helium flow of 100 sccm is frozen in the "freezing tube" by continuously elevating a dewar vessel with liquid nitrogen. The complete freezing is done within 90 s and CO$_2$ is frozen over the whole inner surface of the freezing tube. Then, V1 and V2 are closed and V3 and V4 are opened (see Figure 6b). Now, a low helium flow of 0.1 sccm is flowing through the freezing tube into the ion source. By slowly lowering the dewar vessel, the CO$_2$ is continuously released into that helium flow and transported into the ion source. With this technique, the CO$_2$ content in the helium can be adjusted just by changing the lowering speed. Because of the easier handling, this interface was tested first in a direct coupling of the EA (NC 2500) and a stable mass spectrometer (see Figure 7). A typical CO$_2$ current plot measured with the stable mass spectrometer is shown in Figure 8. The black-filled curve is the measurement with the open-split method (Bronk Ramsey and Hedges 1994a)—typically used for GC-AMS applications—where only ~10% of the oxidized carbon is used for measurement. The second printout was recorded with the cryogenic storage and release technique. The black filled curve shows a steep rise followed by a exponential decrease, whereas the second printout shows an
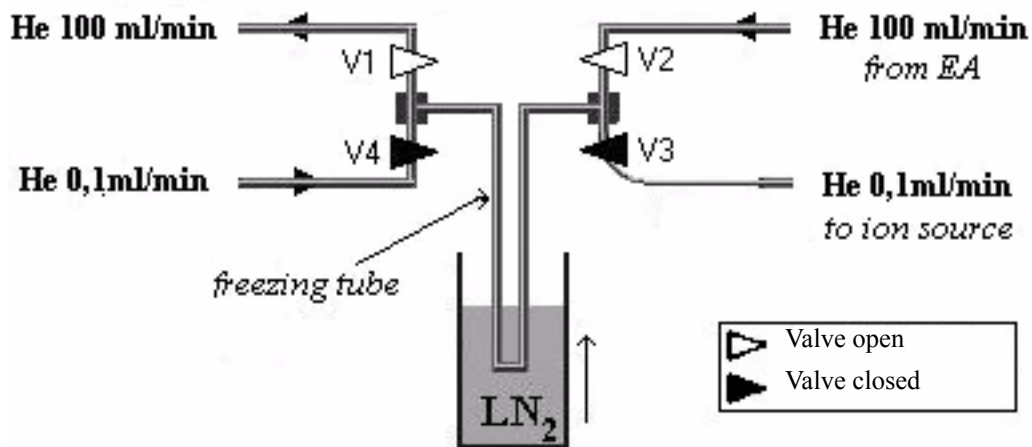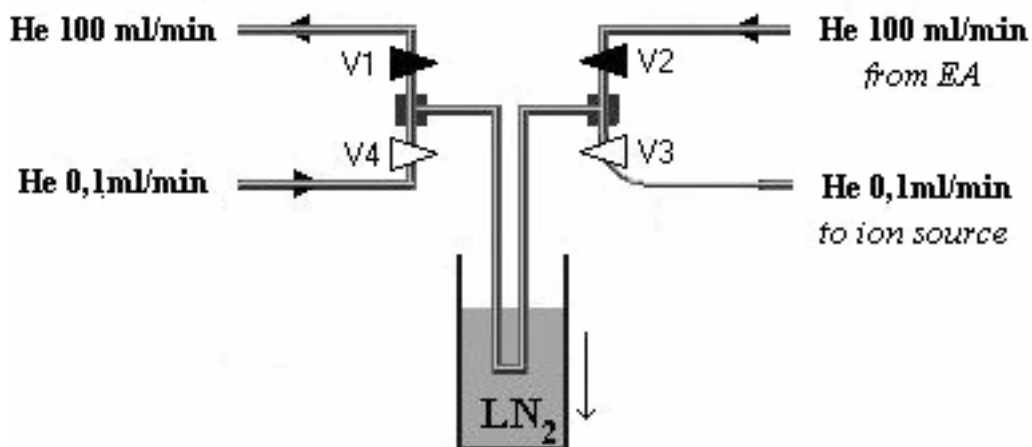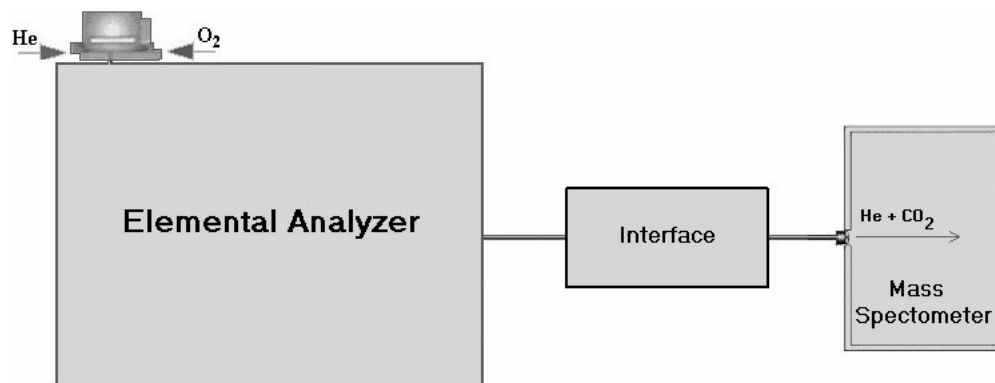
Figure 6a Cryogenic storage of CO_2

Figure 6b Continuous release of CO_2

Figure 7 Set-up for testing an interface between the EA and the ion source

exponential increase followed by a steep fall. This "time inversion" is a consequence from freezing the CO_2 continuously in a forward direction in the freezing tube and subsequent releasing of the CO_2 (beginning with CO_2 that was frozen last) backwards into the mass spectrometer. Also, the second printout is lengthened by a factor of 10 (~40 s to ~400 s) and this is achieved by releasing the CO_2 slowly but continuously into the He flow that leads it into the mass spectrometer.

COUPLING OF THE ELEMENTAL ANALYZER AND THE HYBRID ION SOURCE

The last step was to perform the direct coupling of the elemental analyzer (NC 2500) and the hybrid ion source (modified 40 MC-SNICS) by the interface that is explained above. Figure 9 shows the concept and the realization. A current plot from an online measurement is given in Figure 10. The curve is the convolution of the response of the ion source and the response of the cryogenic storage and release technique. First, the current increases according to Figure 8, but when the CO_2 flow
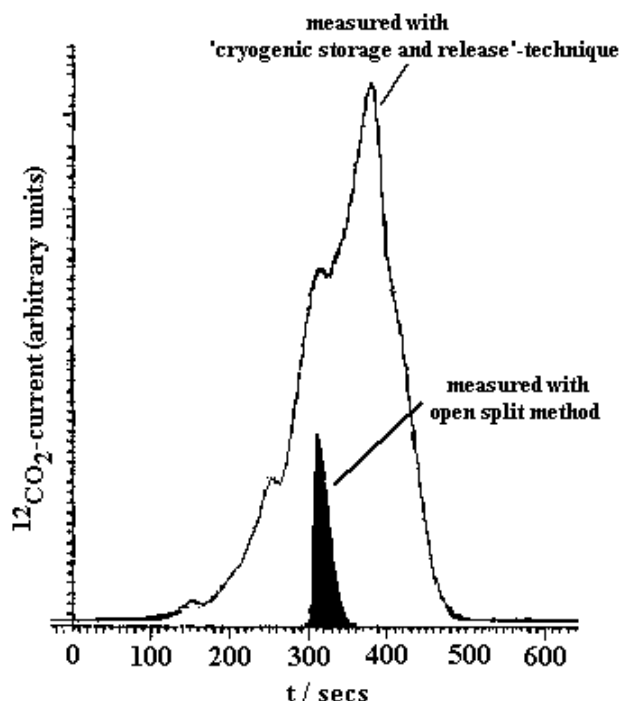

Figure 8 Increasing $^{12}CO_2$ current

exceeds 0.003 sccm, the current is falling as expected from the measurements in Figure 4d. When the CO_2 flow decreases, we see this behavior vice versa followed by an exponential decrease of the carbon current as expected from the curve in Figure 5. The very first online measurements of well-known reference materials are given in Figure 11 in the sequence of the measurements. The gray bars indicate the measured 1-σ range and the black bar over every gray bar marks the actual value of the reference material. The cryogenic storage and release technique proved of value as a GC-AMS online system to measure samples with carbon masses of 1–10 µg (see the estimated combusted carbon mass of every standard, given in brackets). Note that the graphite samples have severe deviations from the actual value compared to the other standards. This could be due also to the fact that no background corrections have been made as to the measuring of modern material before every
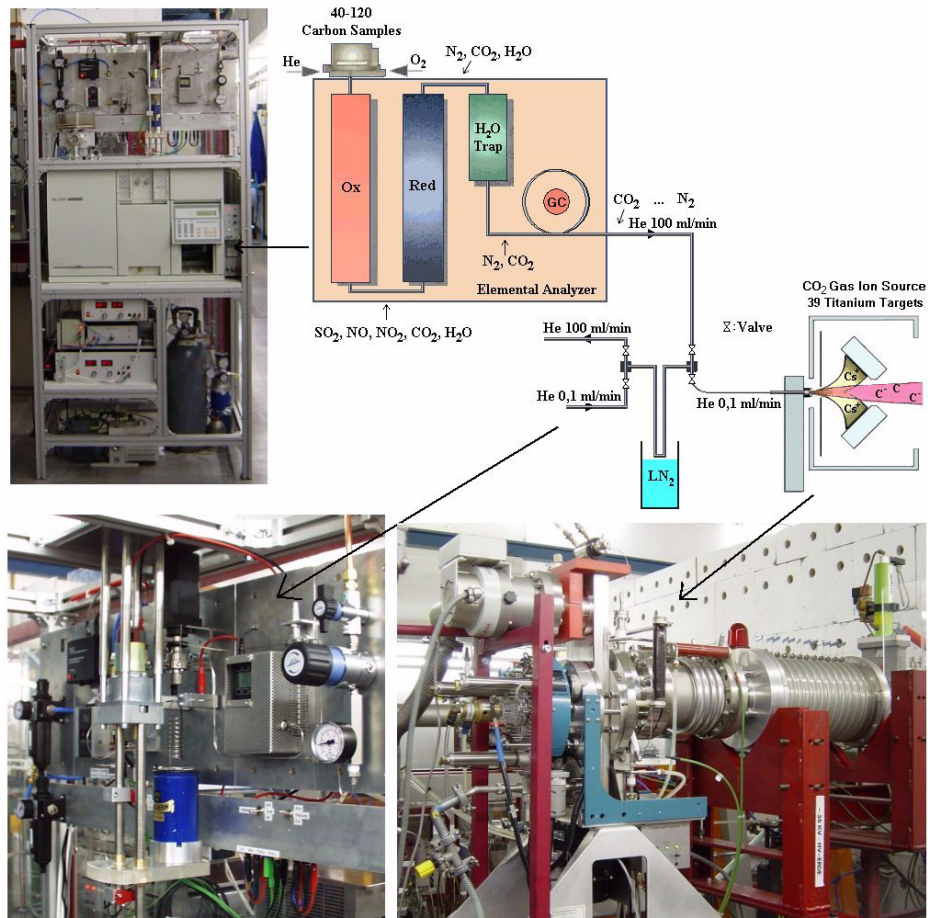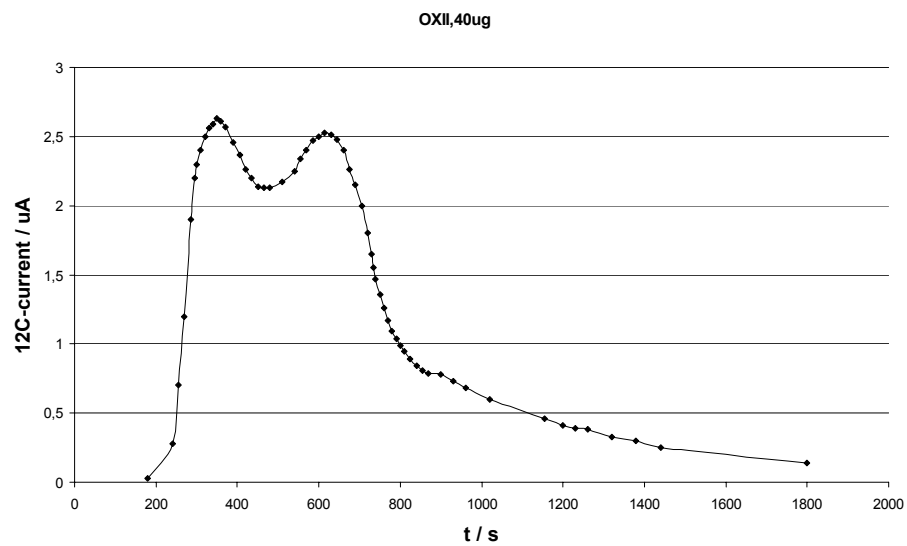
Figure 9 Coupling of EA and hybrid ion source

Figure 10 $^{12}C^-$ current of a gas sample

graphite sample. The last indicates the level of cross-contamination. The measurement of the background curve for the carbon mass and an investigation of cross-contamination is in progress.
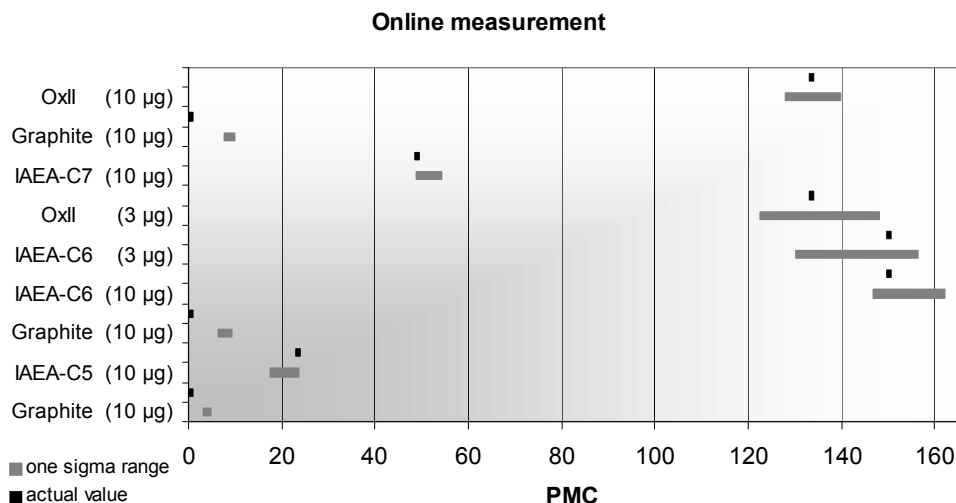
Online measurement

Figure 11 Results of the very first online measurements

CONCLUSION

The direct coupling of an elemental analyzer and a gas ion source for online measurements of samples with carbon masses down to 1 μg is possible with the cryogenic storage and release technique. The advantages of that system are the following:

- Easy handling;
- Omission of the step of the reduction, and so the saving of time and manpower;
- Fast cleaning of the system (within seconds) and, thus, the possibility to change rapidly to another sample;
- Direct (online) measurement and the resulting very low carbon contamination (once the sample is burnt, the CO_2 does not leave the clean system that is steadily self-checking for contamination due to the principle of the configuration);
- Very low minimum carbon mass needed, down to 1 μg (no loss of sample material due to the complete storage of the CO_2 contrary to other GC-AMS online measurement systems);
- Qualification of the technique to simplify investigations in biomedical and environmental science.

An inconvenience is the short range of the best efficiency for the production of carbon ions from CO_2. With the technique presented, it is difficult to keep a constant CO_2 flow rate. Thus, the efficiency is varying (see Figure 10). To adjust a user-defined CO_2 flow rate, the development of a technique to freeze CO_2 in a syringe (CO_2 storing in a bellow and then to dose this CO_2 into the He flow by a pressure difference—similar to the function of the gas-handling system in Figure 1 and according to Bronk Ramsey and Hedges 1994a) is in progress.

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