Note

Automatic Sample Combustion and CO₂ Collection System for AMS-¹⁴C

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A compact accelerator mass spectrometry (AMS) system was installed at Yamagata University in 2010 with the aim of developing technologies for the radiocarbon dating of environmental samples and microdosing clinical tests using radiocarbon. With the installation of this AMS system, we also installed a new automatic sample preparation system comprising an elemental analyzer (EA), an isotope ratio mass spectrometer (IRMS), and a glass vacuum line (GVL). This automatic system can automatically collect CO₂ from samples, measure the stable isotope ratio, quantify the amount of CO₂ and H₂ introduced for reduction, and treat 20 samples in approximately 12.5 hrs, thus enabling the preparation of 60 samples per week.

Key Words : accelerator mass spectrometry, radiocarbon, automatic sample preparation system

1. Introduction

Accelerator mass spectrometry (AMS) has enabled the radiocarbon measurement of minute samples, and its range of applications has been expanding, such as archaeology, environmental science, geology, space and earth science and development of new pharmaceuticals. In particular, active faults around nuclear power plants have been reevaluated after the accident at Fukushima Daiichi Nuclear Power Plant due to the Great East Japan Earthquake. Moreover, preparedness for earthquakes and tsunamis has been emphasized as a result of reevaluating tsunami deposits, increasing the need for radiocarbon dating.

In radiocarbon measurement based on AMS, CO₂ collected from samples is chemically converted into graphite, which is used for measurement. Carbon dioxide is collected from samples by (1) a batch method, in which each

sample is heated in vacuum with an oxidizing agent in a quartz tube¹⁾, or (2) a method using an automatic system that combines an elemental analyzer (EA), a glass vacuum line (GVL), and an isotope ratio mass spectrometer (IRMS)²⁾⁻⁶⁾. The batch method requires several days for the entire process including the encapsulation of each sample into a quartz tube, the oxidation of individual samples in the quartz tube, the purification of the sample gases (CO₂), the quantification of CO₂, and the introduction of H₂ used for CO₂ reduction. In our automatic system, the process from the combustion of sample to the purification of CO₂ is conducted using the EA in approximately 10 min. CO₂ extracted by the EA is introduced into the GVL, where CO₂ is quantified and H₂ is introduced for CO₂ reduction. Because the process from combustion of sample to the extraction of CO₂ is performed by EA only in approximately 10 min, the efficiency of the automatic system is

Fig. 1 Outline of automatic system used for preparing graphite installed at Yamagata University.

Pi, Pirani gauges; P, pressure gauge; CC, cold cathode gauge; TMP, turbo-molecular pump.

much higher than that of the batch method. A rough estimate of 20 samples preparation time indicates half a day for our automatic system and several days for the batch method. In this report, we describe the automatic system combining the EA, GVL, and IRMS of Yamagata University.

2. Outline of System and Operation

Fig. 1 shows an outline of the automatic sample preparation system. The IRMS (Isoprime) and GVL (AG-20, Koshin Rikagaku Seisakusho Ltd.) are connected to the EA (vario MICRO cube, Elementar). Ten percent of the sample gas generated in the EA is introduced into the IRMS for the measurement of the isotope ratio, and 90% of the gas is introduced into the GVL for the preparation of graphite. The EA and IRMS are controlled by the software provided with them, enabling automatic treatment. The

operation of the valves of the GVL, the supply of liquid nitrogen, and the transfer of a Dewar vessel are sequence-controlled by a programmable logic controller (PLC).

A sample is oxidized and decarbonized at 1150°C in a combustion tube. Combustion gases (i.e., N₂, CO₂, H₂O, and SO₂) are transferred with the carrier gas (He, 200 mL/min) and separated in a separation column after excess O₂ gas is removed using reduced copper heated to 850°C. The combustion gases are removed from the separation column in the following order: N₂, H₂O, CO₂, and SO₂. Water vapor is removed by a reagent (SICAPENT®) before reaching the thermal conductivity detector (TCD) of the EA. After the removal of H₂O, the column is heated at 90°C to remove CO₂ from the separation column and then heated at 200°C to remove SO₂. The separated gases are introduced into the TCD to measure the N, C,

and S contents of the sample. To prevent contamination between samples, sample combustion process alternate unknown sample and blank sample. The C content of the sample is measured using the EA, and the result is used to calculate the collection rate of CO₂ transferred from the EA to the GVL. The time required for the treatment in the EA is approximately 10 min for each sample. Ninety percent of the gas passing through the TCD is transferred to the GVL and 10% is transferred to the IRMS. When a signal to start the release of CO₂ is input from the EA to the GVL, the collection of CO₂ and the introduction of H₂ used for CO₂ reduction are automatically conducted following the predetermined procedures. A series of processes, i.e., the operation of valves, the supply of liquid nitrogen to a cold trap, the transfer of the Dewar vessel, the measurement of the pressure of the collected CO₂ gas, the calculation of the amount of H₂ supplied for reducing CO₂, and the recording of the pressure of the supplied H₂, are sequence-controlled by the PLC (Omron Corporation) ; the time required for the treatment of each sample is 26 min. Moreover, the GVL can be equipped with up to 20 CO₂ reduction tubes. With the IRMS, into which 10% of the sample gas is introduced from the EA, $\delta^{15}\text{N}$, $\delta^{13}\text{C}$, and $\delta^{34}\text{S}$ are measured.

3. Results

Fig. 2 shows the measurement results for the C content of sulfanilamide, an EA reference material. The C content of sulfanilamide is 41.81%, which is maintained throughout the entire measurement. Because this value has remained constant for one and a half years since the system was first used, the stable performance of the system has been confirmed.

Fig. 2 Long-term stability of elemental analyzer.

This figure shows stable sulfanilamide C contents value (ave. 41.81%).

Fig. 3 Measurement results of stable carbon isotope ratio.

The measured values for HOxII are in agreement with the consensus value (−17.8‰).

Fig. 3 shows $\delta^{13}\text{C}$ for oxalic acid II (HOxII) gas prepared in the EA, which has remained almost in agreement with the consensus value throughout the entire measurement, indicating that both the EA and the IRMS operate stably. The collection rate of CO₂ introduced with the carrier gas into the GVL has remained stable at approximately 90%. The CO₂ collection rate will probably be further increased by adjusting the GVL ; such adjustment is ongoing. An increase in the CO₂ collection rate will make it

Fig. 4 Measurement results for radio-carbon reference materials.

possible to apply the automatic system to the treatment of minute samples, in line with the recent trend of performing AMS- ^{14}C measurement for minute samples. Fig. 4 shows the measurement result for the International Atomic Energy Agency (IAEA) reference materials C1 – C9 obtained using the compact AMS system installed at Yamagata University⁷⁾. The result shows the relationship among the measured values (pMC) for C2 – C9, which were obtained by normalizing them using the value for HOxII after subtracting the background value (C1). The measured and consensus values are in agreement for each reference material, indicating that graphite was successfully prepared using the automatic system.

4. Summary

The quality of graphite has been verified by regularly examining the linearity of the relationship between the measured and consensus values obtained using IAEA reference materials. Since the automatic system was first operated, the linear relationship for graphite has been maintained, as shown in Fig. 4, which indicates the stable performance of the automatic system. The measurement duration tends to

decrease with increasing performance of the AMS system. In contrast, it is difficult to further speed up the sample preparation in the batch method, resulting in the reduced efficiency of the entire process. Compared with the batch method, the use of the automatic system can markedly reduce the duration of sample preparation because of its highly efficient operation processes. The automatic system at Yamagata University can treat 20 samples in 12.5 hrs, enabling the stable preparation of 60 samples per week. The automatic system has the major advantages of being able to treat multiple samples while maintaining their quality.

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