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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.

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
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 1960’s (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 utilised 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\(^{\circledast}\) 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\(^{\circledast}\) 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 hours.

**Processing of molecular sieve cartridges**

Cartridges are prepared for sample collection by purging with high purity nitrogen (Research Grade 5.0, BOC, UK) and CO\(_2\)-free air while being heated (500°C) over a period of at least 30 minutes. First, the heated cartridge is purged using nitrogen (150 ml/min) for 8 minutes, which desorbs most of the CO\(_2\) trapped on the zeolite. The purge gas is then replaced with CO\(_2\)-free air (ca. 400 ml/min; generated by pumping lab air through soda lime) for 2 minutes to oxidise 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 minutes to further desorb CO\textsubscript{2} from the zeolite. At this stage, an infrared gas analyser (PP Systems EGM-4, Hitchin, UK) is used to ensure that the CO\textsubscript{2} 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 CO\textsubscript{2} continues to desorb from the zeolite until cooled to ca. 430°C, purging with nitrogen continues for another 10 minutes by which time the molecular sieve temperature has fallen to less than 400°C and CO\textsubscript{2} is no longer being desorbed. Valves are then closed to isolate the molecular sieve cartridge, which is left to cool for a further 20 minutes. Next, the cartridge is tested for leaks by flushing with nitrogen (150 ml/min) for 0.5 minutes and checking the CO\textsubscript{2} concentration of the purge gas exiting the molecular sieve (i.e. to determine if ingress of atmospheric CO\textsubscript{2} 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 CO\textsubscript{2} 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\textsuperscript{®} tubing (due to its greater rigidity and lower CO\textsubscript{2} 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 (CO\textsubscript{2} in sealed 6 mm OD glass tubes) a strong 750 ml glass bottle (an empty standard wine bottle cleaned using carbon-free detergent; Decon90\textsuperscript{®}, 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 CO\textsubscript{2} 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 CO\textsubscript{2} 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 (1x10\textsuperscript{-3} mbar) at both ends up to the clips, and then flooded with N\textsubscript{2} (Table 1). Second, the CO\textsubscript{2} concentration is no longer monitored using an infrared gas analyser during desorption, and instead, all cartridges are simply desorbed for a set time of 15 minutes. 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) CO\textsubscript{2} 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 where 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 CO_2 standards (storage time = 3 months; i.e. the cartridges were charged, left three months, used to trap CO_2 standards that were then recovered within the following week). To test for sample carry-over, we ensured that some of the previous CO_2 stored on the molecular sieve cartridge had a ^14C or ^13C concentration that contrasted with the chosen standard. We also performed tests using CO_2 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 CO_2 was determined using a pressure transducer and a calibrated volume, and split into aliquots. One aliquot was used for measurement of δ^13C 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 analysed 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 δ^13C of -25 ‰ using the measured δ^13C values and reported as both pMC and conventional ^14C ages (in BP = years before AD1950; Stuiver and Polach 1977).

RESULTS

Tests of the current cartridge design and procedures

The ^14C concentration of the background standards (CO_2 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 δ^13C 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 CO_2 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 CO_2 and 9 FBC CO_2 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). δ^13C
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 
$^{14}$C analysis is being increasingly recognised, 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 demonstrate that, within the operating parameters that we currently recommend (CO$_2$ sample volume >3 ml, storage time < 3 months), our molecular sieve system is reliable. From a total of 29 measurements on international $^{14}$C standards over two years (6 new cartridge test standards plus 23 known $^{14}$C content standards accompanying samples), only one provided a $^{14}$C value that was >2 σ of the consensus value. Moreover, for the 6 test standards (Table 2) the agreement of $\delta^{13}$C values with consensus values show the absence of fractionation effects. Reliable $^{14}$C measurements from standards of disparate $^{14}$C 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 $^{14}$C 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 $^{14}$C measurement of CO$_2$ (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 CO$_2$ 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 CO$_2$ 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 $^{14}$C and $^{13}$C 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 CO$_2$-free air, slightly over-pressurising 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 CO$_2$ from molecular sieve cartridges is currently in the final phase of development and testing. This rig will be solely for CO$_2$ 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 CO$_2$; 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 CO$_2$-free air purge in the automated charging process (during the air-purge ca. 1 ml CO$_2$ 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 CO$_2$, 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 $^{14}$C measurement of smaller sample volumes (Walker et al. 2015; Wotte et al. 2017a).

ACKNOWLEDGEMENTS

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REFERENCES


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

<table>
<thead>
<tr>
<th>Procedure</th>
<th>Temperature (°C)</th>
<th>Flow rate (ml/min) / carrier gas</th>
<th>Time (min)</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Charging</td>
<td>500</td>
<td>150 / N₂</td>
<td>8</td>
<td>First flush step</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>ca. 400 / CO₂-free air</td>
<td>2</td>
<td>Combustion step</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>150 / N₂</td>
<td>20/&gt;20 if required for CO₂ concentration to be &lt;50 ppm</td>
<td>Second flush step</td>
</tr>
<tr>
<td>Cooling to &lt;400</td>
<td>150 / N₂</td>
<td>10</td>
<td></td>
<td>Cooling flush</td>
</tr>
<tr>
<td>Cooling &lt;250</td>
<td>No flow (isolated)</td>
<td>150 / N₂</td>
<td>20</td>
<td>Cooling</td>
</tr>
<tr>
<td></td>
<td>150 / N₂</td>
<td>1</td>
<td>1</td>
<td>Leak test and refilling cartridge with 1 bar N₂. Cartridge then removed from furnace</td>
</tr>
<tr>
<td></td>
<td>N₂</td>
<td>1</td>
<td>1</td>
<td>Refilled to 1 bar N₂.</td>
</tr>
<tr>
<td>Sample recovery</td>
<td>425</td>
<td>150 / N₂</td>
<td>15</td>
<td>Cryogenic collection</td>
</tr>
</tbody>
</table>
Table 2 Results for aliquots of CO$_2$ derived from $^{14}$C 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). *Superscripts indicate previous gas stored on the molecular sieve cartridge: a-atmospheric CO$_2$, b-TBM CO$_2$, c-ISC CO$_2$, d-FBC CO$_2$, e-unknown.

<table>
<thead>
<tr>
<th>Publication code</th>
<th>Source of CO$_2$ standard</th>
<th>Storage time (months)</th>
<th>CO$_2$ recovered (ml)</th>
<th>Yield (%)</th>
<th>$\delta^{13}$C$_{VPDB}$ (%) ± 0.3‰</th>
<th>$^{14}$C content (pMC ± 1σ)</th>
<th>Conventional $^{14}$C age (BP ± 1σ)</th>
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</thead>
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<tr>
<td>SUERC-74589</td>
<td>TBM$^a$</td>
<td>0</td>
<td>3.01</td>
<td>95</td>
<td>-26.8</td>
<td>116.03 ± 0.54</td>
<td>Modern</td>
</tr>
<tr>
<td>SUERC-74586</td>
<td>ISC$^b$</td>
<td>0</td>
<td>2.86</td>
<td>90</td>
<td>+2.6</td>
<td>0.66 ± 0.01</td>
<td>40356 ± 138</td>
</tr>
<tr>
<td>SUERC-74590</td>
<td>ISC$^c$</td>
<td>0</td>
<td>3.03</td>
<td>92</td>
<td>+2.7</td>
<td>0.41 ± 0.01</td>
<td>44195 ± 150</td>
</tr>
<tr>
<td>SUERC-76518</td>
<td>TBM$^c$</td>
<td>3.4</td>
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<td>-26.8</td>
<td>116.06 ± 0.54</td>
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<tr>
<td>SUERC-76519</td>
<td>ISC$^d$</td>
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<td>2.82</td>
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<td>+2.7</td>
<td>0.77 ± 0.01</td>
<td>39135 ± 131</td>
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<tr>
<td>SUERC-76520</td>
<td>FBC$^e$</td>
<td>3.4</td>
<td>2.93</td>
<td>96</td>
<td>-23.4</td>
<td>57.47 ± 0.33</td>
<td>4449 ± 46</td>
</tr>
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Figure captions

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

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 analyser.

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 ±1 σ. Full lines represent the international consensus value for each standard and dashed line the mean for measured standards.
Fig. 1

Iso-versinic tubing  13X zeolite  Iso-versinic tubing

Coupling  Clip  Quartz wool  Clip  Coupling
Fig. 2

(a) [Image of equipment setup]

(b) [Diagram of flow process with labels: Air in, Soda lime, N₂ in, Furnaces, Flow meter, MSC, Solenoid valve, IRGA, Out]
Fig. 3

TBM

FBC

Date

January 2016  May 2016  October 2016  March 2017  August 2017  January 2018