

## ESTABLISHMENT OF CHEMICAL PREPARATION METHODS AND DEVELOPMENT OF AN AUTOMATED REDUCTION SYSTEM FOR AMS SAMPLE PREPARATION AT KIGAM

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**ABSTRACT.** Many previous studies on the sample preparation of various kinds of radiocarbon dating samples by accelerator mass spectrometry (AMS) have been examined at KIGAM (Korea Institute of Geoscience and Mineral Resources) and our own procedures have been established. Furthermore, an automated reduction system has been developed. The volume of the reduction region was minimized to improve the reduction yield, and air-actuated pneumatic valves and solenoid arrays were used for computer control of the system. Operation of all the valves and vacuum pumps and signals from the temperature sensors and pressure gauges were interfaced to a personal computer with an A/D board. A computer program was also developed to perform automatic operation of the reduction system. This system consistently shows a higher reduction yield than 90%. The reduction time of the system is currently 140 min.

### INTRODUCTION

Many sample preparation techniques have been developed by preceding groups since accelerator mass spectrometry (AMS) began to be applied to radiocarbon dating in the 1970s. The KIGAM (Korea Institute of Geoscience and Mineral Resources) AMS group has set up chemical preparation procedures for various kinds of samples by referring to the previous works of the last 4 yr. Because the demand for analyzing soil samples is high in our institute, extra effort was put into soil sample pretreatment method development.

Since an automatic combustion technique using a commercial elemental analyzer (EA) was developed by Aerts-Bijma et al. (1997), many AMS laboratories have used this method to combust samples automatically. Recently, the Erlangen group and ETH group have developed automatic reduction systems coupled with an EA and automated reduction lines. Since 2005, an automated reduction system has also been developed at KIGAM in order to install a <sup>14</sup>C dating laboratory. A 1MV AMS system was installed in 2007 at KIGAM (details are described in Hong et al. 2010). The automatic and compact reduction system is critical for the KIGAM AMS laboratory because we have only 2 permanent staff members and 2 temporary staff members for sample preparation and AMS operation, and the space to install the AMS machine and all the chemical and physical preparation facilities is also limited.

In the first stage of the development, a prototype reduction system, which is a semi-automated system, was manufactured to collect basic data to design an automatic system. In 2008, a 24-fold reduction system coupled with an EA was developed. This paper reports specifications of the reduction system and preliminary results of the test run.

### CHEMICAL PREPARATION

Since this is the first report of our sample pretreatment procedures and they are very common methods, only a brief summary was presented here. Wood samples are cut into around 100 mesh pieces.

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Currently, a ball mill with a zircon jar and balls is tested at our laboratory for the sample grinding. An ABA procedure based on the method of Lee et al. (2000) is used for conventional analysis at our laboratory. For the precise measurement of wood samples, the alpha cellulose extraction procedure (Hua et al. 2000) is employed.

For each shell sample, the surface treatment was performed using a combination of acid, ultrasonic cleaning, and sandblasting methods. Dissolved inorganic carbon (DIC) is treated by the same method as Sveinbjörnsdóttir et al. (1995). Two methods, direct combustion and hydrolysis, are used to convert carbonates to CO<sub>2</sub>. For routine analysis of calcium carbonates, samples are directly combusted by an EA at 950 °C. However, CaCO<sub>3</sub> samples older than 30,000 yr are converted to CO<sub>2</sub> by hydrolysis with 86% H<sub>2</sub>PO<sub>3</sub> because the background of the hydrolysis method (0.05 pMC) was found to be lower than the direct combustion method (0.1 pMC) in our previous work with IAEA C1 standard samples (Park et al. 2010). BaCO<sub>3</sub> from DIC also should be treated by hydrolysis because it is hard to thermally decompose unlike CaCO<sub>3</sub>. A carbonate preparation line was designed and structured for hydrolysis, which is similar to the carbonate system presented in Tisnérat-Laborde et al. (2001). The recovery yield of this system was found to be approximately 90%, and the typical vacuum condition is  $3 \times 10^{-6}$  Torr. For routine work, 12 mg of carbonates are converted to 120 mTorr of CO<sub>2</sub> after purifying, which is calculated to ~1 mg of carbon. CO<sub>2</sub> gas is cryogenically transferred to a removable container to transfer to a reduction system.

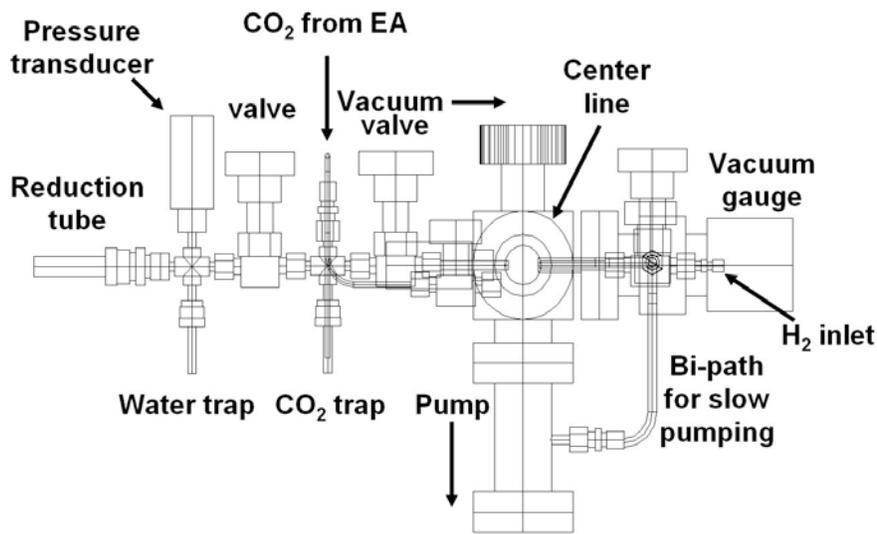
Although accuracy of dating results for soil-related carbon has been discussed, the dating of organic carbon in soil is very important for us because 90% of all samples run at KIGAM are soil samples. Three fractions of organics (humin, humic and fulvic acids) in soil are separated by the ABA procedure, and a humic fraction is measured for age dating. Our method for soil preparation is based on the procedure of Kristiansen et al. (2003), but replacing stirring with the ultrasonic method. The advantages of the ultrasonic method are 1) higher recovery yield of humic acid by 3–10 times so that soil samples with low carbon content can be measured, and 2) no scratches on glassware containers (beaker or test tube) so that chance of contamination by container material decreases. The details of comparison between stirring and ultrasonic extractions were published in Park et al. (2009).

Our procedure for bone sample treatment is mainly based on the Oxford University method (Jacobi et al. 2006). Using a Vivaspin filter, collagen over 30 kD is selectively collected to remove seriously degraded molecules, and then freeze-dried.

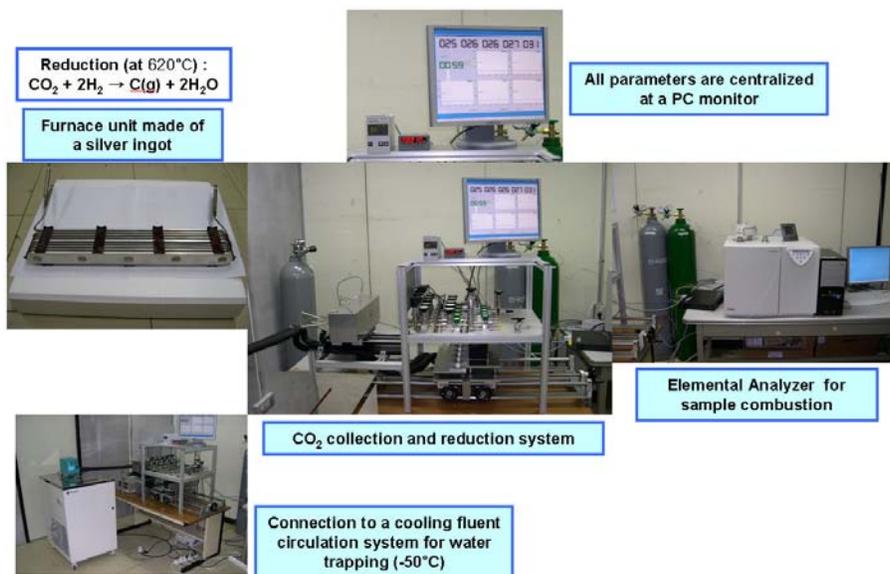
All the experimental conditions and results from the chemical process to AMS measurement are stored semi-automatically to a database system coded by Oracle<sup>TM</sup> so that the data can be accessed any time it is needed in the laboratory.

## **REDUCTION SYSTEM**

A 5-fold semi-automated reduction system, which is a prototype for a fully automated system, was developed to collect basic data for designing a final system. Figure 1a shows a drawing of the reduction region of the semi-automated reduction system, and Figure 1b presents the whole reduction system coupled to an elemental analyzer (EA). A furnace made of a silver ingot was developed to heat 5 reduction tubes without the large temperature differences with simple electronics. Water trapping is carried out by an ethanol circulation system that can cool down ethanol to -70 °C. The reduction system is coupled with an EA (EA1112 CN, Thermo Electron Co.) to combust samples, so that CO<sub>2</sub> from EA is directly transferred at a cryogenic trap of a reduction line. The typical vacuum condition of this system is  $3 \times 10^{-7}$  Torr in the main vacuum line.



(a)



(b)

Figure 1 Layout of the semi-automatic reduction system (prototype): (a) schematic of reduction tube parts; (b) overview of the whole system.

Four mg of Fe catalyst is preheated twice at 500 °C for 20 min in an O<sub>2</sub> atmosphere to remove contamination and in H<sub>2</sub> to reduce the catalyst again. The combustion time is 10 s, and the collection time at a trap is 5 min for each sample. Every sample combustion is followed by the combustion of an empty tin foil to confirm that CO<sub>2</sub> is not detected by the EA any more, which means the previous sample combusted completely. CO<sub>2</sub> is moved to a cold finger close to the reduction tube, and the sample size is measured by a pressure gauge. One mg of carbon is used for routine analysis at

KIGAM. Then, a proper amount of  $H_2$  is inserted in the reduction region. As shown in Figure 2, the optimum condition of  $CO_2/H_2$  ratio was found to be 1:2.1 for our system. The typical reduction time is 140–160 min and the temperature is kept at 630 °C. During the reduction, water is trapped via a  $-50$  °C ethanol trap. The reduction yield is around 85–98%. Variations of pressure and temperature during the reduction reaction are automatically monitored by a personal computer and displayed at a PC monitor in real time. Figure 3a shows the curves of pressure and temperature changes during the reduction. The reduction is completed within  $\sim 140$  min. The computer judges the end of the reduction process of each line when 1 of 2 conditions is satisfied: 1) the pressure drops below 50 Torr or 2) the pressure change for 10 min is smaller than 5 Torr. When all the lines satisfy the ending condition, then the reduction is stopped automatically by the PC. The temperature deviation between lines is within 20 °C, and the pressure change curves of each line have very similar shapes to each other.

The reduction yield distribution in 2008 is shown in Figure 3b. These values are overestimated by 3–5% due to uncertainty of initial  $CO_2$  pressures read by pressure gauges. At the beginning of the operation, the yields converged at 95%. However, the yields increased slowly along with time because the initial carbon was underestimated due to the uncertainty of the pressure reading. We found that frequent calibration of each pressure gauge is needed to get precise reduction yield. Values lower than 80% were measured in the case of a small sample size. For the reduction of small-sized samples, further study and modification of the system is needed. Figure 4 shows the reproducibility and stability of the prototype reduction system. The standard deviation ( $1\sigma$ ) of 200 oxalic acid samples (NIST oxalic acid II) in 2008 was found to be 3.2% of their average value. The average  $^{14}C/^{12}C$  ratio of 120 blank samples,  $3.82 \times 10^{-15}$ , is reasonably small. The accuracy of this reduction system was proved by an interlaboratory comparison (see Hong et al. 2010).

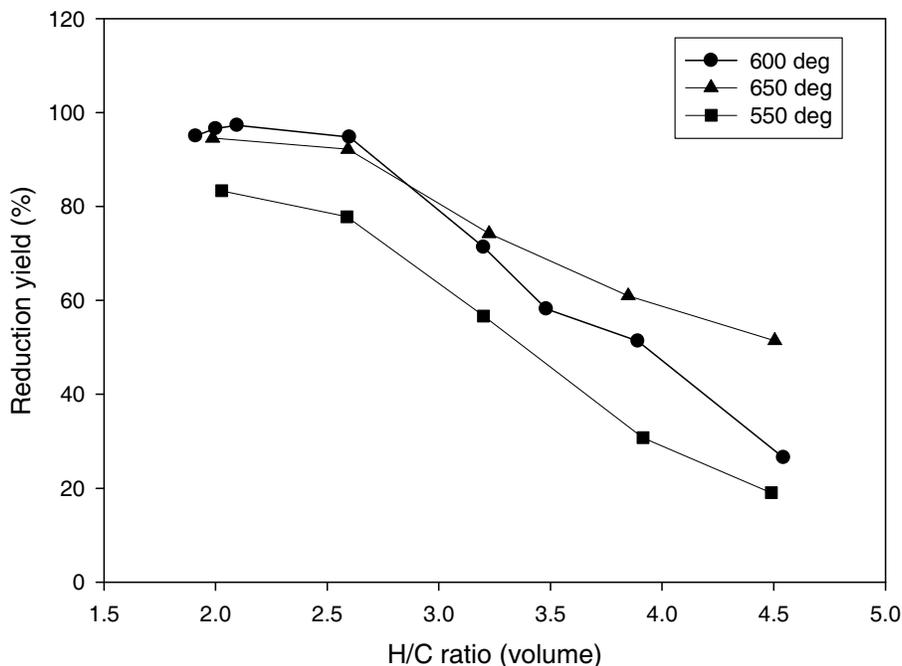
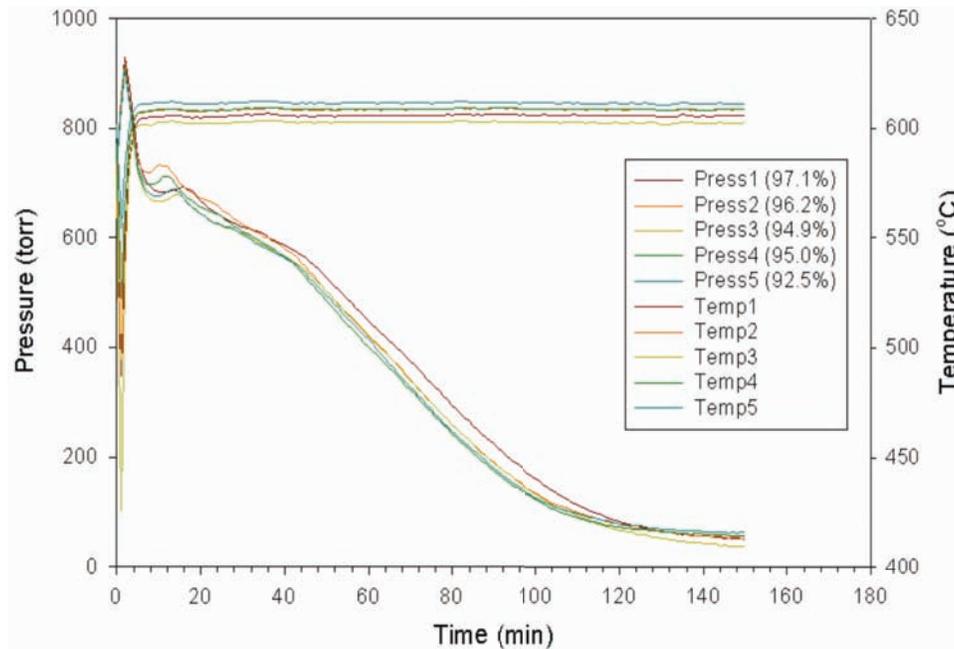
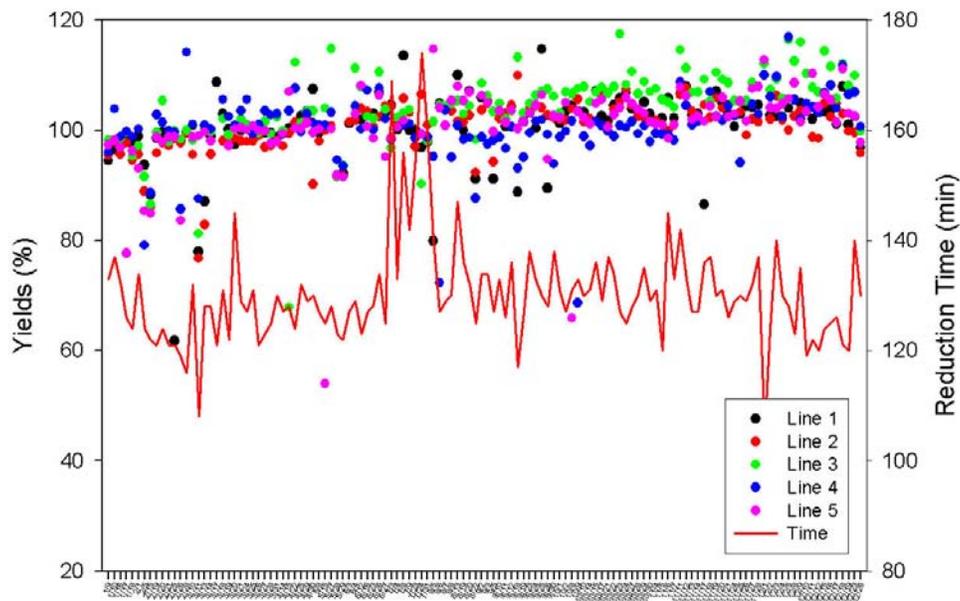


Figure 2 Reduction yield variation along with mixing ratio of  $H_2/CO_2$  obtained by the prototype reduction system.



(a)



Date in 2008

(b)

Figure 3 Performance of the prototype reduction system: (a) curves of pressure and temperature change during reduction reaction; (b) reduction yield distribution in 2008. Reduction yields are overestimated by 2–3% due to pressure gauge uncertainty.

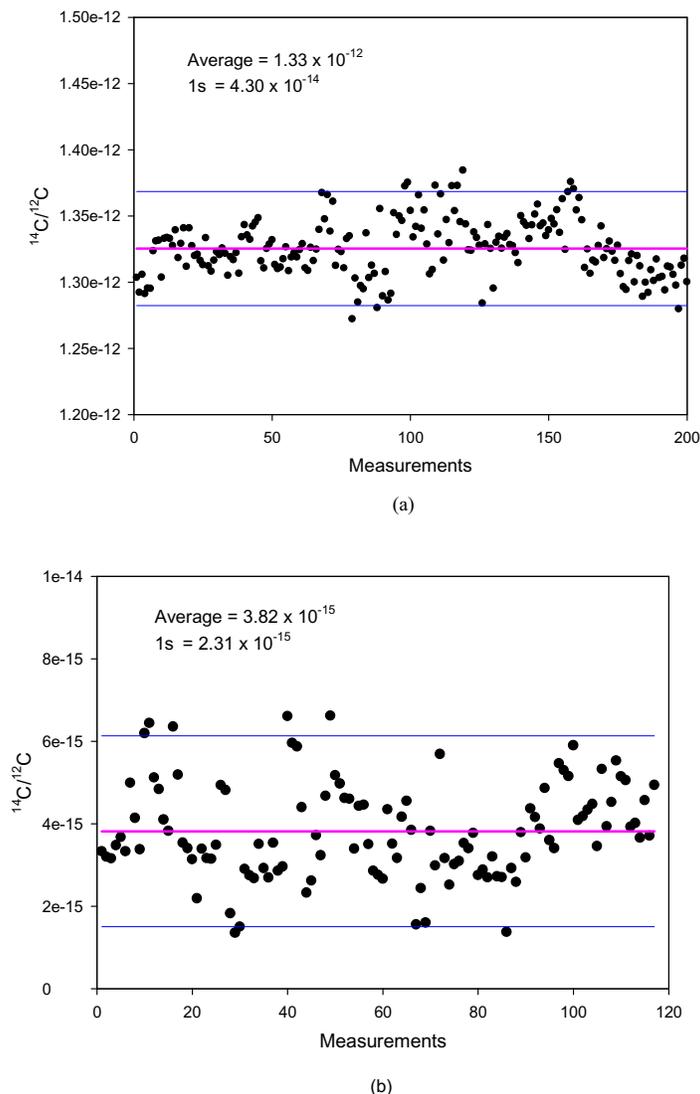


Figure 4 Variation of  $^{14}\text{C}/^{12}\text{C}$  ratios of (a) NIST standard (oxalic acid II) samples and (b) blank samples treated by the prototype reduction system.

With the data obtained from operating the prototype reduction system for 1 yr, an automated 24-fold reduction system with (dimensions of  $234\text{W} \times 75\text{D} \times 160\text{H}$  cm) has been developed (Figure 5) since end of 2008. This system has basically the same structure as the prototype. The major difference is the use of pneumatic valves and air-actuated pistons to move  $\text{LN}_2$  and ethanol dewars. Heaters are run by geared motors. All the units for automatic manipulation and sensors of this new system are interfaced to a personal computer via National Instrument (NI) modules and a board. The software to control the system has been developed by NI-DAQ libraries, NI Measurement Studio<sup>®</sup> and Microsoft Visual Studio<sup>®</sup>. The main screen of the software is presented in Figure 6. Displays of pressures and temperatures are centered on the screen for user convenience. The automatic process is divided into 3 parts: preheating of the catalyst, sample collection, and reduction. The reduction

system is also divided into 2 regions, and they can be operated separately. For instance, while reduction is carried out in one region, the catalyst can be preheated in another region, depending on needs. The software also performs automatic pressure gauge calibration using CO<sub>2</sub> gas and an additional precise and stable pressure gauge, which is calibrated regularly by the Korea Research Institute of Standard and Science (KRISS). Two turbopumps and 2 oil-less backing pumps are used to evacuate the system and typical vacuum was  $8 \times 10^{-7}$  Torr at the center line.



Figure 5 Overview of 24-fold automatic reduction system at KIGAM

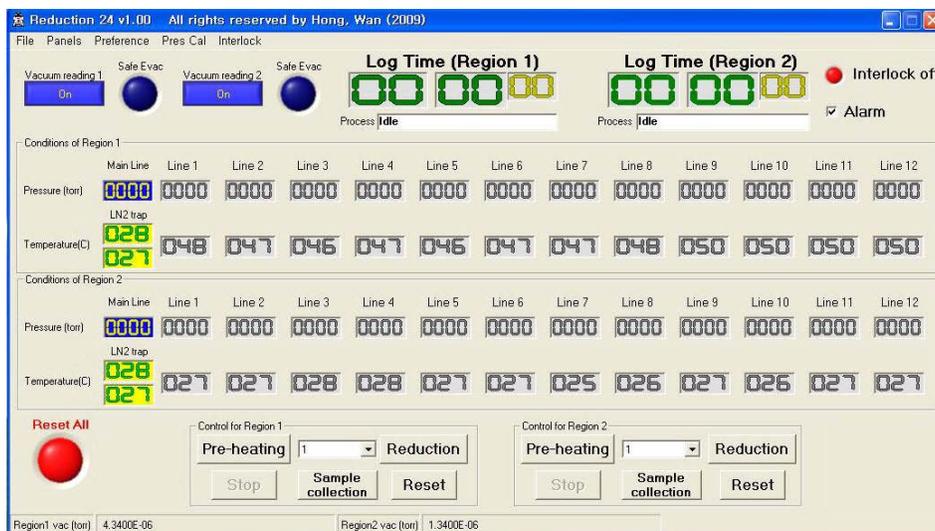


Figure 6 Main screen of the control software of 24-fold automatic reduction system

Performance of the new reduction system is demonstrated in Table 1 and Figure 7. The pressure of each line changes in a very similar way and the pressure drop stopped after 160 min. The reduction time is longer than the prototype by 20 min. The reduction yield was 93.1%. Figure 8 shows the reduction yields distribution of the automatic system for 64 samples. Average yield was found to be 91.6%, which is slightly smaller than the prototype. However, the small standard deviation shows

Table 1 Typical performance of the automatic reduction system.

Line	1	2	3	4	5	6	7	8	9	10	11	12
CO <sub>2</sub> (Torr)	260	278	251	250	248	249	252	249	250	249	251	251
C (mg) <sup>a</sup>	1.20	1.28	1.16	1.15	1.14	1.15	1.16	1.15	1.15	1.15	1.16	1.16
H <sub>2</sub> (Torr)	517	552	503	500	485	495	499	503	503	500	501	503
H <sub>2</sub> /CO <sub>2</sub>	1.99	1.99	2.00	2.00	1.96	1.99	1.98	2.02	2.01	2.01	2.00	2.00
Final pressure	44	38	28	36	33	30	38	39	38	38	36	38
Graphite <sup>b</sup> (mg)	1.09	1.17	1.05	1.04	1.05	1.09	1.13	1.09	1.07	1.07	1.07	1.08
Yield (%)	90.7	91.6	90.7	90.3	92.0	95.0	97.1	94.7	93.2	93.2	92.8	93.5
Line	13	14	15	16	17	18	19	20	21	22	23	24
CO <sub>2</sub> (Torr)	247	249	250	252	253	250	251	251	252	249	250	248
C (mg)	1.14	1.15	1.15	1.16	1.16	1.15	1.16	1.16	1.16	1.15	1.15	1.14
H <sub>2</sub> (Torr)	487	496	500	503	503	505	507	504	509	499	507	501
H <sub>2</sub> /CO <sub>2</sub>	1.97	1.99	2.00	2.00	1.99	2.02	2.02	2.01	2.02	2.00	2.03	2.02
Final pressure	34	36	31	37	51	50	35	35	49	37	33	46
Graphite (mg)	1.10	1.12	1.08	1.10	0.99	1.08	1.06	1.08	1.05	1.09	1.07	1.06
Yield <sup>c</sup> (%)	96.4	98.1	94.3	94.7	85.2	93.5	91.5	93.5	90.2	95.4	92.9	92.7

<sup>a</sup>Calculated values by CO<sub>2</sub> pressure and the average volume of reduction regions.

<sup>b</sup>Values obtained by weighing of quartz boats with Fe catalyst before and after reduction.

<sup>c</sup>Average yield of the 24 lines was 93.1%

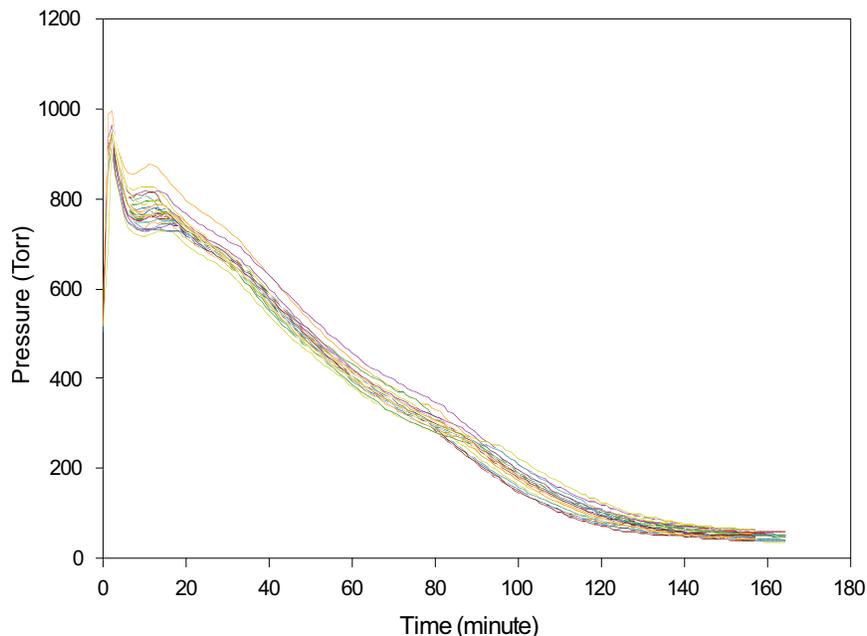


Figure 7 Curves of pressure variation during reduction reaction with automatic reduction system

the system is very stable and confident.  $^{14}\text{C}$  measurements were performed to evaluate the reproducibility of the system, and the results are presented in Figure 9. The average  $^{14}\text{C}/^{12}\text{C}$  ratio of NIST oxalic II sample is  $1.35 \times 10^{-12}$ , which is close to measured value in 2008. Also, the standard deviation is very small. The blank value is  $3.62 \times 10^{-15}$ . The known samples, C8 from IAEA (Le Clercq et al. 1998), were treated by the automatic reduction system and measured to evaluate the accuracy of the system. Table 2 shows the results. The average activity is higher than the consensus value,  $15.03 \pm 0.17$  pMC. More study to solve this problem is needed for precise measurement.

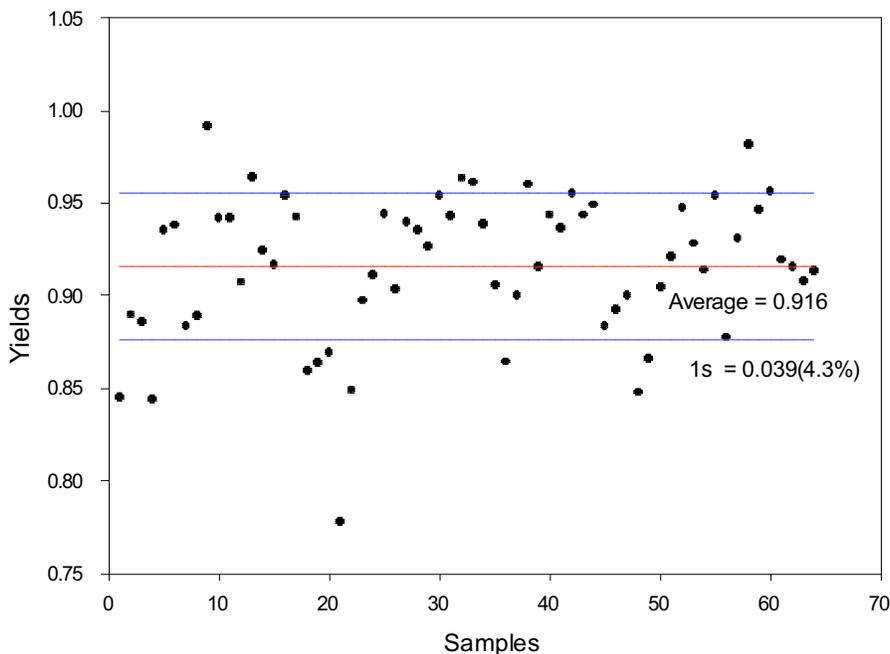


Figure 8 Reduction yield distribution of automatic reduction system. Average yield and standard deviation were 91.6% and 3.9%, respectively.

Table 2 Activities of IAEA C8 reference material treated by the automatic reduction system.

Sample ID	Activity <sup>a</sup> (pMC)	1 $\sigma$
T8C090041	15.58	0.18
T8C090042	15.78	0.18
T8C090045	16.14	0.19
T8C090049	16.19	0.14
T8C090051	15.66	0.16
T8C090054	15.49	0.15
T8C090065	15.15	0.14
T8C090066	15.27	0.16
T8C090067	15.17	0.15
T8C090068	15.28	0.15

<sup>a</sup>Average activity is  $15.56 \pm 0.38$  pMC.

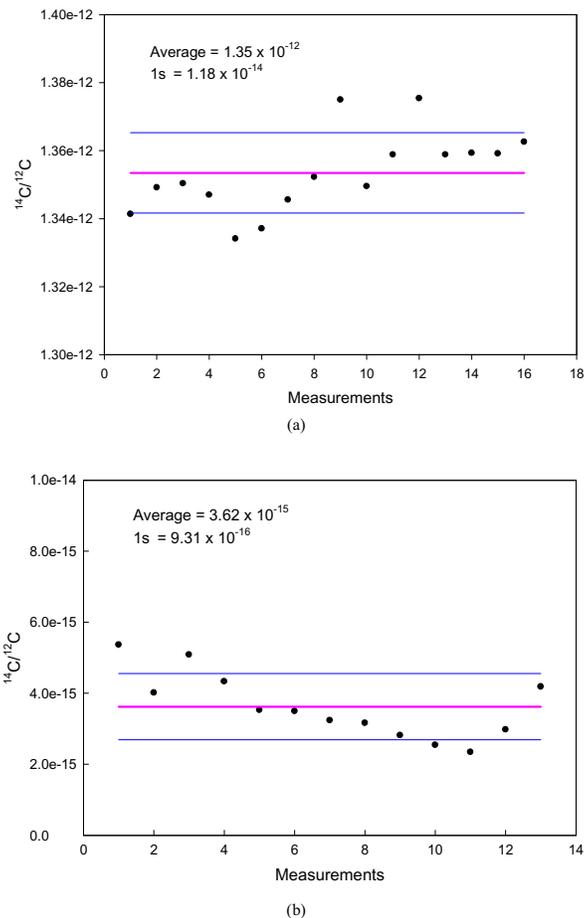


Figure 9 Variation of  $^{14}\text{C}/^{12}\text{C}$  ratios of (a) NIST standard (oxalic acid II) samples and (b) blank samples treated by the automatic reduction system.

## CONCLUSION

Sample preparation procedures for various kinds of samples for  $^{14}\text{C}$  dating have been established at KIGAM AMS laboratory. We have performed  $^{14}\text{C}$  dating since the beginning of 2008, and the overall sample preparation procedures at KIGAM seem to have produced reliable results so far, though several minor modifications such as fine adjustments of acid concentration of ABA and reaction time were needed. The database of results from chemistry, reduction, and AMS measurement for each sample play very important roles in the quality control of age because it makes the inquiry of the sample history very easy. The database also provides a table with several important interim results of the treatment steps for final revision meeting before reporting the sample ages to the customers. We measured more than 500 commercial samples and 500 samples for our own purposes in 2008 using the prototype reduction system. Our throughput is limited by insufficient manpower. As the 24-fold automatic reduction system started routine analysis just recently, it is expected that the throughput could be expanded to as many as 2000 commercial samples per year with only 4 staff members. For the automatic routine work, research on the enhancement of the system accuracy is still being conducted.

## ACKNOWLEDGMENTS

This work has been supported by the General Research Project funded by the Korea Research Council for Industrial Science & Technology and the Ministry of Knowledge Economy.

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