# 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.

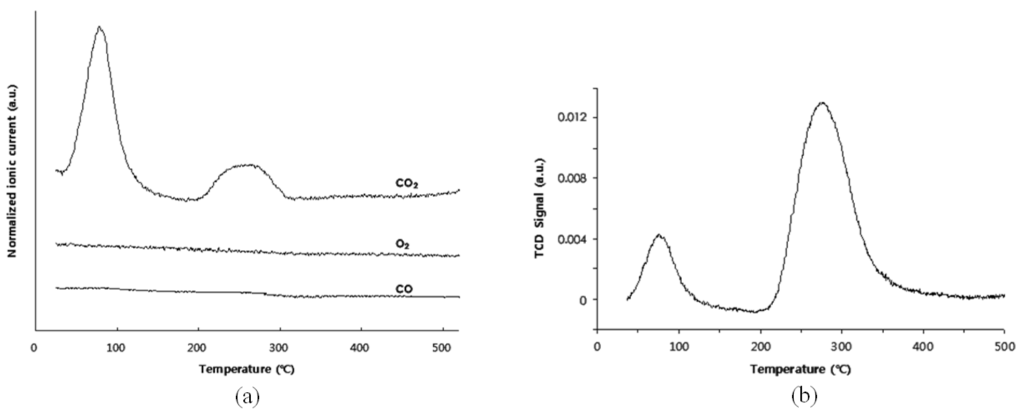


Figure 1 TPD profile of zeolite 13X: (a) absorption characteristics of $CO_2$, $O_2$, and CO; (b) desorption characteristic of $CO_2$.

### 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.

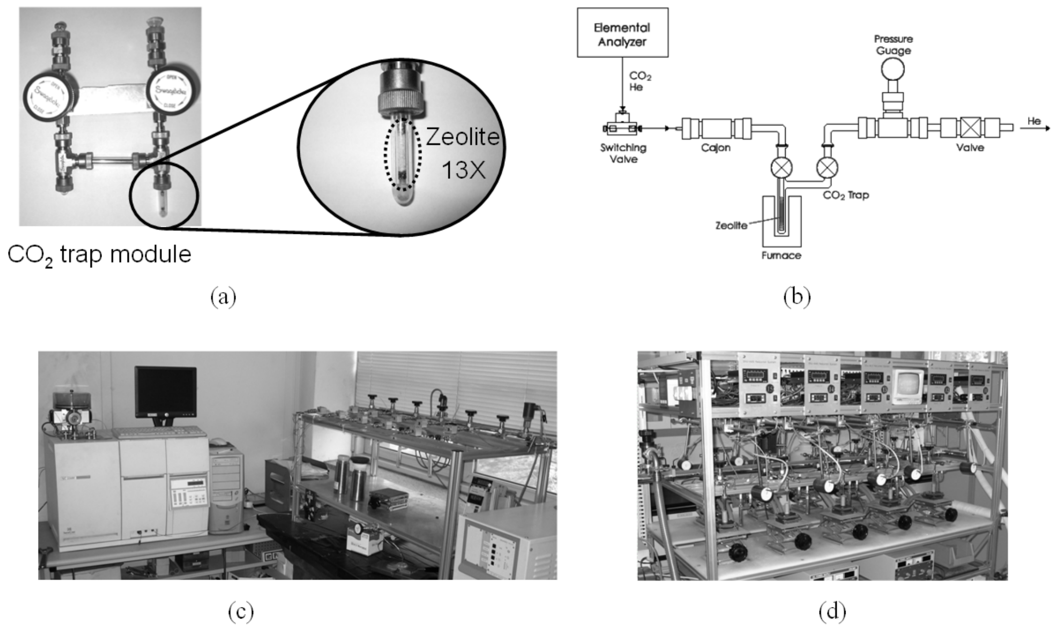


Figure 2 Experimental setup for $CO_2$ trapping: (a) zeolite trap module; (b) schematic diagram of $CO_2$ trapping line; and (c) elemental analyzer combustion and (d) reduction line in the SNU AMS lab.

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.

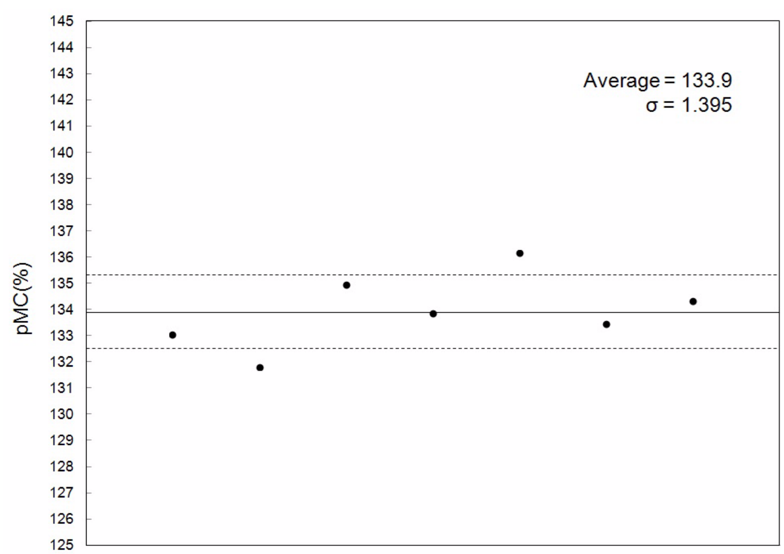


Figure 3 The pMC value of oxalic acid II (NIST SRM 4990C), 7 samples

### 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 | $1.98 \times 10^{-14}$ | $1.92 \times 10^{-14}$ | $1.94 \times 10^{-14}$ | $1.95 \times 10^{-14}$ |
| Old carbon after modern carbon | $4.27 \times 10^{-14}$ | $4.15 \times 10^{-14}$ | $4.31 \times 10^{-14}$ | $4.24 \times 10^{-14}$ |

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 | $9.99 \times 10^{-15}$ |
| Old carbon #2 | $9.59 \times 10^{-15}$ |
| Old carbon #3 | $7.57 \times 10^{-15}$ |
| Old carbon #4 | $1.20 \times 10^{-14}$ |

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.

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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