A STUDY ON TRAPPING CO_2 USING MOLECULAR SIEVE FOR ^{14}C AMS SAMPLE PREPARATION

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ABSTRACT. At the Seoul National University accelerator mass spectrometry (AMS) laboratory, we are planning to develop an automated sample preparation system for higher throughput of radiocarbon dating. This system will consist of several sections, including a combustion line, CO_2 trap, graphitization system, and so on. We usually collect CO_2 by cryogenic trapping. However, since handling liquid nitrogen is expected to be rather difficult, we are interested in replacing the cryogenic method with the molecular sieve method for the collection of CO_2. In this study, we compare the performance of the cryogenic trapping method and molecular sieve method. Zeolite 13X is used as a molecular sieve, and as test samples we use the oxalic acid standard (NIST SRM 4990C), high-purity graphite powder, and archaeological charcoals. The pMC values and the radiocarbon ages (BP) obtained from samples prepared by the above 2 methods are very similar. We especially focused on the memory effect of the molecular sieve, meaning the CO_2 contamination from a previous sample, which can cause errors in age determination. To reduce this effect, we flowed He gas through a zeolite container for several minutes at a high temperature before the CO_2 was introduced. By the adding this step, we have obtained more reliable results.

INTRODUCTION

There is increased demand for radiocarbon dating in Korea, thus an efficient and fast way to treat ^{14}C samples is necessary. Many accelerator mass spectrometry (AMS) laboratories have developed automated sample preparation systems that couple combustion and reduction systems (Hong et al. 2010; Wacker et al. 2010). At the Seoul National University (SNU) AMS laboratory, we are also planning to develop an automated sample preparation system for a higher throughput of ^{14}C dates.

We are especially interested in the method of collecting CO_2 resulting from sample combustion. At the SNU AMS lab, we usually use the cryogenic method to collect CO_2 using liquid nitrogen. Because liquid nitrogen has very a low temperature and is in a liquid state, it is expected to increase the control factors and to make the system complicated when we apply cryogenic CO_2 trapping to the new automated sample preparation system. The AMS group of the Swiss Federal Institute of Technology Zurich (ETH Zurich) have reported on the use of a molecular sieve (zeolite) to trap CO_2 (Wacker et al. 2010).

Zeolite has been used for trapping CO_2 from ice or air (Oeschger et al. 1966; Hardie et al. 2005). A zeolite trap was also used as an alternative to a cryogenic trap for collecting CO_2 from oxidation of organic carbon (Bauer et al. 1992). The selective gas absorption and desorption characteristics of zeolite as a function of temperature will be useful for simplifying the system for trapping CO_2 and transferring the gas to a graphitization reactor. Here, we compare the zeolite trap with a conventional cryogenic trap as a feasibility test for a new automated sample preparation system at the SNU AMS laboratory.

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EXPERIMETAL SETUP

Molecular Sieve – Zeolite 13X

Zeolite has excellent characteristics of absorption and desorption of molecules. Dehydrated zeolite has pores of uniform shape and molecular size, so it can absorb specific molecules selectively. In this experiment, we used 60/80 mesh 13X zeolite based on earlier experiments (Hardie et al. 2005; Ruff 2008; Wacker et al. 2010). At room temperature (25 °C) and atmosphere (100 kPa), 13X zeolite can absorb reaction gas. Figure 1 shows a temperature-programmed desorption (TPD) profile of zeolite 13X, which is scanned from room temperature to about 500 °C at atmosphere. Figure 1a shows the selective gas absorption. At low temperature, it shows good performance for CO_2 absorption and other gases (O_2 and CO) are not absorbed within every temperature range. Figure 1b shows a good desorption characteristic at high temperature.

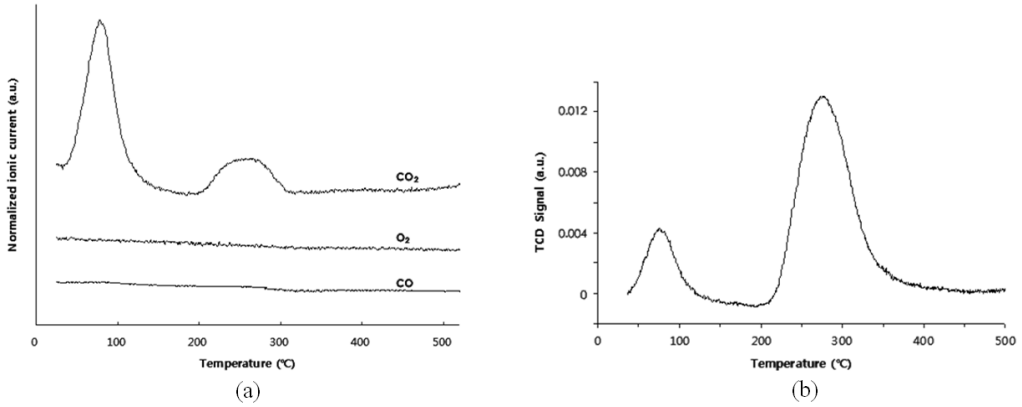


Figure 1 TPD profile of zeolite 13X: (a) absorption characteristics of CO_2, O_2, and CO; (b) desorption characteristic of CO_2.

Zeolite Trap Module and Other Setup

Figure 2a shows the zeolite trap module designed for this experiment. To use the existing CO_2 trapping line for liquid nitrogen, a zeolite trap was made in a similar shape to the CO_2 container used in cryogenic trapping. For this reason, the module is a little bulky, but the zeolite part is small. For the experiment, the combustion and reduction line of the SNU AMS lab was used. We used an elemental analyzer (NC2500, CE Instruments, Figure 2c) to combust samples to CO_2. About 3~5 mg of sample is combusted. The CO_2 is trapped by liquid nitrogen or is trapped in zeolite. Figure 2d shows the reduction line of the SNU AMS lab. CO_2 trapped in zeolite is desorbed to a reduction reactor by heating zeolite to 500 °C. CO_2 transferred to the reactor is reacted with hydrogen and iron powder as a catalyst at 630 °C and is reduced to graphite. The amount of graphite reduced is about 1.5~2.5 mg C. The final graphite sample is pressed into an Al target and then ^{14}C is measured in the SNU 3MV AMS system (Kim et al. 2000; Lee et al. 2000).

RESULTS AND DISCUSSION

As test samples, the oxalic acid II standard (NIST SRM 4990C), high-purity graphite powder (old carbon sample), and archaeological charcoals were used. The test samples were treated using the 2 different trapping methods (zeolite and cryogenic). We compared the pMC values and the ^{14}C ages obtained from the samples.

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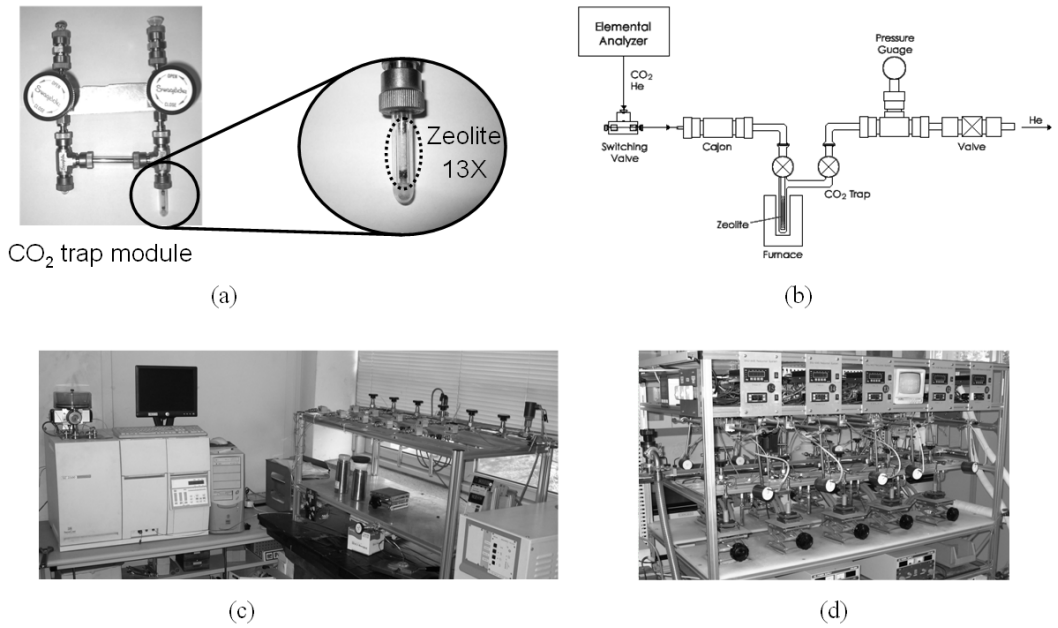


Figure 2 Experimental setup for CO_2 trapping: (a) zeolite trap module; (b) schematic diagram of CO_2 trapping line; and (c) elemental analyzer combustion and (d) reduction line in the SNU AMS lab.

Figure 3 shows the pMC measurements of 7 samples of oxalic acid II, which were prepared with the zeolite trap. The authentic value of oxalic acid II is 134.07 pMC. The average pMC value of the 7 samples (solid line) is 133.9 pMC and standard deviation (dotted line) is 1.395. From the result, the measured values are distributed near the known value.

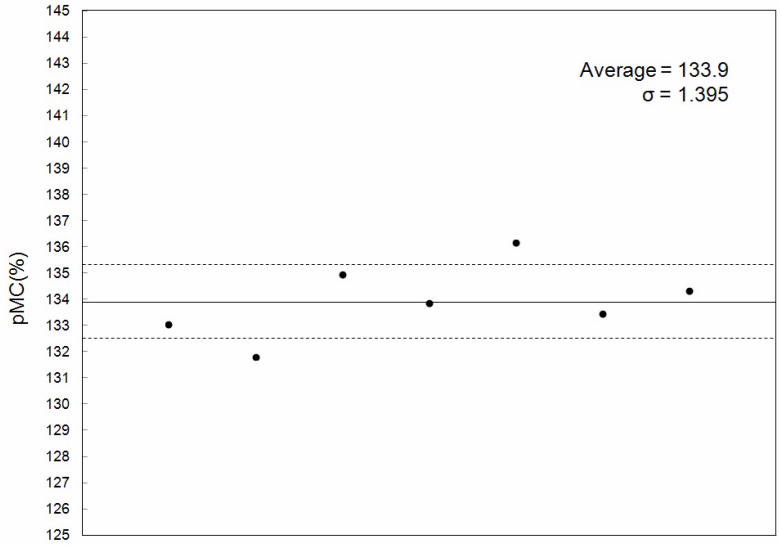


Figure 3 The pMC value of oxalic acid II (NIST SRM 4990C), 7 samples

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Minimization of CO_2 Residue in the Zeolite

We focused on the possibility of a memory effect of the molecular sieve, due to contamination of zeolite by CO_2 from a previous sample, which can cause errors in age determination. In particular, old carbon samples can have their $^{14}C/^{12}C$ ratios seriously affected by the residue of CO_2 from previously trapped samples. To check this memory effect, we trapped CO_2 of samples in the following order: old carbon–oxalic acid II (modern carbon)–old carbon. As an old carbon sample, graphite power (Alfa Aesar, 99.9999%, –200 mesh) was used.

Table 1 Change in the $^{14}C/^{12}C$ ratio of old carbon samples for CO_2 residue in the zeolite after trapping modern carbon CO_2.

	$^{14}C/^{12}C$ ratio			
	Run 1	Run 2	Run 3	Average
Old carbon before modern carbon	1.98×10^{-14}	1.92×10^{-14}	1.94×10^{-14}	1.95×10^{-14}
Old carbon after modern carbon	4.27×10^{-14}	4.15×10^{-14}	4.31×10^{-14}	4.24×10^{-14}

The results in Table 1 show that the $^{14}C/^{12}C$ ratio increased by about 120% when trapping old carbon after modern carbon, so the following sample result is seriously affected by the previously trapped CO_2. To remove the CO_2 residue, we passed a helium gas flow through the heated zeolite. The He gas flow was 120 mL/min for 30 min. Then, the zeolite container was vacuumed at 10^{-4} Torr for 30 min, heating the zeolite to 500 °C. We trapped old and modern carbon alternately 4 times, and between each trapping, heated zeolite and He gas flowed through the zeolite (Table 2).

Table 2 $^{14}C/^{12}C$ ratio of old carbon samples after flowing He gas at high temperature.

	$^{14}C/^{12}C$ ratio
Old carbon #1	9.99×10^{-15}
Old carbon #2	9.59×10^{-15}
Old carbon #3	7.57×10^{-15}
Old carbon #4	1.20×10^{-14}

This result shows that the memory effect from CO_2 residue previously trapped was decreased. However, it takes a long time to extract residual CO_2 from zeolite, so we have to find a more efficient method for a faster reaction time.

Archaeological Charcoals

We measured the ages of several archaeological charcoals by conventional cryogenic trapping and zeolite trapping, respectively. In each experiment, we cleaned zeolite by flowing helium gas before collecting CO_2 from the new sample. The results are consistent regardless of trapping method, as shown in Table 3. Apart from these consistent ages in Table 3, there were some inconsistent results in this experiment, but we think these were not caused by the difference in trapping method. They may be from contamination during pretreatment. We need to further investigate this inconsistency.

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Table 3 Comparison of ^{14}C age of archaeological charcoals.

	LN_2 trap		Zeolite trap		
Lab nr	Age BP	$\delta^{13}C$ ‰	Age BP	$\delta^{13}C$ ‰	Site
SNU10-764	4040 ± 40	–23.96	4090 ± 50	–22.19	Jijwa, Kimcheon
SNU10-769	2440 ± 40	–20.28	2490 ± 50	–18.00	Jijwa, Kimcheon
SNU10-774	2720 ± 40	–20.43	2710 ± 40	–25.53	Jijwa, Kimcheon
SNU10-775	2460 ± 40	–19.77	2480 ± 40	–23.50	Jijwa, Kimcheon
SNU10-776	2680 ± 40	–21.54	2630 ± 40	–25.66	Jijwa, Kimcheon
SNU11-192	2720 ± 50	–23.56	2750 ± 50	–28.66	Cheongun, Gyeongju
SNU11-194	2770 ± 60	–23.85	2720 ± 60	–26.59	Yangchon, Kimpo
SNU11-253	1730 ± 50	–27.53	1710 ± 40	–22.10	Sin-ri, Gokseong
SNU11-337	1720 ± 40	–26.51	1730 ± 50	–30.07	Jangsan, Jangseong
SNU11-410	2730 ± 40	–18.10	2800 ± 40	–21.31	Nokdong, Ulsan
SNU11-490	3000 ± 40	–17.92	2930 ± 40	–19.67	Sinseo, Daegu

CONCLUSIONS

Using molecular sieve zeolite 13X as a CO_2 trapping method for ^{14}C dating, we can get consistent results compared to conventional cryogenic CO_2 trapping. To remove the CO_2 remaining in the zeolite from a previous trapping, we heated the trap in a helium gas flow. Through this treatment, we can get results that are not affected by previous CO_2 trapping. For some charcoal samples, however, there are discrepancies in the yr BP measurements between the 2 trapping methods—conventional and zeolite. We think these results are not from the difference in trapping method, but rather from contamination during another stage of sample treatment. However, we need to further investigate this discrepancy. This study is the start of the development of a new sample preparation system at Seoul National University.

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