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Processing of samples by ramped oxidation at the NEIF Radiocarbon Laboratory, SUERC: Recent technical advances

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Abstract

Carbon occurs as organic and inorganic matter in numerous complex forms and mixtures. Thermal separation of sample mixtures (e.g. sediment or soil), coupled with radiocarbon analysis, is a valuable approach for investigating the source, residence time, or age of different carbon components. At the NEIF Radiocarbon Laboratory we have built equipment for thermally separating samples for radiocarbon analysis using ramped oxidation. The original instrumentation has been successfully tested and validated for the purpose of partitioning samples based on their temperature of thermal decomposition, and for reliable radiocarbon measurement of different sample components. However, the original configuration of our instrument has limitations; a single analysis takes 2–3 hours, and an operator must be present to manually isolate samples from the required temperature ranges. To address this, we have upgraded our ramped oxidation equipment to include computer-controlled solenoid valves. These are activated according to a user-defined sampling scheme which enables autonomous collection of thermally partitioned samples. Here, we describe the latest improvements and present thermograms showing compatibility with the previous version of our equipment. This includes measurements of the radiocarbon background of the equipment, and results for known ^{14}C-content radiocarbon standards. These demonstrate the reliability of the new configuration of our equipment for radiocarbon measurements.

Introduction

Carbon (C) occurs in the environment as organic and inorganic matter, in numerous complex forms and mixtures, and has many different origins and ages (Hanke et al. 2023; Hedges et al. 2000). Unravelling these complex mixtures can allow us to better understand the processing of carbon-containing materials and ultimately better comprehend the Earth's carbon cycle (Hajdas et al. 2021; Hanke et al. 2023; Hedges et al. 2000). Radiocarbon (^{14}C) analysis provides unique information on the age of carbon since atmospheric fixation, and consequently, on the rate of turnover and/or origin of the carbon (Hajdas et al. 2021). While ^{14}C measurement of bulk materials has provided valuable insights (e.g. on cycling of soil carbon; Shi et al. 2020), radiocarbon scientists have long applied methods to refine mixed samples into one or more constituent components prior to ^{14}C measurement, to gain a more nuanced insight (Hajdas et al. 2021). This processing extends from the widely used acid-base-acid pretreatment to remove mobile carbon compounds for chronological studies (Ascough et al. 2024; Hajdas et al. 2021), to fractionation of sample mixtures based on physical characteristics (e.g. density, particle size; Sandeman and Grandy, 2020) and even the isolation of specific chemical compounds (e.g. amino acids and lipids; Blattmann et al. 2020; Casanova et al. 2020).

Another approach to partition mixed samples prior to radiocarbon analysis involves sequential thermal decomposition. This approach exploits the fact that different chemical compounds, or compound groups, thermally decompose at different temperatures, as the input of heat energy reaches the threshold for bond dissociation of the compound in question (Hemingway et al. 2018). Ultimately, this leads to the formation of CO_2, enabling the decomposition products to be isolated and removed for subsequent ^{14}C analysis, leading to a spectrum of radiocarbon age distribution that provides more information on the organic matter age in a sample compared to bulk ^{14}C measurements (Rosenheim and Galy 2012). This has previously been performed using a "stepped" heating approach (e.g. McGeechin et al. 2001), although it has become more common to use "ramped" heating whereby a sample is subjected to a constantly increasing temperature and the combustion products continuously extracted (usually over defined temperature ranges) for subsequent ^{14}C measurement (Hemingway et al. 2017b; Keaveney et al. 2021; Rosenheim and Galy 2012; Rosenheim et al. 2008). Ramped pyrolysis/combustion radiocarbon analysis has been used to investigate a range of issues and sample types such as the turnover of soil C (e.g. Plante et al. 2013; Sanderman and Grandy 2020; Stoner et al. 2023), source contributions to particulate (e.g. Rosenheim and Galy 2012; Rosenheim et al. 2013a) and dissolved organic carbon (e.g. Rogers et al. 2021) and for improved chronological dating of sediments (e.g. Rosenheim et al. 2013b).

Several different approaches to partition radiocarbon samples using ramped heating have been reported, although all rely on the use of a carrier gas to remove evolved combustion products from the sample for subsequent analysis. For instance, Rosenheim et al. (2008) used pyrolysis (thermal breakdown in the absence of oxygen) with a helium carrier gas for their primary thermal decomposition, whereas others have used carrier gases with specific levels of oxygen (e.g. Hanke et al. 2023). These different approaches are likely to have their own advantages and disadvantages (e.g. with how vulnerable they are to "charring effects"; Williams et al 2014), and as yet no standard method has been adopted.

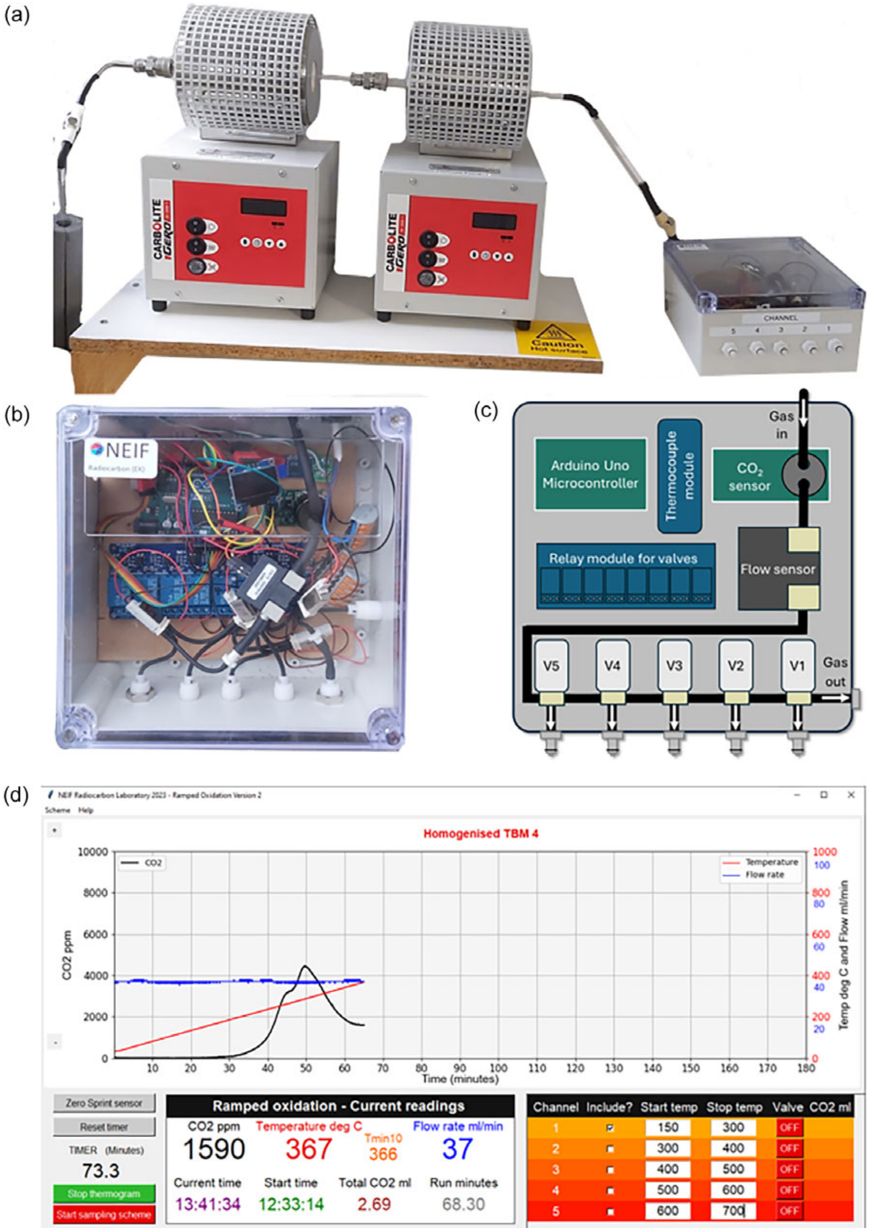
When coupled with a device to measure the CO_2 concentration in the exhaust gases (e.g. an infrared gas analyser or non-dispersive infrared sensor) a plot of the evolved CO_2 versus temperature (thermogram) can be produced which provides a 'fingerprint' reflecting the thermal resistance and abundance of different compounds contained within the sample. Thermograms can provide valuable insight on their own, for example, indicating the proportion of carbon in a sample that is thermally labile versus resistant (Smeaton and Austin 2022), but are even more powerful when coupled with ^{14}C measurement, providing information on source and residence time of the different components (Hemingway et al. 2017b).

With a long history in the radiocarbon analysis of sample mixes in our laboratory, particularly for soils (e.g. Harkness et al. 1986, 1991), and recognising the scientific opportunities available, we decided to develop an instrument for thermally separating samples for ^{14}C analysis using a ramped oxidation approach (Garnett et al. 2023). The original version of our ramped oxidation radiocarbon kit (RO-^{14}C) has proven reliable for thermally separating radiocarbon samples (Garnett et al. 2023) and has been in high demand for projects investigating carbon turnover in solid materials such as soils and sediments. However, a major limitation of the original kit is that the partitioning of thermal fractions requires the continuous presence of an operator over several hours to actuate a manual valve when transferring the sample fractions into separate storage vessels. This makes the equipment labour-intensive in terms of the operator time required to process each sample. Here, we describe recent technical upgrades to our instrumental set-up which, in addition to other improvements, allows autonomous collection of thermally resolved samples for radiocarbon analysis.

Methods

Description of the upgraded ramped oxidation-^{14}C kit

The general principle of operation of the RO-^{14}C equipment and combustion vessels remains the same as previously described (Garnett et al. 2023). High purity oxygen (N5.5, 99.9995% purity, BOC, UK) is



TIMER (Minutes) 73.3

Ramped oxidation - Current readings

CO2 ppm	Temperature deg C	Tmin10	Flow rate ml/min
1590	367	366	37

Current time	Start time	Total CO2 ml	Run minutes
13:41:34	12:33:14	2.69	68.30

Channel	Include?	Start temp	Stop temp	Valve	CO2 ml
1	☑	150	300	OFF	
2	☐	300	400	OFF	
3	☐	400	500	OFF	
4	☐	500	600	OFF	
5	☐	600	700	OFF	

Figure 1. *Illustration of the upgraded ramped oxidation-radiocarbon (RO-^{14}C) kit at the NEIF Radiocarbon Laboratory, showing: (a) Primary (ramp; left) and secondary (right) combustion furnaces connected to the new sensor unit, (b) photograph of the new sensor unit, (c) schematic of the new sensor unit and (d) user interface of the new software (showing an example of a sample being analysed for a thermogram). See text for details.*

used as the carrier gas (ca. 30 mL/min flow rate) which, after passing through a CO_2 scrub (13X zeolite molecular sieve), enters the quartz glass primary combustion vessel. This is held inside a tube furnace (Carbolite MTF 10/15/130–1000 °C, Carbolite, UK) with a temperature ramp program (Figure 1a). A quartz glass insert containing the sample material is placed inside the primary combustion vessel at a precise location to ensure it occupies the hottest part of the furnace. The gas stream exits the primary combustion vessel and enters a secondary combustion vessel. This is identical to the first vessel, except that in the second combustion vessel the sample and quartz insert are replaced by a ca. 3 cm length of platinised wool catalyst (originally Platinum 5% on Triton kaowool, BDH Chemicals Ltd, UK, but due to unavailability we additionally also use High Sensitivity Catalyst 2 g 630-00996, Elemental Microanalysis, UK). This secondary combustion vessel is heated to a constant 950 °C and is used to ensure complete oxidation to CO_2 of carbon-containing combustion products that are generated in the first combustion vessel. The exhaust from the second vessel is dried via a glass tube containing magnesium perchlorate desiccant (Elemental Microanalysis, UK) before being transferred to a sensor unit (Figures 1b–c). Here, the CO_2 concentration and gas flow rate are measured (SprintIR®-WF-5 CO_2 sensor, Gas Sensing Solutions, UK and AWM3100V air flow sensor, Honeywell, USA). An Arduino Uno microcontroller (arduino.org) is used to collect the data from the CO_2 sensors and also to record the temperature of the primary combustion vessel, which is measured by a K-type thermocouple (TCMK150AQ150, TC Ltd, UK). This thermocouple is inserted into the central part of the tube furnace (adjacent to the sample) and differs by <10 °C from manufacturers internal thermocouple of the tube furnace. Both the temperature and CO_2 data are transferred via a serial connection to a computer for logging. From the sensor unit, the gas stream can either be exhausted to atmosphere or collected inside cleaned foil gas bags for subsequent recovery of the evolved CO_2. This is achieved using routine methods of cryogenic purification and collection (Ascough et al. 2024; Garnett et al. 2023).

In the previous version of the RO-^{14}C kit a manually operated 3-way valve was used to direct the carrier gas either to a foil gas bag for sample collection, or to atmosphere. For partitioning into multiple fractions, filled bags were manually exchanged with clean empty ones, as required. In the updated kit, this process has been completely automated. This has been achieved by building a new version of the sensor unit that incorporates five electronically actuated solenoid valves (S070C-6AG-32, SMC, Japan). When activated, these divert the carrier gas into up to five foil gas bags for sample collection (Figures 1b–c). Each valve has three gas ports. These comprise a single inlet that is always open, and two outlet ports that route the gas flow either to a foil gas bag (when the solenoid is activated) or to the next solenoid valve (when the solenoid is inactive). If none of the solenoid valves are activated, the carrier gas is exhausted to atmosphere. Activation of the solenoid valves is controlled by new in-house software (Figure 1d) written in the Python programming language; when required, the software sends a signal to the Arduino Uno which activates the appropriate solenoid valve via a relay module. Thus, using the software, individual solenoid valves are instructed to open and close to allow the collection of sample gas based on the thermocouple-measured temperature of the primary combustion vessel and a preset sampling scheme, enabling automated sample collection.

Procedures and operation of the upgraded ramped oxidation-^{14}C kit

The RO-^{14}C kit is prepared using the same procedures as described in Garnett et al. (2023), with all equipment cleaned between samples either by combustion (quartz glass, at least 2 hours at 900 °C) or using a carbon-free detergent (Decon 90) followed by rinsing with Milli-Q water. Foil gas bags are cleaned by filling and evacuating with ca. 1 L high purity N_2 (N5.5, 99.9995% purity, BOC, UK), three times over at least 24 hours to aid outgassing of residual CO_2 and checked using an SBA-5 CO_2 analyser (accuracy $< 1\%$ calibrated range 0–2000 ppm; PPsystems, USA). After loading a sample into the primary combustion vessel, the carrier gas is tested for leaks using the SBA-5 CO_2 analyser connected to the exhaust of the sensor kit, before combustion proceeds (the SBA-5 is zero-calibrated beforehand with CO_2-free air generated by temporarily diverting the exhaust gases through a cartridge of soda lime before entering the SBA-5). With the new RO-^{14}C software the user can choose to perform a ramped combustion with the entire carrier gas vented to atmosphere to generate a thermogram, by selecting the “Thermogram only” program. This is typically undertaken when investigating a new material where the temperature windows for collection of a ^{14}C sample are unknown. After the analysis is completed the logged sensor data can be used to generate a thermogram.

For automated collection of samples across defined temperature ranges the user first specifies the number of samples to collect and enters the lower and upper temperatures for each fraction (i.e. the "sampling scheme"). A total of 1–5 samples can be collected. The maximum collection number is determined by the number of solenoid valve-controlled gas outlet ports. A small ($<$0.2 mL) volume of "dead space" between the gas port and the solenoid valve is manually flushed with carrier gas to remove CO_2 that may remain from the previous sample, before the clean sample bags are attached and their clips removed.

At the start of an analysis the user is prompted to calibrate the Sprint CO_2 sensor by setting the 0-ppm point. The user can then switch on the furnace of the primary combustion vessel in ramp mode (5 °C/min), and the kit can be left for the next 2–3 hours as the furnace heats from room temperature to the required maximum temperature (usually 800 °C) when the analysis is completed. Recovery of CO_2 from gas bags, conversion to graphite, ^{14}C measurement by accelerator mass spectrometry (AMS) and ^{14}C data reduction follow standard procedures that are described in Garnett et al. (2023) and Ascough et al. (2024). Radiocarbon concentrations are presented as percent modern carbon (pMC) where pMC = fraction modern ($F^{14}C$) × 100 (Reimer et al. 2004). $F^{14}C$ is determined from the $^{14}C/^{12}C$ ratio of the unknown sample or standard ($_S$) and oxalic acid international radiocarbon reference ($_{Ox}$):

$$F \text{ or } f = (^{14}C/^{12}C)s/(^{14}C/^{12}C)_{Ox} \tag{1}$$

Where F and f are the raw fraction modern values (normalised to $\delta^{13}C$ of −25‰ using $\delta^{13}C$ of the recovered CO_2 measured by isotope ratio mass spectrometry; Delta V, Fisher Scientific, Germany) of the ramp-combusted sample and the process background standard (based on measurements of ^{14}C-dead anthracite), respectively. Background correction is applied based on Donohue et al. (1990) to determine $F^{14}C$:

$$F^{14}C = F \cdot (1 + f) - f \tag{2}$$

Tests used to verify the reliability of the upgraded ramped oxidation-^{14}C kit

We undertook the following tests to determine whether the new RO-^{14}C kit produced thermograms that were consistent with the previous version of the kit, and to assess whether the new kit was reliable for radiocarbon analysis:

Thermograms for standard materials (anthracite coal and barley mash from the Third International Radiocarbon Intercomparison; TIRI; Gulliksen and Scott, 1995) were generated using the original and the new version of the RO-^{14}C kit and compared.

A suite of five anthracite background radiocarbon standards was processed using the new kit to determine its ^{14}C background and to test whether it was significantly different to the previous kit (commissioning standards). Additional anthracite standards, subsequently processed alongside samples, were also added to this assessment (post-commissioning process standards).

Known ^{14}C content/age radiocarbon standards (TIRI barley mash, 116.35 ± 0.0084 pMC, ca. 45 % C; and 96H humin, 65.63 ± 0.54 pMC, ca. 52 %C; Xu et al. 2004) were processed using the new kit and the measured radiocarbon contents compared to consensus values.

When thermally partitioning a sample into multiple fractions, the amount of sample required is calculated so that the smallest partition will yield at least 3 mL CO_2. Therefore, depending on the shape of the thermogram, this can mean that some samples will evolve a total of many tens of mL of CO_2 during analysis. With the new RO-^{14}C kit we observed some smoothing of the thermograms, evidenced by fewer sharp peaks and shallowing of valleys between peaks. We suspected this was due to a small amount of mixing of combustion products in the primary combustion vessel. To address this, we replaced the standard quartz insert sample holder, which was completely sealed at one end, with a new version that was open at one end, and only partially sealed at the other end using a quartz glass frit. Thus, the new sample

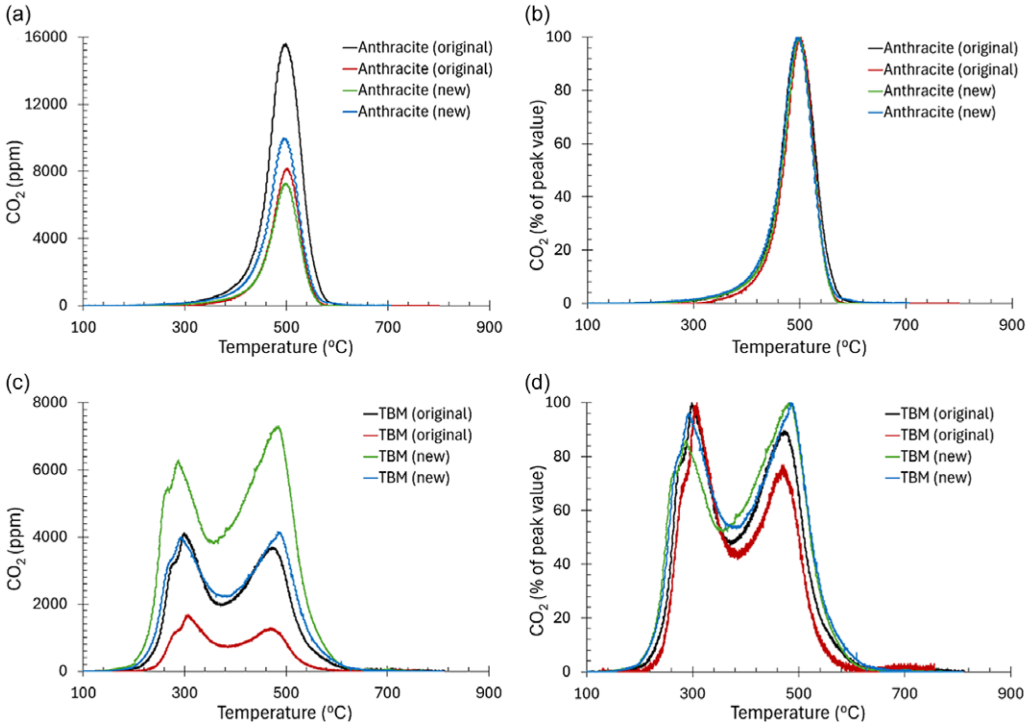


Figure 2. *Comparison of thermograms generated using the original version of the RO-^{14}C kit and the new version. Representative thermograms presented for anthracite coal (a & b) and TIRI barley mash (c & d) as measured CO_2 concentrations (ppm) (a & c) and normalised % of peak CO_2 (b & d) to account for different sample sizes.*

holder securely contains the sample material but should allow better flushing of combustion products out of the primary combustion vessel. Therefore, we also report here thermograms for standard materials with high carbon contents processed by the RO-^{14}C kit using the original and new sample holder.

All statistical tests were performed using Minitab 19 (T-tests) or Microsoft Excel (all other data analysis).

Results

Tests used to verify the reliability of the upgraded ramped oxidation-^{14}C kit

Thermograms generated using the new RO-^{14}C kit and its predecessor are presented in Figure 2 for anthracite and barley mash. There is strong agreement in the thermograms of the two kits, with for example, peak CO_2 concentration for the anthracite occurring at 503 ± 3 °C for the old kit (n = 5; Garnett et al. 2023), and 495 ± 2 °C for the updated kit (commissioning standards n = 5). When the thermograms are normalised by scaling to the peak CO_2 concentration (to adjust for differences in sample size), the thermograms from both kits plot on top of each other (Figures 2b and d).

All ^{14}C concentrations for the anthracite background standard plot within the 2 σ range of the long-term background used to correct sample results for the small amount of contamination introduced during laboratory processing and AMS ^{14}C measurement (Figure 3). However, the first five anthracites used to test the new kit during the initial commissioning phase had a higher mean ^{14}C content (0.42 ± 0.07 pMC) than the anthracites used to test the previous version of the kit (0.34 ± 0.08 pMC), although the difference was not statistically significant (T-test; $p = 0.116$). Four anthracites subsequently processed alongside samples returned ^{14}C values in agreement with both versions of the kit (Figure 3).

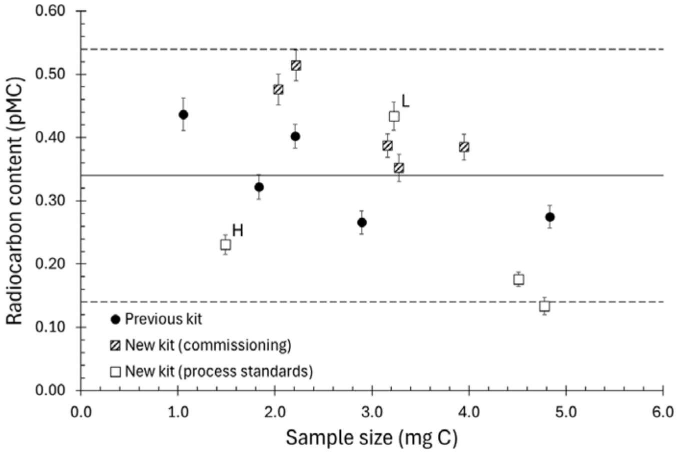


Figure 3. *Radiocarbon concentration of an anthracite coal background standard determined using the original RO-^{14}C kit, and the new version during commissioning and for post-commissioning process standards. Current background correction applied to samples and ± 2 σ uncertainty are represented by the solid and dashed lines, respectively. Low (200–500 °C; L) and high (500–800 °C; H) temperature fractions are indicated for one thermally partitioned standard. Error bars represent 2 σ AMS measurement uncertainty.*

Table 1. *Results for quality assurance standards processed with the new RO-^{14}C kit in 2024. All ^{14}C results for combined and full samples are ≤ 2 σ of the consensus values*

Standard	Weight (mg)	SUERC-	Temperature range (°C)	CO_2 (mL)	$\delta^{13}C_{VPDB}$ ± 0.3‰	pMC ± 1σ
96H humin	7.8	124832	100–380	3.82	–28.2	65.47 ± 0.31
		124833	380–700	2.69	–27.8	65.11 ± 0.31
			Combined	*6.51*	*–28.0*	*65.32 ± 0.43*
TIRI Barleymash	8.4	124834	100–380	3.19	–27.4	115.96 ± 0.54
		124838	380–700	3.91	–27.7	114.85 ± 0.51
			Combined	*7.10*	*–27.6*	*115.35 ± 0.74*
TIRI Barleymash	13.8	126721	60–380	4.54	–27.1	115.82 ± 0.53
		126722	380–800	6.23	–27.0	116.92 ± 0.54
			Combined	*10.77*	*–27.1*	*116.45 ± 0.76*
TIRI Barleymash	6.0	128331	60–600	4.75	–26.8	116.40 ± 0.51
TIRI Barleymash	6.6	126693	150–650	5.32	–27.0	115.17 ± 0.59

The radiocarbon concentrations for known-^{14}C standards are shown in Table 1. These comprise of three standards which were each split into two temperature fractions (to simulate thermally partitioning a sample; i.e. six ^{14}C measurements in total), and two more standards where the entire sample CO_2 was collected into a single gas bag. For the samples that were split during processing, the ^{14}C content of the mathematically combined whole sample (weighted by volume of CO_2 recovered for each fraction) was within 2 σ of the consensus values. Similarly, the samples that were not split during combustion were also within measurement uncertainty (≤ 2 σ) of the consensus value.

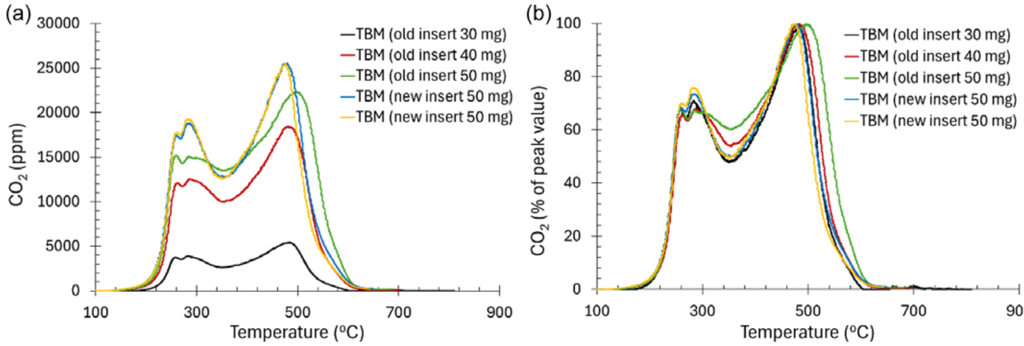


Figure 4. *Comparison of thermograms generated for large (up to 50 mg d/w) samples of TIRI barley mash using the original and new sample holder. Thermograms presented as measured CO_2 concentrations (a) and normalized % of peak CO_2 concentration (b) to account for different sample sizes.*

Figure 4 plots the thermograms for TIRI barley mash when processed with the new RO-^{14}C kit using the old and new sample holders. The peak-CO_2 normalised plot clearly shows the progressively shallower valley between the two main CO_2 peaks and shift of the second peak to higher temperature when sample size increased up to 50 mg using the old sample insert. Despite the same sample size of 50 mg, the two TIRI barley mash standards processed with the new sample holder provided thermograms very similar to the smallest sample (30 mg) with the old sample holder.

Discussion

We developed equipment to perform the radiocarbon dating and analysis of thermally separated carbon pools after recognizing the scientific opportunities it provided for studies in ^{14}C chronology (e.g. Keaveney et al. 2021; Rosenheim et al. 2008) and carbon cycling (e.g. Hemingway et al. 2018; Plante et al. 2013). It soon became apparent that our original RO-^{14}C kit, created mostly from components already available in our laboratory, was hindered by its manual operation. While the kit could be left to run autonomously for several hours during the acquisition of thermogram data, collection of thermally partitioned samples for ^{14}C analysis required almost continuous presence of an operator to manually switch a valve and swap out foil gas bags at specific times over a period of 2-3 hours. Moreover, a small mistake such as missing the correct moment to manually flip the valve would result in the entire sample having to be discarded and re-run. This obviously presents a problem if sample material sizes are limited. After starting an analysis, the new version of our RO-^{14}C kit can be left to autonomously complete either a thermogram measurement, or the collection of evolved CO_2 from up to five individual thermally resolved fractions. As well as reducing the likelihood of human error, this frees up time for the operator, which is of particular benefit given that the RO-^{14}C method can usually only process 1–2 samples per day.

We undertook tests to determine whether the new version of our RO-^{14}C kit produced the same results as the original kit, although we did not expect significant differences as most of the hardware of the kit including the combustion vessels, and most procedures, were unchanged. Thermograms for standard materials processed with the old and new version of the kit are visually almost identical (when normalised to eliminate the effect of sample size; Figures 2b and 2d) meaning that for routine-sized samples (< ca. 30 mg C) we can safely make comparisons of thermograms collected from both kits, without being concerned about artifacts arising from discrepancies between the kits. We stress that the new kit has retained the same temperature ramp rate (5 °C/min) as the original kit; initial tests with alternative temperature ramp rates have resulted in slightly modified thermograms with peak CO_2 concentrations occurring at different temperatures.

When processing samples that produced tens of mL of CO_2 we observed a smoothing of the thermogram which we attributed to mixing effects. This results if the CO_2 evolves at a faster rate than it is flushed from the primary combustion vessel (Figure 4). Modifying the quartz sample holder so that it is permeable at both ends, and thus allows smoother throughput of carrier gas, appears to have resolved this issue. With the new sample holder we observed that the shape of thermograms for 50 mg d/w (ca. 40 mL CO_2) barley mash standards was identical to the thermograms generated from much smaller barley mash standards, indicating consistent thermograms irrespective of sample size. Consequently, the slightly modified insert has been adopted for routine processing of all our RO-^{14}C samples.

With the new RO-^{14}C kit, we processed aliquots of the same anthracite laboratory background standard that was used to determine the ^{14}C background of the original kit. From five aliquots of the standard, the ^{14}C background of the original kit was established as 0.34 ± 0.08 pMC (Garnett et al. 2023) which was subsequently revised to 0.34 ± 0.10 pMC for use in the background correction of samples following the acquisition of more data. Five aliquots of the anthracite processed with the new RO-^{14}C kit gave a slightly higher mean ^{14}C content of 0.42 ± 0.07 pMC, although this was not statistically different, and all results fell within the 2 σ uncertainty of the routine background correction. Assuming a value of 100 pMC for the contamination in the blank (Fernandez et al. 2014), samples processed using our new RO-^{14}C kit have a total blank (i.e. all steps including AMS measurement) equivalent to 12.0 ± 0.2 µg C, which compares to 8.1± 3.3 µg C for the original kit, and literature values of 3.7 ± 0.6 µg C (Hemingway et al. 2017a) and 8.8 ± 4.4 µg C (Fernandez et al. 2014).

The higher ^{14}C background for the five anthracite standards used in the blank assessment of the new instrument may at least partly be due to a greater amount (mean 500 mL more) of carrier gas used in the new kit tests. This is due to higher carrier gas flow rates of 40 mL/min (increased from 30 mL/min) to counter the thermogram smoothing effects caused by the original sample insert. While high purity research grade oxygen (N5.5, 99.9995% purity, BOC, UK) is used for the carrier gas it could still contain up to 0.0005% (or 5 ppm) in impurities, and measurements with the SBA-5 suggest that typically 1–2 ppm CO_2 is detected after the carrier gas has passed through the combustion furnaces (although this is close to the limit of detection, and we cannot rule out other sources within the RO-^{14}C equipment). Furthermore, we have observed a significant positive relationship ($p < 0.02$) between the radiocarbon-calculated blank (µg C) and the volume of carrier gas used for anthracites from both kits ($n = 12$), which predicts a contribution to the blank of at least 2 µg C per 1000 mL of carrier gas. This mechanism explains part of the difference in the blanks for the two kits and suggests that the flow rate and volume of the carrier gas used in a combustion should be minimised and more closely regulated to ensure lower and more consistent ^{14}C blanks. However, it also confirms that other factors contribute to the ^{14}C blank. For instance, we note that when thermally partitioning anthracite the low temperature component is significantly ^{14}C-enriched compared to the high temperature part (Figure 3 and Garnett et al. 2023), even when an identical carrier gas volume was used (Figure 3). This suggests possible ^{14}C-inhomogeneity in this standard which potentially could be reduced by pre-baking (Fernandez et al. 2014), for example, to remove adsorbed CO_2. Further insight into the ^{14}C background of the new kit will be achieved as more data are acquired, however, the tests so far suggest a similar overall background contribution to the original kit. Indeed, four results for anthracites subsequently processed alongside samples using the new kit have returned ^{14}C contents of 0.13–0.43 pMC (Figure 3), and a blank of 7.9 ± 4.4 µg C which is almost identical to the original kit. Importantly, despite being produced with a wide range of carrier gas volumes (1920–4840 mL) all anthracite standards have provided ^{14}C values that fall within the 2 σ uncertainty of the background correction applied to samples (Figure 3). This confirms that the current blank correction applied to sample results correctly accounts for the small amount of processing-induced contamination, and that it should be reliable for samples collected with different carrier gas volumes (a consequence of collection over different-sized temperature ranges).

A key test of the new RO-^{14}C kit involves the radiocarbon measurement of standards of known ^{14}C concentration (or age). So far, five of our usual laboratory process standards have been analysed using the new kit, with three being thermally partitioned. All standards provided radiocarbon concentrations within 2 σ measurement uncertainty of the consensus values, indicating that the new kit is reliable for ^{14}C measurement (Table 1).

Based on the results from the above tests, we believe that our new RO-^{14}C kit, like the previous version, is reliable for the radiocarbon analysis of samples that yield at least 2 mL CO_2 (ca. 1 mg C) in each fraction. However, as a rule we aim for a minimum of 3 mL CO_2 as the higher volume allows us to archive part of the CO_2 for use in the event of a failure during graphitisation or AMS measurement.

Other developments and future plans

Our RO-^{14}C kit typically produces over thirty-thousand datapoints for every thermogram generated (since time, temperature, CO_2 concentration and flow rate are recorded every second). To manage the large amount of data generated, and enable easy access to it, we import all thermogram data into a database. Software has been developed to access the data allowing us to rapidly generate thermogram plots comparing multiple samples. Thermograms can be generated using the raw CO_2 ppm measurements, or after normalising the thermograms based on the peak CO_2 concentration or sample weight. The software also allows us to predict the amount of sample material required to generate sufficient CO_2 for radiocarbon analysis, based on the thermogram and the selected temperature windows, which has proven very useful.

We believe our current RO-^{14}C kit is performing reliably and provides high-quality radiocarbon measurements. However, the method can be further improved in a number of areas. Future development will focus on reducing the ^{14}C background of the kit, for example, by minimising the volume of carrier gas used (without affecting the thermograms), which should benefit close-to-background samples and may enable a reduction in the minimum sample size. Additionally, we are currently developing an automated method for isolating the sample CO_2 from the foil gas bags using a zeolite molecular sieve trap (Bauer et al. 1992) which should enable more efficient processing of RO-^{14}C samples.

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Data access. All data supporting this study are provided in the “Results” section of this paper.

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