

ADVANCES IN THE RADIOCARBON ANALYSIS OF CARBON DIOXIDE AT THE NERC RADIOCARBON FACILITY (EAST KILBRIDE) USING MOLECULAR SIEVE CARTRIDGES

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ABSTRACT. Radiocarbon (^{14}C) analysis of carbon dioxide (CO_2) provides unique information on the age, turnover and source of this important greenhouse gas, raising the prospect of novel scientific investigations into a range of natural and anthropogenic processes. To achieve these measurements, cartridges containing zeolite molecular sieves are a reliable and convenient method for collecting CO_2 samples. At the NERC Radiocarbon Facility (East Kilbride) we have been refining our molecular sieve methods for over twenty years to achieve high-quality, reproducible and precise measurements. At the same time, we have been developing novel field sampling methods to expand the possibilities in collecting gas from the atmosphere, soil respiration and aquatic environments. Here, we present our latest improvements to cartridge design and procedures. We provide the results of tests used to verify the methods using known ^{14}C content standards, demonstrating reliability for sample volumes of 3 mL CO_2 (STP; 1.6 mg C) collected in cartridges that had been prepared at least three months earlier. We also report the results of quality assurance standards processed over the last two years, with results for 22 out of 23 international ^{14}C standards being within measurement uncertainty of consensus values. We describe our latest automated procedures for the preparation of cartridges prior to use.

KEYWORDS: automation, carbon dioxide, molecular sieve, radiocarbon, Zeolite.

INTRODUCTION

Concentrations of the greenhouse gas carbon dioxide (CO_2) continue to increase in the Earth's atmosphere and most predictions are that this will lead to a rise in global temperature of at least 1.5°C before the end of the current century (IPCC 2013). Although it is accepted that anthropogenic activities are driving the increase in CO_2 levels (IPCC 2013), sources of CO_2 to the atmosphere are complex and include both direct (e.g. fossil fuel emissions) and indirect (e.g. land-use change) anthropogenic emissions, as well as natural emissions of the Earth's carbon cycle. Moreover, the response of the carbon cycle to climatic warming, and whether this will result in the loss of carbon stores that have been “locked away” for centuries/millennia, adds further complexity, but is important because it could lead to a positive feedback to further increase the rate of warming (Walker et al. 2016).

Radiocarbon (^{14}C) analysis of CO_2 provides unique information on the age (since photosynthetic fixation from the atmosphere) of emissions and rate of carbon turnover and can help to identify the contribution of different sources (Levin and Hesshaimer 2000). For example, Campeau et al. (2017) found that aquatic emissions of carbon dioxide from a boreal fen were predominantly modern (i.e. with a ^{14}C concentration >100 pMC) implying that they were substantially composed of carbon that had been fixed within the last ca. 60 years. In contrast, Newsham et al. (2018) reported that discrete taxa of fungi respired carbon from Antarctic soil that was over a thousand years old, providing direct evidence for the release of old organic carbon to the atmosphere.

Cartridges containing zeolite molecular sieve (Hardie et al. 2005; Garnett and Murray 2013) are convenient for collecting CO_2 samples for ^{14}C analysis and are particularly useful when the CO_2 occurs at less than several thousand ppm. The porous molecular sieve has a crystalline structure, which, when a gas flows through it, precludes large molecules from entering

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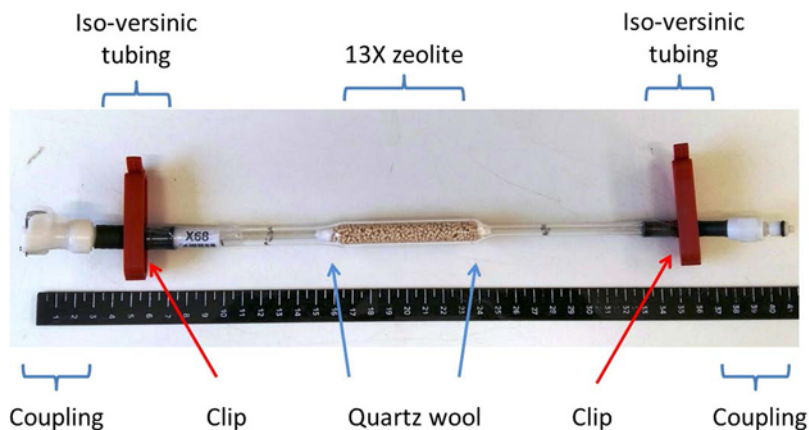


Figure 1 Molecular sieve cartridges used at the NERC Radiocarbon Facility (East Kilbride) for routine samples.

(Breck 1974). In addition, the adsorption properties of the zeolite are such that unlike other gases (e.g. nitrogen and oxygen) the polar molecule CO_2 is rapidly trapped and concentrated into a relatively small and therefore highly portable volume (Breck 1974). The sampled CO_2 can be released from the zeolite by heating and purified using routine cryogenic methods (Hardie et al. 2005; Garnett and Murray 2013).

Molecular sieves have been used for collecting carbon dioxide for ^{14}C analysis since at least the 1960s (Godwin and Willis 1964). At the NERC Radiocarbon Facility (East Kilbride, UK), we have used cartridges containing zeolite molecular sieves for sample collection for over 20 years, with development of the technique being documented at various stages (Bol and Harkness 1995; Hardie et al. 2005; Garnett and Murray 2013). The cartridges have been utilized in novel field sampling methods to enable the ^{14}C analysis of soil-respired CO_2 (Hardie et al. 2005), aquatic CO_2 (Garnett et al. 2012) and atmospheric CO_2 (Garnett and Hartley 2010). Development of our molecular sieve methods continues, most recently with a focus on further improving the reliability of the method and quality of results, and to increase capacity and throughput to meet demand from users. Here, we describe the latest refinements to our methods, present the results of tests used to verify our latest procedures, and report the results of all known ^{14}C content quality assurance standards processed alongside samples over the last two years.

METHODS

Design of the Molecular Sieve Cartridge

An earlier version of our molecular sieve cartridge was built from quartz glass (Hardie et al. 2005), but since cartridge temperature does not exceed 500°C we now use tubular borosilicate glass. The cartridge has a central compartment for containing the molecular sieve material (Figure 1) and is designed for processing using a tube furnace (MTF 10/15/130, Carbolite, UK). The dimensions of the three compartments are: centre (14 mm OD, 11 mm ID by 80 mm long), inlet (10 mm OD, 7 mm ID by 95 mm long), exhaust (6 mm OD, 4 mm ID by 95 mm long). At either end of the cartridge, 50 mm lengths of Iso-versinic® tubing (770260-05 and 770360-05, Saint-Gobain, France) are attached into which couplings (cPMCD22-03

and cPLCD170-06, Colder Products Company, USA) are inserted to facilitate connection to sample collection and recovery equipment. The couplings have auto-shutoffs that automatically seal when disconnected. Primary sealing of the cartridge is achieved by placing clips (PA50, Weloc, Scandinavia Direct, UK) across the Iso-versinic[®] tubing at both ends. The molecular sieve material (3–4 g, 1.6-mm pellets, Type 13X zeolite, 334340, Sigma-Aldrich, UK) is held within the central compartment using quartz wool. Prior to cartridge construction, the molecular sieve material is combusted in a furnace at 500°C for 24 hr.

Processing of Molecular Sieve Cartridges

Cartridges are prepared for sample collection by purging with high purity nitrogen (Research Grade 5.0, BOC, UK) and CO₂-free air while being heated (500°C) over a period of at least 30 min. First, the heated cartridge is purged using nitrogen (150 mL/min) for 8 min, which desorbs most of the CO₂ trapped on the zeolite. The purge gas is then replaced with CO₂-free air (ca. 400 mL/min; generated by pumping lab air through soda lime) for 2 min to oxidize any contaminants that may be present within the zeolite (Table 1). The purge gas is then switched back to nitrogen for at least another 20 min to further desorb CO₂ from the zeolite. At this stage, an infrared gas analyzer (PP Systems EGM-4, Hitchin, UK) is used to ensure that the CO₂ concentration in the exhaust gas is below 50 ppm, and if so, heating of the molecular sieve is stopped. However, because a small amount of CO₂ continues to desorb from the zeolite until cooled to ca. 430°C, purging with nitrogen continues for another 10 min by which time the molecular sieve temperature has fallen to less than 400°C and CO₂ is no longer being desorbed. Valves are then closed to isolate the molecular sieve cartridge, which is left to cool for a further 20 min. Next, the cartridge is tested for leaks by flushing with nitrogen (150 mL/min) for 0.5 min and checking the CO₂ concentration of the purge gas exiting the molecular sieve (i.e. to determine if ingress of atmospheric CO₂ has occurred). Finally, the cartridge is filled with nitrogen to ca. 1 bar above atmospheric pressure and the cartridge removed from the furnace. These stages are all performed using a bespoke automated system (Figure 2) built using solenoid valves (PU220AR-01, Shako, Taiwan), microcontrollers (Arduino Uno and Mega, Arduino, Italy; www.arduino.cc) and PC software written in the Processing 2 programming language (www.processing.org). To maintain positive pressure within the cartridge, a further addition of nitrogen is performed manually once the cartridge has achieved room temperature. Using these procedures, we have found that the same molecular sieve cartridge can be recharged and reused for multiple samples, without any loss in performance.

Collection of samples and quality assurance standards on cartridges is usually undertaken by active sampling (at a flow rate of ca. 500 mL/min) using a molecular sieve CO₂ sampling system originally described by Hardie et al. (2005), but with the following improvements. First, all Tygon E-3603 tubing has been replaced with Iso-versinic[®] tubing (due to its greater rigidity and lower CO₂ permeability). Second, instead of calcium sulphate, we now use cartridges containing magnesium perchlorate (0.7–1.2-mm grains, Elemental Microanalysis, UK), which we believe to be superior for drying the sample gas before collection on the molecular sieve. Third, for processing quality assurance standards (CO₂ in sealed 6 mm OD glass tubes) a strong 750 mL glass bottle (an empty standard wine bottle cleaned using carbon-free detergent; Decon90[®], Decon Laboratories Limited, UK) fitted with a rubber bung and two stainless steel sampling ports is used to provide an air-tight chamber into which the gas standards can be released. This is achieved by firstly removing atmospheric

Table 1 Summary of molecular sieve charging and sample recovery procedures.

Procedure	Temperature (°C)	Flow rate (mL/min) / carrier gas	Time (min)	Comment
Charging	500	150 / N ₂	8	First flush step
	500	ca. 400 / CO ₂ -free air	2	Combustion step
	500	150 / N ₂	20/>20 if required for CO ₂ concentration to be <50 ppm	Second flush step
	Cooling to <400	150 / N ₂	10	Cooling flush
	Cooling <250	No flow (isolated)	20	Cooling
		150 / N ₂	1	Leak test and refilling cartridge with 1 bar N ₂ . Cartridge then removed from furnace
		<25	N ₂	1
Sample recovery	425	150 / N ₂	15	Cryogenic collection

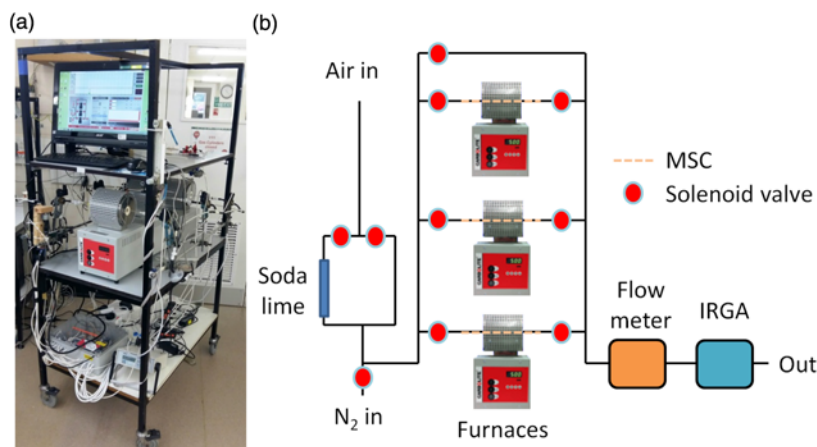


Figure 2 (a) Photograph and (b) schematic of the automated rig for charging molecular sieve cartridges at the NERC Radiocarbon Facility (East Kilbride). MSC = molecular sieve cartridge. IRGA = infrared gas analyzer.

CO₂ from the bottle by circulating the headspace through soda lime (Hardie et al. 2005), and then by shaking the bottle to break the scored glass tube against the bottle wall, thus releasing the standard gas.

Recovery of CO₂ from molecular sieve cartridges is performed by purging (150 mL/min) the molecular sieve with high purity nitrogen while heating the cartridge inside a tube furnace, followed by cryogenic collection. The method is similar to that described by Garnett and Murray (2013), except for the following changes. First, prior to heating, the cartridge is connected to the vacuum rig and evacuated (1×10^{-1} mbar) at both ends up to the clips, and then flooded with N₂ (Table 1). Second, the CO₂ concentration is no longer monitored using an infrared gas analyzer during desorption, and instead, all cartridges are simply desorbed for a set time of 15 min. Third, cartridges are now desorbed at 425°C and not 500°C as in the earlier method.

Tests of Current Cartridge Design and Procedures

The current molecular sieve cartridge and procedures were tested using ca. 3 mL (STP; standard temperature and pressure) CO₂ standards of known carbon isotope concentration produced from reference materials (Iceland Spar Calcite (ISC), background; TIRI Barley Mash (TBM), 116.35 ± 0.0084 pMC; Gulliksen and Scott 1995; FIRI Belfast Cellulose (FBC), 57.22 ± 0.04 pMC; Boaretto et al. 2002). The first tests were performed on freshly prepared cartridges for which the charging, gas collection, and gas recovery were undertaken within one week (i.e. storage time = 0 months). To assess the cartridges after a period of storage, tests were also performed on cartridges that had been charged at least three months before being used to trap CO₂ standards (storage time = 3 months; i.e. the cartridges were charged, left three months, used to trap CO₂ standards that were then recovered within the following week). To test for sample carry-over, we ensured that some of the previous CO₂ stored on the molecular sieve cartridge had a ¹⁴C or ¹³C concentration that contrasted with the chosen standard. We also performed tests using CO₂ produced from the abovementioned standard materials with each batch of molecular sieve samples

submitted for analysis. For these tests, the volume of the standard used was selected to be similar to the samples and where possible undertaken using molecular sieve cartridges that had been prepared at the same time as those used for the samples, and often had accompanied the submitter to the field site.

After recovery, the volume of CO₂ was determined using a pressure transducer and a calibrated volume, and split into aliquots. One aliquot was used for measurement of δ¹³C using isotope ratio mass spectrometry (Thermo-Fisher Delta V, Germany) with results expressed in per mil relative to VPDB. A second aliquot was transformed to graphite using Fe-Zn reduction (Slota et al. 1987) and analyzed by accelerator mass spectrometry (AMS) at the Scottish Universities Environmental Research Centre. Following convention, ¹⁴C measurements were corrected for isotopic fractionation by normalising to a δ¹³C of −25 ‰ using the measured δ¹³C values and reported as both pMC and conventional ¹⁴C ages (in BP = years before AD 1950; Stuiver and Polach 1977).

RESULTS

Tests of the Current Cartridge Design and Procedures

The ¹⁴C concentration of the background standards (CO₂ derived from Iceland Spar Calcite) used to test the latest cartridge design and procedures ranged from 0.41 to 0.77 pMC and are below the long-term background for molecular sieve cartridges at the NERC Radiocarbon Facility (1.0 ± 0.5 (SD) pMC based on n = 15 measurements between 2010 and 2015; Table 2). The ¹⁴C results for the non-background standards were all within 1 σ measurement uncertainty of consensus values, for both freshly-prepared and stored cartridges (Table 2). The δ¹³C values for all standards were also within measurement uncertainty (<1 σ) of the accepted values derived from measurements of bulk gas at NERC Radiocarbon Facility (TBM −26.9 ± 0.3 ‰; FBC −23.7 ± 0.3 ‰; ISC 2.4 ± 0.3 ‰).

The results for CO₂ derived from Iceland Spar Calcite showed that during 2016–2017 the ¹⁴C background of the method was 1.08 ± 0.51 pMC (n = 10), which is similar to the long-term background for molecular sieve cartridges at the NERC Radiocarbon Facility (1.0 ± 0.5 pMC). During the same period a total of 14 TBM CO₂ and 9 FBC CO₂ standards were processed alongside samples. For TBM, all results except one differed from the consensus value (116.35 pMC) by <2 σ and the mean (116.13 ± 0.61 SD pMC) was not significantly different (p=0.20; 1-sample T-test, Minitab 18; Figure 3). For FBC, the mean (56.99 ± 0.24 SD pMC) was slightly lower than the consensus value (57.22 pMC; p=0.02), but with measurement uncertainty all results overlapped with the consensus value at <2 σ (Figure 3). δ¹³C values for all quality assurance standards (mean ± SD; TBM −26.8 ± 0.2‰; FBC −23.6 ± 0.1‰) agreed with accepted values.

DISCUSSION

The benefit of cartridges containing zeolite molecular sieve for collecting carbon dioxide samples for ¹⁴C analysis is being increasingly recognized, with new systems having been recently reported from several other labs (Hämäläinen et al. 2010; Palonen 2015; Walker et al. 2015; Wotte et al. 2017b). At the NERC Radiocarbon Facility, development of our molecular sieve method has continued with a focus on improving the reliability of the method and quality of results, and to increase capacity and throughput to meet demand from users. The analyses performed to test our latest cartridge design and procedures

Table 2 Results for aliquots of CO₂ derived from ¹⁴C standard material trapped on molecular sieve cartridges and recovered using the latest procedures described in the text and Table 1. Consensus values for reference materials are: ISC = Iceland Spar Calcite, background; TBM = TIRI Barley Mash, 116.35 ± 0.0084 pMC (Gulliksen and Scott 1995); FBC = FIRI Belfast Cellulose, 57.22 ± 0.04 pMC (Boaretto et al. 2002).

Publication code (SUERC-)	Source of CO ₂ standard*	Storage time (months)	CO ₂ recovered (mL)	Yield (%)	δ ¹³ C _{VPDB} (‰ ± 0.3 ‰)	¹⁴ C content (pMC ± 1 σ)	Conventional ¹⁴ C age (BP ± 1 σ)
74589	TBM ^a	0	3.01	95	-26.8	116.03 ± 0.54	Modern
74586	ISC ^b	0	2.86	90	+2.6	0.66 ± 0.01	40356 ± 138
74590	ISC ^a	0	3.03	92	+2.7	0.41 ± 0.01	44195 ± 150
76518	TBM ^c	3.4	3.18	95	-26.8	116.06 ± 0.54	Modern
76519	ISC ^d	3.4	2.82	90	+2.7	0.77 ± 0.01	39135 ± 131
76520	FBC ^e	3.4	2.93	96	-23.4	57.47 ± 0.33	4449 ± 46

*Superscripts indicate previous gas stored on the molecular sieve cartridge: ^aatmospheric CO₂, ^bTBM CO₂, ^cISC CO₂, ^dFBC CO₂, ^eunknown.

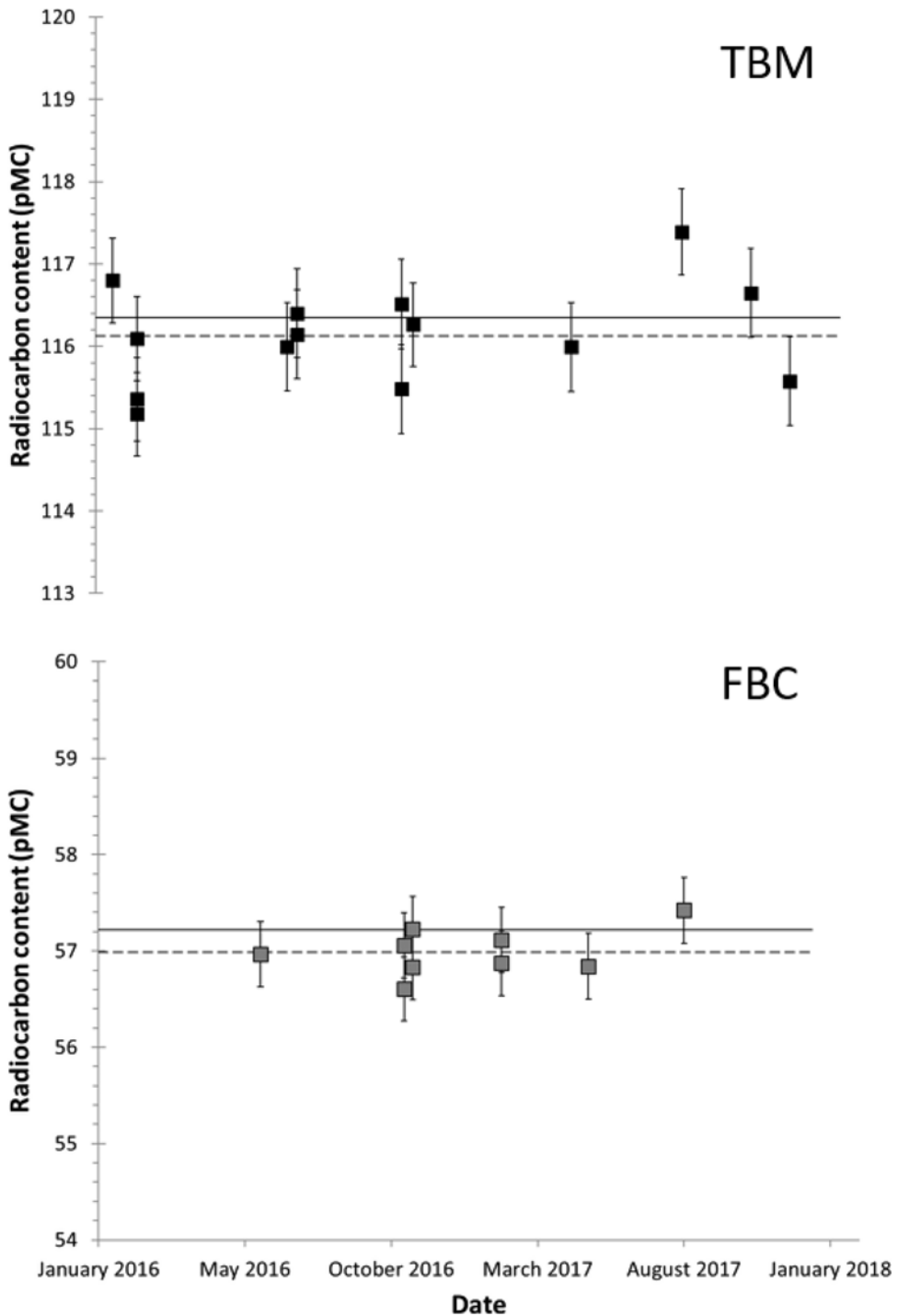


Figure 3 Radiocarbon concentration of known ^{14}C content quality assurance standards collected on, and recovered from, molecular sieve cartridges during 2016–2017. CO_2 derived from TIRI Barley Mash (TBM; top) and FIRI Belfast Cellulose (FBC; bottom). Error bars are $\pm 1 \sigma$. Full lines represent the international consensus value for each standard and dashed line the mean for measured standards.

demonstrate that, within the operating parameters that we currently recommend (CO₂ sample volume >3 mL, storage time < 3 months), our molecular sieve system is reliable. From a total of 29 measurements on international ¹⁴C standards over two years (6 new cartridge test standards plus 23 known ¹⁴C content standards accompanying samples), only one provided a ¹⁴C value that differed from the consensus value by >2 σ . Moreover, for the 6 test standards (Table 2) the agreement of $\delta^{13}\text{C}$ values with consensus values show the absence of fractionation effects. Reliable ¹⁴C measurements from standards of disparate ¹⁴C concentrations demonstrate the absence of contamination and sample carry-over effects in both newly charged cartridges and cartridges that have been in storage for 3 months.

The performance of our molecular sieve sampling method compares well with similar systems developed in other laboratories. Radiocarbon concentrations of our background ¹⁴C standards are similar to those reported by Wotte et al. (2017a), and lower than those of Walker et al. (2015; calculated by Wotte et al. 2017a). While our developments have enabled a reduction in the recommended sample size from ca. 10 mL (Hardie et al. 2005) to >3 mL for the current system, the results of Wotte et al. (2017a) suggest that a further reduction in sample size may be possible (although they acknowledge that smaller samples are vulnerable to contamination and carry-over effects).

We have previously demonstrated that our molecular sieve methods are reliable for stable-carbon and ¹⁴C measurement of CO₂ (Garnett and Murray 2013). To construct more cartridges to meet higher demand from users, it has been necessary for us to source new supplies of Type 13X zeolite. Although molecular sieve traps can be reused, we had limited quantities of the BDH (British Drug Houses) 13X used in earlier cartridges (Hardie et al. 2005; Garnett and Murray 2013) and were unable to obtain new supplies. We found that the performance characteristics of new Type 13X zeolite from several suppliers differed slightly, and that they did not completely desorb all the CO₂ that they had trapped when processed using the earlier reported methods (Garnett and Murray 2013), leading to significant sample carry-over (typically ca. 0.1 to 0.3 mg C). We found that we could overcome this problem when using Sigma-Aldrich Type 13X molecular sieve (used for all results presented here) by preparing the cartridges at 500°C but recovering the sample CO₂ at a lower temperature of 425°C. Although this results in a slightly lower yield (by ca. 5%, presumably due to incomplete desorption at the lower temperature), it prevents significant sample carry-over and as shown in the results reported here, enables reliable ¹⁴C and ¹³C measurement (Table 2, Figure 3).

A considerable improvement to our molecular sieve method has been the construction of an automated charging rig for preparing the molecular sieve cartridges before use. This system ensures that all cartridges are prepared consistently, incorporates several different charging steps (purging with nitrogen and CO₂-free air, slightly over-pressurizing cartridges with nitrogen) and performs a leak test to check the integrity of the cartridges. Moreover, after a minimal set up, the rig can be left to process three cartridges with no further operator input required until the charging processes is completed. Thus, up to 9 molecular sieve cartridges can be prepared in a standard working day, with a total operator time of less than one hour. An automated rig for recovering sample CO₂ from molecular sieve cartridges is currently in the final phase of development and testing. This rig will be solely for CO₂ recovery for analysis, with used cartridges being recharged on the existing automated charging rig as required.

Presently, we are undertaking tests to make cartridges more robust since even though they are provided to users in protective housing (polyethylene foam pipe insulation), they occasionally break in transit. Metal cartridges offer one solution (e.g. Wotte et al. 2017b), though we have often found it useful to observe inside the cartridge to check for the presence of water (particularly when using the cartridges for passive sampling aquatic CO₂; Garnett et al. 2012) or contamination. For example, on at least one occasion a carbon-rich black deposit has formed on the 13X zeolite during sample recovery, which we suspect was due to the reduction of hydrocarbons (likely present on the molecular sieve due to the sample type). Since this was a potential contaminant for future samples processed using the cartridge, we incorporated the CO₂-free air purge in the automated charging process (during the air-purge ca. 1 mL CO₂ was observed in the exhaust gases and the black deposits were removed). Other modifications currently under trial include the replacement of quartz wool in the cartridges with stainless steel wool, which reduces back pressure during sampling, and should enable the cartridges to perform more consistently during sample collection.

Finally, the results presented here demonstrate the reliability of our methods under currently recommended operating parameters (>3 mL CO₂, and <3 months storage time). Future investigations will seek to more accurately resolve the limitations of the current methods, and to find improvements that will enable reliable ¹⁴C measurement of smaller sample volumes (Walker et al. 2015; Wotte et al. 2017a).

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