MOLECULAR SIEVES IN $^{14}CO_2$ SAMPLING AND HANDLING

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ABSTRACT. Molecular sieves are a promising way to sample and manipulate gaseous samples for radiocarbon analyses. Molecular sieve material can adsorb CO_2 selectively, enabling sampling of CO_2 from large air volumes in a small amount of adsorbent. The sieve material can be regenerated via heating and reused without removing the sieve material from its container. This results in ease of use and reduced risks of atmospheric contamination. Because sieve container volume is small and can be filled with synthetic air or nitrogen, it does not introduce underpressure to the system under study. Hence, sieves are suitable for many different experimental setups, from collection of CO_2 from small soil chambers to atmospheric CO_2 collection. The most common sieve material in use for sampling CO_2 is the 13X zeolite. For environmental measurements starting this year, we have studied the properties of 13X zeolites in more detail. For reliable $^{14}CO_2$ sampling, there are several caveats that should and can be avoided. In this contribution, we discuss these caveats and solutions to optimize the molecular sieve sampling process.

INTRODUCTION

Molecular sieve material contains tiny nanometer-scale pores that adsorb molecules. With suitable selection of pore size and polarity, molecular sieve material can adsorb CO_2 highly selectively, enabling sampling of CO_2 from large air volumes in a small amount of adsorbent. The sieves are not caustic and they can be regenerated via heating and reused without removing the sieve material from its container. This results in ease of sampling and reduced risks of atmospheric contamination. Due to the selectivity of the sieve and the small volume of the container, changes in the pressure of the target system remain negligible. The flow rate of gas through the sieve can be easily adjusted by a flow controller or by adjusting the pumping. This makes molecular sieve-based sampling suitable for a wide variety of field settings. Indeed, our portable field sampling equipment has already been used with environmental-research chambers with volumes ranging from 10 L to 1 dL; for sampling from soil, wetland, and laboratory chambers; and for taking direct atmospheric $^{14}CO_2$ samples.

The most common sieve material used with CO_2 is the 13X zeolite due to its high selectivity for CO_2 (Bayer et al. 1992; Hardie et al. 2005). Particularly, we have used 13X zeolite in our previous work (Hämäläinen et al. 2010; Palonen et al. 2013). Within the process development, we have occasionally observed memory effects up to some percents and up to 10‰ fractionation effects when using 13X sieves.

Especially for atmospheric samples, the differences in the ^{14}C and ^{13}C concentrations of the samples are often low. For this reason, high precision, and hence negligible memory effects and low fractionation, is required from the sampling setup. Low fractionation is also highly preferable because there is often a demand for using the ^{13}C result from the samples for research purposes and not just for correcting the ^{14}C signal. While memory effects result mostly from inadequate sieve desorption, fractionation can occur both during sampling of the CO_2 and during the CO_2 desorption phase. In the current work, we report more detailed measurements on the properties of 13X zeolites for $^{14}CO_2$ sampling. With an improved sieve-collection procedure, we are able to minimize the memory and fractionation effects to negligible levels.

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Proceedings of the 21st International Radiocarbon Conference edited by A J T Jull & C Hatté
RADIOCARBON, Vol 55, Nr 2–3, 2013, p 416–420

https://doi.org/10.1017/S0033822200057544 Published online by Cambridge University Press

DESORPTION MEASUREMENTS

There are different types of adsorption sites in zeolites (Ruthven 1984; Yang 1997, 2003). If CO_2 molecules in all the sites are not desorbed, memory effects will ensue and fractionation may occur. Figure 1 shows gas flow from a sieve under vacuum and increasing temperature. Even after baking the sieve for 1.7 hr at 590 °C, a detectable gas flow results when the temperature is increased to 690 °C. However, as the water adsorption efficiency exceeds that of CO_2 and the binding energy of the water molecules to the sieve material is higher than that for CO_2 molecules, one would expect more of the molecules desorbing at higher temperatures to be water. It is noted that some of the observed gas molecules at 690 °C may also originate from the sieve material itself. The pressure in the system at the maximum of the peak at t = 0.3 hr was 6 mbar. Residual gas analyzer (RGA, VTI Odyssey) measurements in Figure 2 show relevant masses (water and CO_2) desorbing from the sieve as a function of the temperature.

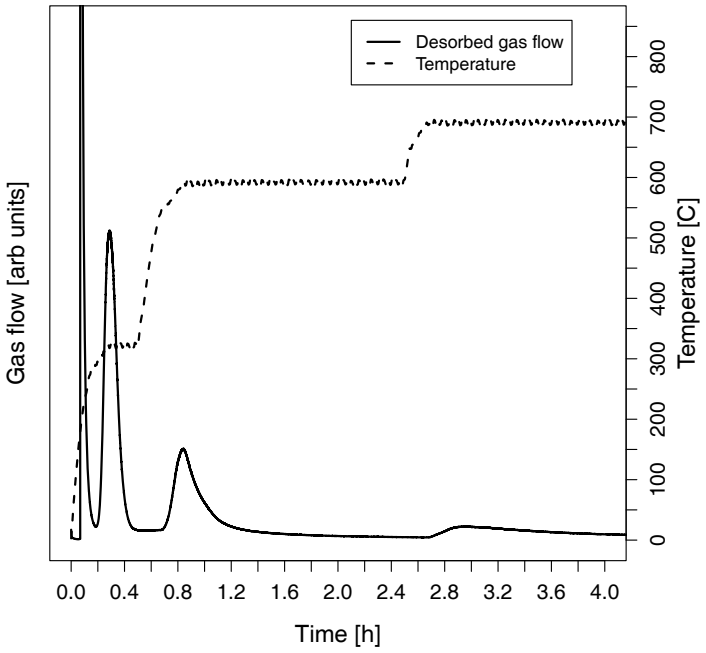


Figure 1 Gas flow from a sieve container under vacuum as a function of increasing oven temperature. Sieve container held 1.7 g of 2-mm-diameter grain 13X sieve (Merck 1.05703.1000). Similar results were obtained for 45–60 mesh (0.25–0.35 mm diameter).

It is noted that the sieve grains had to be pumped to $<10^{-7}$ mbar along with the RGA system, with the sieve releasing an unknown amount of molecules prior to the analysis. It is seen that after 2.5 hr of desorption at 500 °C, there is still some CO_2 left. After 1 hr at 600 °C, the amount of CO_2 has dropped off below the detection level, whereas water molecules are observed well over the detection level. Later, when increasing the oven temperature to 700 °C, the CO_2 signal remained below the detection level.

https://doi.org/10.1017/S0033822200057544 Published online by Cambridge University Press

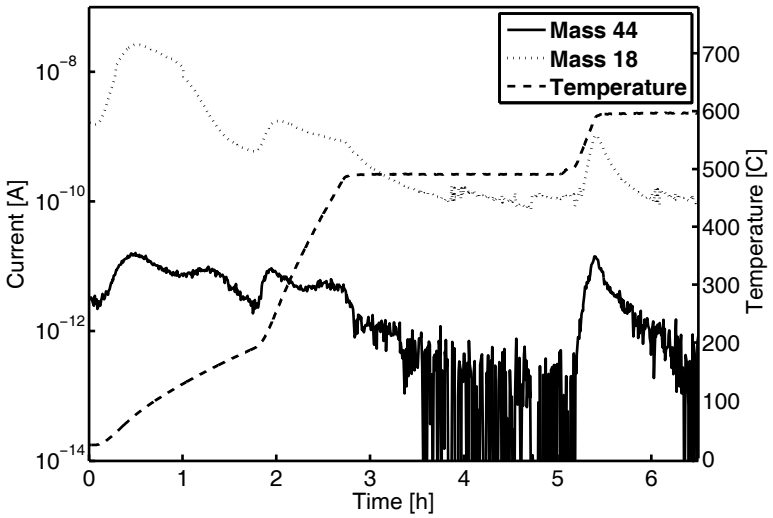


Figure 2 Residual gas analyzer spectra results from 4 grains of 45–60 mesh 13X sieve (Supelco 2-0304) under vacuum as a function of temperature.

ADSORPTION MEASUREMENTS

Because the sieve may preferably adsorb molecules with heavier isotopes, it is important that all CO_2 molecules in the target gas are captured by the sieve. Furthermore, sorption is a 2-way process. The sieve material is also releasing some of the sampled CO_2 already at room temperature and the more abundant and stronger-binding H_2O tends to replace CO_2 in the sieve. Both of these factors can result in fractionation of CO_2 if the capture is not complete. Figure 3 shows results from an adsorption measurement for a 13X sieve. The plot was obtained by measuring the CO_2 concentration with a LI-840A CO_2 /H_2O analyzer in the gas stream immediately exiting the sieve (Supelco 2-0304, in a 9-mm-inner-diameter quartz tube). Flow rate was 0.5 L/min. It is seen that for 1 g of 13X sieve material, the fractionation-safe sampling volume is roughly 10 L of 1-ppt-H_2O air.

IMPROVED PROCEDURE AND RESULTS

Based on the above desorption and adsorption results, we have updated our sieve sampling procedure (Hämäläinen et al. 2010; Palonen et al. 2013) to the following:

- Prior to sampling, the sieve material is purified by baking the central part of the sieve container under vacuum for 30 min at 240 °C, 1 hr at 540 °C, and 1 hr at 640 °C. The sieve is baked first at 240 °C to minimize the hydrothermal damage to the material from H_2O molecules in the higher temperatures.
- The CO_2 sample is then collected in the field by circulating target gas through the sieve container. Usually, we collect CO_2 with 1 g of 13X, 1 L/min flow rate, and a Nafion dryer to 1 ppt H_2O. Hence, to ensure no fractionation during sampling, the maximum sampling time is 10 min.
- The adsorbed CO_2 sample is released in the laboratory by first pumping the sieve to below 1 mbar pressure at room temperature through an attached liquid nitrogen (LN) trap. The sieve container is then placed in an oven for 2.5 hr, the sieve material now in a closed volume with the LN trap. For the first 30 min, the oven is held at 240 °C, and for the remaining 2 hr at 530 °C.

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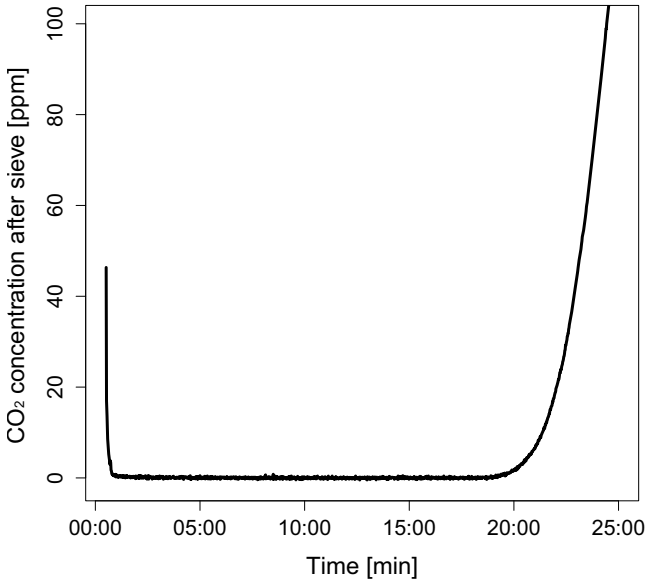


Figure 3 CO_2 concentration of air (400 ppm CO_2, 1 ppt H_2O) after a sieve container with 1 g of 13X sieve as a function of time. Flow rate was 0.5 L/min. Complete capture of CO_2 occurs during the first 20 min.

To check the reliability of the above procedure, OxII, humic acid (VIRI T), and background samples were combusted, collected to a sieve, released from the sieve, and graphitized for high-precision measurements at the VERA AMS laboratory. A different sieve container was used for each sample. Based on capacitive pressure readouts on the amount of CO_2, the efficiency of the current process is 98–100%. The ^{14}C concentration and $\delta^{13}C$ values are given in Table 1.

Table 1 ^{14}C and $\delta^{13}C$ results for OxII, background, and humic acid reference samples after sieve collection, desorption from the sieve, and graphitization. The uncertainties have 68.3% probability coverage. Reference values are given with respect to the original CO_2 gas. The $\delta^{13}C$ uncertainties represent our observed overall between-sample scatter from gas handling, ampoule storage, and MS measurements.

Sample	Description	Mass (mg)	^{14}C (pMC)	^{14}C ref (pMC)	$\delta^{13}C$ (‰)	$\delta^{13}C$ ref (‰)
HU154	OxII	1.03	134.27 ± 0.19	134.07	–18.0 ± 0.2	–17.8
HU155	OxII	1.13	134.42 ± 0.19	134.07	–17.6 ± 0.2	–17.8
HU139	OxII	1.50	133.84 ± 0.19	134.07	–17.9 ± 0.2	–17.8
HU154	OxII	0.38	133.12 ± 0.23	134.07	–17.9 ± 0.2	–17.8
HU153	Humic acid	0.93	65.61 ± 0.12	65.82	–28.4 ± 0.2	–28.9
HU164	Diesel	1.34	0.27 ± 0.01	0.25	–30.0 ± 0.2	–30.0

From the ^{14}C results it is evident that the sieve-sampling process is reliable to 0.2% precision for normal 1-mg samples. The $\delta^{13}C$ values are also reproducible within uncertainties, indicating minimal fractionation due to sieve collection. The somewhat higher deviation of the small OxII sample (HU154) may be due to statistical fluctuation, due to the sieve process, or due to the AMS measurement. Usually the AMS measurements would not be suspect, but for this sample the scatter in

https://doi.org/10.1017/S0033822200057544 Published online by Cambridge University Press

the AMS measurements was high and the AMS-measured $\delta^{13}C$ value was –21.8‰, in contrast to the –17.9‰ measured from the sample gas after the sieve collection.

CONCLUSIONS

When collecting CO_2 with a molecular sieve, it should be remembered that sorption is still a 2-way process: During CO_2 capture, the sieve material releases some of the sampled CO_2 already at room temperature with possible preference to the lighter isotope. Also, the stronger-binding H_2O molecule can replace the CO_2 molecule. It follows that fractionation of the $^{14}CO_2$ can occur if the $^{14}CO_2$ capture is not complete. This can occur, for example, when H_2O removal of the target gas is inadequate or the sampling time is too long.

The sieve material can have a memory effect of a few percents if the regeneration/desorption time is less than 2 hr. Fractionation can also occur if the desorption of the sample from the sieve is not done properly, i.e. if some of the sample is pumped away in lower desorption temperatures or the time reserved for desorption is too short. Interestingly, it may be possible to reduce the desorption time significantly with the use a of purge gas flowing through the sieve (Garnett and Murray 2013).

Based on the presented measurements on 13X sieve properties, we have been able to minimize the previously seen fractionation and memory effects (Palonen et al. 2013) to negligible levels. This forms a solid foundation for our work in collecting gaseous samples within the broad operational framework of atmospheric and environmental studies.

ACKNOWLEDGMENTS

This research was supported by the Academy of Finland, project number 139036. We wish to thank laboratory analyst Joni Niemi for his careful work preparing several of the samples in this study.

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