



STATUS OF THE AMS GRAPHITIZATION SYSTEM IN THE DENDROCHRONOLOGICAL LABORATORY AT AGH-UST, KRAKÓW

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Abstract

A new system for the preparation of graphite samples for radiocarbon (^{14}C) measurement using an accelerator mass spectrometer (AMS) has been built in the Dendrochronological Laboratory at AGH-UST, Kraków. This system consists of three independent components. The first is the equipment for mechanical and chemical sample pre-treatment. The second is the vacuum line for sample sealing and the purification of CO_2 . The third and central part of this system is a graphitization line, where graphite is produced from CO_2 . In the first stage, chemical sample preparation was carried out to remove impurities. IAEA and NIST OxII standard materials were converted to CO_2 without pre-treatment. In the next step, samples were combusted to CO_2 . The resulting CO_2 was released under vacuum and cryogenically purified for subsequent graphitization. The performance of the system was tested with NIST OxII, IAEA standards (IAEA C5, C6 and C7) and background samples. The test confirms good reproducibility of results obtained for the samples prepared using this system. The results of the 49 samples of NIST Ox-II, IAEA standards and blank samples were presented in this article.

Keywords

AMS, graphitization system, radiocarbon measurements, sample preparation.

1. Introduction

One of the most important considerations for ^{14}C dating by accelerator mass spectrometry (AMS) is the method of target preparation. Measurements precision is limited by the C^- current obtainable from material in a Cs sputter-ion source (0.5–2 μA). For high precision, it is necessary to fabricate targets from material such as graphite, which gives a high C^- current (Jull *et al.*, 1986). In the AMS technique of radiocarbon dating, the ^{14}C concentration is measured in graphite, which is prepared from the carbon contained in the sample. Graphite is pressed into a tablet, which is used as a target in the Cs-sputtering ion source of the accelerator (Czernik and Goslar, 2001).

The whole process of the radiocarbon dating consists of sample preparation and measurement. The sample preparation includes mechanical and chemical processes of cleaning, combustion and graphitization. A new system for the preparation of graphite samples for radiocarbon (^{14}C) measurement using AMS has been built in the Dendrochronological Laboratory at AGH-UST, Kraków. This system consists of three independent components. The first is the equipment for mechanical and chemical sample pre-treatment. The second is the vacuum line for sample sealing and purification of CO_2 . And, the third and central part of this system is graphitization line, where graphite is produced from CO_2 (Krąpiec *et al.*, 2018).

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The cathodes produced in this system were measured at the Center for Applied Isotope Studies at the University of Georgia, and the results of these measurements were presented in this article.

2. Samples and methods

Organic samples, such as charcoal and plant fragments are pre-treated with the AAA method (acid-alkali-acid), following standard protocols (e.g. Jull *et al.*, 2006). In our laboratory, we treat samples with 2% HCl at 75°C, next rinsing with deionized H₂O to a neutral pH. As the next step, we treat the samples with 1 M NaOH at 75°C and rinsing with deionized H₂O to a neutral pH again. Finally, we treat the samples with 2% HCl at 75°C again and rinse with deionized H₂O to a neutral pH. We then dry the prepared sample and it is ready for the next stage.

For wood samples, alpha cellulose extraction was performed since it is the most stable compound from plant material; therefore, the separation and utilization of this cellulose content is the most suitable for a ¹⁴C-age determination (Molnár *et al.*, 2013). Lignin and hemicellulose, being components of wood, contain carbon that is easier to replace and is therefore not suitable for determining age (Nemec *et al.*, 2010). The Green (1963) protocol was used to extract α -cellulose from wood. Additionally, this method was modified using an ultrasonic bath (Pazdur *et al.*, 2005), and it used HCl instead of acetic acid to avoid any possible acetylation (Nemec *et al.*, 2010) (Fig. 1).

IAEA and NIST OxII standard materials were converted to CO₂ without pre-treatment. The background material (vitrinite) was prepared by AAA extraction

to remove inorganic (carbonates) and organic components (fulvic and humic acid) (Krapiec *et al.*, 2018).

Samples were weighed and transferred to quartz ampoules, pre-baked at 850°C together with cupric oxide and silver wool. Thus, the prepared samples were flame-sealed in evacuated quartz ampoules to a pressure of 10⁻⁵ mbar and combusted for 6 h at 900°C in a muffle oven. Resulting CO₂ was released under vacuum and cryogenically separated from water in a glass vessel cooled in a dry ice/ethanol slurry (~177 K). Next, the purified CO₂ was

trapped in the glass valve cooled by liquid nitrogen and transferred to the reduction line (Czernik and Goslar, 2001) (Fig. 2b).

The reduction line consists of five ports (Fig. 2a). Each port is connected to a vacuum pump and contains manual valves for pressure control; a glass valve with sample CO₂, a tube with a Fe catalyst and electric furnace and tube with cooling trap (Krapiec *et al.*, 2018). For CO₂ reduction, we used ~200 mbar CO₂, which corresponds to 1 mg of carbon. Graphite is produced during the reaction with H₂ at 600°C, on 2 mg Fe as catalyst:



Before the reduction of CO₂, the iron powder is oxidized for 15 min at 400°C and then reduced in H₂ for 30 min at 400°C. During graphitization, for water separation, we used cooling trap from mixture of dry ice and alcohol (Goslar and Czernik 2000) (Fig. 2c). This is all monitored and controlled by manual pressure recordings at 5-min intervals. The cathodes produced in this system were measured at the Center for Applied Isotope Studies at the University of Georgia, USA (Labcode UGAMS; Cherkinsky *et al.*, 2010).

3. Results

The graphitization process is monitored and controlled by manual pressure recordings at 5-min intervals. It shows that the graphitization process is completed after approximately 65 min (Fig. 3). According to the equation of efficiency (Osborne *et al.*, 1994), the efficiency EF_p is >95%.

$$\text{EF}_p = \frac{P_{\text{all_start}} - P_{\text{all_end}}}{3 * P_{\text{CO}_2}}$$

The results of the previous measurements and details of our system and procedures are described by Krapiec *et al.*, (2018). This article presents the results of 49 samples, including 20 samples of NIST Ox-II, 21 background samples and eight samples of IAEA standards (three samples of IAEA

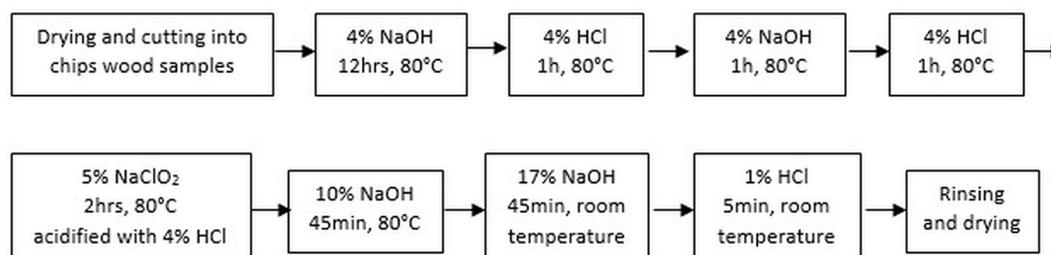


Fig 1. Scheme of alpha cellulose extraction.

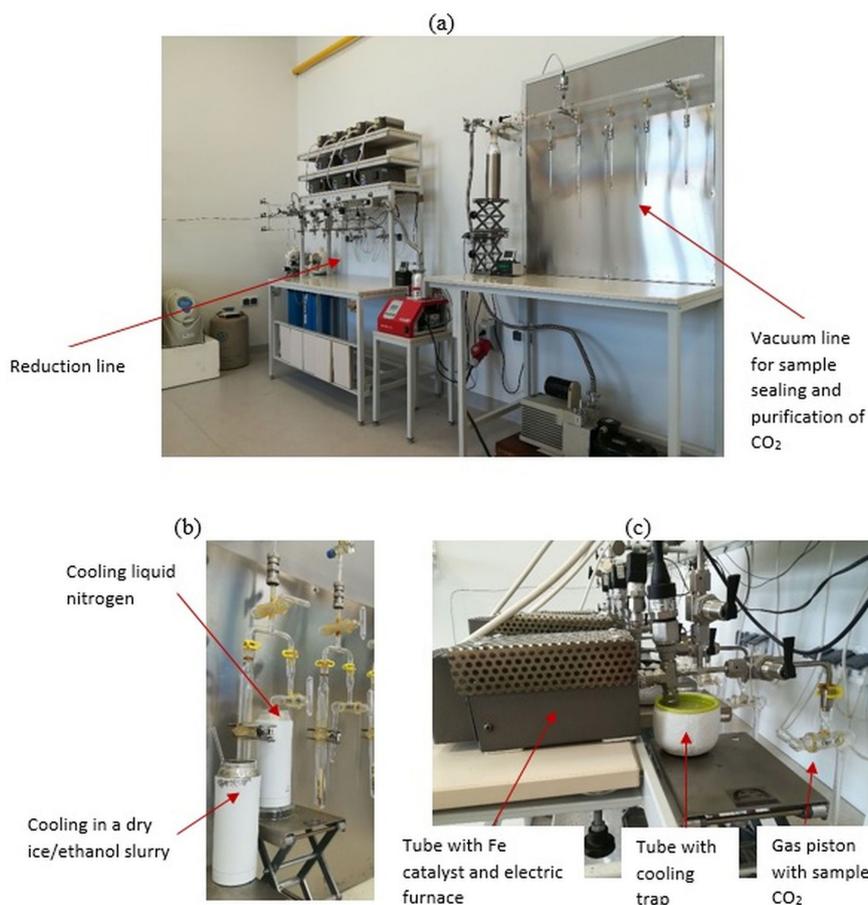


Fig 2. AMS graphitization system in the Dendrochronological Laboratory at AGH-UST, Kraków: a) Reduction line and vacuum line for sample sealing and purification of CO₂; b) cryogenically separation CO₂ from water in glass vessel cooled in a dry ice/ethanol slurry and trapping CO₂ in the glass valve cooled by liquid nitrogen; c) shows the vacuum line for graphite preparation.

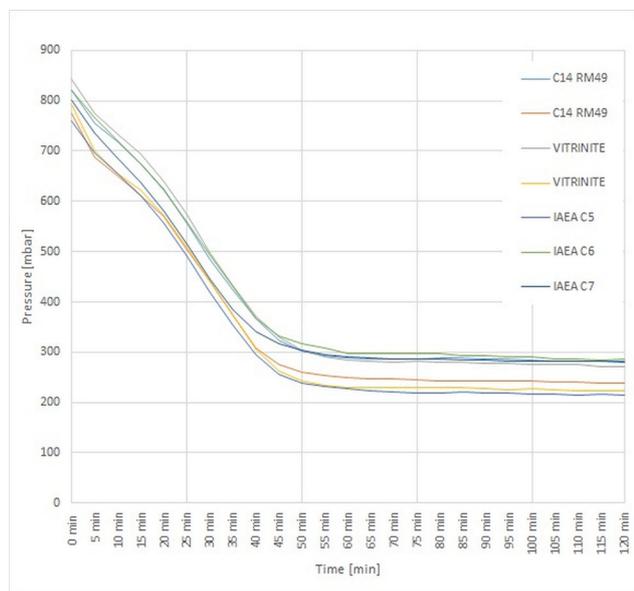


Fig 3. Changes in CO₂ pressure during reduction for some of the reduced samples.

C5, one sample of IAEA C6 and four samples of IAEA C7) (Table 1). These samples were used to test the performance of the system.

The relationship between the measured and expected values for all samples is presented in Table 2. For most of the samples, there are no significant differences between the measured values and the consensus values. An average value of samples NIST Ox-II of 134.05 ± 0.17 pMC was obtained from 20 measurements and corresponds well with the expected value. The measurement of standards samples (IAEA C5, IAEA C6 and IAEA C7) also have very good results. An average value of samples IAEA C5 of 23.31 ± 0.35 pMC was obtained from three measurements, of samples IAEA C6 of 149.44 ± 0.44 pMC was obtained from one measurement and of samples IAEA C7 of 50.38 ± 0.15 pMC was obtained from four measurements. Those results are satisfying and correspond rationally well to the consensus values.

The biggest scatter of results can be observed for the background samples (vitrinite), with an average

Table 1. The results of ^{14}C AMS measurements of the samples prepared using the graphitization line in the Dendrochronological Laboratory at AGH-UST Krakow.

N	Lab code	Sample ID	Material	pMC	±	^{14}C age years	±	Weight C [mg]
1	UGAMS 40065	C14_10	OXII	133.82	0.33			1
2	UGAMS 34241	C14_5	OXII	134.69	0.28			1
3	UGAMS 34242	C14_5A	OXII	133.43	0.28			1
4	UGAMS 41465	C14_11	OXII	135.11	0.30			1
5	UGAMS 41466	C14-12	OXII	133.07	0.30			1
6	UGAMS 41699	C14_13	OXII	134.78	0.41			1
7	UGAMS 41702	C14_15	OXII	133.31	0.41			1
8	UGAMS 41700	C14-13B	OXII	134.68	0.33			0.3
9	UGAMS 41701	C14-14	OXII	133.45	0.33			0.36
10	UGAMS 42224	C14_11A	OXII	135.20	0.26			1
11	UGAMS 42225	C14_12A	OXII	132.83	0.36			1
12	UGAMS 35610	C14_7	OXII	134.02	0.31			1
13	UGAMS 35611	C14_7A	OXII	134.11	0.32			1
14	UGAMS 36945	C14_7B	OXII	135.21	0.31			1
15	UGAMS 36946	C14-9	OXII	132.89	0.31			1
16	UGAMS 37297	C14_9A	OXII	134.48	0.31			1
17	UGAMS 37298	C14_9B	OXII	133.64	0.31			1
18	UGAMS 43566	C14_16	OXII	133.99	0.34			1
19	UGAMS 43567	C14_16A	OXII	134.48	0.43			0.34
20	UGAMS 43568	C14_16B	OXII	132.88	0.39			0.1
21	UGAMS 40066	WIT_10	vitrinite	0.391	0.011	42096	147	1
22	UGAMS 40067	WIT_10A	vitrinite	0.385	0.011	42200	155	0.65
23	UGAMS 34243	WIT_3D	vitrinite	0.546	0.013	41854	195	1
24	UGAMS 34244	WIT_5	vitrinite	0.576	0.014	41427	198	1
25	UGAMS 41467	WIT_11	vitrinite	0.549	0.013	41811	194	1
26	UGAMS 41468	WIT_12	vitrinite	0.765	0.047	39141	512	1
27	UGAMS 41695	WIT_11A	vitrinite	0.568	0.012	41532	203	1
28	UGAMS 41696	WIT_12A	vitrinite	0.684	0.016	40043	184	1
29	UGAMS 41697	WIT_13B	vitrinite	0.942	0.021	37471	177	0.32
30	UGAMS 41698	WIT_13C	vitrinite	0.951	0.020	37400	166	0.35
31	UGAMS 42222	WIT_13	vitrinite	1.020	0.016	36834	124	1
32	UGAMS 42223	WIT_14	vitrinite	0.672	0.014	40187	166	1
33	UGAMS 35612	WIT_6	vitrinite	1.961	0.025	30010	83	1
34	UGAMS 35613	WIT_7	vitrinite	0.432	0.010	43770	179	1
35	UGAMS 36947	WIT_7A	vitrinite	0.696	0.024	39899	280	1
36	UGAMS 36948	WIT_9	vitrinite	0.658	0.021	40316	256	1
37	UGAMS 37299	WIT_7B	vitrinite	1.410	0.060	34233	165	1
38	UGAMS 37300	WIT_9A	vitrinite	1.385	0.081	34377	225	1
39	UGAMS 43569	WIT15	vitrinite	0.388	0.010	44601	207	1

Table 1. Continued

N	Lab code	Sample ID	Material	pMC	±	¹⁴ C age years	±	Weight C [mg]
40	UGAMS 43570	WIT15A	vitritinite	0.482	0.013	42862	214	0.34
41	UGAMS 43571	WIT15B	vitritinite	0.943	0.038	37461	325	0.1
42	UGAMS 31703	C5_1	IAEA C5	23.32	0.11	11696	36	1
43	UGAMS 42226	C5_2	IAEA C5	23.47	0.85	11644	29	1
44	UGAMS 36949	C5_1B	IAEA C5	23.16	0.09	11750	30	1
45	UGAMS 34245	C6_1B	IAEA C6	149.44	0.44			1
46	UGAMS 35614	C7_1	IAEA C7	50.55	0.15	5479	23	1
47	UGAMS 35615	C7_2	IAEA C7	50.99	0.14	5410	21	1
48	UGAMS 41489	C7_2A	IAEA C7	50.26	0.16	5526	25	1
49	UGAMS 37301	C7_1A	IAEA C7	49.72	0.15	5616	27	1

Table 2. Relationship between measured and expected values.

Material	n	Consensus value ¹⁴ C (pMC)	Average measured value ¹⁴ C (pMC)
NIST OxII	20	134.07±0.17	134.05±0.17
Background (vitritinite)	21	0	0.781±0.023
IAEA C5	3	23.05±0.02	23.31±0.35
IAEA C6	1	150.61±0.11	149.44±0.44
IAEA C7	4	49.53±0.12	50.38±0.15

value of 0.781 ± 0.023 pMC that was obtained from 21 measurements. The average value of measured background is not bad, but the result is inflated by several samples. The measurements oscillating around ~ 0.350 pMC are acceptable and comparable with values reported by other laboratories (Krajcar-Broni \acute{c} *et al.*, 2010; Molnar *et al.*, 2013). A few results are much higher (for example samples: WIT_13 – 1.020 ± 0.016 pMC, WIT_7B – 1.410 ± 0.060 pMC and WIT_9A – 1.385 ± 0.081 pMC), which can probably be explained by leakage during sealing or by the graphitization of the samples (Krapiec *et al.*, 2018).

Another explanation may also be the contamination of samples during weighting or transferring. However, a relationship was noted between the weight of C (amount of CO₂ used for reduction) and the measured value of ¹⁴C. If we used ~ 200 mbar CO₂, which corresponds to 1 mg of carbon, it is easier to obtain the expected result. The lower the carbon content of the sample (the smaller the amount of CO₂ used for reduction), the lower the accuracy of the results. For example, see samples WIT_15, WIT_15A and WIT_15B.

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First sample (WIT_15): we used ~ 200 mbar carbon dioxide, which corresponds to 1 mg of carbon – result, 0.388 ± 0.010 pMC ($44\,601 \pm 207$ ¹⁴C age years).

Second sample (WIT_15A): we used ~ 68 mbar carbon dioxide, which corresponds to 0.34 mg of carbon – result, 0.482 ± 0.013 pMC ($42\,862 \pm 214$ ¹⁴C age years).

Third sample (WIT_15B): we used ~ 20 mbar carbon dioxide, which corresponds to 0.1 mg of carbon – result, 0.943 ± 0.038 pMC ($37\,461 \pm 325$ ¹⁴C age years).

4. Conclusions

The measurements conducted thus far provide evidence for the reliability of the AMS graphitization system in the Dendrochronological Laboratory at AGH-UST, Kraków. The results of measurements are satisfying and correspond rationally well to the consensus values. The tests conducted thus far show that a relationship was noted between the weight of C (amount of CO₂ used for reduction) and the measured value of ¹⁴C. The small deviations are probably caused by leakage during sealing or the graphitization of the samples. Further tests are necessary to constantly improve the line and eliminate any contamination of samples.

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