STUDIES ON THE PREPARATION OF SMALL ^{14}C SAMPLES WITH AN RGA AND ^{13}C-ENRICHED MATERIAL

Jakob Liebl • Roswitha Avalos Ortiz • Robin Golser • Florian Handle • Walter Kutschera • Peter Steier[1] • Eva Maria Wild

Vienna Environmental Research Accelerator (VERA), Faculty of Physics, Isotope Research, University of Vienna, Währinger Straße 17, A-1090 Vienna, Austria.

ABSTRACT. The minimum size of radiocarbon samples for which reliable results can be obtained in an accelerator mass spectrometry (AMS) measurement is in many cases limited by carbon contamination introduced during sample preparation (i.e. all physical and chemical steps to which samples were subjected, starting from sampling). Efforts to reduce the sample size limit down to a few μg carbon require comprehensive systematic investigations to assess the amount of contamination and the process yields. We are introducing additional methods to speed up this process and to obtain more reliable results. A residual gas analyzer (RGA) is used to study combustion and graphitization reactions. We could optimize the reaction process at small CO_2 pressures and identify detrimental side reactions. Knowing the composition of the residual gas in a graphitization process allows a reliable judgment on the completeness of the reaction. Further, we use isotopically enriched ^{13}C (≥98% ^{13}C) as a test material to determine contamination levels. This offers significant advantages: 1) The measurement of ^{12}C/^{13}C in CO_2 is possible on-line with the RGA, which significantly reduces turnaround times compared to AMS measurements; 2) Both the reaction yield and the amount of contamination can be determined from a single test sample.

The first applications of isotopically enriched ^{13}C and the RGA have revealed that our prototype setup has room for improvements via better hardware; however, significant improvements of our sample processing procedures were achieved, eventually arriving at an overall contamination level of 0.12 to 0.15 μg C during sample preparation (i.e. freeze-drying, combustion, and graphitization) of μg-sized samples in aqueous solution, with above 50% yield.

INTRODUCTION

Radiocarbon is probably the radionuclide with the most versatile applications. Many of these applications are limited by the minimum amount of carbon that can be measured. The most relevant samples for investigations in life and earth sciences are often difficult to obtain in large quantities.

Our approach to reduce the sample size limit down to a few μg carbon pursues investigations presented in Steier et al. (2006) and Drosg et al. (2007). Studies at our own laboratory and work by other groups (Gagnon et al. 2000; Hua et al. 2004; Santos et al. 2007; Southon 2007) suggest that the standard procedure to convert sample carbon into graphite (Vogel et al. 1984), suitable for standard accelerator mass spectrometry (AMS) ion sources, has the potential to be extended down to samples of 10 μg carbon or below. A complementary approach using a so-called gas ion source, where the sample is introduced into the AMS ion source as CO_2, is emphasized at other laboratories (e.g. Ruff et al. 2007).

At VERA, we have installed very small graphitization reactors of only 0.9 cm^3 volume. This modification (and every other change in the procedure) may require that graphitization parameters (such as reduction temperature, amount of reactant gases, and catalyst used) are verified to optimize the new procedure. Determination of the process yield and background is also desirable after every change in the procedure. This is, however, hampered by the difficulty of these determinations.

In the simplest approach, used at VERA and other laboratories, the yield of sample pretreatment and combustion (i.e. the amount of carbon recovered as CO_2 against the initial amount of carbon) is calculated from the CO_2 pressure measured in a calibrated volume. The carbon contamination might be

---

[1]Corresponding author. Email: peter.steier@univie.ac.at.

assessed from the CO_2 pressure obtained when processing sample material without any carbon. Depending on the process under study, this might be a vacuum-sealed quartz tube previously filled with reagents only (a "combustion blank") or an inert or sometimes "virtual" material subjected to all steps applied to the unknown samples (a "full processing blank") (e.g. Vandeputte et al. 1998; Steier et al. 2006; Jenk et al. 2007). We see problems in this simple approach: In yield determination, background carbon will contribute to the measured pressure, and, therefore, results in an overestimation of the yield. For background determination, the small amount of background carbon will react under completely different conditions compared to being processed together with a larger amount of sample carbon. Thus, the contamination of the samples will be underestimated if the yield for very small CO_2 amounts is lower (as it is usually expected). As an exaggerated example, the processing of 10 µg sample carbon with 100% yield and no background could not be distinguished from 50% yield and 5 µg contamination.

Besides this simple approach, an elaborate measurement protocol is usually required to precisely extract the average contamination mass, involving a complete series of AMS measurements on samples of different known carbon mass and $^{14}C/^{12}C$ ratios (e.g. Brown and Southon 1997; Hua et al. 2004; Steier et al. 2006; Santos et al. 2007). This method suffers from the large effort involved. The yield of the graphitization reaction is usually estimated from the pressure change during the reaction (e.g. Hua et al. 2004). However, side reactions may take place, only mimicking successful graphite production. Additional information on the gas composition during or after the graphitization reaction is desirable (McNichol et al. 1992).

With trial and error and the long turnaround time of AMS measurements, the optimization of a new procedure is a very time-consuming (and expensive) process. To speed up the systematic investigations, we have explored additional analytical tools: a residual gas analyzer (RGA) and ^{13}C-enriched material. An RGA has been used already for the investigation of "large" samples by McNichol et al. (1992), and we found it very advantageous for small samples. Isotopic analyses of small graphitized samples with an elemental analyzer coupled on-line to a stable isotope ratio mass spectrometer were successfully used at other laboratories (Santos et al. 2007), without applying isotopically enriched material. Their results showed a tendency towards isotopic fractionation, an indication for decreased yield, when optimum conditions for graphitization were not achieved.

We want to note that the uncertainty contributed by the contamination correction to a ^{14}C AMS measurement result of a small sample is increased not only by a larger amount of contamination, but also by a smaller sample processing yield: the ratio of sample mass to contamination is reduced in both cases. Both figures have to be optimized for a good measurement.

METHODS

Use of a Residual Gas Analyzer (RGA)

The RGA (VG Instruments Monitorr 100 F) is essentially a small RF quadrupole mass spectrometer with an electron-impact ion source. The instrument has a mass range of 1 to 100 amu and is connected via a capillary and a precision valve to the individual sample ports of the graphitization reactors (Figure 1). The analyzer volume is pumped with a turbomolecular pump (Pfeiffer Vacuum TMH 065), resulting in a pressure of about 10^{-6} mbar in the instrument. We have equipped the RGA assembly with heating ribbon, which allows to bake it before use. For sampling of gas from a running reaction, we have constructed a special reactor valve, which allows sampling of small aliquots during the reaction.
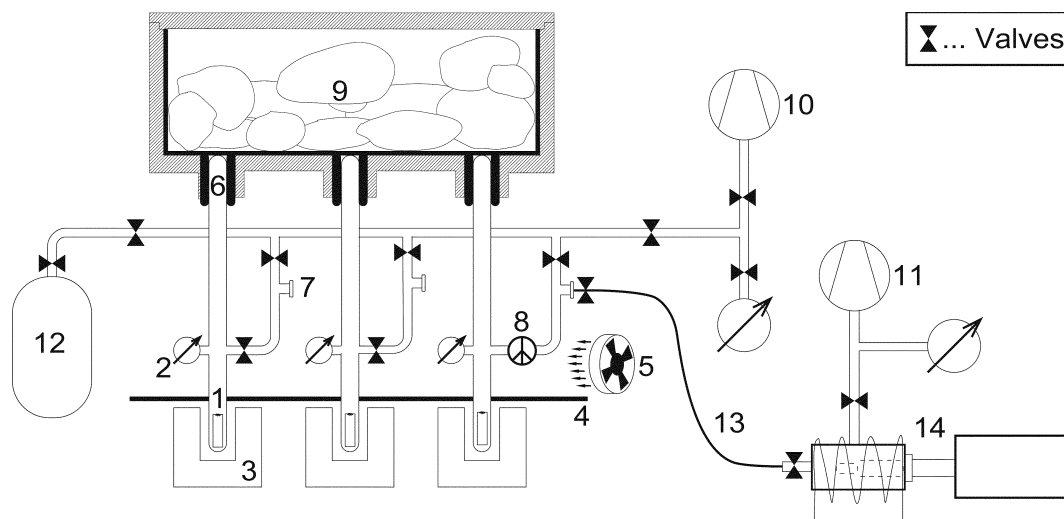
Figure 1 The graphitization setup (with 3 graphitization reactors) connected to the RGA. 1: Fe catalyst in Cu sample holder (pressed as Fe_2O_3 powder); 2: manometer; 3: graphitization oven; 4: heat shield; 5: blower; 6: Al cold finger; 7: port for loading sample and connecting RGA capillary; 8: sampling plug valve; 9: dry ice cold trap; 10, 11: high vacuum pump; 12: hydrogen bottle; 13: RGA capillary; 14: RGA with heating ribbon.

^{13}C-Enriched Material

The use of isotopically pure ^{13}C ($\geq$98% ^{13}C) offers significant advantages for the development of the method. The measurement of ^{12}C/^{13}C of CO_2 is possible online with the RGA, or offline with AMS for the graphitized sample. While the ^{14}C/^{12}C ratio of the contaminant is not well defined (depending on its origin), the ^{12}C/^{13}C ratio of the contamination will show natural isotopic ratios (^{12}C:^{13}C about 99:1) with a variability negligible for our application. This removes an unknown variable from the equations, thus allowing to determine both the yield of a process and the amount of contamination it introduces from a single test sample.

Since CO_2 is needed in an RGA measurement, a combustion step has to be the final step in the process under study. However, the processing may start at any earlier stage (e.g. separation of the carbon compound of interest, or freeze-drying), if suitable ^{13}C-enriched test material is available. The background introduced by the graphitization process and during later handling steps cannot be studied with the RGA, but only with an AMS measurement.

For pure ^{13}C material subjected to the procedures, the isotopic ratio ^{12}C/^{13}C in the produced CO_2 directly reflects the proportion of carbon contamination:

$$N_{\text{cont}} \approx N(CO_2) \times \left(\frac{^{12}C^{16}O_2^+}{^{13}C^{16}O_2^+}\right)_{\text{RGA}}$$

where $N(CO_2)$ is the number of moles of CO_2 recovered in the reactor and determined manometrically, N_{cont} is the number of moles of carbon contamination present in the reactor, and $(^{12}C^{16}O_2^+/$ $^{13}C^{16}O_2^+)_{\text{RGA}}$ is the isotopic ratio measured with the RGA. Small amounts of ^{13}C in natural carbon and mass fractionation in the RGA are neglected for simplicity.

Additionally, the chemical yield ε for these very small samples can be determined taking into account the additional mass of the contamination:

$$\varepsilon = \frac{N(CO_2) - N_{cont}}{N(^{13}C_{initial})}$$

where $N(^{13}C_{initial})$ is the original number of moles of ^{13}C. Processing of a single sample provides both information, without the need to perform an AMS measurement.

The isotopic ratio in the RGA is measured as mass 45 ($^{13}C^{16}O_2^+$) to 44 ($^{12}C^{16}O_2^+$). Our RGA quotes a peak-to-valley ratio of 10:1 between neighboring masses. An inspection of the peak shape for an RF frequency scan of the quadrupole showed a tail of the peaks towards lower masses, which suggests a cross-talk of a few percent from mass 45 to mass 44. To study backgrounds below 1 µg ^{12}C, the amount of ^{13}C applied has to be kept well below 10 µg for an unambiguous identification of the background carbon.

Some of the enriched samples were also graphitized and measured with AMS at VERA. The AMS measurement of the $^{13}C/^{12}C$ allows not only a check of the RGA measurement, but also allows to study the contamination in graphitization, graphite sample handling, and AMS measurement. Small samples of natural isotopic composition were measured in the same sample wheel, to check for a possible cross-contamination in the ion source from the highly ^{13}C-enriched samples.

As mentioned (e.g. McNichol et al. 1992; Gagnon and Jones 1993; Turner et al. 2004), quantitative measurements of chemical gas compositions with an RGA are hampered by differences in the ionization yield and especially by deionization and molecular breakup due to interaction with residual gas in the analyzer quadrupole. However, the isotope ratio measurement $^{13}C^{16}O_2^+/^{12}C^{16}O_2^+$ is effected only by isotopic fractionation, which is expected to be at maximum a few percent.

For measurements of the chemical composition of sample gas, we bake the instrument at 120 °C overnight under high-vacuum pumping. This strongly reduces the molecular breakup and improves the sensitivity. We can achieve quasi-quantitative results with this protocol, despite the optimal conditions degrade, within a few hours even under continued high-vacuum pumping. The instrument needs only very small sample amounts (<0.1 mbar mL) for a measurement. In comparison, 10 µg C correspond to ~20 mbar mL CO_2.

While the molecules $^1H_2$ (mass 2) and $^{12}C^{16}O_2$ (mass 44) can be measured directly as $^1H_2^+$ and $^{12}C^{16}O_2^+$, other masses are ambiguous. This is especially the case for $^{12}C^{16}O$ versus $^{14}N_2$ (mass 28) and $^{12}C^1H_4$ versus ^{16}O (mass 16), where certain unambiguous breakup products (mass 14, $^{14}N^+$ from $^{14}N_2$; and mass 15, $^{12}C^1H_3^+$ from $^{12}C^1H_4$) are used. However, the quantitative measurement of CO turned out to be difficult, since it requires a subtraction of the $^{14}N_2$-induced signal for mass 28, based on the (varying and 4 to 10 times smaller) mass 14 signal. $^{14}N_2$ is often observed as a background, which we attribute to outgassing of the vacuum tubing.

For convenience, we want to recapitulate the main points of our sample preparation procedure described in Drosg et al. (2007), including modifications found with the RGA and ^{13}C-enriched material. However, the investigation of the procedures is still ongoing, and not all steps are yet investigated. A comprehensive description will be published in a separate paper, once the investigations are complete. The most recent and best data presented in this paper was obtained with the following, preliminary procedure:

Iron powder to be used as a catalyst was oxidized at 900 °C in atmosphere to remove traces of carbon. Aliquots of several 100 µg of the resultant iron oxide were pressed with a pressure of ~0.3 GPa into copper sample holders (cylindrical, outer diameter 1.8 mm, inner diameter 1 mm, bore depth 1 mm), and inserted into the graphitization reactors. The volume of the reactors (~0.9 mL) was determined for every sample by expansion of air of atmospheric pressure from the reactor volume to a calibrated reference volume. This allowed to handle the intrinsic variability of the reactors without transferring the samples to the reference volume, therefore avoiding the risk of cross-contamination. The pressure in the graphitization reactor can be measured with a precision of 0.2 mbar. The iron oxide (together with the copper holder) was baked in vacuum at 815 °C for 30 min and then reduced to iron in 850 mbar H_2 at 815 °C. During this step, H_2 was replaced every 15 min until no further pressure drop was observed (approximately 2 hr).

The samples available in aqueous solution (up to 1 mL) were transferred to quartz vials (3 mL), closed with valves, frozen, and connected to the graphitization unit through a separate port for each reactor. After this step, no opening of the hermetically sealed system is required, which excludes any introduction of carbon from laboratory air. The samples were freeze-dried by applying an oil-free vacuum, then baked in vacuum at up to 200 °C, depending on the material. Gaseous oxygen was cleaned in a liquid N_2 cold trap (−196 °C) and about 220 mbar were added to the sample vial. The samples were combusted at 900 °C for 30 min. The resulting CO_2 was cryogenically purified by freezing with liquid N_2 (−196 °C) and pumping off non-condensable gases. The CO_2 was transferred to the graphitization reactors while water was kept in the combustion vials with a dry ice/isopropanol slurry (−78 °C). H_2 was added for the graphitization reaction, at a pressure of 2.5 times the CO_2 pressure (typically 23 mbar for 10 µg C) plus 50 mbar. Graphitization took place at 915 °C for 1 hr, followed by 600 °C until the reactor pressure became constant. Water was trapped with a dry ice/isopropanol trap (−78 °C). The RGA was used to verify that the residual gas consisted only of H_2. The copper sample holders with the iron/graphite mixture can be mounted into the sample wheel for our AMS ion source directly, which avoids transfer losses. Only some of the parameters (amounts, temperatures, durations) were up to now systematically investigated. However, by using the methods described in this paper, we have already achieved significant improvements compared to the status described in Drosg et al. (2007).

FIRST RESULTS

Figure 2 and Table 1 show results from measurement series where different sample preparation methods were tried out to find the optimum procedure. In general, the data represents the development from what is described in Drosg et al. (2007) towards the procedure given above. Different amounts of ^{13}C-enriched glucose (^{13}C >99%) and DNA (^{13}C >98%) were applied. The samples were freeze-dried and combusted, the resulting CO_2 amount was determined manometrically, and its isotopic composition, i.e. the $^{13}C^{16}O_2^+/^{12}C^{16}O_2^+$, ratio was measured with the RGA. Though isotope ratio measurements are in principle possible without baking the RGA, baking at 120 °C overnight is now our routine procedure and was applied for all data shown here.

Table 1 also shows the $^{13}C/^{12}C$ ratio measured with AMS after graphitization for some of the samples. Precision is not critical for background studies, so the raw $^{12}C^{3+}/^{13}C^{3+}$ ratio can be used directly (we typically observe −20‰ fractionation in AMS measurements of $^{13}C^{3+}/^{12}C^{3+}$ for carbon samples at VERA). There is an acceptable agreement of the RGA measured ratio $^{13}C^{16}O_2^+/^{12}C^{16}O_2^+$ of CO_2 samples and the AMS measured $^{13}C^{3+}/^{12}C^{3+}$ ratio of the respective graphitized samples (±20%), but for the largest sample (100 µg ^{13}C, out of scale in Figure 2) where the (expected) cross-talk of the large peak at mass 45 to mass 44 leads to an overestimation of the contamination with the RGA mea-
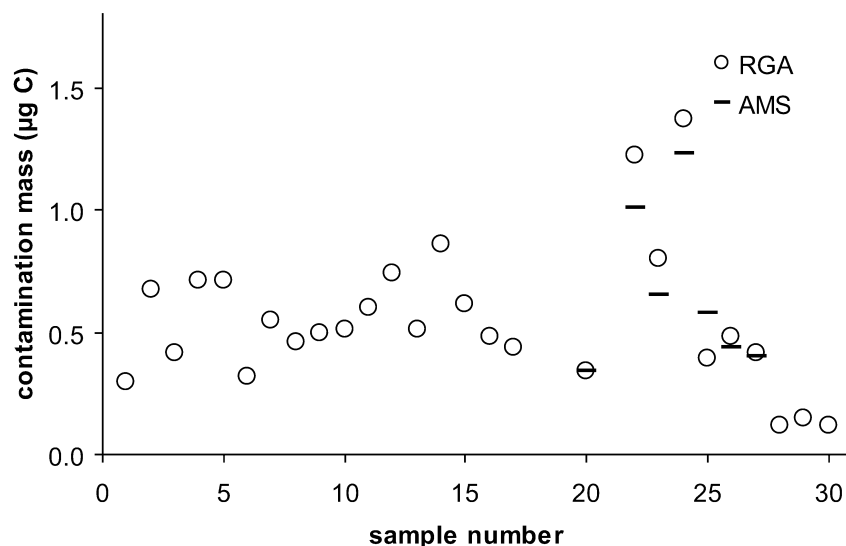
Figure 2 Determination of carbonic contamination during sample preparation by RGA and AMS measurements on small samples enriched in ^{13}C. Sample numbers are ordered chronologically. Sample 21 is not visible here (AMS: 4.3 µg C; RGA: 11.0 µg C).

surement. We think that the agreement of the $^{13}C/^{12}C$ ratios determined with AMS and the RGA is the best estimate for the accuracy of our contamination masses quoted (±20%). Surprisingly, there is no indication for an additional contamination during graphitization and AMS measurement in our data at the present limit of detection (~0.1 µg C); however, additional investigations are required in this context.

Small samples of natural isotopic composition (down to 17 µg C), which were mounted next to graphitized ^{13}C-enriched samples on the AMS target wheel, showed no cross-contamination coming from ^{13}C-enriched samples during the AMS measurement. The $\delta^{13}C$ values of the natural samples measured before and after sputtering of the highly enriched ^{13}C samples remained unchanged within measurement uncertainties (2‰).

With the help of ^{13}C-enriched material and the RGA, the average contamination in sample preparation involving a freeze-drying and a combustion step could be reduced from 0.6 ± 0.2 to 0.15 ± 0.05 µg C for the most recent measurements (sample numbers 28 to 30). These numbers compare favorable to the best recently published contamination levels: Hua et al. (2004) report 0.6 ± 0.1 µg C actually incorporated into small graphite samples during sample processing. The data presented in Santos et al. (2007) corresponds to a total carbon contamination of 0.3 to 1.5 µg C during graphitization (0.2 to 1 µg of modern carbon and 0.1 to 0.5 µg of dead carbon).

We also used the RGA to study the reaction process at small CO_2 pressures. This was done by analyzing the residual gas after the reaction (see Figure 3, panels c and d, for an example), which is routinely possible for true samples (if mass 14, $^{14}N^+$, is found, a correction for the contribution of $^{14}N_2$ to the $^{12}C^{16}O$ mass (mass 28) is required; see above).

The gas composition in the graphitization reactors was also measured during graphitization with the RGA using a sampling valve. Small gas aliquots from the reactor were sampled repeatedly during a reaction run and analyzed with the RGA (Figure 4). These investigations were hampered by the rel-

Table 1 Investigation of laboratory contamination of small carbon samples utilizing an RGA and AMS. $^{13}C^{16}O_2^+/^{12}C^{16}O_2^+$ RGA measurements typically have a repeat accuracy of ~5%; $^{13}C^{3+}/^{12}C^{3+}$ AMS measurements a precision of about 1%. The contamination masses were determined as $M_{cont} = N_{cont} \times 12$ amu (see Methods section). Samples 1–17 are ^{13}C glucose; samples 20–30 are ^{13}C DNA.

Sample nr	^{13}C (µg)	C as CO_2 in graphitization reactor (µg)	$^{13}C^{16}O_2^+/$ $^{12}C^{16}O_2^+$ RGA	$^{13}C^{3+}/^{12}C^{3+}$ AMS	M_{cont} RGA (µg)	M_{cont} AMS (µg)	Chemical yield (%)
1	5.0	3.5	12.0		0.29		65
2	2.5	1.8	2.7		0.67		46
3	5.0	2.8	6.7		0.42		47
4	2.5	1.8	2.5		0.71		42
5	2.7	3.1	4.3		0.71		88
6	5.0	2.9	9.0		0.32		51
7	2.5	1.9	3.4		0.55		52
8	2.7	3.5	7.5		0.46		111
9	5.0	2.9	5.8		0.49		48
10	2.5	1.7	3.4		0.51		49
11	2.7	3.1	5.3		0.60		94
12	5.0	2.6	3.5		0.74		37
13	2.5	1.4	2.8		0.51		36
14	2.7	2.8	3.2		0.86		71
15	5.0	4.2	6.8		0.62		72
16	2.5	2.2	4.5		0.48		67
17	2.7	2.7	6.3		0.44		85
20	3.3	1.7	4.9	4.96	0.34	0.34	41
21	108.4	107.4	9.8	25.07	11.02	4.29	95
22	10.8	8.4	6.9	8.31	1.22	1.01	68
23	5.4	5.0	6.2	7.62	0.80	0.65	80
24	3.3	4.8	3.5	3.92	1.37	1.23	111
25	3.3	3.8	9.8	6.59	0.39	0.58	99
26	3.3	3.5	7.2	7.94	0.48	0.44	94
27	2.2	2.6	6.2	6.45	0.42	0.40	101
28	1.1	0.7	5.6		0.12		51
29	0.9	0.7	4.7		0.15		63
30	1.1	0.9	7.7		0.12		74

atively fast degradation of the RGA sensitivity after baking. The reliability of the measured CO concentrations were affected by this. Since we have not in parallel calibrated our instrument with standard gas mixtures, no absolute values were obtained in gas composition measurements. Still, important findings were possible: we discovered that the first step of the graphitization reaction, reduction of CO_2 to CO ($CO_2 + H_2 \leftrightarrow CO + H_2O$), takes place quickly (usually within less than 2 hr) with our standard reaction conditions. For small samples, however, the duration of the second step, the conversion of CO to graphite ($CO + H_2 \leftrightarrow C + H_2O$), was very sensitive to small variations of the reaction parameters, especially to the low partial pressure of H_2O. Based on this finding, we now replace the dry ice in the cold trap by liquid nitrogen after the reduction of the CO_2 to CO if the reaction proceeds too slowly (Figure 5). This results in a quick completion of graphite formation. A possible explanation for the observed increased reaction rate at lower cold trap temperatures is given by Němec et al. (2010).
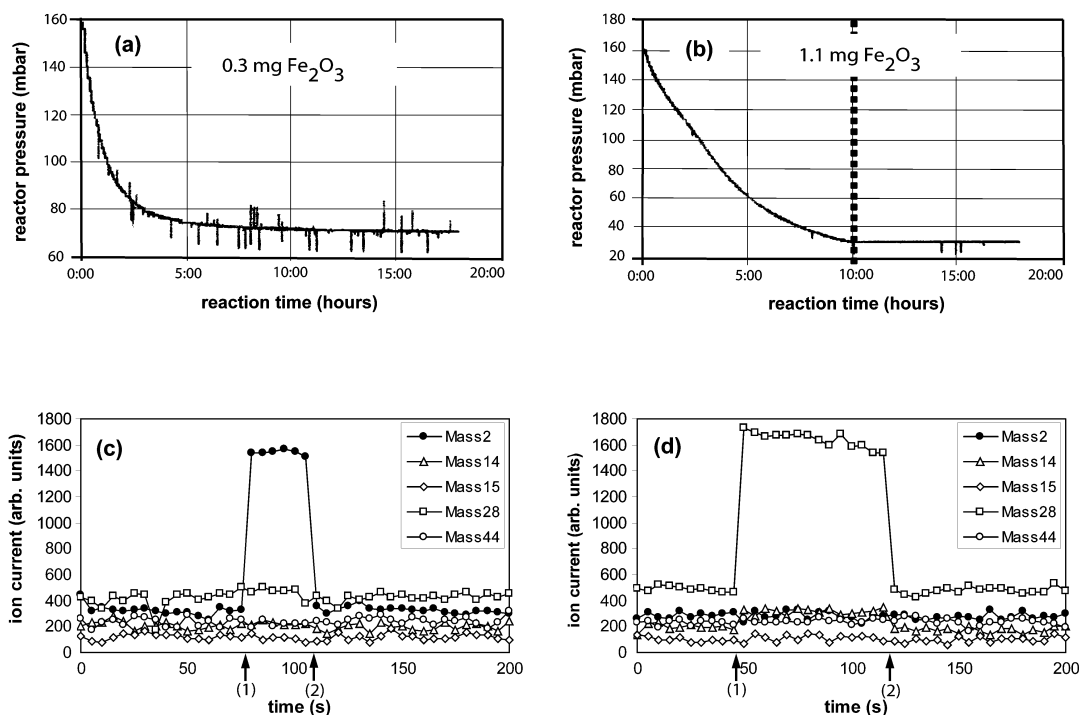
Figure 3 Identification of an unwanted side reaction in the graphitization process by analyzing the residual gas. Panels (a) and (b) show the pressure-vs.-time curves of graphitization reactions using 2 different amounts of iron oxide, which was reduced for 1 hr at 815 °C in 845 mbar H_2 atmosphere to serve as iron catalyst for the graphitization reaction (the glitches on the curve are electronic noise and bear no information about the process). For case (b), insufficient reduction resulted in residual iron oxide, which consumed the H_2 during the graphitization, causing incomplete CO processing. The point in time where we suspect exhaustion of H_2 is marked with the vertical dashed line in (b). For the smaller amount of iron catalyst (a), the reaction completed regularly. The panels (c) and (d) show the RGA analysis of the residual gas from the reactions (a) and (b), respectively. The points in time where the valve from the reactor into the RGA was opened (1) and closed (2) are indicated. The instrument background is visible before and afterwards. While in (c) only mass 2 (H_2) is found as expected, the residual gas of (d) exhibits mass 28 (CO). We now have extended the procedure of baking the Fe catalyst in H_2 atmosphere.

Small samples are more sensitive to detrimental side reactions. Impurities in the sample gas, reactor leakage, or residual oxygen on the iron catalyst lead to relatively large deviations from optimal reaction conditions even if disturbances are small in absolute size. Knowing the composition of the residual gas allows a reliable judgment of the completeness of the graphitization. We have already found and solved one problem in our usual procedure (Figure 3): though the pressure-vs.-time curves look regular for these reactions, the RGA revealed that residual oxygen on the iron catalyst had consumed the available hydrogen in cases where larger amounts of catalyst were used. Another side reaction, $C + 2H_2 \leftrightarrow CH_4$, is most prominently discussed in the literature (e.g. Vogel et al. 1984; McNichol et al. 1992). The product CH_4 can be unambiguously identified with the RGA as mass 15. Up to now, we have seen mass 15 marginally above background in a test where we reduced the graphitization temperature to 450 °C during the second step of the reaction. In another case, in which we cooled down the ovens for the reactors slowly to room temperature after 1 hr of graphitizing, CH_4 contributed significantly to the residual gas. No CH_4 was detected for our "routine" procedure.
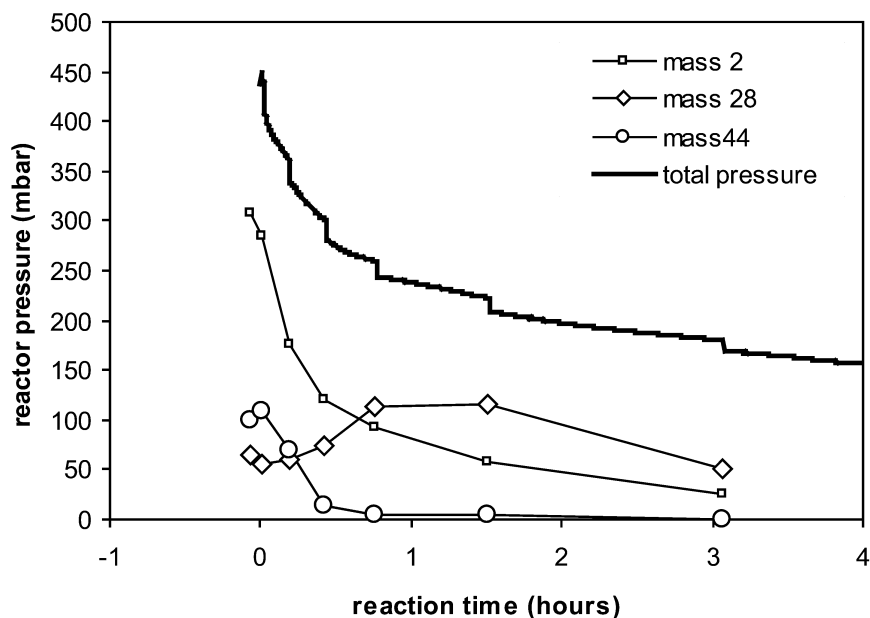
Figure 4 Change of the gas composition during the graphitization reaction. Steps in the pressure curve result from gas sampling (5% of the reactor volume each). The RGA readings for H_2 (mass 2) and CO_2 (mass 44) were scaled to match the composition before the reaction started (time 0:00). However, due to the long duration of this measurement, the RGA probably degrades, so the plots should be understood as qualitative data only. Mass 28 is presently always visible from N_2 outgassing when using the sampling valve, which partly obscures the detection of CO. Nevertheless, the fast reduction of CO_2 to CO is obvious.
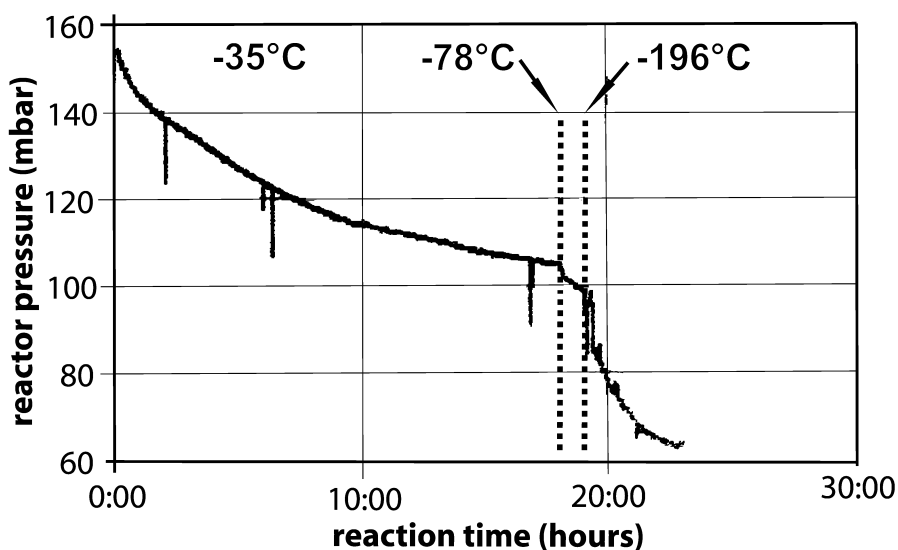

Figure 5 Influence of liquid nitrogen cooling on the graphitization process. Once all CO_2 is reduced to CO, cooling of the cold trap with liquid N_2 can be applied, speeding up the reaction significantly. The different temperatures were achieved with electric cooling (−35 °C), dry ice slurry (−78 °C), and liquid nitrogen (−196 °C). The dotted lines indicate the application of dry ice slurry and liquid nitrogen cooling.

SUMMARY AND OUTLOOK

The fast turnaround time of the described procedure allows one to study several variations of sample preparation procedures quickly, especially to reduce the carbon contamination introduced during sample preparation. Different ^{13}C materials are available commercially, which enables to study differences in the sample behavior during sample preparation. We want to emphasize, however, that the combined use of ^{13}C materials and the RGA cannot substitute the measurement of small-mass procedural blanks measured by AMS, since no information on the ^{14}C content of the contamination is obtained.

The development of a sample preparation procedure for ultra-small carbon samples is an ongoing process at our laboratory. Nevertheless, we have already gained some insight into the graphitization reaction, which would hardly have been possible without the RGA measurements. The RGA consumes only a very small amount of gas per measurement, and is therefore well suited for the investigation of small sample procedures. Even monitoring the reaction of valuable samples by repeated gas sampling is feasible without significant loss of sample material. Presently, repeated calibration of the RGA with a calibration gas throughout the measurement is required. Recent tests with a new RGA indicate that the procedures described in this paper can be facilitated: no vacuum baking required, better stability, and reduction of cross-talk between neighboring masses.

However, it should be pointed out that the ^{13}C/^{12}C ratio measurements with ^{13}C-enriched material are not influenced by the shortcomings of the present RGA instrument. This makes ^{13}C-enriched materials and the RGA a perfect combination to systematically develop the preparation of small ^{14}C samples.

ACKNOWLEDGMENTS

REFERENCES

Brown TA, Southon JR. 1997. Corrections for contamination background in AMS ^{14}C measurements. *Nuclear Instruments and Methods in Physics Research B* 123(1–4):208–13.

Drosg R, Kutschera W, Scholz K, Steier P, Wagenbach D, Wild EM. 2007. Treatment of small samples of particulate organic carbon (POC) for radiocarbon dating of ice. *Nuclear Instruments and Methods in Physics Research B* 259(1):340–4.

Gagnon AR, Jones GA. 1993. AMS-graphite target production methods at the Woods Hole Oceanographic Institution during 1986–1991. *Radiocarbon* 35(2): 301–10.

Gagnon AR, McNichol AP, Donoghue JC, Stuart DR, von Reden K. 2000. The NOSAMS sample preparation laboratory in the next millennium: progress after the WOCE program. *Nuclear Instruments and Methods in Physics Research B* 172(1–4):409–15.

Hua Q, Zoppi U, Williams AA, Smith AM. 2004. Small-mass AMS radiocarbon analysis at ANTARES. *Nuclear Instruments and Methods in Physics Research B* 223–224:284–92.

Jenk TM, Szidat S, Schwikowski M, Gäggeler HW, Wacker L, Synal H-A, Saurer M. 2007. Microgram level radiocarbon (^{14}C) determination on carbonaceous particles in ice. *Nuclear Instruments and Methods in Physics Research B* 259(1):518–25.

McNichol AP, Gagnon AR, Jones GA, Osborne EA. 1992. Illumination of a black box: analysis of gas composition during graphite target preparation. *Radiocarbon* 34(3):321–9.

Němec M, Wacker L, Gäggeler H. 2010. Optimization of the graphitization process at AGE-1. *Radiocarbon* 52(2–3):1380–93.

Ruff M, Wacker L, Gäggeler H, Suter M, Synal H-A, Szidat S. 2007. A gas ion source for radiocarbon measurements at 200 kV. *Radiocarbon* 49(2):307–14.

Santos GM, Southon JR, Griffin S, Beaupre SR, Druffel ERM. 2007. Ultra small-mass AMS ^{14}C sample preparation and analyses at KCCAMS/UCI facility. *Nu-*

clear Instruments and Methods in Physics Research B 259(1):293–302.

Southon J. 2007. Graphite reactor memory—Where is it from and how to minimize it? *Nuclear Instruments and Methods in Physics Research B* 259(1):288–92.

Steier P, Drosg R, Fedi M, Kutschera W, Schock M, Wagenbach D, Wild EM. 2006. Radiocarbon determination of particulate organic carbon in nontemperated, alpine glacier ice. *Radiocarbon* 48(1):69–82.

Turner P, Taylor S, Clarke E, Harwood C, Cooke K,

Frampton H. 2004. Calibration effects during natural gas analysis using a quadrupole mass spectrometer. *Trends in Analytical Chemistry* 23(4):281–7.

Vandeputte K, Moens L, Dams R, van der Plicht J. 1998. Study of the ^{14}C-contamination potential of C-impurities in CuO and Fe. *Radiocarbon* 40(1):103–10.

Vogel JS, Southon JR, Nelson DE, Brown TA. 1984. Performance of catalytically condensed carbon for use in accelerator mass spectrometry. *Nuclear Instruments and Methods in Physics Research B* 5(2):289–93.