

## AUTOMATED SAMPLE COMBUSTION AND CO<sub>2</sub> COLLECTION SYSTEM WITH IRMS FOR <sup>14</sup>C AMS IN YAMAGATA UNIVERSITY, JAPAN

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**ABSTRACT.** Accelerator mass spectrometry (AMS) was introduced at Yamagata University in 2010, including the measurement of radiocarbon. In the Yamagata University laboratory (YU-AMS), the application of <sup>14</sup>C AMS is aimed at micro-dose pharmacokinetics investigation and the development of improved sample preparation techniques. The lab also measures environmental samples. With the installation of this AMS system, a new automated sample production system was installed, which is composed of an elemental analyzer, a glass vacuum line, and an isotope ratio mass spectrometer (IRMS). In this system, it is also possible to measure stable isotopes ( $\delta^{13}\text{C}$ ,  $\delta^{15}\text{N}$ , and  $\delta^{34}\text{S}$ ) of the sample gas using a mass spectrometer. To increase the amount of CO<sub>2</sub> gas introduced into the glass vacuum line, the gas mass flow introduced into the MS was reduced, and the change of  $\delta^{13}\text{C}$  accompanying this reduction was monitored. The sample gas split was changed to set the glass vacuum line (GVL):isotope ratio mass spectrometer (IRMS) ratio to 5:5, 8:2, and 9:1, and  $\delta^{13}\text{C}$  was measured for each ratio. It was confirmed that there was no effect on the isotopic fractionation accompanying the change in the sample gas split ratio. To prioritize the use of gas in the production of graphite, the GVL:IRMS ratio of 9:1 was chosen for this setup. The components are connected on-line, and up to 20 samples can be processed automatically.

### INTRODUCTION

Since Aerts-Bijma et al. (1997) reported sample combustion using an elemental analyzer (EA), the introduction of an automated CO<sub>2</sub> collection system has been carried out in various laboratories (Gagnon et al. 2000; Hong et al. 2010). A fully automated sample combustion, CO<sub>2</sub> collection, and graphitization system was recently reported by Wacker et al. (2009). An automated sample preparation system and a compact accelerator mass spectrometry (AMS) system were introduced into the YU-AMS laboratory in 2010 (Tokuai et al. 2011). The advantage of an automated system is that it makes sample production more reproducible. Although the procedure from sample pretreatment to graphitization is performed by one person at YU-AMS, many sample production processes can be performed stably using this automated system.

The automated sample preparation system (Figures 1A and 1B) is composed of an elemental analyzer (Vario MICRO cube, Elementar), an isotope ratio mass spectrometer (IRMS; Isoprime Ltd.), and a glass vacuum line (GVL; Koshin Rikagaku Seisakusho Co., Ltd.). Samples are combusted in the EA. The sample gas is then separated into nitrogen, carbon dioxide, and sulfur dioxide using a temperature-programmed desorption (TPD) column. The sample gas generated in the EA is introduced into the GVL and IRMS at rates of 90% and 10%, respectively. The EA and IRMS are controlled by software (Vario MICRO and IonVantage, respectively), and the GVL is automated by the sequence control. Blank processing is carried out after sample processing to prevent cross-contamination owing to the memory effect that may arise in the adsorption column of the EA. Up to 20 samples can be processed in ~12.5 hr (Kato et al. 2012) and the graphite production rate is 60 samples per week. The carbon dioxide generated in the EA is distributed to the GVL and IRMS. In the usual EA-IRMS system consisting of a Vario MICRO cube and the Isoprime, 50% of total helium carrier gas flow is introduced into the IRMS from the EA, which is the default setting, and stable isotope measurements are performed. However, in YU-AMS, to prioritize gas use over graphite production, the gas volume introduced into the IRMS is changed to 10%. In order to prevent isotopic fractionation of  $\delta^{13}\text{C}$  by changing the split ratio,  $\delta^{13}\text{C}$  measurements were performed at a split ratio of 5:5 (GVL:IRMS) of the default setting and at 9:1 as a maximum setting to deliver CO<sub>2</sub> to the GVL.

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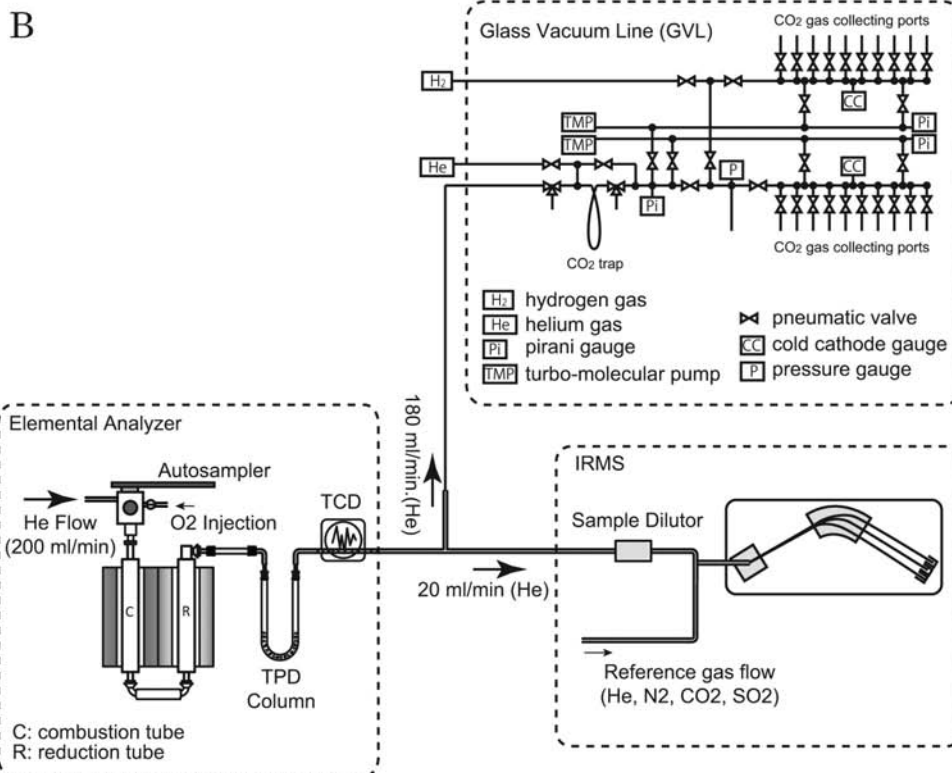
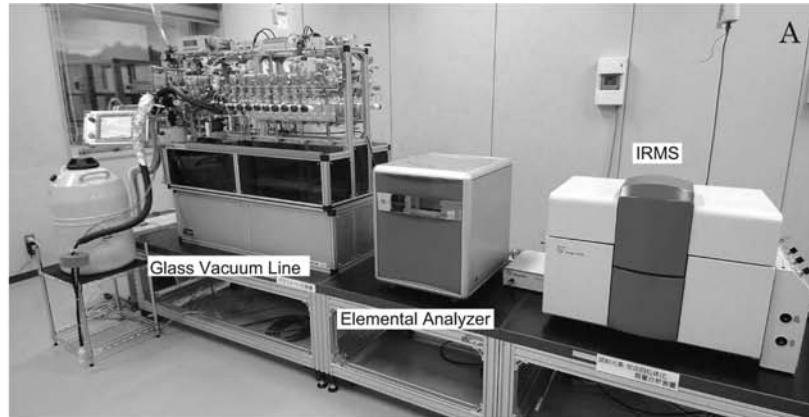


Figure 1 (A) An overview photograph of the automated sample production system, and (B) shows a schematic image of this system. The automated sample preparation system is composed of the EA, IRMS, and GVL. Since a maximum of 20 sample adjustments are possible, a sample is wrapped in tin and set in the autosampler of the EA. Sample gas is introduced into the GVL and IRMS at rates of 90% and 10%, respectively. In the GVL, recovery and volume measurement of CO<sub>2</sub> are performed and CO<sub>2</sub> is subsequently moved to the collection port. Recovery and movement are performed using liquid nitrogen and controlled by the sequencer program. As for the gas introduced into the IRMS, stable isotope measurements are performed using software (IonVantage).

## METHODS

International standard samples (IAEA CH-7, IAEA CO-8, and IAEA C-6) and sulfanilamide, a standard reagent of EA with an unknown  $\delta^{13}\text{C}$ , were used for measurement. The EA and IRMS were used for CO<sub>2</sub> sample gas production and  $\delta^{13}\text{C}$  measurement, respectively. With helium carrier gas flow at a rate of 200 mL/min, CO<sub>2</sub> emitted from the EA's adsorption column was introduced to the IRMS to measure  $\delta^{13}\text{C}$  as well as into the GVL. With the current equipment, the gas volume introduced into the MS usually allows to perform stable isotope measurements using 50% of the emitted CO<sub>2</sub>. This setup corresponds to the gas split ratio of 5:5 in this study. The split ratio was changed to set the GVL:IRMS ratio to 5:5, 8:2, and 9:1. After adjusting the flow of He carrier gas discharged from the EA to the flow corresponding to each split ratio,  $\delta^{13}\text{C}$  measurement was carried out for each split ratio. Measurement at a split ratio of 8:2 was also performed as a reference to verify that the results were not influenced by the split ratios.

## RESULTS AND DISCUSSION

The value of reference gas was determined using the value of CH7, C08, and C6 references at all split ratios. Although some differences were observed for  $\delta^{13}\text{C}$ , its dependence on the split ratio was not observed (Figure 2). The measurement was performed three times at each distribution ratio and split ratio, and nine measurement results were obtained on the whole. The average of these nine measurement results was determined. Measured values agreed with the 1 $\sigma$  range relative to the nine measurements. The recommended  $\delta^{13}\text{C}$  values of CO8 and CH7 are in the 1 $\sigma$  range, and that of C6 is in the 2 $\sigma$  range. However, some of the measurement results of the split ratio of 8:2 were outside the 1 $\sigma$  range. Although the recommended  $\delta^{13}\text{C}$  value of C6 is outside the 1 $\sigma$  range of measurement values (Figure 2c), the reason for this difference between measured value and a recommended value has not yet been identified.

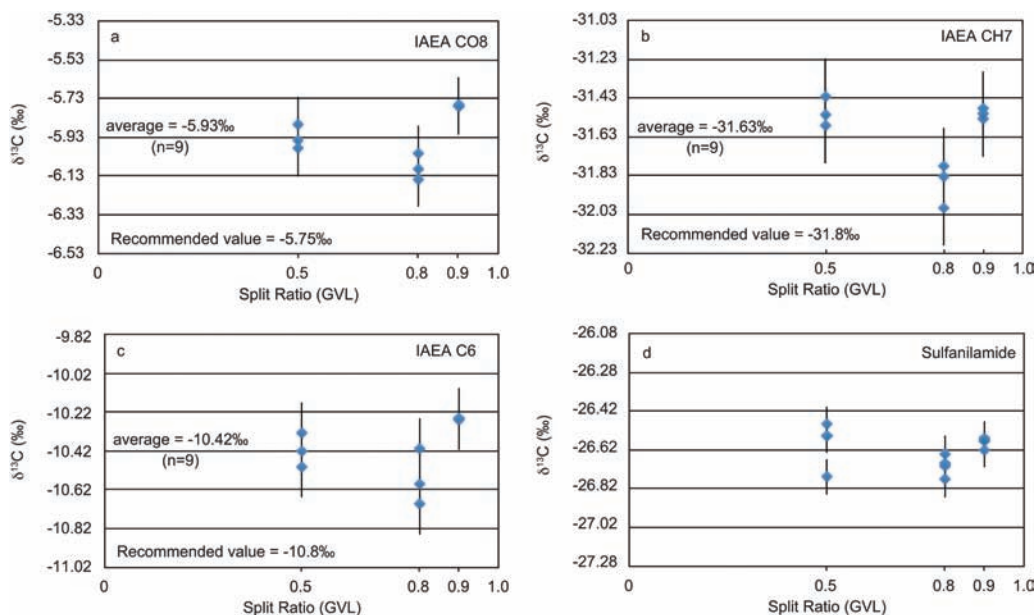


Figure 2  $\delta^{13}\text{C}$  values of IAEA CO6 (a), IAEA CH7 (b), IAEA C6 (c), and sulfanilamide (d) at each split ratio. The  $\delta^{13}\text{C}$  value of each sample remains almost constant with the change in split ratio. The error bar shows the standard deviation relative to the nine total measurements.

Table 1 Absence of cross-contamination between samples in the EA.

Pro- cessing order	Sample name	$\delta^{13}\text{C}$ (‰)
1	Sulfanilamide	-26.68
2	Sulfanilamide	-26.64
3	Sulfanilamide	-26.63
4	Sulfanilamide	-26.62
5	IAEA CH7	-31.49
6	IAEA CH7	-31.54
7	IAEA CH7	-31.51
8	IAEA CO8	-5.76
9	IAEA CO8	-5.77
10	IAEA CO8	-5.77
11	IAEA C6	-10.26
12	IAEA C6	-10.25
13	IAEA C6	-10.26

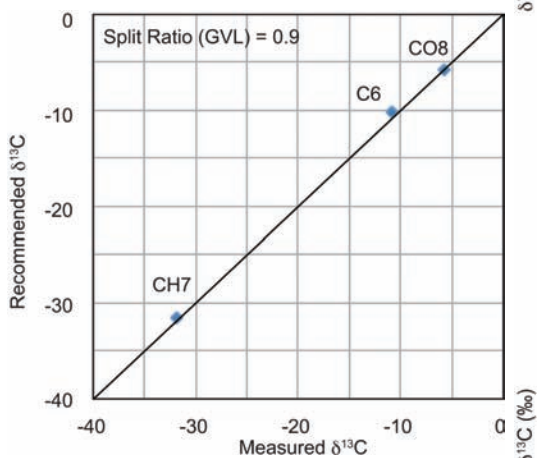
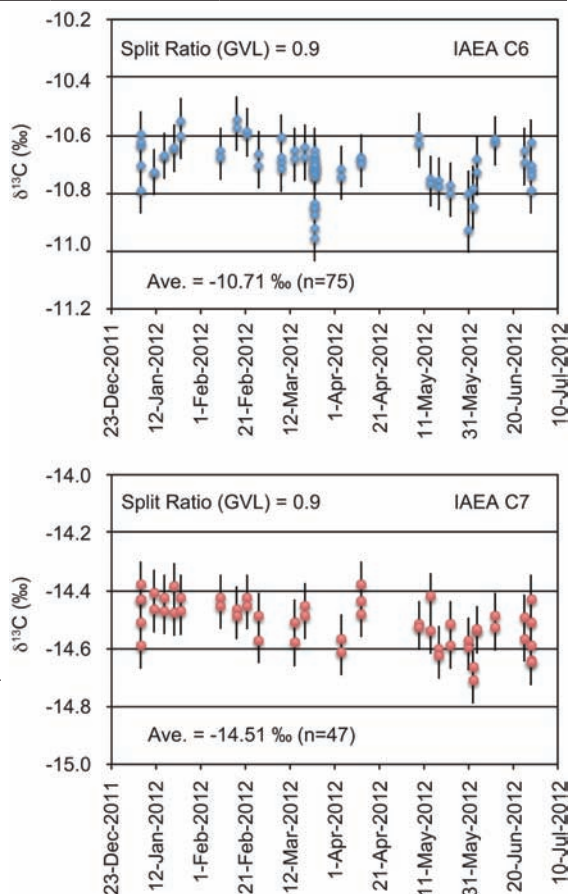
Figure 3 Relationship between the recommended and measured  $\delta^{13}\text{C}$  values at split ratio of 0.9 in the GVL.

Table 2 Graphite quality comparison between batch method and automated graphite production system. The result of the batch method is reported by Tokanai et al. (2011).

Sample type	Consensus value (pMC)	Batch method	Automated
		measured value (pMC) 24 Mar 2010	system measured value (pMC) 3 Dec 2010
IAEA-C2	41.14 ± 0.03	41.06 ± 0.25	41.66 ± 0.11
IAEA-C3	129.41 ± 0.08	130.13 ± 0.24	129.81 ± 0.43
IAEA-C4	0.20 - 0.44	0.04 ± 0.03	0.03 ± 0.02
IAEA-C5	23.05 ± 0.02	22.98 ± 0.07	22.97 ± 0.30
IAEA-C6	150.61 ± 0.11	150.09 ± 1.14	150.54 ± 0.30
IAEA-C7	49.53 ± 0.12	49.77 ± 0.29	49.85 ± 0.13
IAEA-C8	15.01 ± 0.17	15.09 ± 0.06	15.07 ± 0.18
IAEA-C9	0.12 - 0.21	-	0.12 ± 0.02

Figure 4 Long-term variation in  $\delta^{13}\text{C}$  at split ratio of 0.9 in GVL. The average value of C6 and C7 is  $-10.71\text{‰}$  and  $-14.51\text{‰}$ , respectively. The error bar shows standard deviation relative to measurements of C6 and C7.

The isotopic measurement results of C08, C07, and C06 at the split ratio of 9:1 were confirmed to be generally in agreement with the recommended values (Figure 3). From the results, it was confirmed that the isotopic fractionation accompanying the change in split ratio had not occurred. To prioritize gas use over graphite production, the GVL:IRMS ratio was set to 9:1 in the setup.

Figure 4 shows long-term changes of  $\delta^{13}\text{C}$  of C6 ( $n = 75$ ) and C7 ( $n = 45$ ) with a distribution ratio of 9:1, from which the measured values of C6 and C7 were confirmed to be stable. However, the difference in the  $\delta^{13}\text{C}$  of C6 is larger than that of C7, which may be reflected by the difference in standard deviation between C6 (0.5) and C7 (0.2).

Table 1 shows the  $\delta^{13}\text{C}$  results obtained by continuous measurement of a different standard specimen. Since the absence of cross-contamination by the residual gas that may exist in the EA adsorption column was confirmed, the measured  $\delta^{13}\text{C}$  value is not affected by the different  $\delta^{13}\text{C}$  values. Despite confirmation of this efficient sample gas collection, blank processing was performed after sample processing.

Table 2 shows the measurement results of the IAEA C series standard obtained by a batch method and the automated system. Since these results mostly agree with the consensus value, the measurement that uses the C series has been performed periodically and the result has been reported by Tokanai et al. (2013). Although the reason for the deviation of the values of C2, C4, and C7 from the consensus value in Table 2 is unknown, the agreement between the measured values and recommended values over a long period of time (Tokanai et al. 2013) confirms the validity of sample production using the automated system presented.

## CONCLUSION

The results obtained confirmed that isotopic fractionation had not occurred due to the change in split ratio. To prioritize gas use over graphite production, the GVL:IRMS split ratio was set to 9:1 in the setup. Since the pMC value of the IAEA standard obtained with the automated system agrees with the recommended value, the validity of this automated system is confirmed.

## ACKNOWLEDGMENTS

The author (KK) would like to thank Mari Sugihara, Satoru Ohkubo, and Shigeru Ito of JASCO International Co., Ltd., and Hisashi Uno and Rie Shitara of YU-AMS for their help.

## REFERENCES

- Aerts-Bijma AT, Meijer HAJ, van der Plicht J. 1997. AMS sample handling in Groningen. *Nuclear Instruments and Methods B* 123(1–4):221–5.
- Gagnon AR, McNichol AP, Donoghue JC, Stuart DR, von Reden K, NOSAMS. 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.
- Hong W, Park JH, Kim KJ, Woo HJ, Kim JK, Choi HW, Kim GD. 2010. Establishment of chemical preparation methods and development of an automated reduction system for AMS sample preparation at KIGAM. *Radiocarbon* 52(3):1277–87.
- Kato K, Tokanai F, Anshita M, Sakurai H. 2012. Automatic sample combustion and CO<sub>2</sub> collection system for AMS-<sup>14</sup>C. *Radioisotopes* 61(9):469–73.
- Tokanai F, Kato K, Anshita M, Izumi A, Sakurai H, Saito T. 2011. Compact AMS system at Yamagata University. *AIP Conference Proceedings* 1336:70–4.
- Tokanai F, Kato K, Anshita M, Sakurai H, Izumi A, Toyoguchi T, Kobayashi T, Miyahara H, Ohyama M, Hoshino Y. 2013. Present status of the YU-AMS system, Yamagata University. *Radiocarbon* 55(2):251–9.
- Wacker L, Němec M, Bourquin J. 2009. A revolutionary graphitisation system: fully automated, compact and simple. *Nuclear Instruments and Methods in Physics Research B* 268(7–8):931–4.