

ONLINE COUPLING OF PURE O₂ THERMO-OPTICAL METHODS – ¹⁴C AMS FOR SOURCE APPORTIONMENT OF CARBONACEOUS AEROSOLS

Konstantinos Agrios ^{1,2,3} • Gary Salazar ^{1,2} • Yanlin Zhang ^{1,2,3,#} • Chiara Uglietti ^{1,2,3} • Michael Battaglia ^{1,2} • Marc Luginbühl ¹ • Viorela Gabriela Ciobanu ^{3,*} • Matthias Vonwiller ^{1,2,3} • Sönke Szidat ^{1,2,4}

1. Department of Chemistry and Biochemistry, University of Bern, Bern, Switzerland.
2. Oeschger Centre for Climate Change Research, University of Bern, Bern, Switzerland.
3. Paul Scherrer Institute, Villigen, Switzerland.
4. Corresponding author szidat@dcb.unibe.ch

Now at: Yale-NUIST Center on Atmospheric Environment, Nanjing University of Information Science and Technology, 210044 Nanjing, China

* Now at: Centre for Ice and Climate, Niels Bohr Institute, University of Copenhagen, Copenhagen, Denmark

Accepted version

Published in

Nuclear Instruments and Methods in Physics Research B 361 (2015) 288-293

<http://dx.doi.org/10.1016/j.nimb.2015.06.008>

ABSTRACT

This paper reports on novel separation methods developed for the direct determination of ^{14}C in organic carbon (OC) and elemental carbon (EC), two sub-fractions of total carbon (TC) of atmospheric air particulate matter. Until recently, separation of OC and EC has been performed off-line by manual and time-consuming techniques that relied on the collection of massive CO_2 fractions. We present here two on-line hyphenated techniques between a Sunset OC/EC analyzer and a MICADAS (**MI**ni radio**CA**rbon **DA**ting **S**ystem) accelerator mass spectrometer (AMS) equipped with a gas ion source. The first implementation facilitates the direct measurement in the low sample size range ($<10 \mu\text{g C}$) with high throughput on a routine basis, while the second explores the potential for a continuous-flow real-time CO_2 gas feed into the ion source. The performance achieved with reference materials and real atmospheric samples will be discussed to draw conclusions on the improvement offered in the field of ^{14}C aerosol source apportionment.

Keywords: Radiocarbon; Aerosols; Organic Carbon; Elemental Carbon; Hyphenation

INTRODUCTION

The carbonaceous aerosol (total carbon, TC) and its sub-fractions organic carbon (OC) and elemental carbon (EC) constitute a significant portion of the atmospheric fine air particulate matter, influencing the global climate and human health [1, 2]. The application of radiocarbon (^{14}C) in the field of carbonaceous aerosols is different from radiocarbon dating. Emission sources of OC and EC fractions can be traced back by different radiocarbon levels, as ^{14}C is extinct in emissions from fossil-fuel usage, whereas carbonaceous aerosols from modern material are on the contemporary ^{14}C level. Therefore, ^{14}C characterization provides an unambiguous quantification of fossil and non-fossil aerosols sources. As the partition of these two source types is often quite different for OC and EC, it is necessary to perform radiocarbon measurements on both fractions individually [1, 2].

For this type of analysis, we take advantage of the new Accelerator Mass Spectrometer AMS facility MICADAS at University of Bern [3] and its gas-accepting ion source for the direct analysis of CO₂ gas, eliminating the need to graphitize samples. The existing gas introduction system (GIS) [2] has been lending itself very well to the hyphenation with a variety of analytical instruments throughout several joint works between University of Bern and ETH Zurich [3-7]. This allows aerosol analysis with high sample throughput, which substantially improves the source apportionment by ¹⁴C. However, sample preparation is still impeded by the use of manual cryogenic CO₂ trapping deriving from the THEODORE setup [8]. This **Two-step Heating** system for the **EC/ OC Determination of Radiocarbon in the Environment** was used until recently for the production of CO₂ ampoules after being coupled to the combustion instrument. The subsequent use of a semi-automatic ampoule cracking apparatus further made the methodology more complex for environmental routine analysis.

We present here two different methodologies for the direct coupling of an Organic Carbon/Elemental Carbon (OC/EC) analyzer using pure O₂ as carrier gas to the AMS gas ion source following the recent installation of a 200 kV MICADAS facility in the University of Bern [3]. By using these methods, we demonstrate that it is feasible to bypass CO₂ cryogenic trapping and ampoule cracking methodology for the measurement of real atmospheric samples as an improvement of an older work [7]. Additionally, for a first series of reference materials analysis, CO₂ gas is directly fed into the ion source without using the GIS. Both methods are best suited to large series of environmental samples ~5-100 µg C.

MATERIALS AND METHODS

The OC/EC analyzer and trapping offline ¹⁴C analysis

Our group uses a thermo-optical OC/EC analyzer (Model4L, Sunset Laboratory Inc., USA) [9].

This instrument produces CO₂ gas as combustion product of atmospheric filters. In this study, we

used a temperature program of one step at 760 °C for 170 s for total carbon combustion and an OC/EC thermo-optical separation program of 4 thermal steps (Swiss_4S) developed and characterized previously [1]. For the total carbon combustion program, the carrier gas is pure O₂ (99.9995 %). For the Swiss_4S protocol, the carrier gases used are pure O₂ for steps 1, 2 and 4 and He (>99.999 %, pre-cleaned with a moisture/O₂/hydrocarbon trap) for step 3. The filter transmittance is monitored by a 660-nm tuned-diode laser. The gas flow parameter of the OC/EC analyzer is set at 60 mL/min. The gaseous carbonaceous species released from the combustion pass through a MnO₂ bed heated to 850 °C and get oxidized to CO₂. The CO₂ fractions are then detected and quantified by a non-dispersive infrared (NDIR) detector before being released to the GIS. The CO₂ can then be trapped cryogenically and, later on, transferred and sealed in glass ampoules. CO₂ samples prepared in this way are introduced in the GIS via means of an ampoule cracker, which utilizes mechanical bellows to crack delicately the glass vessel. We denote this method as trapping offline, which we used in previous studies [e.g., 1, 2].

For the validation of both systems, trapping online and continuous-flow coupling, we prepared aqueous solutions of C7 (oxalic acid), C6 (sucrose) as well as combusted grains of C5 (wood) as such in the sample holder (all reference materials from the International Atomic Energy Agency, IAEA) and aqueous solutions of oxalic acid 2 (HOx2, reference material SRM 4990c, National Institute of Standards and Technology, NIST) and fossil sodium acetate, (NaOAc, p.a., Merck, Germany) in the range of 2-10 g/L. For the aqueous solutions, we then pipetted 5-10 µL on 1.5 cm² prebaked quartz-fiber filters before inserting them in the OC/EC analyzer. The filters were then dried for 2 min before initiating a total carbon combustion temperature program by a dedicated drying program of the Sunset OC/EC analyzer. This approach is contrasting the online trapping from [7], where the punches were dried in a flow box, thus exposing the filter to contaminant volatile organic compounds.

For the validation of the trapping online method, we used filters from 2010-2011 that were part of a five-years Swiss air pollution study and were collected with high-volume samplers for 24 h on quartz fibre filters [2]. After the sampling, all filters were wrapped in aluminium foil, packed in air-tight polyethylene bags and stored at $-18\text{ }^{\circ}\text{C}$. All filters were heavily loaded with particulate matter (typical loading: $30\text{-}100\text{ }\mu\text{gC}/\text{cm}^2$ and $10\text{-}30\text{ }\mu\text{gC}/\text{cm}^2$ for OC and EC, respectively). For the analysis, one single 1.5 cm^2 quartz filter punch per sample was used.

Trapping online CO₂ via GIS

In the trapping online method, the CO₂ is collected in a zeolite trap of the GIS (Figure 1). The control of the GIS and the communication with the Sunset Analyzer and the MICADAS is performed by a LabView program. The carrier gas flow of the OC/EC analyzer is set to 60 mL/min measured after the CO₂ trap with an electronic flow meter (Restek, USA). When connected to the CO₂ trap, the OC/EC analyzer exhibits a backpressure of 200 hPa. This was in agreement with similar findings of [7], where the operators observed a backpressure of 240 hPa – albeit while using a different Sunset OC/EC analyzer model (i.e., RT 3080, Sunset Laboratory Inc, USA). Due to this, a prime/purge solenoid valve used by the instrument for switching the flow from the combustion tube to the NDIR or to the vent leaked a significant portion of the gas to the vent during our first tests. This resulted in a 50 % loss in CO₂ recovery. On account of that, the OC/EC analyzer connection was adjusted in order to bypass the valve and lead the combustion products directly to the NDIR detector without purging option. The internal calibration constant of the instrument requires correction by a factor of 0.8 based on analyzing known amounts of sucrose solutions (multi-point calibration with 3 repetitions of 10, 20 and 40 $\mu\text{g C}$ yielding sucrose solutions, D(+)-Sucrose, Fluka Analytical) under that backpressure. There is another pressure increase of about 20-30 hPa on heating the sample (Figure 5) due to the thermal expansion of the gas. This is taken into consideration for recalibrating the instrument by

commencing trapping of each fraction after the pressure has equilibrated.

A 2 m 1/8" I.D. stainless steel tube directs the CO₂ fractions into the zeolite trap after previously passing through a water trap (Sicapent, Merck, Germany). The connection starts with a 1/8" O.D. stainless steel tube ending in a 1/8" x 1/16" reduction union about 30 cm before the CO₂ trap. The 4-port 2-way valve (VICI, USA) (valve A) positioned after the OC/EC analyzer performs the interchangeable connection between the OC/EC analyzer and the CO₂ trap or the vent. A He stream flushes the line to the GIS whenever the OC/EC analyzer is vented so that air contamination is minimized. By switching valve B, the OC/EC analyzer combustion products pass through the CO₂ trap while analyzing a fraction of interest. The syringe cleaning from remains of the previous sample is conducted in parallel with the trapping. After collection is complete, valve B is switched to the atmosphere and the trap is back-flushed with He at room temperature to minimize contamination from other adsorbed combustion products or O₂ traces from the carrier gas.

We use the trapping online hyphenation for the measurement of ¹⁴C from reference materials and water-extracted filters prepared and analyzed by the Swiss_4S method [1]. Alternatively, for standard material measurements, a total carbon combustion program allows for the total carbon load of a filter to be desorbed and quantified as one single peak. 50 seconds before the commencement of the temperature ramp, the OC/EC analyzer outlet is directed to the packed CO₂ trap by switching valve B. This period is adequate for pressure stabilization before the loading of a CO₂ fraction on the trap. The OC/EC analyzer outlet remains connected to the CO₂ trap for 1 minute after the peak has been fully resolved in the NDIR spectrum. At this moment, valve B is switched automatically to the atmosphere.

Continuous-flow coupling of the OC/EC analyzer with the MICADAS

The continuous-flow coupling scheme explores the potential of real-time injection of CO₂ fractions without using CO₂ enrichment steps. For a continuous-flow coupling, the CO₂ mixed with the O₂ carrier gas passes through a heated Cu reactor that scrubs the O₂ away prior to injection into the ion source. A substantial improvement arises from continuous-flow ¹⁴C measurements of the thermograms provided by the commercial Sunset OC/EC analyzer, as the averaging of the ¹⁴C signal over trapped fraction is omitted. However, real-time ¹⁴C measurements are currently hindered by the fact that the gas flow outlet of the Sunset OC/EC analyzer is about two orders of magnitude higher than what may be tolerated by the gas ion source. Additionally, the nature of the carrier gas (pure O₂) renders ionization problematic so that O₂ shall be removed prior to injection.

The heart of this implementation (Figure 2) lies on a vertically positioned quartz tubular reactor (11 × 300 mm) filled with 25 g Cu fine wires (Elementar AG, Germany) that are kept in position by quartz wool plugs on both sides. The Cu bed has a length of 140 mm and is enclosed in a resistively heated coil oven (12 I.D. × 150 mm) that heats the Cu on average at 580 °C throughout the hot zone that encloses the reactor. At this temperature, the Cu scrubs the combustion gases from free O₂ via the reaction $2\text{Cu} + \text{O}_2 \rightarrow 2\text{CuO}$. Furthermore, it reduces nitrogen oxides to elemental nitrogen, while CO₂ remains unchanged. A supplementary minimal He flow of 0.5 mL/min regulated by a mass flow controller (Alicat Scientific Inc., USA) is added before the Cu reactor to carry the CO₂ into the ion source. The He gas is supplied via 0.1 mm I.D. / 0.363 mm O.D., 5 mm long fused silica capillary coaxially fitted into a 1/16" O.D., 0.13 mm I.D. PEEK tube sleeve. The low He flow and the exhaust stream from OC/EC analyzer meet in a 1/8" tee (Swagelok, USA), the outlet of which is connected to the Cu reactor. Valve A interchangeably connects the Cu reactor to the OC/EC analyzer or to a He stream of 10 mL/min when the instrument is vented. The reactor ends in a narrow 1/8" I.D. and 70 mm long quartz

nozzle that is connected with the ion source fused silica capillary by a 1/16" O.D., 0.13 mm I.D. and 900 mm long PEEK tube, which also serves as an insulator for the transfer from ground potential to about -40 kV inside of the ion source [6].

Initially, the Cu reactor is being flushed by an external He stream at medium flow (10 mL/min), which exits to the atmosphere via an open valve (B) that serves as an artificial leak after the reactor. Prior to the analysis, the OC/EC analyzer is purged with 60 mL O₂ for 2 min, while valve A is switched to the atmosphere. On initiating the actual measurement, valve A is switched to the Cu reactor and the medium flow He stream is turned off. The O₂ flow is then recorded by a digital flow meter (Restek, USA) at the leak valve after the Cu reactor. At that moment, two carrier gas streams are passing from the Cu-filled compartment: the O₂ from the instrument and an additional minimal He flow of 0.5 mL/min. It should be noted that after switching valve A to the Cu reactor the oxygen background needs around 150 s to be reduced to 0 mL/min. The leak valve is then closed and the heating of the filter begins ~50 seconds later. For the continuous-flow online coupling, the carrier gas flow of the OC/EC analyzer is set to 20 mL/min of pure O₂. Under these flow conditions, the active lifetime of the reactor filled with 25 g of Cu is sufficient for the injection of 35 total carbon combustion analyses (5 minutes analysis time), which is equivalent to a total capacity of ~3 L of O₂.

RESULTS AND DISCUSSION

Trapping online measurements

Carbonaceous fractions separated as described above were analyzed by AMS. ¹⁴C results are reported as percent Modern Carbon (pMC) that is derived as the ratio of ¹⁴C/¹²C measured in the samples to the ¹⁴C/¹²C ratio in 1950, which is defined as 0.95 times the value of the contemporary standard SRM4990B, multiplied by 100%.

Table I presents the measurements of different standard materials as unknowns. In general, the nominal pMC values lay well within the $1\text{-}\sigma$ uncertainty range of the measured values. The ^{14}C pMC values and the standard deviation of all analyses for the certified standards were calculated from 3 injections per sample that were combined and averaged.

For the determination of cross contamination and constant contamination contributions of the system, we combusted solid grains of a fossil NaOAc and the modern reference material NIST-HOx2 for different sample sizes and followed the procedure as in [11] (Figure 3). The constant contaminant mass was estimated as $0.4\pm 0.2\ \mu\text{g C}$ with a ^{14}C value of $80\pm 36\ \text{pMC}$. The mass of the constant contamination is slightly higher than for the trapping offline method (i.e., $0.055\ \mu\text{g C}$ at $50\ \text{pMC}$ [6]), as the zeolite trap introduces a larger uncertainty than the ampoule sealing-cracking method [11]. After analyzing fossil and modern samples alternately, 0.5% of the carbon of the previous sample was found to mix and cross contaminate the next injection (cross contamination factor, $\varphi = 0.5\pm 0.4\%$). Both parameters, the constant contamination and the cross contamination, induce slightly higher measurement uncertainties than the trapping offline method especially for very small samples ($<5\ \mu\text{g C}$), which are typically negligible though compared to other uncertainty components for such small samples. Consequently, no significant changes in the analytical precision and accuracy are to be expected in comparison with [6].

In general, the method is improved compared to a previous proof-of-principle study [7], which discussed how a coupling of a Sunset OC/EC analyzer with the AMS MICADAS may be realized by measuring a pair of standards. It reported difficulties with operation of the Sunset OC/EC analyzer under high backpressure, which is now solved by using a different Sunset model and modifying the internal valve setup of the instrument (see above). Further technical improvements involve exchange of the water trap at the outlet of the Sunset instrument and a fully automatic control of the interface with the LabView program. Moreover, we now achieve

$^{12}\text{C}^+$ currents that are higher by an order of magnitude and a constant contamination contribution to the blank that is a factor of 5 lower than what was reported in [7].

The performance of the trapping online setup is evaluated by ^{14}C measurements of filter samples that had been measured in the past. Older results [2] obtained by the offline technique were compared with our method (Figure 4). While the OC measurements agree well, the measured ^{14}C of EC samples in the low pMC value range seem to tend towards lower values than the reference. However, the dataset is too small to determine, whether this deviation is significant. Figure 5 compares a typical thermogram of a water-extracted filter analyzed by both methodologies. It seems that there is a slightly greater loss of native EC at step 2 and a subsequent lower EC yield during step 4 as indicated by the laser signal. Apart from that, the peak resolution is maintained and the laser course does not indicate any significant difference in charring elsewhere. The system experiences higher backpressure during the trapping times, a fact that does not alter the resolving power of the system. For both methods, the exhaust is let to the atmosphere during the He step of the Swiss_4S protocol by switching valve A while keeping the trap flushed with 10 mL/min He. This is due to excessive flow restriction by the narrow tubing of the GIS when He is passed through.

From the operation performance point of view, preparation and analysis of small CO_2 samples are carried out within the same day and with a reduction of the turnaround time of a factor of 4 for analyzed samples when compared to the trapping offline setup [5, 6]. Where it is sensible, collection and analysis by ^{14}C of OC and EC fractions can be performed in one single run of Sunset OC/EC analyzer (e.g., when water-insoluble OC shall be evaluated or in particulate matter analysis from ice cores).

First pure O_2 continuous-flow ^{14}C gas measurements

An initial test of a continuous-flow ^{14}C AMS measurement is performed without any intermediate CO_2 trapping and usage of the gas-tight syringe or an open split system. During the analysis of samples ranging 20-40 $\mu\text{g C}$, average $^{12}\text{C}^+$ currents amounted to 1.4-1.9 μA . Lower carbon masses (10 μg) were measured by this method producing comparable currents, although this seemed to be dependent on the ion source condition. HOx_2 analysis resulted on the average in a pMC value of 134.9 ± 2.9 and for NaOAc in 7.7 ± 0.5 (Table II) for a FWHM of 200 s under stable conditions. The signal decayed very slowly to background levels resulting in a broadened and tailed peak (Figure 6) with a turning point after the signal had started to drop. $^{13}\text{C}/^{12}\text{C}$ ratio starts to raise with ^{12}C current increase and is as stable as it usually is for normal offline gas measurements. In the first runs, the pressure in the ion source was $1.5 \cdot 10^{-6}$ hPa starting to increase to $>10^{-5}$ hPa after the peak has been resolved in the NDIR plot. Since then, stable pressure conditions throughout the measurement have been maintained by disconnecting the Cu reactor from the OC/EC analyzer in an attempt to minimize the dead volume as soon as the CO_2 pulse had exited the Sunset OC/EC. The teed-in extra He flow is varied in the range 0.2-0.5 mL/min in order to test for different He/ CO_2 proportions and peak broadening. 0.5 mL/min carrier He flow rate is chosen here as most satisfactory, but this issue is investigated in next section.

The combination of inevitable dead volumes with the low He carrier flow results in air intrusion from the vent outlet. This is especially the case at the instance when oxygen background has completely been reduced and before the valve after the Cu reactor is switched to the ion source. For this reason we believe that several reference materials resulted in elevated pMC concentrations (Table II), which will be investigated further. The low carrier flow causes a peak broadening and the poor resolution compromises the real-time aspect of the setup and hampers the separation of closely resolved peaks in Sunset. On the other hand, this allows us to measure

for longer period resulting in a gain of ^{14}C counts.

Ion current optimization – first real-time measurements

In order to optimize the CO_2 :He dilution ratio, maintain stable vacuum conditions of the ion source throughout the analysis and improve the efficiency of the peaks, it is possible to increase the He carrier flow by a factor of 5, while experimenting with three different reduction capillaries with I.D.'s of 0.13, 0.18 and 0.25 mm. Inlet flows in the ion source mentioned in this section is measured with the system exhaust after the Cu reactor open to the air (valve B in Figure 2). We found that the best response resulted from combustion of masses lower than $2\ \mu\text{g}$ C using the 0.13 mm I.D. capillary as it is demonstrated in Figure 7. For the analysis of $1.75\ \mu\text{g}$ C derived from combustion of HOx_2 as an example, the ion source pressure throughout the analysis was 5×10^{-6} hPa with an average $^{12}\text{C}^+$ current of $2.8\ \mu\text{A}$ and a total number of $^{14}\text{C}^+$ counts of 1873. For higher flow rates or bigger capillary I.D.'s, the excess of carbon dioxide in the center of the peak causes a reduction of the ionization efficiency of the ion source, which induces an artificial double peak. This makes the analysis of higher masses problematic, because this ionization suppression effect becomes more intense producing even completely negatively inversed peaks. For more complex ambient aerosol mixtures, we expect that thermal protocols need to be modified so that decomposition products evolve more gradually.

Conclusion and outlook

The trapping online setup has been proven successful for the collection and analysis of ^{14}C derived from a series of standards and real atmospheric samples. Measured $^{14}\text{C}/^{12}\text{C}$ of individual carbonaceous fractions are consistent with those determined by conventional methods. First continuous-flow ^{14}C measurements of reference materials were successfully performed without intermediate steps such as split systems or intermediate CO_2 storage in a syringe and traps. Next

steps include the optimization of the proportion of CO₂ to carrier gas after the Cu reactor in order to improve the efficiency of the resolved CO₂ pulses. The modification of the Sunset OC/EC temperature program will also be performed in order to make the ¹⁴C characterization of thermal degradation products more efficient for continuous-flow analysis.

Acknowledgement

We are grateful to the help of E. Vogel (University of Bern) during this study.

References

1. Y. L. Zhang, N. Perron, V. G. Ciobanu, P. Zotter, M. C. Minguillón, L. Wacker, A. S. H. Prévôt, U. Baltensperger, S. Szidat, *Atmos. Chem. Phys.*, 12 (2012) 10841.
2. P. Zotter, V. G. Ciobanu, Y. L. Zhang, I. El-Haddad, M. Macchia, K. R. Daellenbach, G. A. Salazar, R.-J. Huang, L. Wacker, C. Hueglin, A. Piazzalunga, P. Fermo, M. Schwikowski, U. Baltensperger, S. Szidat, A. S. H. Prévôt, *Atmos. Chem. Phys.*, 14 (2014) 13551.
3. S. Szidat, G. A. Salazar, E. Vogel, M. Battaglia, L. Wacker, H.-A. Synal, A. Türlér, *Radiocarbon*, 56 (2014) 561.
4. L. Wacker, S. M. Fahrni, I. Hajdas, M. Molnar, H.-A. Synal, S. Szidat, Y. L. Zhang, *Nucl. Instr. Meth. Phys. Res. B*, 294 (2013) 315.
5. M. Ruff, L. Wacker, H. W. Gäggeler, M. Suter, H. A. Synal, S. Szidat, *Radiocarbon*, 49 (2007) 307.
6. M. Ruff, S. M. Fahrni, H. W. Gäggeler, Hajdas I., M. Suter, H.-A. Synal, S. Szidat, L. Wacker, *Radiocarbon*, 52 (2010) 1645.
7. N. Perron, S. Szidat, S. M. Fahrni, M. Ruff, L. Wacker, A. S. H. Prévôt, U. Baltensperger, *Radiocarbon*, 52 (2010) 761.
8. S. Szidat, T. M. Jenk, H. W. Gäggeler, H.-A. Synal, I. Hajdas, G. Bonani, M. Saurer, *Nucl. Instr. Meth. Phys. Res. B*, 223-224 (2004) 829.
9. J. J. Bauer, X.-Y. Yu, N. S. Laulainen, *J. Air Waste Manag. Assoc.*, 59 (2009)
10. S. M. Fahrni, L. Wacker, H.-A. Synal, S. Szidat, *Nucl. Instr. Meth. Phys. Res. B*, 294 (2013) 320.
11. G. Salazar, Y. L. Zhang, K. Agrios, S. Szidat, *Nucl. Instr. Meth. Phys. Res. B*, this issue (2015), <http://dx.doi.org/10.1016/j.nimb.2015.03.051>.

Tables

Table I. Radiocarbon analysis with the trapping online method of reference materials from 3 determinations with mean measurement uncertainty (calculated referring to the single analysis) and average $^{12}\text{C}^+$ currents.

Sample	Nominal $^{14}\text{C}/^{12}\text{C}$, pMC	$^{14}\text{C}/^{12}\text{C}$ measured, pMC	Mean $^{12}\text{C}^+$, μA
IAEA-C5	23.05±0.02	23.7±1.4	4.0±0.2
IAEA-C7	49.53±0.12	48.7±1.5	4.0±0.1
IAEA-C6	150.61±0.11	151.0±2.0	4.1±0.1
NIST-HOx2	134.07±0.05	134.9±2.0	3.9±0.4

Table II. ^{14}C analysis of reference materials by continuous-flow online measurements.

Sample	carbon mass, μg	Nominal $^{14}\text{C}/^{12}\text{C}$, pMC	$^{14}\text{C}/^{12}\text{C}$ measured, pMC	$^{12}\text{C}^+$, μA
NaOAc	36	0	7.7 ± 0.5	1.5
IAEA-C5	20	23.05 ± 0.02	25.9 ± 1.4	1.2
IAEA-C7	20	49.53 ± 0.12	52.1 ± 3.1	0.4
NIST-HOx2	40	134.07 ± 0.05	134.9 ± 2.9	2.0
IAEA-C6	20	150.61 ± 0.11	153.3 ± 3.8	1.3

Figure Captions

Figure 1. Schematic of the gas handling system (GIS) for the MICADAS gas ion source at University of Bern. The main elements of the system are two VICI 2-position multi-port valves (labeled A and B) and the CO₂ trap. The valves are shown here in the configuration for collection of CO₂ in the trap.

Figure 2. The technical scheme for continuous-flow online ¹⁴C measurements. Valve A is shown here in the configuration for ¹⁴C measurement of CO₂.

Figure 3. (a) ¹⁴C/¹²C (pMC) of reference material NIST-HOx2 and (b) of fossil NaOAc as a function of the sample size. The drift model is described by the continuous line with 1σ confidence bands. Large confidence bands for the fossil reference are due to the calculation based on the same mathematical model [11] as for the modern samples.

Figure 4. Comparison of ¹⁴C measurement (pMC values) of OC (a) and EC (b) using the trapping offline and trapping online methods with aerosol samples from Switzerland [2].

Figure 5. Typical thermo-optical separations with the OC/EC analyzer displaying the CO₂ response of the NDIR detector, the optical laser signal and the backpressure inside of the system (for temperature programming see [1]). **Top:** OC/ EC analyzer exhaust passes through the GIS and trapping online of refractory OC (non-trapped second peak is resolved under similar pressure, indicating the large backpressure exerted by the narrow GIS tubing itself) and EC at a pressure of 200 hPa. **Bottom:** trapping offline of the EC fraction with OC/EC analyzer operating at near ambient outlet pressure.

Figure 6. Continuous-flow ¹⁴C measurement profile for combustion of 40 μg C NIST-HOx2, and 0.5 mL/min carrier He flow rate delivered to the ion source by a 0.13 mm I.D. 1 m long

PEEK capillary. The respective IR trace for total carbon combustion is overlaid with the $^{12}\text{C}^+$ current and $^{14}\text{C}/^{12}\text{C}$ as well as $^{13}\text{C}/^{12}\text{C}$ ratios (time resolution 10 seconds).

Figure 7. Continuous-flow ^{14}C measurement profile for combustion of 1.75 μg C NIST-HOx2 at 2.5 mL/ min carrier He flow rate delivered to the ion source by a 0.13 mm I.D. 1 m long PEEK capillary. The respective IR trace for total carbon combustion is overlaid with the $^{12}\text{C}^+$ current and $^{14}\text{C}/^{12}\text{C}$ as well as $^{13}\text{C}/^{12}\text{C}$ ratios (time resolution 3 seconds).

Figures

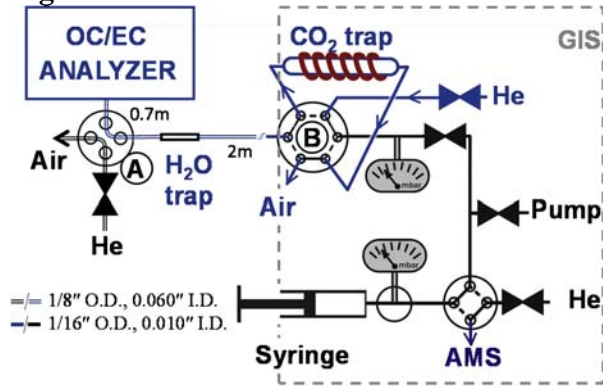


Figure 1

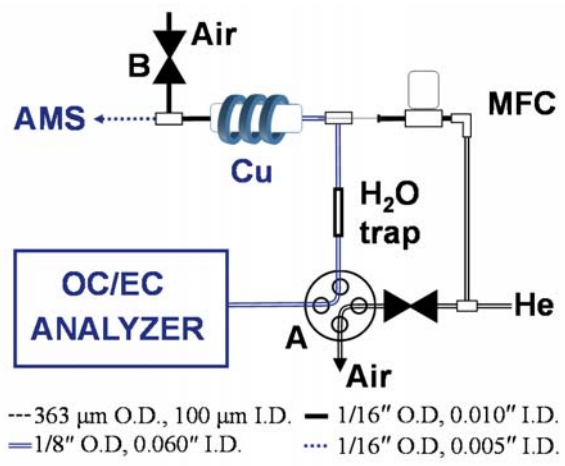
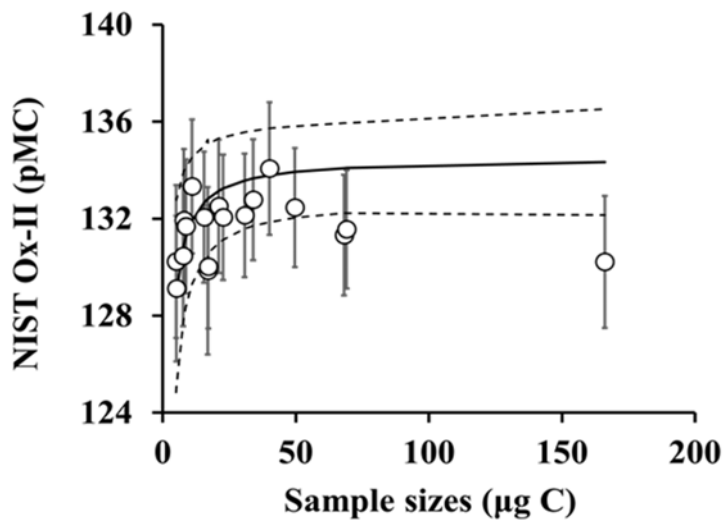
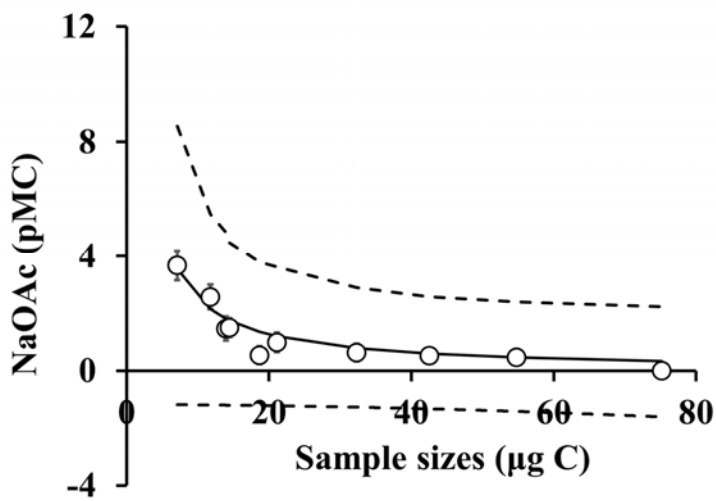


Figure 2

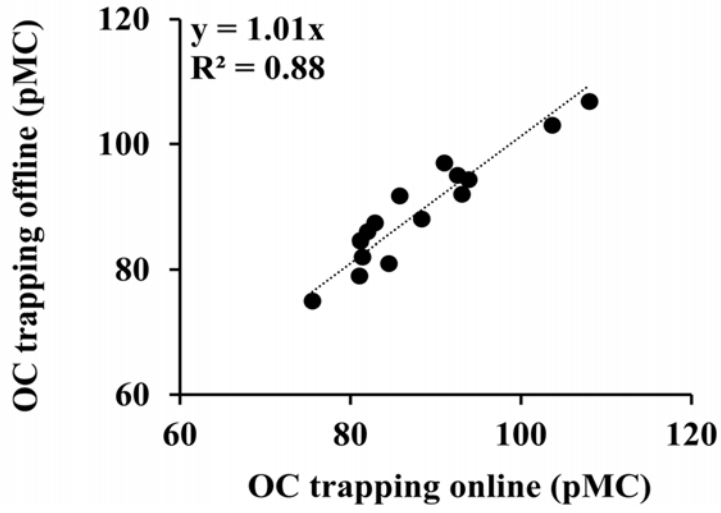


(a)

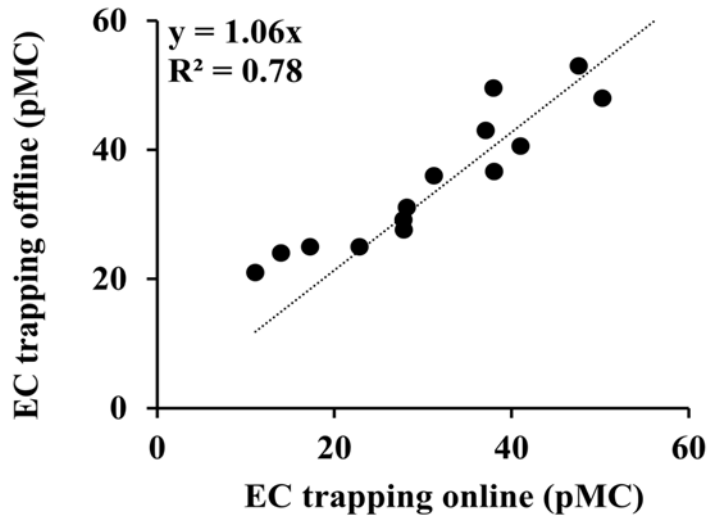


(b)

Figure 3



(a)



(b)

Figure 4

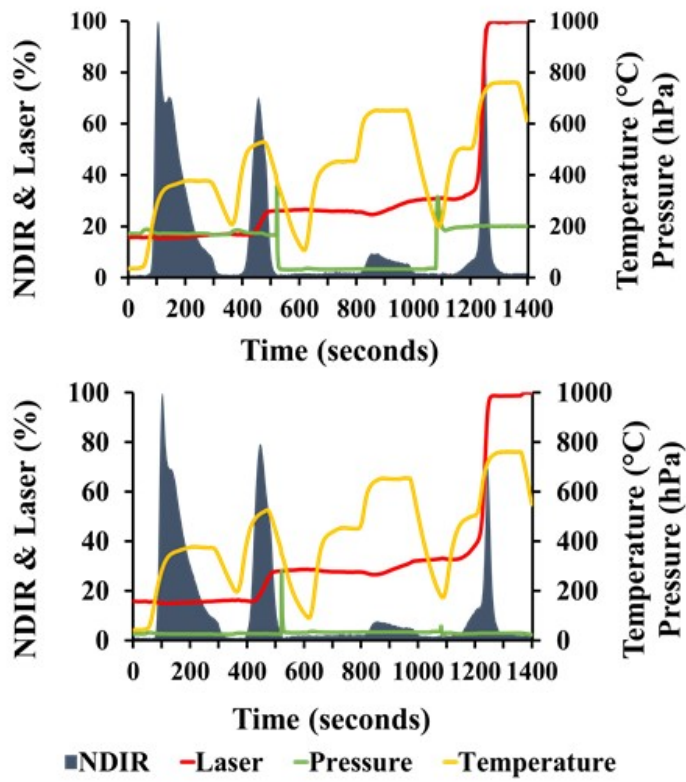


Figure 5

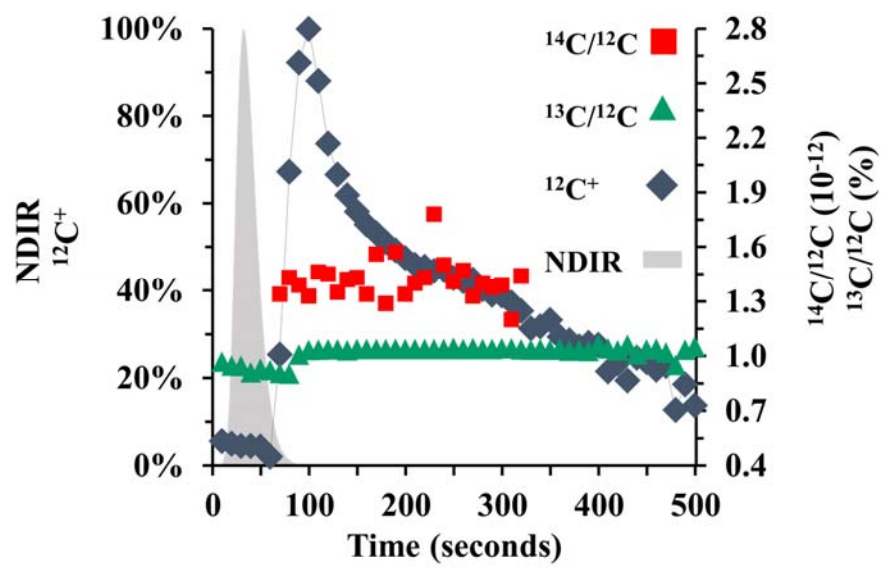


Figure 6

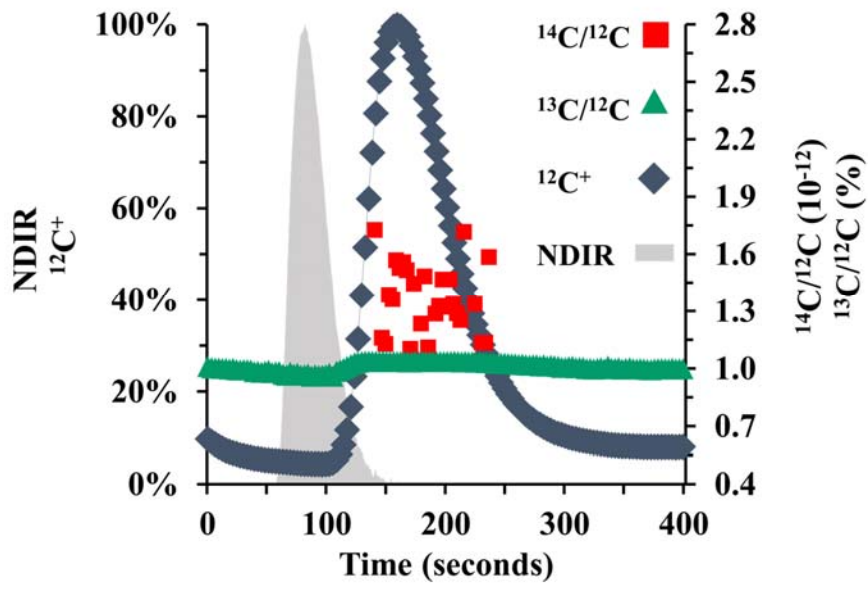


Figure 7