

PERFORMANCE TEST OF A NEW GRAPHITE TARGET PRODUCTION FACILITY IN ATOMKI

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ABSTRACT. We present our new graphite target production system, developed in the Institute of Nuclear Research of the Hungarian Academy of Sciences (ATOMKI), for accelerator mass spectrometry (AMS) radiocarbon dating measurements. The system consists of a gas handling line and a graphite target production system. Results of AMS measurements, stable isotope mass spectrometry measurements, and gravimetric/pressure yield determinations have been used to find the proper conditions for the graphitization process. We have also investigated the ¹⁴C contamination and the memory effect of the system during the graphitization processes. This paper covers the details of these experiments and a discussion of the results.

INTRODUCTION

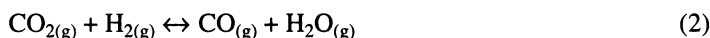
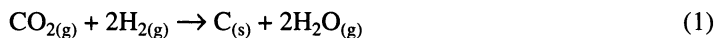
Radiocarbon dating by gas proportional counter (GPC) system has a long tradition in the Institute of Nuclear Research of the Hungarian Academy of Sciences (ATOMKI). The institute aimed to enlarge its ¹⁴C dating possibilities by the installation of the Tandetron accelerator facility obtained from the Oxford Radiocarbon Accelerator Unit (ORAU). Our laboratory has been developing a sample preparation system for accelerator mass spectrometry (AMS) radiocarbon dating measurements. Performance tests of the gas handling line and the graphite target production system were the first step towards the realization of the system in collaboration with CEDAD, University of Lecce, Italy.

METHODS

The schematic of our gas handling line is shown in Figure 1. All parts of the line were made of stainless steel, and Swagelok[®] valves were utilized in the system. The vacuum is applied with a BOC Edwards oil-sealed 2-stage pump, yielding a minimum line pressure of 7.5×10^{-3} mbar. The system can handle up to 5 samples simultaneously. The volume of the reaction rig is ~ 7 cm³ and consists of a Hy-Lok plug valve, a Swagelok Ultra-Torr[®] Union Tee fitting, a quartz tube, and a reusable glass water trap tube. The use of a quartz tube decreases modern carbon contamination (Vogel et al. 1987), and a new quartz tube is used for each graphitization process.

The graphite target production system is similar to the one used in ORAU (Bronk Ramsey and Hedges 1997). It was developed by the Special Control Devices Company in Hungary. The system consists of 2 independent furnaces and Peltier cooling devices, each with 5 positions for the reaction rigs. The temperature of the furnaces and the Peltier coolers was monitored by a digital control system. Set-point accuracy for the furnace and the Peltier cooler was 1.0 °C and 0.1 °C, respectively.

Graphite is produced by hydrogen reduction of CO₂ gas over an iron powder catalyst (Vogel et al. 1984). The overall graphitization equation (Equation 1) is the net result of the possible competing steady-state reactions (Equations 2–5) (Dee and Bronk Ramsey 2000):



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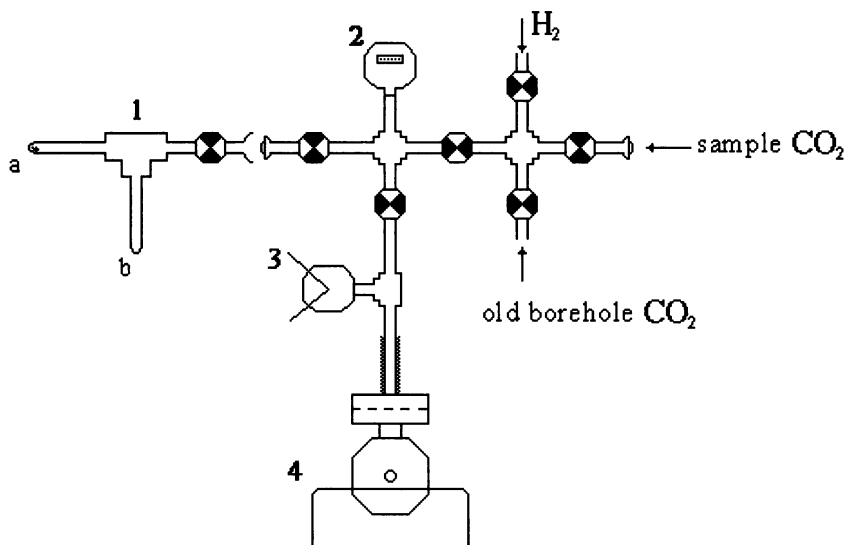
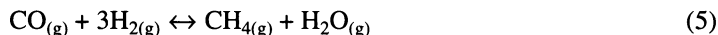


Figure 1 The gas handling line: 1) reaction rig; a) quartz tube containing the iron powder; b) reusable water trap tube; 2) digital pressure gauge; 3) vacuum gauge; 4) oil-sealed vacuum pump.

We used iron powder of <325 mesh (Alfa Aesar®), which is 98% pure. The powder was obtained from CEDAD (D'Elia et al. 2004), where it is used for routine AMS measurements. Before beginning the graphitization process, the iron powder was pre-activated in 2 different ways: 1) by oxidation with 0.7-bar O₂ (purity 99.95% v/v, Linde AG, Répcelak, Hungary) at 450 °C for 15 min, followed by H₂ (purity 99.999% v/v, Linde AG, Répcelak, Hungary) reduction at 450 °C for 30 min; or 2) by using only the reduction step.

¹⁴C background of the gas handling line and the graphite target production system was tested by graphitization of ¹⁴C-dead CO₂ gas (harvested from an old borehole, purity 99.995% v/v, Linde AG, Répcelak, Hungary) at different furnace temperatures (500, 540, and 580 °C) and by using different iron powder pre-activation methods.

We also checked the memory effect of the system by graphitization of modern CO₂ gas, which has significant ¹⁴C activity, between graphitization of inactive old borehole CO₂ gases. The “modern” CO₂ gas was prepared in the gas preparation line of our GPC system from a VIRI A sample we obtained in the framework of the Fifth International Radiocarbon Intercomparison (VIRI; Scott et al. 2003) program.

Initial pressure of the CO₂ gas was close to 510 mbar, temperature of the water trap during the iron powder pre-activation and the graphitization process was 0 °C, and graphitization time was 300 min during these experiments.

We also carried out a pressure run investigation during the graphitization process for various initial H₂:CO₂ ratios. Total conversion of CO₂ to graphite was monitored in 2 ways: 1) by gravimetric yield data with the following yield calculations (Osborne et al. 1994):

$$\text{Gravimetric yield} = \frac{m_1 - m_2}{m_3} \times 100\% \quad (6)$$

where m_1 = common weight of iron powder, graphite, and quartz tube (in mg) after graphitization; m_2 = common weight of iron powder and quartz tube (in mg) before graphitization; and m_3 = the estimated total mass of carbon in the CO₂ gas form according to ideal gas law, $m_3 = P \times V \times \text{const}$, where P = initial pressure of CO₂ sample in the reaction rig (in mbar) before graphitization, V = volume of the reaction rig (in cm³), and $\text{const} = 4.92 \times 10^{-4} \frac{\text{mg}}{\text{cm}^3 \times \text{mbar}}$.

and 2) by pressure yield data with yield calculations as follows (Osborne et al. 1994):

$$\text{Pressure yield} = \frac{P_{\text{initial}} - P_{\text{final}}}{3 \times P_{\text{sample}}} \times 100\% \quad (7)$$

where P_{initial} = initial pressure of gases in the reaction rig before graphitization; P_{final} = final pressure of gases in the reaction rig after graphitization; and P_{sample} = initial pressure of CO₂ sample gas in the reaction rig before graphitization.

RESULTS AND DISCUSSION

In order to evaluate the possibility of using both the pressure and the gravimetric yield calculations to characterize the graphitization process, the gas tightness of the reaction rig was checked without CO₂ gas. The iron powder was activated as discussed previously, but after the evacuation step we added only hydrogen gas (at 1500 mbar) to the reaction rig. All the other conditions were identical to those used in a standard graphitization process. The measured final and initial pressures were equal, within error limits. We also weighed the quartz tube and the iron powder before and after the process and the values also showed good agreement with each other. This means there was not any surface contamination effect during graphitization that we can account for within the mass-weight error limits.

The pressure run as a function of time for 3 different initial H₂:CO₂ pressure ratios (3.32, 2.92, and 2.11) during the graphitization step is shown in Figure 2. The pressure immediately increases after inserting the quartz tube into the preheated furnace, and it reaches the maximum value within 5–7 min. After this short period, the pressure decreased slowly, indicating the start of the chemical reactions. Results showed that with an initial gas ratio of 3.32, the overall net reaction was virtually finished after 320 min. In case of a 2.11 initial gas ratio, this reaction time was longer, as we can see in Figure 2. On the other hand, the lowest final P/P_{max} value was obtained with an initial gas ratio of 2.11.

Table 1 presents the gravimetric and pressure yield data for different initial gas ratios and different reaction times. The highest gravimetric yield (73.3%) was achieved with a 2.00 initial ratio and 1260 min reduction time. If we consider those situations where we use a “normal” reduction time (360 min), we obtained the highest gravimetric yield (about 62%) from a 2.11 initial gas ratio.

The pressure yield values (Table 1) produced an interesting pattern: in some cases, the values were higher than 100%. There was another notable correlation: when the pressure yield exceeded 100%,

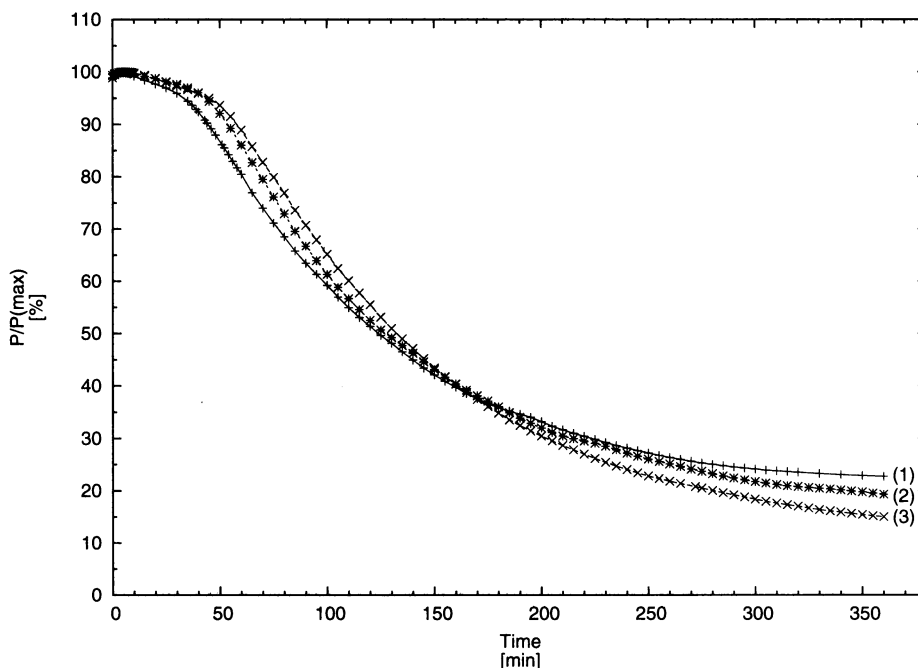


Figure 2 Graphitization reaction rates for various initial $H_2:CO_2$ pressure ratios. The temperature of the furnace was $580\text{ }^\circ\text{C}$, the temperature of water trap was $0\text{ }^\circ\text{C}$, and the initial pressure of the CO_2 gas was 509 mbar in the reaction rig. The gas ratios were 3.32:1 (1), 2.92:1 (2), and 2.11:1 (3).

Table 1 Calculated gravimetric and pressure yield data for various initial $H_2:CO_2$ pressure ratios and different reaction times.

$H_2:CO_2$ ratio	Reduction time (min)	Gravimetric yield (%)	Pressure yield (%)
3.32	360	49.8 ± 1.7	110.3 ± 0.1
3.32	360	52.2 ± 1.0	109.3 ± 0.1
2.92	360	61.6 ± 0.9	105.6 ± 0.1
2.12	360	63.6 ± 1.6	88.2 ± 0.1
2.11	360	61.2 ± 2.1	86.8 ± 0.1
2.11	470	68.5 ± 1.5	90.7 ± 0.1
2.00	1260	73.3 ± 2.4	90.3 ± 0.1

the gravimetric yield always gave smaller values. If we look back at the equations of possible steady-state reactions (Equations 2–5), we found that this behavior might come from either the presence of methane in the gas phase formed during the graphitization process (Equation 5) or the domination of the CO formation reaction (Equation 2). Only these 2 reactions decrease the partial pressure of the CO_2 gas without increasing the mass of the formed graphite. It also seems that a higher volume of initial hydrogen gas improves the efficiency of these obstructive reactions.

If we investigate the definition of pressure yield, we see that it gives values $>100\%$ when the pressure difference is larger than triple the value of the initial pressure of the sample CO_2 gas. However, if we consider that the reduction proceeded as the overall net equation (Equation 1), the pressure yield could never be higher than 100% . According to McNichol et al. (1992), after the graphitization

process, generally a mixture of CO, CO₂, and CH₄ gas is obtained. It followed from this that we should not eliminate any of the possible steady-state reactions (Equations 2–5) and we might get a pressure yield higher than 100% after the graphitization process. On the other hand, those reactions that increased the pressure yield and did not lead to graphite formation naturally decreased the gravimetric yield of the reduction too.

We also investigated the influence of the furnace temperature on the gravimetric yield for the same initial gas ratio (Figure 3). We found that, at least in the investigated temperature range, higher temperatures increase the gravimetric yield. We also observed that the oxidation step during iron powder pre-activation decreased the gravimetric yield for identical temperature and initial gas ratios.

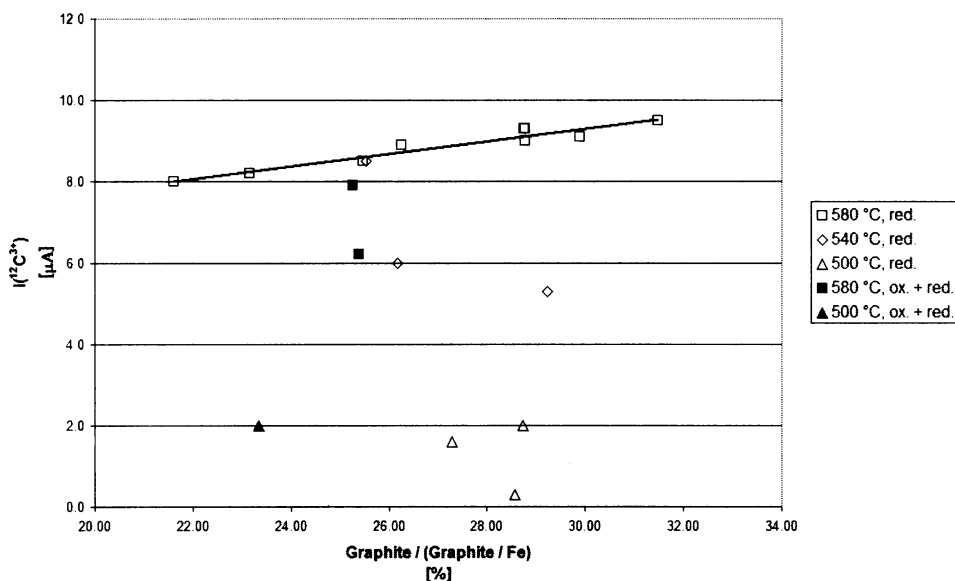


Figure 3 Calculated gravimetric yield vs. furnace temperature for various graphite target preparation conditions

The graphite samples were also analyzed at CEDAD, Italy, with a 3MV HVEE Tandem accelerator (Calcagnile et al. 2004). The typical mass of the iron powder weighed into the quartz tube was 2–2.5 mg and the mass of the formed graphite was ~1 mg. As seen in Figure 4, we achieved acceptable and reproducible ¹²C³⁺ post-accelerated beam current values only by applying 580 °C furnace temperatures and leaving the oxidation step out during iron powder pre-activation. Results of δ¹³C (Figure 5) and ¹⁴C concentration (Figure 6) measurements also confirmed the graphitization conditions described above. We concluded that the higher furnace temperatures along with application of the reduction step alone during pre-activation of the iron powder gave the optimum results for our equipment.

The result for the ¹⁴C background level investigation of the gas handling line and graphite target production system was 0.31 ± 0.05 pMC, after averaging 3 measurements. This is close to the sample processing background level at CEDAD (D'Elia et al. 2004).

Finally, we investigated the memory effect in the system (Table 2). Two of the 3 memory effect sample runs did show a slight increase between the ¹⁴C-dead CO₂ gas before the modern sample and the ¹⁴C-dead CO₂ gas run after the modern sample. Results indicated that the ¹⁴C memory of the gas handling line and reaction rigs is low for 580 °C furnace temperatures.

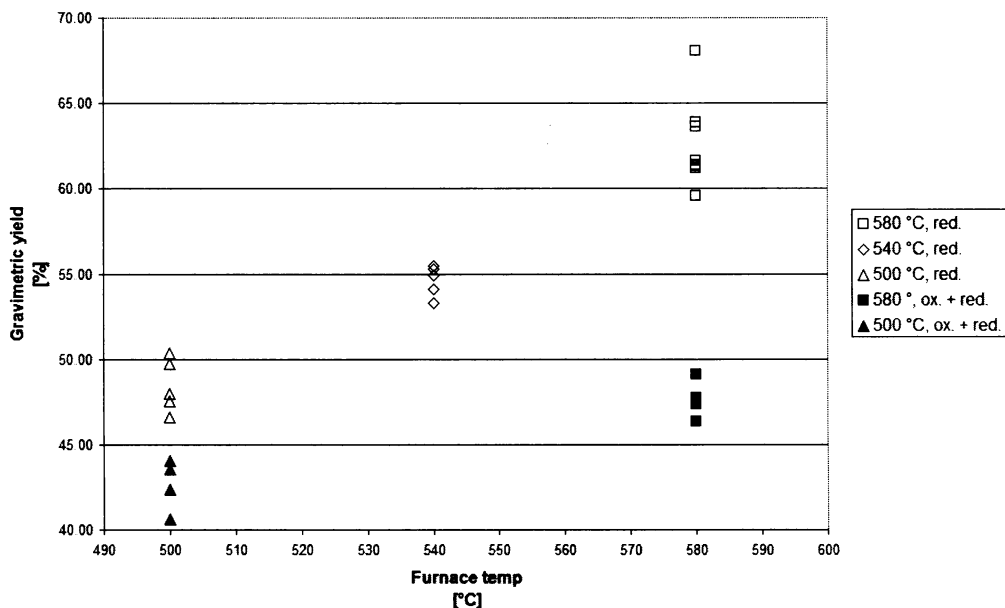


Figure 4 $^{12}\text{C}^{3+}$ post-accelerated beam current vs. formed graphite mass ratio for various graphite target preparation conditions.

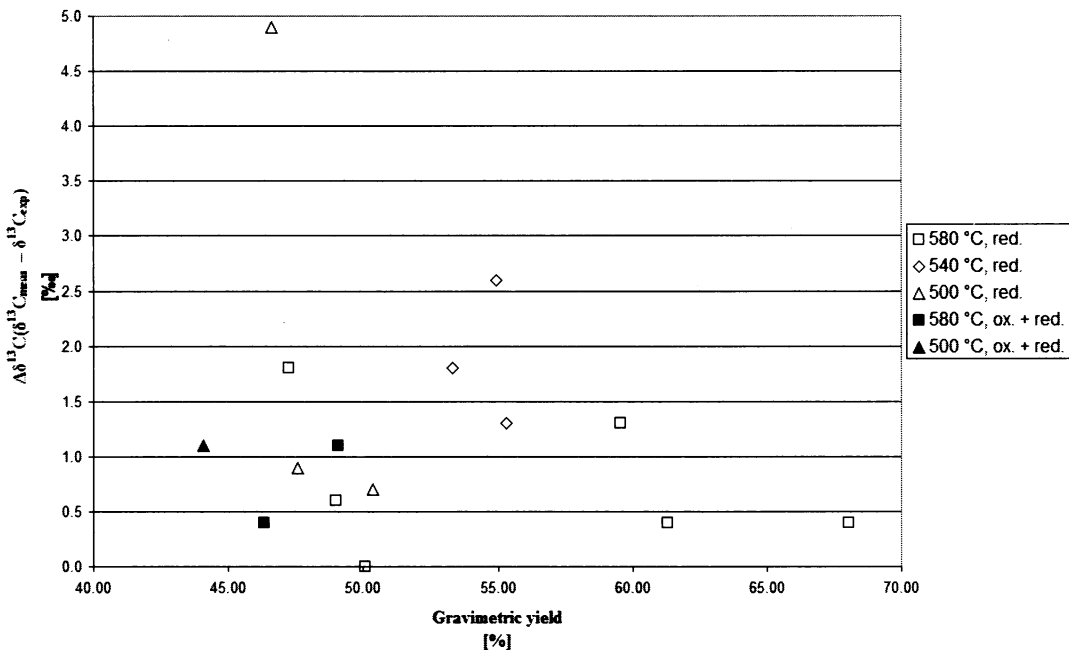


Figure 5 $\Delta\delta^{13}\text{C}$ ($\delta^{13}\text{C}_{\text{meas}} - \delta^{13}\text{C}_{\text{exp}}$) versus gravimetric yield for graphite targets prepared from ^{14}C -dead CO_2 gas ($\delta^{13}\text{C} = 2.8\%$, purity 99.995% v/v, Linde AG, Répcelak, Hungary).

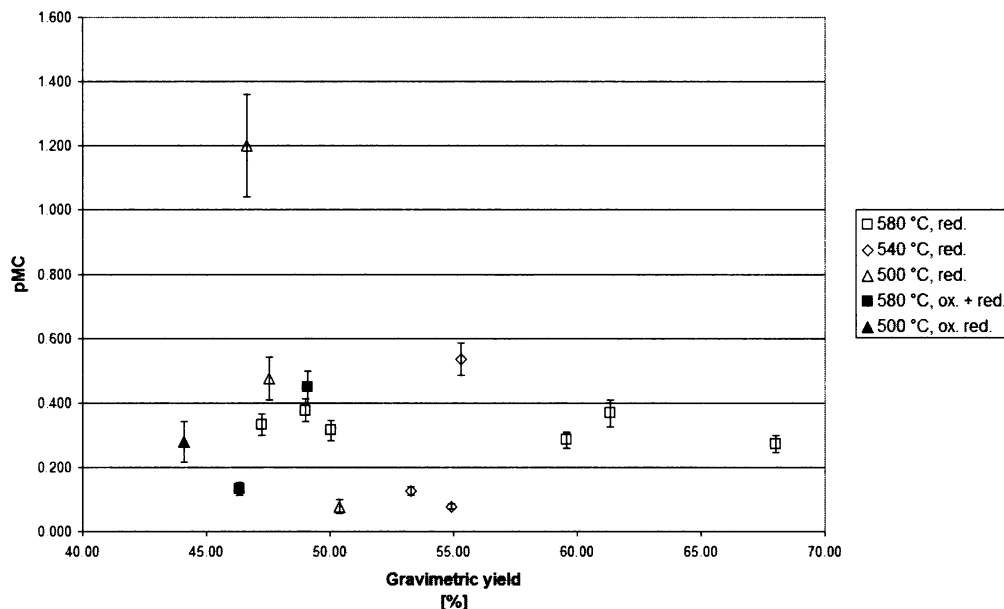


Figure 6 ¹⁴C activity in pMC vs. gravimetric yield for graphite targets prepared from ¹⁴C-dead CO₂ gas (purity 99.995% v/v, Linde AG, Répcelak, Hungary).

Table 2 Results of the memory effect investigation with usage of ¹⁴C-dead CO₂ gas ($\delta^{13}\text{C} = 2.8 \pm 0.2\text{‰}$ measured by our stable isotope mass spectrometer, purity 99.995% v/v) and modern sample gas (VIRI A, 109.7 ± 0.5 pMC measured by our GPC; $\delta^{13}\text{C} = -30.3 \pm 0.2\text{‰}$ measured by our stable isotope ratio mass spectrometer). Measurements were carried out at CEDAD, Italy.

¹⁴ C-dead CO ₂ gas before the modern sample		Modern CO ₂ gas		¹⁴ C-dead CO ₂ gas after the modern sample	
pMC	$\delta^{13}\text{C}$ (‰)	pMC	$\delta^{13}\text{C}$ (‰)	pMC	$\delta^{13}\text{C}$ (‰)
0.286 ± 0.025	-4.1 ± 0.1	109.45 ± 0.68	-30.5 ± 0.3	0.334 ± 0.033	-4.6 ± 0.2
0.274 ± 0.027	-2.4 ± 0.1	109.36 ± 0.65	-30.5 ± 0.4	0.376 ± 0.035	-2.2 ± 0.5
0.368 ± 0.042	-2.4 ± 0.1	110.55 ± 0.67	-30.9 ± 0.1	0.315 ± 0.031	-2.8 ± 0.3

The mean value of the VIRI A sample measured by AMS (109.8 ± 0.7 pMC) was consistent with what we measured by our GPC system (109.7 ± 0.5 pMC) and with the consensus value for this sample (109.1 ± 0.04 pMC) as published in the first report of the VIRI project (Scott et al., these proceedings).

CONCLUSION

After the performance tests on our new system, we found that the optimum hydrogen to CO₂ ratio was approximately 2.1, the optimum temperature of the furnace during the graphitization process was 580 °C, and that we got better results when we left out the oxidation step from the iron powder activation process. All of these conditions are for mg-size graphite samples.

The investigation of the ¹⁴C background level of the gas handling line and the graphitization system gave good agreement with CEDAD’s sample processing background value. The measurements do

not indicate a significant memory effect for the system. The AMS results of modern ^{14}C graphite samples were also in good agreement with the consensus value.

The results also show that the pressure yield alone does not give an all-inclusive description of the graphitization process in case of non-ideal conditions. The use of gravimetric yield in addition to the pressure yield gives extra information about the possible reactions and products and may assist in finding the proper conditions for the graphitization process.

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