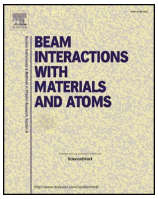
Nuclear Inst. and Methods in Physics Research B 455 (2019) 165–170

Contents lists available at ScienceDirect

Nuclear Inst. and Methods in Physics Research B

journal homepage: www.elsevier.com/locate/nimb



Investigation of the combustion of methane using CuO for radiocarbon dating

Bin Yang*, A.M. Smith

Australian Nuclear Science and Technology Organisation, Locked Bag 2001, Kirrawee DC, NSW 2232, Australia

ARTICLE INFO

Keywords:
Accelerator mass spectrometry
Radiocarbon
Methane
Carbon dioxide
Combustion
Bosch reaction
Copper oxide

ABSTRACT

For the combustion of methane (CH_4) gas to carbon dioxide (CO_2), we investigated the use of copper oxide (CuO) as the source of oxygen, using our type 2 Micro Conventional Furnaces (MCF-II), traditionally used for the reduction of CO_2 to graphite for AMS measurement Yang and Smith, 2017 [1]. Experiments showed that both graphite and CH_4 can be oxidised to CO_2 rapidly at a temperature at 780 °C. The reaction is complete within just a few minutes for graphite and within about one hour for CH_4 gas. However, this method is only suitable for combustion of CH_4 when the concentration > 3% due to the small internal volume of MCF-II. To combust gases of lower CH_4 concentration, we installed a gas circulation loop with additional components including 1) a novel, newly designed MCF-III with a dual tube furnace for heating 6 mm OD quartz tubes up to 850 °C; 2) a gas circulating unit comprising a miniature diaphragm pump and flow meter along with a needle valve for adjusting gas flow rate; 3) differently sized gas storage tubes and bags, permitting optimisation of the carbon sample size; 4) a water trap and miniature CO_2 gas traps −65 °C and −150 °C respectively Yang et al., 2013 [2]. This system is also suitable for collecting CO_2 from air at atmospheric concentrations. It also has the flexibility to assemble a specific gas trapping/combustion system to suit the composition of individual gas samples. We report on the early performance with some samples and our evaluation of the cross contamination between CO_2 and CH_4 based AMS measurement of a set of mixing gas $CO_2/CH_4/N_2$ samples.

1. Introduction

Having the capability for the measurement of the ^{14}C (radiocarbon) activity of methane (CH_4) samples opens many commercial and scientific opportunities for Australian Nuclear Science & Technology Organisation (ANSTO). Recently, a number of requests have been made by researchers and private consultants for this service which is presently not offered in Australia. Many of these studies are concerned with discriminating fossil from biogenic methane sources, for which ^{14}C is the ideal tracer. Such studies do not require high precision measurements and the sample sizes are very large for accelerator mass spectrometry (AMS) measurement. Often ^{14}C of carbon dioxide (CO_2) is requested simultaneously, as are $\delta^{13}C$ (stable isotope) analyses for both gases. Like all other ^{14}C samples measured at ANSTO, the CH_4 sample must be firstly be converted to CO_2. The final stage is conversion of the CO_2 to graphite which is then loaded into a target ('cathode') for accelerator mass spectrometry (AMS) measurement in ANSTO's Centre for Accelerator Science (CAS) platform.

A few systems have already been developed for separation of CO_2 and combustion of CH_4 to CO_2 in environmental gas samples with CuO [3–5]. We decided to design our own miniature system based upon the Micro Conventional Furnace (MCF). From a safety perspective, we needed to know how Cu(II)O to Cu(I)O behaved at high temperature and the chemical reactions that occur when CuO is heated in the presence of graphite and CH_4 gas. The decomposition of CuO in the high temperature range between 850 °C and 1100 °C has been experimentally investigated via quartz-fibre microbalance by measuring mass changes due to excess of O_2 [6]. The phase diagram of CuO, Cu_2O and O_2 was also reported in the literature [7], shows O_2 pressure vs temperature for CuO and Cu_2O. The pressure will depend largely on the ratio between mass of CuO and volume of gas reactor. To verify this result, we performed experiments directly using the MCF as a chemical gas reactor to investigate O_2 pressure as CuO was heated and cooled. Based on our experimental results, we developed a simple miniature system for separation and combustion of methane (CH_4) to CO_2 by using our novel Micro Conventional Furnace type III (MCF-III).

2. Modified MCFs for combustion

Based on our experience in developing laser heated furnaces [8,9]

---

* Corresponding author.
E-mail address: bin.yang@ansto.gov.au (B. Yang).

https://doi.org/10.1016/j.nimb.2018.12.018
Received 30 January 2018; Received in revised form 6 December 2018; Accepted 7 December 2018

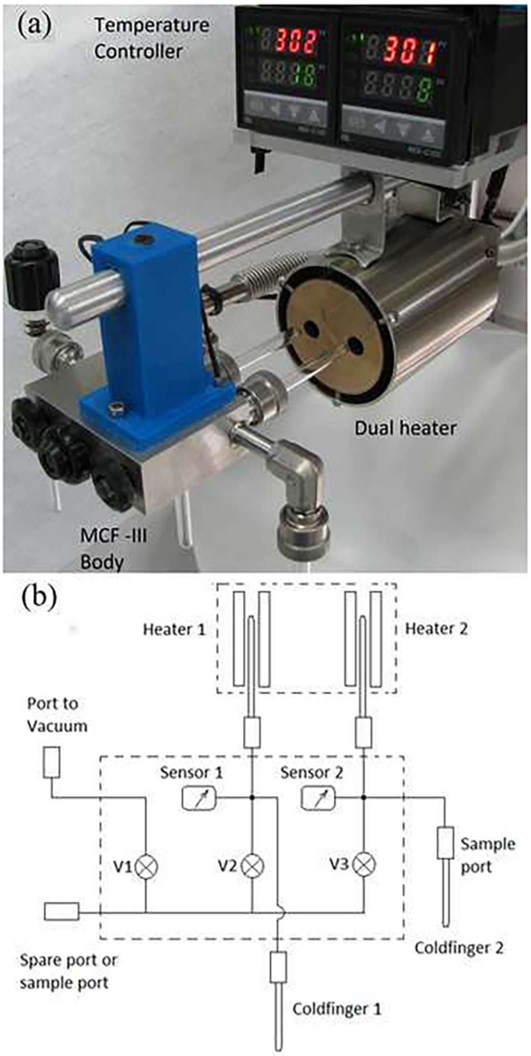


Fig. 1. a) Photograph of stainless steel body of MCF-III fitted with two pressure sensors, two front ports plus dual heaters with independent PID temperature controllers. b) Block diagram of MCF-III that has dual reactors when V2 and V3 were closed and a secondary glass cold finger was inserted into the "sample port". In this case, each of the reactors has a cold finger and a pressure sensor to monitor pressure changes during graphitisation. Therefore, it can be applied to graphitise two samples at same time. Before graphitisation, two samples should be admitted through the spare port one by one into each of the dual reactors.

for graphitisation of CO_2, the MCFs were initially designed for the graphitisation of over a wide mass range (5–2000 µg) carbon samples [1] via Bosch (H_2) reaction [10–13]. For the combustion of CH_4 and graphite samples, we modified the tube heater of MCF-II by increasing the temperature of the hot finger (T_{HF}) to 850 °C from 700 °C. The maximum depth for the quartz tube insert into the furnace is 44 mm. We normally insert about 30 mm in depth. In addition, we also developed another miniaturised heater that can heat T_{HF} to 1100 °C in order to study CuO properties at even higher temperatures. The maximum depth for the quartz tube insert into this furnace is 46 mm. Hence, MCF-II can be operated as a chemical gas reaction chamber for studying oxygen liberation and combustion processes.

In addition, we also designed and manufactured two type 3 MCF (MCF-III) for graphitisation mass range (5–2000 µg) carbon samples and for some other applications such as separation of CO_2, and combustion of CH_4. Fig. 1 shows MCF-III. Compared with MCF-II, the main differences are the following: 1) two pressure sensors are installed in each stainless steel MCF block body; 2) one additional port was opened at the front of the MCF body so that two graphitisation tubes (hot fingers) can be connected to the body; 3) the heater contains two parallel heating tubes, with the temperature of the tubes controlled by two individual PID controllers up to 850 °C; 4) the sample port can be connected with another changeable glass cold finger to form a secondary gas reactor with volume 1.8+ ml. The primary reactor has volume 1.3+ ml same as the volume of MCF-II. Hence, MCF-III provides the flexibility to be used either normally to graphitise one sample at a time or to process dual samples at one run for increasing the productivity. In the second case, two CO_2 samples were transferred through the spare port into dual reactor in sequence than to be graphitised simultaneously by the MCF-III.

3. Combustion of graphite with CuO

We apply MCF-II to investigate thermal behaviours of CuO. At ANSTO, CuO needles (1 mm OD ~ 5 mm L, Sigma-Aldrich 310433-500G) was utilised for combustion of samples. The CuO was pre-sieved to remove dust and was combusted 2 h at 600 °C in O_2 at ~1000 mbar to remove any carbon. We measured the evolved O_2 pressure as a function of the temperature (T_{HF}) for pure CuO by heating 503 mg of the CuO needles in the hot finger (a 6 mm OD, 65 mm length quartz tube, and reactor volume 1.43 mL). After evacuation to 2×10^{-5} mbar, the reactor was isolated and the reactor pressure, P_R, was recorded as T_{HF} was manually increased from room temperature (RT) to 1050 °C and then gradually decreased back to RT. The pressure curve shown in Fig. 2 indicates that 1) during heating, P_R began to noticeably increase from 2.2 mbar at $T_{HF} = 750$ °C, rising exponentially to 380 mbar as the temperature increased to 1047 °C; 2) during cooling, P_R behaved similarly for a given T_{HF}; 3) P_R was independent of the mass of CuO, over the range of 50–500 mg that we tested. This result basically agrees with the experimental data of O_2 pressure along the Cu_2O-CuO transition curve reported in the literature [7].

In the next step, we added small amount (~0.5 mg) of pure graphite with CuO into a quartz tube and recorded the pressure of CO_2 during the heating process. Fig. 3 shows the pressure curve under two conditions: a) temperature of cold finger T_{CF} = RT and b) $T_{CF} = -170$ °C

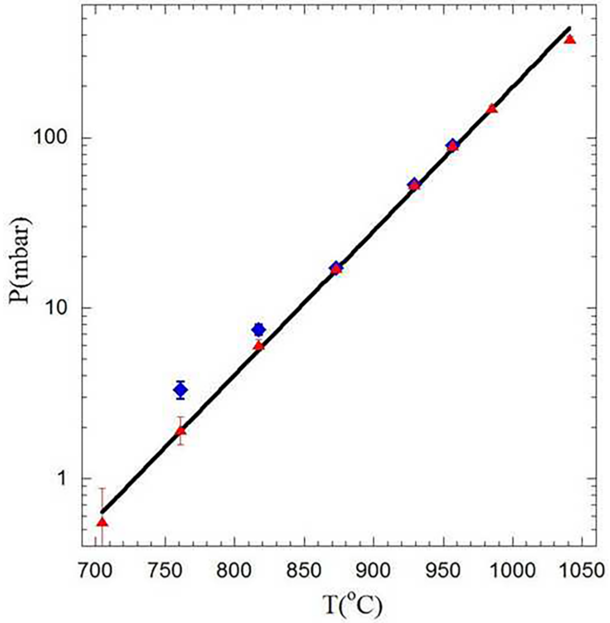


Fig. 2. Pressure of O_2 vs T_{HF} for 503 mg of CuO during heating (red triangle) and cooling (blue diamond). These results show that 1) pressure rises exponentially with increasing temperature. 2) The pressure is reversible during cooling. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

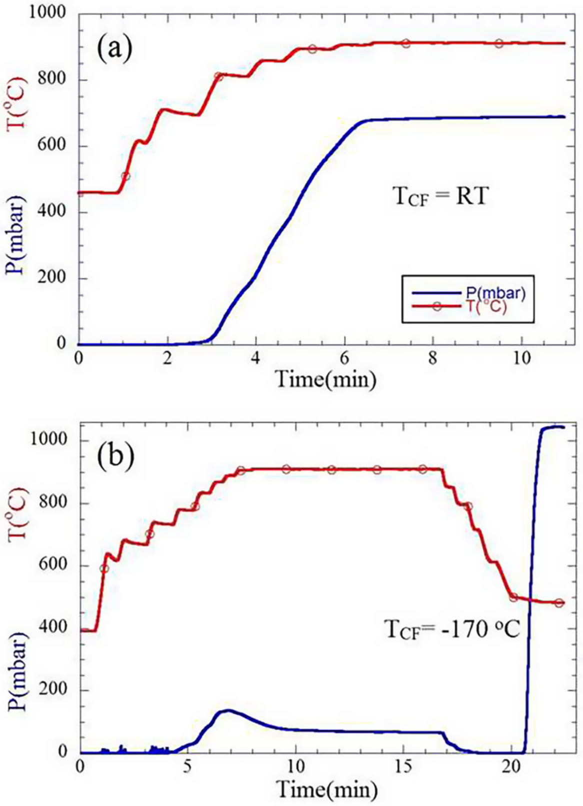


Fig. 3. Pressure changes during combustion of pure graphite with CuO under different conditions: a) T_{CF} = RT pressure rising when carbon convert to CO_2, and b) $T_{CF} = -170$ °C for trapping both water and CO_2 during oxidation. The peak may be contributed by CO, the plateau corresponds to O_2 pressure produced by CuO at the T_{HF} = 910 °C.

which will trap both water and CO_2 produced during combustion by using a miniature trap [2]. The results indicate that 1) the oxidation of graphite starts at 700 °C as CO_2 pressure rises; 2) the oxidation is complete within 10 min; 3) 100% conversion of C to CO_2 is independent of T_{CF}.

4. Combustion of CH_4 with CuO

We trialled a simple approach, loading the reactor of MCF-II with about 300 mg of CuO in a quartz tube, evacuating it to 2×10^{-5} mbar, then filling with CH_4 at atmospheric pressure from a 500 mL Cali5Bond™ GSB-P/0.5 gas sampling bag via sample port. Then, we close valve of the reactor, set $T_{CF} = -65$ °C and record the pressure of CH_4 as P_{CH4}. For combustion of CH_4, we set $T_{CF} = -130$ °C and T_{HF} = 910 °C. Fig. 4 shows that when the hot finger was heated, P_R began dropping at $T_{HF} \sim 800$ °C, with $T_{CF} = -130$ °C to trap CO_2 and H_2O. When T_{HF} rose to 910 °C, P_R dropped constantly as the CH_4 was combusted and the products CO_2 trapped. After about one hour, P_R dropped to a minimum value of 68 mbar, corresponding to P_R of pure O_2 at 910 °C. Then, we turned off the heater's power and kept $T_{CF} = -130$ °C. As we observed, when T_{HF} dropped below 710 °C, P_R decreased to zero. It indicates the absence of any residual CH_4 in the reactor. For recording P_R of CO_2 (P_{CO2}), T_{CF} was set at -65 °C again to release CO_2 and to keep H_2O trapped in the cold finger. The yield of CO_2 was calculated as ratio P_{CO2}/P_{CH4} = 99.9%. It is important to mention that $T_{CF} = -130$ °C was chosen for combustion of CH_4 to prevent partial trapping of CH_4, and yet to efficiently trap CO_2. Another experiment demonstrates that CH_4 was completely combusted within two hours with T_{HF} = 800 °C and T_{CF} = RT. This indicates that trapping CO_2 and H_2O is not necessary during the combustion. To check the combustion yield of lower concentration CH_4 in gas mixtures, we prepared a mixed gas of 18% CH_4 with 82% argon that was combusted for 2 h by MCF-II. Our results showed that 99.3% of CH_4 was converted to CO_2, demonstrating that, the MCF-II can be used for the combustion of CH_4. However, it isn't suitable for combustion of gas containing $CH_4 < 3\%$ in volume (corresponding ~70 µg carbon) because of the small volume of the reactor.

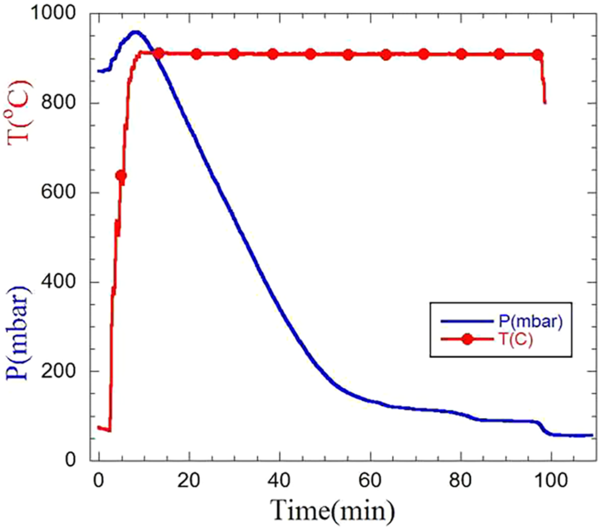


Fig. 4. Combustion of pure CH_4 with $T_{CF} = -130$ °C. There are three stages: 1) The pressure rise caused by thermal expansion as the T_{HF} increases before oxidation of CH_4 begins; 2) the rapid pressure drops as CH_4 is oxidised and the product CO_2 and H_2O is trapped in the cold finger; 3) the pressure drops to a constant value after 60 min, corresponding to the pressure of pure O_2. This implies that the oxidation is finished.

We also tried to use MCF-II for separating and combusting CH_4 in environmental samples that contain CO_2, CH_4, N_2 and other gases. This is accomplished by using an additional cold finger on a spare port of the MCF, permitting separation of CO_2, H_2O and other condensable gases from the remainder which is then isolated in the reactor and combusted. However, the experiment was unsuccessful because CO_2 could not be trapped completely into the cold finger and consequently the residual CO_2 contaminated the CH_4 gas fraction.

5. A setup for separation and combustion gas samples

Based on above experiments, we designed a gas circulation loop that can separate CO_2 and combust CH_4 at lower concentrations. This system is designed to process one gas sample at a time as presented in Fig. 5a and a block diagram in b. The loop contains the following components: 1) MCF-III with dual tube furnaces for heating 6 mm OD U-shaped quartz tubes (been packed with CuO) which pass through the furnace to combust the gas twice for improving the efficiency of the combustion; 2) a gas circulating unit including a model of a miniature diaphragm pump (D-pump) and flow meter along with a needle valve for adjusting the gas flow; 3) differently sized gas storage tubes and bags to permit optimisation of the carbon sample size; 4) a water trap operating at -70 °C (dry ice/ethanol) and 5) two miniature CO_2 traps by using a pair of (6 mm OD, 65 mm length) micro traps inserted into cold finger coolers, operated in the range -170 °C and -60 °C. Two CO_2 micro traps are used in line to increase trapping efficiency and eventually to reduce cross contamination of CH_4 fraction by residual CO_2 gas. This system has the flexibility to be assembled in different ways to build a specific gas trapping/combustion system to suit the composition of individual gas samples.

As an example, we tested an open loop for trapping CO_2 from air. About 500 mL air was collected into a 500 mL gas sampling bag, then

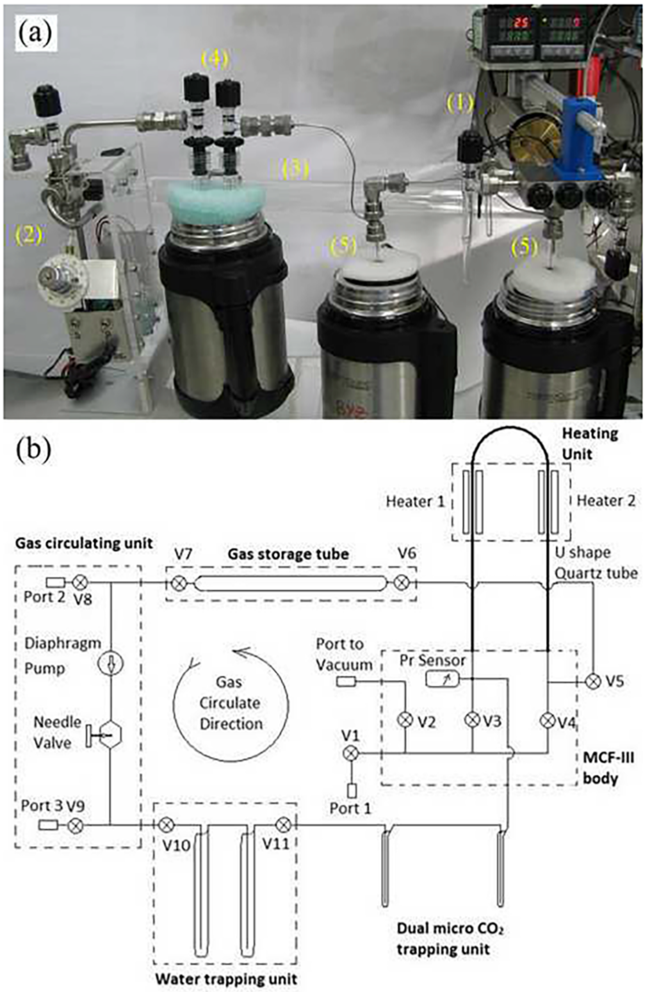


Fig. 5. a) Over view of the loop and b) block diagram of the loop system that contains 1) MCF-III with a dual tube furnaces for combustion CH_4 inside the U-shaped quartz tubes that was packed with CuO 2) a gas circulating unit; 3) gas storage tubes 4) a water trap, operating at −70 °C degree C (dry ice/EtOH) and 5) Two miniature CO_2 traps, operating at $T_{CF} = -150$ °C. The temperature of the dual furnaces were set at RT, 400 °C and 780 °C for separation of CO_2, combustion of CO and combustion of CH_4 respectively.

connected to port 2 as an inlet gas, with another empty sampling bag connected to port 1 as an outlet; closing V2, V3, V5, V6, V7, V9 and opening V1, V4, V10 and V11. Then, the air sample was pulled through the line by turning on the D-pump and setting water trap at −70 °C and a pair of CO_2 traps at −150 °C that are optimised to freeze CO_2 efficiently. After about 15 min, the air sample was moved completely from the inlet bag to the outlet bag and more than 93% of CO_2 was collected in the pair of cold fingers. After transferring the CO_2 gas from the cold fingers to a storage vessel, we switched the two bags and made a second run for another 15 min to collect the remaining of ~7% of CO_2 from the outlet bag. The efficiency (*Ef* = 93%) was calculated by equation: $Ef = m_{1st}/(m_{1st} + m_{2nd})$, where, m_{1st} and m_{2nd} is carbon mass collected in first and second run respectively. Combining m_{1st} and m_{2nd}, we obtained more than 99% of CO_2 from the air sample for graphitisation by using other MCF. Applying this method, we analysed an air sample collected from ANSTO campus on 6th March 2017 and obtained a reasonable pMC value of 103.22 ± 0.30.

To evaluate separation and combustion efficiency, we prepared a known gas sample mixture inside the loop that was pre-evacuated to a pressure below 1×10^{-4} mbar. CO_2 was transferred into the loop through port 1 and froze it in the micro cold finger. CH_4 was transferred to the loop by using a gas storage tube of ~270 mL. With the volume of the whole loop ~300 mL, the pressure of 2.8 mbar equates to 350 mgC. Next, high purity N_2 was admitted to $P_R \sim 1000$ mbar and the three gases were mixed homogenously by circulating them in the loop for 10 min with both the heater and cooler off.

For trapping the CO_2 fraction from the gas mixture, we kept the dual heater off, closed V1, V2 V3, V4, V8 and V9; opened V5, V6, V7, V10 and V11 to form a closed loop so that the gas could be circulated inside the loop. We trapped H_2O and separated CO_2 from the gas mixture by turning on the D-pump with a flow rate about 30 mL/minute, setting the water trap at −70 °C and CO_2 trap at −150 °C; after 40 min, we stopped the D-pump and collected the first fraction of CO_2. To get optimised temperature for trapping CO_2 in the loop, we tested previously a few different temperatures between −120 °C and −150 °C. As we found that it is crucial to set trap temperature at −150 °C to ensure only CO_2 is trapped without any CH_4 or O_2. Because of the operating conditions (near 1000 mbar of pressure), if liquid nitrogen is used instead, both CH_4 and O_2 will be trapped significantly along with CO_2.

To freeze CO_2 in a sample vessel from the cold fingers, we applied 5 steps: 1) connect the sample vessel to port 1 and close V11 and V5; 2) set $T_{CF} = -170$ °C for frozen CO_2 in the two cold fingers, open V2, V1 and V3 in sequence to evaluate any incondensable gas in the part of the loop; 3) close V3 and set $T_{CF} = -65$ °C so that the CO_2 was released from cold fingers; 4) close V2, open V3 and freeze CO_2 into the sample vessel by liquid nitrogen; 5) close V1 and open V2 to evaluate the part to $Pr = 5 \times 10^{-5}$ mbar for next run. It is important to pre-remove incondensable gas in order to transfer CO_2 effectively.

To combust CH_4 and to collect CO_2 of this fraction, we close V1 and V3, open V5 and V11, set the two cold fingers at −150 °C, set temperature of the dual heater at 780 °C, and turn on the D-pump to circulate the sample gas again. In this run, the CH_4 was eventually converted to CO_2 inside a U-shaped quartz tube (6 mm OD) with ~1g of pre-sieved CuO needles at 780 °C; CH_4 derived CO_2 was trapped into the two micro cold fingers. The dual heater was used for improving efficiency of the combustion, because effective heating length for each of the heater is only 40 mm. It was observed that the amount of CuO can be used to combust at least three gas samples without being changed or refreshed, by combusting it at 600 °C in O_2. The CuO was also combusted in air at 600 °C for 30 min between samples. After 40 min, we transfer the second fraction of CO_2 that was trapped in the cold fingers for AMS measurement. It takes about 3 h to process each environmental gas sample in this way.

6. Results and discussion

To characterise the gas circulation loop and evaluate the cross contamination CO_2/CH_4 and extraneous carbon added (system background) and memory during the processing, we used four gases: a) 'blank or dead' CO_2 (activity = 0.03 ± 0.01 pMC) from a gas cylinder (99.5% purity), b) 'modern' CO_2 produced by combustion of OX2 standard (activity = 134.06 ± 0.04 pMC), c) 'blank' CH_4 (activity = 0.23 ± 0.04 pMC) from a gas cylinder (99.9% purity) and 'modern' CH_4 (activity = 103.73 ± 0.4 pMC) landfill gas from Energy Developments Pty Limited near ANSTO. High purity (99.9%) N_2 was used to dilute these gases. The samples were processed in three ways, were reported in Table 1: a) (No. 1–4) Standard CH_4 blank and modern, also diluted with N_2 to evaluate extraneous carbon added from the environment (air in laboratory) and from the N_2 gas, b) (No. 5) 120 µgC blank CH_4 was combusted following with combusting of 900 µg C of modern CH_4 and diluted them in ~1000 mbar of N_2 to quantify the system memory between the modern and the blank CH_4 during combustion, c) to quantify the contamination CO_2/CH_4 caused by separation, two gas samples was prepared by mixing (No. 6–8) modern CO_2 (by oxidation of OX2) with blank CH_4, (No. 9–11) modern CH_4 with blank CO_2 and diluted them in N_2 to a volume ratio between 0.1% and 0.4%. Samples 1 and 4 were combusted by MCF-II. All the other samples were processed by circulating gas in the loop with MCF-III. Based

Table 1

Measured radiocarbon activities and calculated cross-contamination for separated fractions, assuming $\delta^{13}C = -25‰$ for all pure gases and gas mixtures. No. 1: Standard blank CH_4 gas with 99.9% purity was combusted directly by MCF-II; No. 2: The blank CH_4 (0.3% in volume) with N_2 (99.7%), were combusted in the circulation loop. The C mass of contamination from air was calculated by the equation: *323 × (0.37–0.23)/(100–0.23)*; No. 3: Standard modern CH_4 gas with 71% purity was combusted directly by MCF-II; No. 4: 0.1% of blank CO_2 gas was mixed with N_2, then was separated by the circulation loop. The contamination from air (assuming pMC = 100) was calculated by the equation: *112.1 × (0.53–0.03)/(100–0.03)*; No. 2 and 4 indicate that only about 0.5–0.6 µg of carbon contamination from air (system background) during separation and combustion process. No. 5 The cross contamination (memory) between modern and blank CH_4 was evaluated by: *117.3 × (0.93–0.23)/(103.73–0.23)*; No. 6: mixture of three gases, the cross contamination is obtained: *240.6 × (2.41–0.23)/(134.06–0.23)*; No. 9 The contamination is calculated: *282.3 × (103.73–102.64)/102.64–0.03)*.

Sample no.	Sample type	Gas composition	CH_4 fraction			CO_2 fraction			Cross contamination		
			C mass [µg]	Activity [pMC]	Error [pMC]	C mass [µg]	Activity [pMC]	Error [pMC]	C mass [µg]	Ratio %	Assumed activity [pMC]
1	Pure standard gas or mixed with N_2	Blk CH_4 99.9%	336.8	0.23	0.04	0.0					
2		Blk CH_4 0.3% + N_2	323.0	0.37	0.04	0.0			0.5	0.14	100.0
3		Mod CH_4 71%	245.3	103.73	0.40						
4		Blk CO_2 0.1% + N_2	0.0			112.1	0.53	0.04	0.6	0.50	100.0
5	Cross contamination	Blk CH_4 post combust. Mod CH_4	117.3	0.93	0.05				0.8	0.68	103.7
6	OX2 CO_2 + Blk CH_4	Blk CH_4 0.2% + Mod CO_2 0.3% + N_2	240.6	2.41	0.10	367.0			3.9	1.63	134.1
7		Blk CH_4 0.3% + Mod CO_2 0.3% + N_2	269.3	2.57	0.06	347.0			4.7	1.75	134.1
8		Blk CH_4 0.6% + Mod CO_2 0.2% + N_2	435.0	0.99	0.04	280.5	134.95	0.45	2.5	0.57	134.1
9	Mod CH4 + Blk CO_2	Blk CO_2 0.25% + Mod CH_4 0.3% + N_2	282.3	102.62	0.35	234.0	0.88	0.04	3.1	1.08	0.03
10		Blk CO_2 0.4% + Mod CH_4 0.3% + N_2	189.0	99.57	0.39	360.3	1.22	0.05	7.9	4.18	0.03

on the measured ^{14}C activity of the samples and assuming $\delta^{13}C = -25‰$ for all pure gases and gas mixtures, the calculated mass of C introduced by cross contamination is listed in Table 1.

Mass of carbon in Table 1 was calculated in the following way. If we combine two carbon sources (CO_2 gases) that have carbon mass and pMC value: m_1, pMC_1 and m_2, pMC_2 respectively, than after mixed the two sources, we have:

$$pMC_3 \times (m_1 + m_2) = pMC_1 \times m_1 + pMC_2 \times m_2$$

where, pMC_3 is the post-mixed pMC value. In addition, we have the total mass of the mixture:

$$M = m_1 + m_2$$

Based on the above two equations, we can get:

$$m_1 = M \times (pMC_3 - pMC_2)/(pMC_1 - pMC_2)$$

And

$$R = m_1/M = (pMC_3 - pMC_2)/(pMC_1 - pMC_2)$$

where, m_1 is carbon mass of cross contamination; R is relative value of the contamination; pMC_1 is the value of contamination source.

The result of No. 1–4 indicates that the extraneous carbon added from the environment (air, assuming pMC = 100) and from the N_2 gas is less than 1 µgC, much less than the carbon mass of sample. Therefore, the extraneous carbon from air added during separation/combustion process (system background) is not an issue. It also can be concluded that the purity of the N_2 gas is sufficient for this experiment. Result of No. 5 shows that the cross contamination from 900 µg modern CH_4 to 120 µg of blank CH_4 is only 0.8 µg. It indicates system memory isn't significant. However, the cross contamination CO_2/CH_4 (No. 6–8) is a few times higher than the system background. It is clearly caused by that CO_2 has not been completely removed from gas before the combustion of CH_4. The modern CH_4 fraction for samples No. 9–10 suggest some blank (dead) carbon contamination. The source of blank carbon isn't from air but from the pre-mixed blank CO_2 gas. Similar as No. 6–8, this result confirmed the problem of contamination between CO_2 and CH_4 because the blank CO_2 hasn't been removed clearly in first run. The residual blank was mixed with modern CH_4 derived CO_2 in the second run and inducing the contamination.

Compared with the flow-through process line [3], our system has very high cross contamination CO_2/CH_4. However, our system has a much simpler structure, is smaller in size and has an adjustable CO_2 trapping temperature. It is suitable for the ^{14}C analysis of gas samples that do not require high precision measurements, for example to discriminate fossil from biogenic methane sources.

In recent experiments, a few ways were found to improve CO_2 trapping efficiency: 1) loading glass beads (1.5 mm in diameter) into two cold fingers and 2) improving water trapping efficiency by increasing length of water trap and 3) increasing time of circulation for CO_2 trapping. The contamination between CO_2 and CH_4 can be reduced by 2 or 3 fold. In the future, for high accuracy measurements, we may insert a glass tube filled with soda-lime [4] in the loop to remove residual CO_2 gas before combustion of CH_4.

To deal with carbon monoxide (CO), methanol and ethanol gas existing in the natural CH_4 samples [3], we tried to combust of pure CH_4 at 400 °C with CuO in the loop. The result confirms that CH_4 cannot be oxidated at all at this temperature. For combustion CO, an environmental gas was loaded into the loop; CO_2 fraction was pre-removed the through a run. Then, the gas was circulated again with T_{HF} = 400 °C to combust CO. After 30 min, amount of CO_2 was trapped, was produced by oxidation of CO and/or other organic fractions in the gas. Therefore, with an additional circulating/combustion at 400 °C, we can remove CO and may be some organic fractions from the environmental gas and collect CO_2 for AMS measurement. However, it is unable to discriminate between CO and other organic fractions unless a Gas Chromatography been applied.

7. Summary

We measured O_2 pressure as a function of the temperature from 700 °C to 1050 °C for pure CuO in an equilibrium state in a fixed reactor volume. The pressure increased exponentially up to 370 mbar with the T_{HF} = 1047 °C, in good agreement with the literature [6,7]. The oxidation of pure graphite with CuO at temperature 780 °C or higher is very fast, with the reaction complete in just a few minutes. This result indicates that the combustion of conventional radiocarbon samples with CuO can be completed at 800 °C within 20 min, important for processing samples rapidly. High concentration CH_4 gas is easily combusted at 780 °C with CuO. For radiocarbon dating, CH_4 gas can be completely converted to CO_2 within 1 h in a sealed quartz tube. For separation of CO_2 and combustion of CH_4 gas, we made and tested a miniature loop. It can be used to extract CO_2 from air and to combust of low concentration CH_4 gas. However, the cross contamination between CO_2 and CH_4 needs to be reduced if high precision measurements are to be achieved.

Acknowledgements

We acknowledge the financial support (Portal number 10106) from the Australian Government for the Centre for Accelerator Science at ANSTO through the National Collaborative Research Infrastructure Strategy (NCRIS), Australia. We are very grateful for discussions with Mr Alan Williams concerning safety and experimental details for the combustion of CH_4 gas.

References

[1] B. Yang, A.M. Smith, Radiocarbon 59 (3) (2017) 859–873.
[2] B. Yang, et al., Nucl. Instr. Meth B 294 (2013) 262–265.
[3] M.A. Pack, et al., Org. Geochem. 78 (2015) 89–98.
[4] M.H. Garnett, S.M.L. Hardie, C. Murray, M.F. Billett, Biogeochemistry 114 (1–3) (2013) 213–223.
[5] K.W. Anthony, R. Daanen, P. Anthony, T.S. Deimling, C.L. Ping, J.P. Chanton, G. Grosse, Nat. Geosci. 9 (2016) 679–682.
[6] M. O'Keeffe, W.J. Moore, J. Chem. Phys. 36 (1962) 3009.
[7] R.D. Schmidt-Whitney, M. Martinez-Clemente, A. Revcolevschi, J. Cryst. Growth 23 (1974) 133–1120.
[8] A.M. Smith, B. Yang, Q. Hua, M. Mann, Radiocarbon 52 (2010) 769.
[9] B. Yang, A.M. Smith, S. Long, Nucl. Instr. and Meth. B 361 (2015) 363.
[10] M.P. Manning, R.C. Reid, Industr. Eng. Chem. Process Design Dev. 16 (3) (1977) 358–361.
[11] J.S. Vogel, J.R. Southon, D.E. Nelson, T.A. Brown, Nucl. Instr. Meth. B 5 (1984) 289.
[12] A.M. Smith, V.V. Petrenko, Q. Hua, J. Southon, G. Brailsford, Radiocarbon 49 (2007) 245.
[13] A.M. Smith, Q. Hua, A. Williams, V. Levchenko, B. Yang, Nucl. Instr. Meth. B 268 (2010) 919.