PROCESSING OF CO_2 SAMPLES COLLECTED USING ZEOLITE MOLECULAR SIEVE FOR ^{14}C ANALYSIS AT THE NERC RADIOCARBON FACILITY (EAST KILBRIDE, UK)

M H Garnett[1] • C Murray

NERC Radiocarbon Facility, Rankine Avenue, East Kilbride G75 0QF, United Kingdom.

ABSTRACT. Cartridges containing a zeolite molecular sieve are used for the field collection of CO_2 from a variety of environments (e.g. atmosphere, soil respiration, evasion from surface waters) for accelerator mass spectrometry (AMS) radiocarbon analysis by the NERC Radiocarbon Facility. Previously, sample CO_2 was recovered from the sieves by heating under vacuum prior to cryogenic purification and graphitization. An additional heating and evacuation stage was used to prepare the cartridge for the next sample. We have recently developed an alternative method using heating and purging with nitrogen gas to remove sample CO_2 from the molecular sieve. An infrared gas analyzer (IRGA) is used to continuously monitor CO_2 content in the purge gas. The preparation of the molecular sieve cartridge for the next use is performed simultaneously and the IRGA reading is used to verify that all sample CO_2 has been removed from the sieve, ensuring insignificant carryover of CO_2 into the next sample. We present the results of a suite of standards of distinctly different ^{14}C and stable-carbon isotope composition, which we used to confirm the reliability of the new procedure. The new method has considerably reduced the time required to process a single sample from at least 2 hr to less than 40 min, and reduced the minimum sample size by 50%.

INTRODUCTION

A zeolite molecular sieve is a crystalline alumino-silicate with selectivity and adsorption properties that make it particularly useful to trap or purify carbon dioxide (Bol and Harkness 1995). It has been utilized in radiocarbon science from at least the 1960s for sampling atmospheric CO_2 (e.g. Godwin and Willis 1964). It is particularly valuable as an alternative to cryogenic methods for purifying CO_2 on vacuum systems (e.g. Bauer et al. 1992), facilitating its use in the recent automation of laboratory procedures in the preparation of ^{14}C samples (e.g. Wacker et al. 2010).

At the NERC Radiocarbon Facility (East Kilbride, UK), we use cartridges containing zeolite molecular sieves for the field collection of CO_2 from a variety of environments for ^{14}C analysis by accelerator mass spectrometry (AMS). For example, the molecular sieve cartridges (MSCs) have been used with a pump-based sampling system (Hardie et al. 2005) to collect CO_2 respired in various environments (e.g. arctic tundra, Hartley et al. 2012; temperate peatlands, Hardie et al. 2009; or evaded from surface waters, Billett et al. 2006, or subsurface pipes, Billett et al. 2012). They have also been deployed as passive samplers, for example, to recover CO_2 for ^{14}C analysis from the atmosphere (Garnett and Hartley 2010), the permanently waterlogged layers of peats (using hydrophobic filters; Garnett and Hardie 2009), or surface emissions of soils (Garnett et al. 2009).

Hardie et al. (2005) describe the methods we previously used for processing molecular sieve samples, involving heating under vacuum to recover sample CO_2 from the sieve prior to cryogenic purification and graphitization (based on earlier methods described by Bol and Harkness 1995). An additional heating and evacuation stage was used to prepare the cartridge for the next sample. We have recently developed a more efficient method to process CO_2 samples collected using a molecular sieve and to prepare the cartridges for next use. Here, we describe the new method to process samples collected using MSCs and demonstrate the reliability of the method with the results of a suite of standards.

[1]Corresponding author. Email: M.Garnett@nercrcl.gla.ac.uk.

© 2013 by the Arizona Board of Regents on behalf of the University of Arizona
Proceedings of the 21st International Radiocarbon Conference edited by A J T Jull & C Hatté
RADIOCARBON, Vol 55, Nr 2–3, 2013, p 410–415

https://doi.org/10.1017/S0033822200057532 Published online by Cambridge University Press

METHODS

Processing of Molecular Sieve Cartridges

Figure 1 illustrates the vacuum rig used to process MSCs. High-purity N_2 gas (150 mL/min) is introduced to the MSC via a coupling (Colder Products Company, USA). The MSC (containing Type 13X zeolite molecular sieve [BDH, UK] and identical to the design used by Hardie et al. 2005) is placed within a tube furnace (Carbolite, UK) that is initially at room temperature, then heated to 500 °C to release the trapped CO_2. Purge gas exiting the MSC enters the vacuum rig where it is first dried using a slush trap (mixture of dry ice and methylated spirits; –78 °C) and then directed to an infrared gas analyzer (IRGA; PPSystems EGM-4, Hitchin, UK) where the CO_2 concentration is measured. Next, the purge gas passes through 2 liquid nitrogen-cooled traps (–196 °C), retaining the CO_2 and directing non-condensable gases to atmosphere (via a flow gauge). Once the majority of CO_2 has been desorbed from the MSC (when the IRGA readout is <10 ppm), collection of CO_2 in the liquid nitrogen traps is stopped by isolating the traps from the MSC. A vacuum pump is then used to remove non-condensibles from the liquid nitrogen traps, and sample CO_2 is dried for a second time by replacing the second liquid nitrogen trap with a slush trap, and the gas transferred to a calibrated volume to quantify the volume of CO_2 recovered. At the same time as the recovered sample CO_2 is being processed, purge gas continues to flow through the MSC via the IRGA to atmosphere, in order to ensure complete removal of CO_2 from the cartridge (indicated when CO_2 concentration of the purge gas reaches 0 ppm).

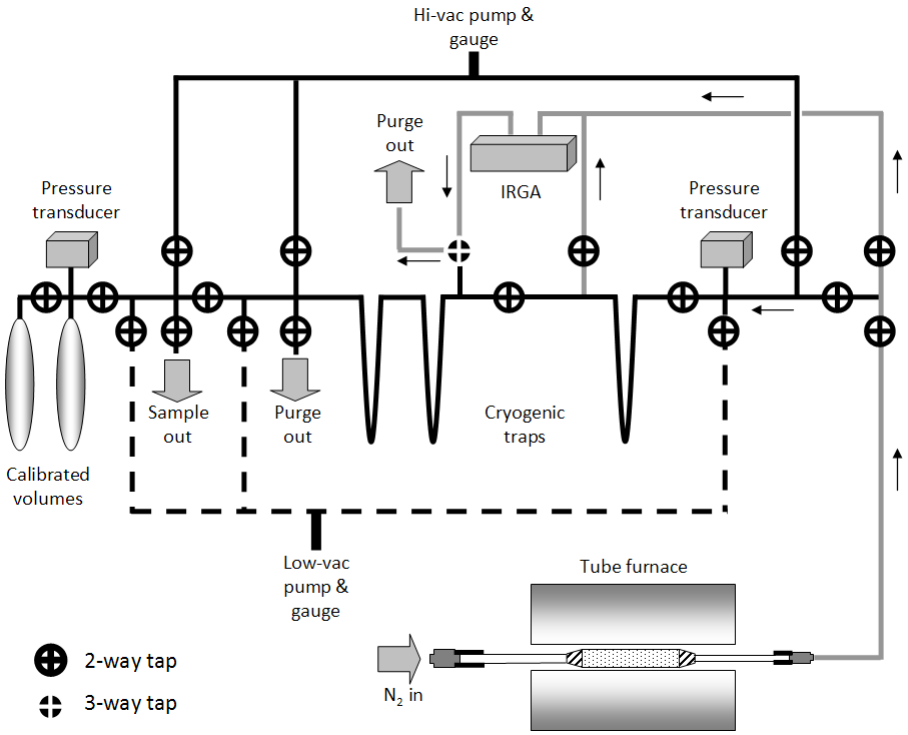


Figure 1 Design of the vacuum rig used to process molecular sieve samples by purging with nitrogen gas. A molecular sieve cartridge is shown within the tube furnace. An infrared gas analyzer (IRGA) is used to monitor CO_2 concentration in the purge gas. Small arrows indicate the direction of the purge gas. See Methods for further details.

https://doi.org/10.1017/S0033822200057532 Published online by Cambridge University Press

Test of Laboratory Methods

Tests were performed to verify the new procedure, and especially check for sample carryover (memory effects) since the cartridges had previously been shown not to be affected by fractionation effects (Hardie et al. 2005). A suite of standards (Table 1) of distinctly different ^{14}C and stable-carbon isotope composition were sampled consecutively on 2 MSCs, and processed with the new procedures.

Table 1 Results for standards used to test the new procedures. Two molecular sieve cartridges (MSC; labeled 1 and 2) were used to consecutively sample CO_2 derived from known-age or background standards, after initially being used to sample atmospheric CO_2 (assumed to be ~104 pMC). Consensus values for standards reported by Gulliksen and Scott (1995)[a] and Boaretto et al. (2002)[b].

MSC–Run order	Source of CO_2	Volume CO_2 recovered (mL)	Recovery (%)	$^{13}C_{VPDB}$ standard CO_2 ±0.1‰	$^{13}C_{VPDB}$ recovered CO_2 ±0.1‰	^{14}C standard CO_2 (pMC ±1σ)	Lab code (SUERC-)	^{14}C recovered CO_2 (pMC ±1σ)
1–1	Atmosphere	5.8	—	—	–9.9	—	—	—
1–2	Iceland spar calcite	8.9	>98	+1.6	+1.4	Background	32517	0.34 ± 0.01
1–3	TIRI Barley mash	2.6	>99	–26.8	–26.6	116.35 ± 0.0084[a]	32521	116.79 ± 0.54
1–4	FIRI Belfast cellulose	2.9	>95	–23.6	–23.9	57.22 ± 0.04[b]	32523	57.08 ± 0.25
2–1	Atmosphere	6.1	—	—	–10.1	—	—	—
2–2	TIRI Barley mash	9.0	>98	–26.8	–27.0	116.35 ± 0.0084[a]	32518	116.85 ± 0.54
2–3	Iceland spar calcite	3.1	100	+2.7	+2.2	Background	32522	0.40 ± 0.01
2–4	FIRI Belfast cellulose	2.6	>97	–23.6	–23.8	57.22 ± 0.04[b]	32516	57.62 ± 0.26

Standard gases had been initially prepared to CO_2 using routine laboratory procedures (combustion/hydrolysis) and stored in sealed glass tubes. To collect each of the standard gases on a MSC, the glass tube containing the standard CO_2 was placed in a 1-L air-tight chamber ("Kilner" jar; John Lewis, UK). This chamber was connected to the molecular sieve sampling system described by Hardie et al. (2005) using couplings (Colder Products Company, USA). Atmospheric CO_2 was first removed from the chamber by scrubbing with soda-lime, and then the standard CO_2 released by breaking the glass tube against the side of the chamber. An air pump (Pulse Pump III, MiDan Co., Chino, California, USA; flow rate ~500 cc/min) was used to circulate chamber air in a closed-loop via a MSC, enabling trapping of the standard CO_2. The CO_2 trapped on the molecular sieve was then recovered using the new procedures, the MSC recharged and reused for collecting the next standard.

Aliquots of the recovered CO_2 were analyzed for $\delta^{13}C$ and ^{14}C concentration. $\delta^{13}C$ was determined on a dual-inlet isotope ratio mass spectrometer (VG Optima, UK) at the NERC Radiocarbon Facility and expressed in per mil relative to the Vienna-PDB reference standard. An aliquot of the recovered CO_2 was converted to graphite using Fe-Zn reduction (Slota et al. 1987) and passed to the Scottish Universities Environmental Research Centre (SUERC) AMS Laboratory for ^{14}C measurement. ^{14}C results were normalized to a $\delta^{13}C$ of –25‰ and expressed as pMC following convention (Stuiver and Polach 1977).

https://doi.org/10.1017/S0033822200057532 Published online by Cambridge University Press

RESULTS

Measurements of the CO_2 concentration in the purge gas taken by the IRGA show that CO_2 was rapidly released from the molecular sieve when heated (Figure 2). In fact, it was observed that in some cases within the few minutes that it took for the furnace to reach the target temperature of 500 °C, the CO_2 concentration in the purge gas had already started to decline, indicating that the majority of the CO_2 had been released at a slightly lower temperature. CO_2 concentration fell to 0 ppm (and therefore the MSC recharged for next use) in all samples within less than ~40 min from the commencement of heating the sieve.

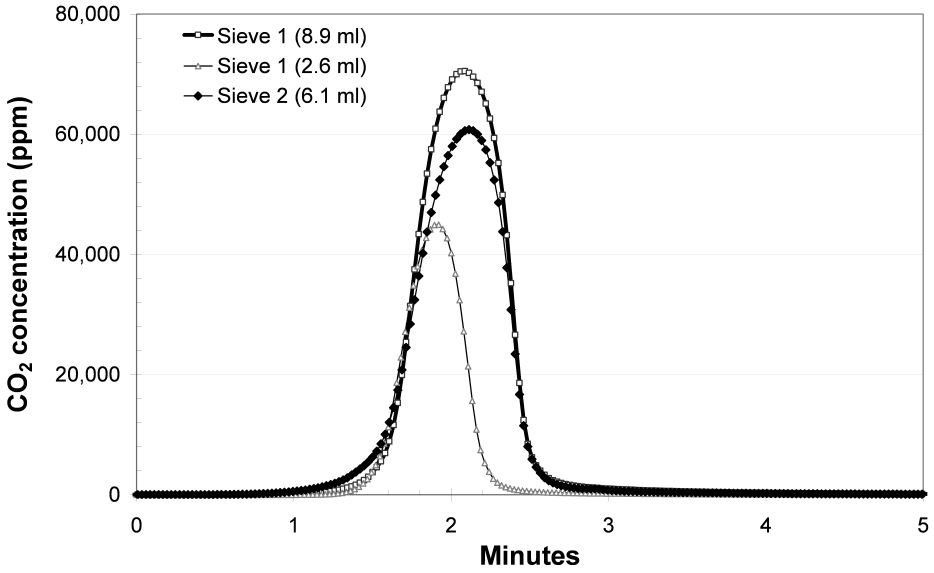


Figure 2 Carbon dioxide concentration of the purge gas when heated to release the sample (for standards 1–2, 1–3, and 2–1). Heating of the sieve (starting at room temperature) began at ~0 min. The figure shows that the vast majority (>99%) of sample CO_2 is desorbed from the sieve within 4 min.

The volume of CO_2 recovered from the MSCs processed with the new methods was 95–100% of that expected based on the volume of the standard gas used (Table 1). In all cases, the ^{14}C concentration of the recovered CO_2 was within measurement uncertainty (2σ) of the reference values for known-age standards (Table 1). Background (^{14}C-dead) standards had ^{14}C contents (0.34 ± 0.01 and 0.40 ± 0.01 pMC) only slightly higher than the laboratory background for combusted samples, and were considerably lower than background standards processed using the previous molecular sieve procedure (Hardie et al. 2005). All $\delta^{13}C$ values were within measurement uncertainty (2σ) with the exception of 1 result (sample 2–3, which was just >2σ).

DISCUSSION

Several studies have previously demonstrated the reliability of zeolite molecular sieve for trapping and purifying CO_2 in samples for ^{14}C analysis. Some of these studies applied heat and vacuum to recover the sample CO_2, although Wacker et al. (2010) showed that purging with helium efficiently removed adsorbed CO_2 (using N_2 as the purge gas could result in the condensation of N_2 in liquid nitrogen traps [Bauer et al. 1992], but this is not something that we have observed using our method). When incorporated within a vacuum rig system, Bauer et al. (1992) successfully demon-

https://doi.org/10.1017/S0033822200057532 Published online by Cambridge University Press

strated the use of a purge gas approach for processing ^{14}C samples with molecular sieve, as an alternative to cryogenic trapping with liquid nitrogen.

The vacuum and heating procedure previously used at the NERC Radiocarbon Facility for processing our field-collected samples had been shown to be reliable for samples of ~10 mL CO_2 through testing with a suite of ^{14}C and stable-carbon isotope standards. We used a similar testing approach, but with smaller volumes (2.6–9.0 mL) to test the new procedures. It should be noted that the cartridges and sampling system used to trap the CO_2 were almost identical to those used by Hardie et al. (2005); therefore, essentially it was only the new procedures that were being tested.

The results in Table 1 show that the new procedures are reliable for the processing of CO_2 samples collected using MSCs and do not result in significant memory effects, contamination, or isotopic fractionation. Despite consecutively processing samples of distinctly different ^{14}C concentration on the same MSC, the ^{14}C results remained within measurement uncertainty ($<2\sigma$) of consensus values. The ^{14}C concentration of background standards (0.34 ± 0.01 and 0.40 ± 0.01 pMC) was only slightly higher than the background associated with routine combustion methods at the laboratory. The results for background standards were also considerably lower than when using the previous method (1.23 ± 0.02 and 1.28 ± 0.02 pMC; Hardie et al. 2005) despite the much smaller size of most of the samples processed using the new procedures. The fact that sample recovery for each of the CO_2 standards was almost 100% further demonstrates the reliability of the new procedures, indicating that no significant quantities of CO_2 remained on the molecular sieve following charging.

The results for test standards demonstrate the reliability of the new procedures, and while we consider that there is still potential for further improvement and refinement (e.g. further reduction in background and/or sample size), the new procedures bring significant benefits. Firstly, the time to process a sample using the new procedures is less than ~40 min, compared with the ~2.5 hr typically required to process a single sample using the previous method. Part of the saving in time is a result of being able to complete the recharging of the MSC at the same time as the recovered sample is still being processed (e.g. aliquoted). However, the greatest saving in time is a result of the rapidity that CO_2 is desorbed from the molecular sieve when purged (Figure 2). Secondly, the new procedures enable the minimum sample size to be processed to be considerably reduced; results from our tests indicate that the new method is reliable for samples with as little as 2.6 mL of CO_2 (compared with the recommended 5–10 mL of CO_2 associated with the earlier method). Finally, incorporation of an IRGA into the purge gas stream allows for a much greater control when processing samples, for example, reliably informing when the molecular sieve has been completely desorbed of sample CO_2.

ACKNOWLEDGMENTS

We thank staff at the NERC Radiocarbon Facility (East Kilbride) and SUERC AMS Laboratory. The UK Natural Environment Research Council (NERC) is gratefully acknowledged for facility support.

REFERENCES

Bauer JE, Williams PM, Druffel ERM. 1992. Recovery of submilligram quantities of carbon dioxide from gas streams by molecular sieve for subsequent determination of isotopic (^{13}C and ^{14}C) natural abundances. *Analytical Chemistry* 64:824–7.

Billett MF, Garnett MH, Hardie SML. 2006. A direct method to measure $^{14}CO_2$ lost by evasion from surface waters. *Radiocarbon* 48(1):61–8.

Billett MF, Dinsmore KJ, Smart RP, Garnett MH, Holden J, Chapman P, Baird AJ, Grayson R, Stott AW. 2012. Variable source and age of different forms of carbon released from natural peatland pipes. *Journal of Geophysical Research* 117:G02003, doi:02010.01029/02011JG001807.

Boaretto E, Bryant C, Carmi I, Cook G, Gulliksen S, Harkness D, Heinemeier J, McClure J, McGee E,

https://doi.org/10.1017/S0033822200057532 Published online by Cambridge University Press

Naysmith P, Possnert G, Scott M, van der Plicht H, Van Strydonck M. 2002. Summary findings of the fourth international radiocarbon intercomparison (FIRI) (1998–2001). *Journal of Quaternary Science* 17(7): 633–7.

Bol RA, Harkness DD. 1995. The use of zeolite molecular sieves for trapping low concentrations of CO_2 from environmental atmospheres. *Radiocarbon* 37(2):643–47.

Garnett MH, Hardie SML. 2009. Isotope (^{14}C and ^{13}C) analysis of deep peat CO_2 using a passive sampling technique. *Soil Biology and Biochemistry* 41(12): 2477–83.

Garnett MH, Hartley IP. 2010. A passive sampling method for radiocarbon analysis of atmospheric CO_2 using molecular sieve. *Atmospheric Environment* 44(7):877–83.

Garnett MH, Hartley IP, Hopkins DW, Sommerkorn M, Wookey PA. 2009. A passive sampling method for radiocarbon analysis of soil respiration using molecular sieve. *Soil Biology and Biochemistry* 41(7):1450–6.

Godwin H, Willis EH. 1964. Cambridge University natural radiocarbon measurements VI. *Radiocarbon* 6: 116–37.

Gulliksen S, Scott M. 1995. Report of the TIRI workshop, Saturday 13 August 1994. *Radiocarbon* 37(2): 820–1.

Hardie SML, Garnett MH, Fallick AE, Rowland AP, Ostle NJ. 2005. Carbon dioxide capture using a zeolite molecular sieve sampling system for isotopic studies (^{13}C and ^{14}C) of respiration. *Radiocarbon* 47(3):441–51.

Hardie SML, Garnett MH, Fallick AE, Ostle NJ, Rowland AP. 2009. Bomb-^{14}C analysis of ecosystem respiration reveals that peatland vegetation facilitates release of old carbon. *Geoderma* 153(3–4):393–401.

Hartley IP, Garnett MH, Sommerkorn M, Hopkins DW, Fletcher BJ, Sloan VL, Phoenix GK, Wookey PA. 2012. A potential loss of carbon associated with greater plant growth in the European Arctic. *Nature Climate Change* 2:875–9.

Slota Jr PJ, Jull AJT, Linick TW, Toolin LJ. 1987. Preparation of small samples for ^{14}C accelerator targets by catalytic reduction of CO. *Radiocarbon* 29(2):303–6.

Stuiver M, Polach HA. 1977. Discussion: reporting of ^{14}C data. *Radiocarbon* 19(3):355–63.

Wacker L, Nemec M, Bourquin J. 2010. A revolutionary graphitisation system: fully automated, compact and simple. *Nuclear Instruments and Methods in Physics Research B* 268(7–8):931–4.

https://doi.org/10.1017/S0033822200057532 Published online by Cambridge University Press