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An improved setup for radiocarbon analysis of water-soluble organic carbon in environmental matrices

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Abstract

This paper presents an improved setup for radiocarbon analysis of water-soluble organic carbon based on wet chemical oxidation as installed at the Laboratory for the Analysis of Radiocarbon with AMS (LARA) at the University of Bern. The implementation of a non-dispersive infrared CO_2 detector allows more precise and accurate quantification of carbon amounts in samples and establishes the possibility of simple monitoring of the efficacy of flushing and sampling processes. A detailed blank assessment unveiled undesired oxidation of different materials and sample temperature as critical factors regarding the level of constant contamination. Contamination arising from oxidation of septum pieces and carbon-based glues in conventional sampling needles was minimized by developing a glass-sintered needle. This new needle was also designed to be longer, reducing the minimum amount of sample solution needed to 2 mL. The oxidation time and temperature (1 hr at 75°C) were optimized to further decrease contamination during analyses of samples with carbon amounts of up to ~50 μg. With these improvements, we now report low constant contamination levels of 0.62 ± 0.12 μg C (with $F^{14}C$ of 0.19 ± 0.04), whereas the cross contamination factor was determined to be $0.25 \pm 0.07\%$.

Introduction

Water-soluble organic carbon (WSOC)—here used synonymously with dissolved organic carbon (DOC) or non-purgeable organic carbon (NPOC)—is defined as the fraction of organic carbon (OC) which is soluble in water, independent of whether it is in solution or not (Tao 2000). The radiocarbon analysis of WSOC is a versatile, rapid and low-blank method that finds application among different research fields. In atmospheric sciences for instance, the radiocarbon content in the WSOC fraction of airborne particulate matter is an important measure during source apportionment (e.g. Kirillova et al. 2014; Rauber et al. 2023; Zhang et al. 2018). Radiocarbon measurements of the water-soluble portion of aerosols are a powerful tool that facilitates clear discrimination between its fossil and non-fossil emission sources (Szidat et al. 2004). More examples are the investigation of non-saline waters to learn about carbon cycling dynamics (Lang et al. 2016), of marine samples to understand oceanic up- and downwelling cycles (Druffel et al. 2019), and of speleothem organic matter to reconstruct past terrestrial ecosystem sensitivity to climate change (Lechleitner et al. 2019; Xue et al. 2023). Finally, ice core research makes use of this approach as well and implemented the radiocarbon measurement of DOC as a dating tool to determine the age of mid- and low-latitude glaciers (Fang et al. 2021). This variety of

applications demonstrates the importance of high-precision radiocarbon analyses on WSOC from environmental materials.

Given the wide range of environmental matrices and applications for WSOC ^{14}C analysis, a number of methods have been developed for sample preparation and analysis. One common approach is the oxidation of dissolved organic matter using ultraviolet (UV) light (Beaupré et al. 2007). UV oxidation allows the measurement of a large range of sample sizes (~30 mL to 1 L) and is advantageous for low concentration samples where large amounts of material are needed. Furthermore, this method allows exceptionally low blanks. The biggest drawback of UV oxidation is low sample throughput, as simultaneous treatment is limited to 4–12 samples with up to 5 hr oxidation time per cycle (Xue et al. 2015). The usage of catalysts (Fang et al. 2019) or time-saving modifications (Griffin et al. 2010) enable significant decrease of the oxidation and sample preparation time, but overall sample turnaround times remain high. Another popular method for sample treatment is to concentrate WSOC by freeze-drying, followed by combustion either in vacuum-sealed quartz tubes with cupric oxide (Csank et al. 2019) or in an elemental analyzer (EA) for direct ^{14}C measurement (Rethemeyer et al. 2019; Ruff et al. 2010; Salazar et al. 2015). This method allows the preparation of multiple samples simultaneously, however, freeze-drying makes the preparation steps rather time consuming and energy intensive. Beside UV oxidation and combustion, potassium permanganate has been used as an oxidizing agent after removing all liquid from the samples (Thomas et al. 2021). Similar as for UV oxidation, this method allows large samples and reactors of ~1 L are not exceptional, however, oxidation times of 12 hr limit the sample throughput drastically.

Wet chemical oxidation of OC is another method that has gained popularity more recently due to its applicability to a wide range of sample types (e.g. Lang et al. 2013; Lechleitner et al. 2019; McIntyre et al. 2016). Briefly, aqueous samples are oxidized to carbon dioxide (CO_2) by spiking them with a chemical oxidizer under elevated temperatures. This method allows the measurement of small samples (< 7 mL), as well as a high sample throughput as multiple samples can be prepared simultaneously. Furthermore, it lowers the potential of cross contamination between samples and profits from low blanks (Lang et al. 2016).

CO_2 evolving from different oxidation procedures can either be graphitized for subsequent analysis on an accelerator mass spectrometer (AMS) (Vogel et al. 1984) or directly measured using an AMS equipped with a gas ion source (Ruff et al. 2007).

Here, we present an optimized setup for the routine processing and radiocarbon analysis of WSOC samples applying wet chemical oxidation as implemented at the Laboratory for the Analysis of Radiocarbon with AMS (LARA) at the University of Bern (Szidat et al. 2014). The method is based on the procedure as described by Rauber et al. (2023), but with the implementation of several substantial improvements regarding issues with contamination levels and sample recovery that we observed using the previous setup. A newly developed glass-sintered needle was incorporated with benefits on both sample recovery and contamination levels. Additionally, the insertion of a non-dispersive infrared (NDIR) CO_2 detector between autosampler and AMS allows monitoring of flushing and sampling processes and increases the accuracy of sample amount quantification. By dint of the NDIR detector, time consuming measurements with an AMS can be skipped for a first estimation of contamination amounts and are only needed for a final blank determination. This allows fast and detailed blank assessment as it was performed on this new setup to reach low contamination levels.

Methods

General sample preparation procedure

Wet chemical oxidation (Lang et al. 2013, 2016; Rauber et al. 2023) is performed in 12 mL Exetainer® vials (Round Bottom, Borosilicate, 938W, Labco Limited, Lampeter, UK) equipped with a screw cap and a pierceable chlorobutyl septum. Prior to single use, Exetainer® vials are cleaned in a ~1 M acid

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bath (H_3PO_4 for analysis EMSURE®, 85%, ACS grade, Merck KGaA, Germany) for at least 24 hr, rinsed three times with ultrapure water (18 MΩ·cm, total organic carbon (TOC) < 5 ppb, Purelab flex 2, ELGA LabWater, High Wycombe, UK) and baked at 500°C for 5 hr as suggested by Lang et al. (2012). During this cleaning procedure, screw caps are wrapped in aluminum foil for storage and re-mounted on the vials as soon as the baking process has finished. Before attaching them on the freshly cleaned vials, caps are blown out with a commercially available dust-off spray (Dust Off 67, Kontakt Chemie, Germany) to minimize any potential contamination. To test the clean Exetainer® vials for tightness, they are pressurized to ∼ 4 bar with nitrogen (99.999%, Carbagas, Switzerland), heated to 75°C over-night and then pierced with a needle (0.029" × 0.012″ × 2″, 943052, VICI AG, Switzerland). Vials not making a clear sound of depressurization after this procedure are assumed to be leaking and are discarded, all other vials are stored under overpressure (∼ 3.5 bar) until usage.

Liquid samples (2–5 mL) containing WSOC from environmental materials are transferred into the clean Exetainer® vials and sealed with a cap. The transfer can either be done through a needle (21 G × 4.75", B. Braun Medical AG, Switzerland) piercing the septum while having the screw cap half a turn opened or by completely removing the cap, depending on the type of sample and its pretreatment. Audible depressurization of the vial at this stage guarantees tightness during the storage since leak testing. In a next step, samples are acidified with H_3PO_4 to remove inorganic contaminants. To this end, each sample is manually spiked through the septum with 0.5 mL of a freshly prepared 8.5% phosphoric acid solution from concentrated H_3PO_4 (Suprapur®, 85%, Merck KGaA, Germany) by using a rinsed 1 mL glass syringe (1001 LTN, ga22/51mm/pst5, Hamilton Company, Reno, USA). Samples are then flushed with helium (99.999%, Carbagas, Switzerland) at room temperature for 3 min each to remove air as well as CO_2 evolved from the treatment of inorganic carbon with acid in the previous step. The helium flow is controlled by a flowmeter (red-y compact series, Vögtlin Instruments GmbH, Switzerland) and set to ∼55 mL/min. The flushing with He is performed using an in-house made glass-sintered needle (described in more detail below) mounted on an autosampler (PAL HTC-xt, CTC Analytics AG, Switzerland), which is part of a carbonate handling system (CHS, Ionplus AG, Switzerland). During the automatically performed flushing with the robotic system, a 10% sodium persulfate solution is prepared by dissolving $Na_2S_2O_8$ (purum p.a., ≥99.0% (RT), Merck KGaA, Germany) in a 5% phosphoric acid solution. This solution was prepared in a separate vial (N 24, 5 × 72.5 mm, 30.0 mL, 702132, Macherey-Nagel AG, Switzerland) equipped with a pierceable butyl/PTFE septum containing cap (N 24, PP, 702130, Macherey-Nagel AG, Switzerland). After its preparation the oxidizer is pre-oxidized at 90°C for 30 min and subsequently flushed with helium (99.999%, Carbagas, Switzerland) for 3 min. This has shown to effectively remove contamination from impurities in the oxidizer (Rauber et al. 2023). Samples are heated to 75°C and 0.25 mL of the freshly prepared oxidizer are added through the septum of each vial using the same 1 mL Hamilton glass syringe as for the acidification step. Samples are then kept at 75°C for 1 hr for the oxidation to take place and cooled down to room temperature afterwards. Samples are stored at room temperature until ^{14}C analysis is performed, preferably the next day to keep contaminations at a low level. All sample-treatment steps and preparation of solutions are executed under clean conditions in a laminar flow cabinet (Telstar PV-100, Telstar, Azbil Group, Japan).

The setup and procedure described here is not only suitable to analyze WSOC, but it can also be adapted to measure dissolved inorganic carbon (DIC). For this purpose, samples must be flushed with helium prior to acidification to remove atmospheric CO_2 from the vials. Adding 0.5 mL 8.5% phosphoric acid solution to the sample after the flushing converts the DIC into CO_2 which can subsequently be sampled from the headspace of the Exetainer® vial for ^{14}C analysis. This option gives the opportunity to measure both DIC and WSOC sequentially on the same sample. An additional flushing step with helium is suggested in between to remove any potential remaining CO_2 from the acidification of DIC.
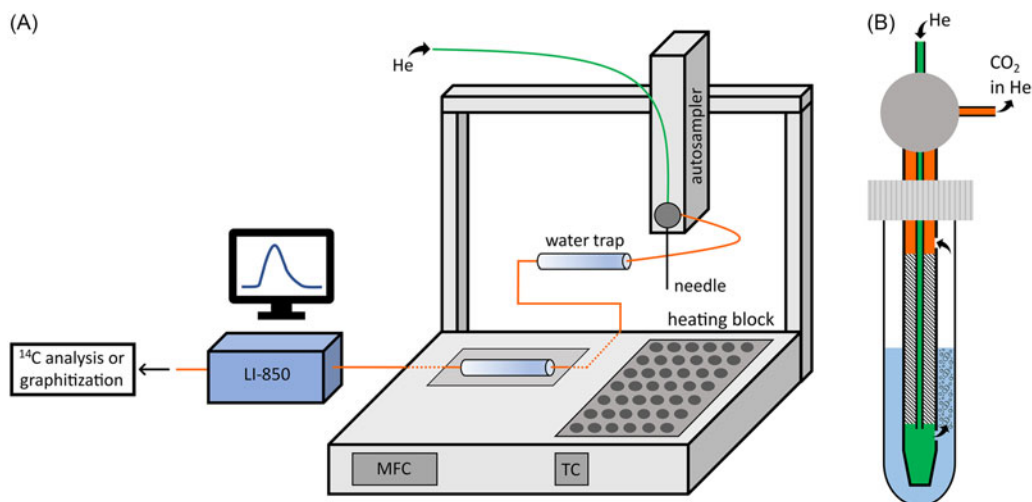
Figure 1. *A: Setup for wet chemical oxidation at LARA. The heating block of the CHS has 42 positions for vials and its temperature is set with a temperature controller (TC). The helium flow is regulated with a mass flow controller (MFC) (the connection of the gas line to the MFC is not shown for the sake of simplicity). The needle is operated with an autosampler to flush CO_2 from the headspace of the vials towards the LI-850 for detection passing two intermediary water traps. B: Closeup of the glass-sintered needle. Helium (green) enters the vial through the bottom side port to flush the CO_2 (orange) from the headspace through the upper side port towards the LI-850. The shaded area represents the soda lime glass that seals the space between the inner and the outer capillary. The needle is not true to scale compared to the vial, but made wider in favor of perceptibility.*

Setup

The instrumentation used for the treatment of WSOC samples at LARA is illustrated in Figure 1A. Exetainer® vials containing samples and standards are placed in the heating block of the CHS device. The needle enters the individual vials during the flushing procedure or during the sampling step to flush the CO_2 via a gas interface system (GIS) (Wacker et al. 2013) towards the AMS for direct ^{14}C analysis using a gas ion source (see below). Alternatively, the CO_2 can also be flushed towards the Automated Graphitization Equipment (AGE) (Wacker et al. 2010b) for graphitization. Two serial glass tubes filled with phosphorus pentoxide (Sicapent® with indicator, Merck KGaA, Germany) serve as water traps to remove any water vapor from the gas stream after flushing or sampling.

We installed a NDIR detector (LI-850 CO_2/H_2O gas analyzer, LI-COR Biosciences, Lincoln, USA), herein after referred to as LI-850, to monitor CO_2 during flushing and sampling. The LI-850 was modified by replacing the original plastic tubing in its housing by PEEK tubing (1/8" OD × 2.0 mm ID, BGB Analytik AG, Switzerland). This prevents any outgassing from the unknown plastic tubing material installed by default, as well as losses of CO_2 during sampling due to potential diffusion through the tubing. Furthermore, an in-line particulate filter (stainless steel, 1/8", 2 micron pore size, Swagelok, Solon, USA) was installed directly in front of the inlet to protect the optical bench of the NDIR from any particles that may enter the gas flow. The LI-850 records data at 2 Hz resolution during flushing and measurement and the data are stored as.txt files. All recorded CO_2 concentration values are automatically compensated by the LI-850 for any changes in pressure and are standardized to conditions with a pressure of 990 mbar. The total gas volume is derived from the simultaneously recorded volumetric gas flow (mL/min) by attaching a flowmeter (ProFLOW 6000, Restek Corporation, Bellefonte, USA) to the vent of the GIS. We developed a dedicated peak integration script written as an R Shiny application (Chang et al. 2023) for data evaluation. This application (available on GitHub:

https://github.com/DylanGeissbuhler/LICOR-CHS, last access: 14 June 2023) uses the recorded gas flow to calculate the total gas volume. After conversion to the amount of substance by applying the ideal gas law, the amount of carbon is calculated considering the CO_2 concentration (ppm) logged by the LI-850. Integration over the complete CO_2 peak of a sample delivers its total carbon content.

Glass-sintered needle

As commercially available needles appeared to have multiple disadvantages for our new setup, we developed a dedicated one. The final needle construction process is the result of a multi-stage optimization process based on several experiments. The in-house made glass-sintered needle is composed of an outer capillary (RN NDL, ga19/120mm/pst5, Hamilton Company, Reno, USA) and an inner capillary (Tube AISI 316L, 0.50/0.35 x 1000 mm, Unimed S.A., Lausanne, Switzerland) as shown in Figure 1B. The space between the inner and outer capillary is sealed with a soda lime glass capillary (outer diameter: 0.65 mm, inner diameter: 0.52 mm, length: 80 mm, Hilgenberg GmbH, Germany) via a glass-sintering process. For the construction of the needle, the support sleeve of the outer capillary is removed with a rotary tool and an additional side port (diameter: 0.3 mm, distance to needle tip: 80 mm) is drilled for the extraction of CO_2 from the headspace. The three capillaries are then put together to align one end of the glass capillary with one end of the inner capillary. Alignment with the outer capillary is made ensuring that the glass is positioned between the two side ports of the outer capillary. The resulting construct is inserted in a quartz glass tube. While a stream of pure nitrogen (99.999%, Carbagas, Switzerland) is applied to the inner part of the quartz tube to avoid oxidation of the needle at higher temperatures, the tube is heated up stepwise with a resistive heating element. First, the oven is heated to ~300°C for at least 1 hr to condition the system and to remove any contaminants. Afterwards, the temperature is stepwise increased to ~900°C within 30 min and then kept balanced for another hour. During this step, the soda lime glass softens and seals the space between the inner and the outer capillary completely. Lastly, the heating is switched off and the cooling process is manually supported by a pressurized air stream from the outside while maintaining the nitrogen stream inside the oven. The ready-made needle is mounted on a tee (1/16″, 1.0 mm bore, SS, VICI Valco Instruments Co. Inc., Houston, USA) to connect it with the inlet and outlet tubings (TubPEEK Ora, 1/16 × 0.020 × 10ft, Merck KGaA, Germany).

Routine online ^{14}C measurement

For the radiocarbon measurement of the oxidized WSOC samples, the CO_2 is sampled directly from the headspace of the Exetainer® vials and flushed from the vial towards the GIS (Wacker et al. 2013) with helium (~55 mL/min) as carrier gas. Quantification is performed with the intercalated LI-850. In the GIS, CO_2 is collected on a zeolite trap, mixed with helium and by means of a moving syringe continuously fed into a MIni CArbon DAting System (MICADAS) equipped with a gas ion source (Ruff et al. 2007; Wacker et al. 2013). Results measured with this AMS are evaluated with the BATS software (Wacker et al. 2010a) to obtain standard and blank corrected results and their uncertainties. OxII (Oxalic Acid, Standard Reference Material 4990C, National Institute of Standards and Technology, Gaithersburg, MD, USA) and NaOAc (Sodium acetate, puriss. p.a., ACS reagent, anhydrous, No. 71180, Merck KGaA, Germany) (Szidat et al. 2014) are used as standard and blank, respectively. They are added as aqueous solutions into Exetainer® vials and treated according to the same wet chemical oxidation procedure as the WSOC samples. For standards, amounts are adjusted to yield 50 µg of carbon (µg C) each. During a normal measuring day, five standards and blanks each are included in the procedure, split for both into three at the beginning and two at the end of the day. Different, but well-known amounts of OxII (100 µg C, 25 µg C, 5 µg C) are additionally prepared for mass calibration of the LI-850 device to enable the quantification of the carbon content in the analyzed

samples. While the 100 µg C OxII can be used as a standard and replace one of the five 50 µg C, the two smaller OxII (25 µg C, 5 µg C) should not be considered as standards for ^{14}C evaluation as they may be biased by any potential constant contamination. Consequently, the measurements of these small amounts are not defined as runs of standards in BATS, but they are treated as normal samples instead. Finally, all data are corrected for constant and cross contamination. The factors for these two correction steps were experimentally determined for this specific measurement setup and are discussed in detail in the results and discussion section.

Blank assessment

We conducted an extensive blank assessment to detect and quantify possible contamination sources in the system. The experiments can be split in two main parts, (i) exploring the influence of different potential contamination sources and (ii) testing the contamination dependency on temperature. For the first set of experiments, different components of the wet chemical oxidation protocol were varied while monitoring the evolving CO_2 amounts. Additionally, three main suspects of contamination contributors were added to an Exetainer® vial and treated according to the wet chemical oxidation procedure: pieces of Exetainer® septa, septa from the oxidation vial and dried two-component adhesive (Araldite® rapid, Huntsman Advanced Materials, Salt Lake City, USA). To investigate the temperature dependency of the contamination over time, several samples of ultrapure water were prepared following the wet chemical oxidation procedure and kept either at 75°C or at room temperature (20°C). No extraneous carbon was added to these vials. Headspace sampling of the CO_2 was performed in different time lags (up to 48 h) with regard to the time when the oxidizer was added.

For both types of experiments calibration of the LI-850 data was performed by means of a logarithmic fit (Figure S1). The fit is based on the measurement of different amounts of OxII standard. As the detected amounts in these two experiments were very small (< 4 µg C), a logarithmic fit was found to best describe the ratio of the measured quantities to the prepared standard amounts. For quantities larger than 5 µg C, as it normally is the case for ^{14}C analyses, a linear fit between measured and prepared carbon amounts is sufficient.

Quantification intercomparison

The performance of our new setup in terms of carbon quantification was verified by means of an intercomparison with another instrumentation. Aliquots of the same solutions were measured both with our new wet oxidation setup and with a total organic carbon (TOC) analyzer (TOC-L CPH, Shimadzu Corporation, Japan) coupled with an autosampler (ASI-L, Shimadzu Corporation, Japan) installed at the Laboratory of Atmospheric Chemistry at the Paul Scherrer Institute (PSI, Switzerland). For the calibration of the TOC analyzer, a 10 ppm solution was prepared out of a commercially available standard (TOC standard according to ISO/CEN EN1484, 1000 mg/L ± 10 mg/L, Merck KGaA, Germany). The measured samples for comparison include water extracts from different atmospheric particulate matter samples as well as a solution with a well-known concentration of sucrose (D(+)-Sucrose, ACS reagent, ≥99.0%, Merck KGaA, Germany).

Results and discussion

Contamination characteristics

Contamination from extraneous carbon influences the results of ^{14}C analyses and in particular small samples can be highly affected. Therefore, the characterization of the constant contamination level of a setup is crucial to correct the final data. As the contamination amount is usually too low to be accurately quantified via direct measurement, we determined the constant contamination for the new wet oxidation
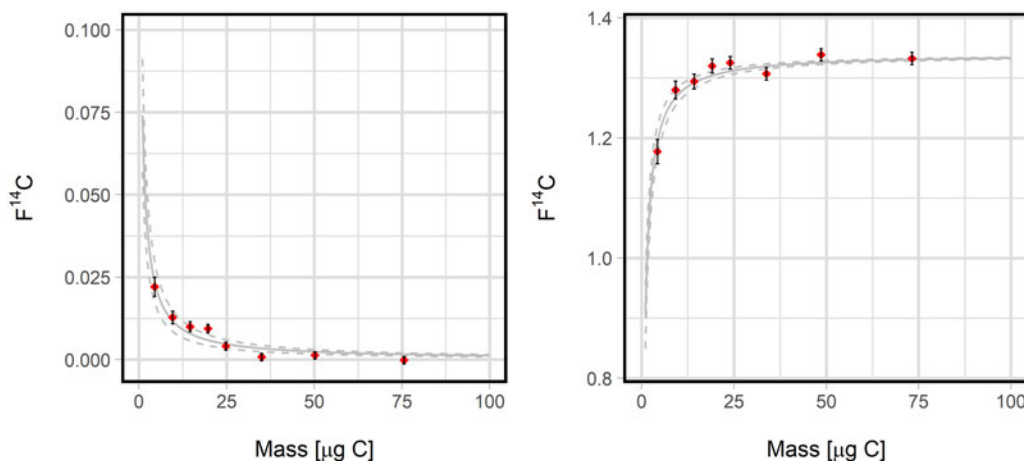
Figure 2. *Measured $F^{14}C$ values (red diamonds) for different amounts of NaOAc (left) and OxII (right). Error bars indicate the measurement uncertainty. The grey line represents the chi-square-fitted curve with the uncertainty range (dashed lines), as described in Hanke et al. (2017).*

protocol as described in Hanke et al. (2017). In brief, different amounts of two contrasting standard materials were measured, one depleted in ^{14}C and one with modern ^{14}C values. The measured values are then fitted by minimizing chi-squares. Based on this fit, the total contamination mass and $F^{14}C$ value, consisting of the modern and the depleted contamination, are estimated. We measured NaOAc ($F^{14}C = 0$) and OxII ($F^{14}C = 1.3407$) in the range of 5–75 μg C each (Figure 2). Our new setup yields a constant contamination of 0.62 ± 0.12 μg C with an $F^{14}C$ of 0.19 ± 0.04 (data evaluation is provided in supplementary material). This result confirms the low background level of the optimized method. As the constant contamination may slightly vary depending on laboratory and analysis conditions and may also be influenced based on sample pretreatment, we suggest to freshly determine the constant contamination for every measurement campaign.

In addition to constant contamination, cross contamination between subsequent samples also needs to be considered when performing GIS-AMS measurements. According to Salazar et al. (2015) the drift in the measured $F^{14}C$ can be written as

$$drift = F^{14}C_m - F^{14}C_S = \phi \cdot \frac{m_x}{m_S} \left(F^{14}C_x - F^{14}C_S \right) \tag{1}$$

The drift in Equation (1) describes the difference between the measured $F^{14}C$ of a sample ($F^{14}C_m$) and its real $F^{14}C$ ($F^{14}C_S$), where m_S is the mass of the sample, m_x the mass of the previous sample, $F^{14}C_x$ the $F^{14}C$ of the previous sample and ϕ is the fraction of carbon from the previous sample cross-contaminating the current sample. Rewriting this equation leads to an expression for the calculation of ϕ as shown in Equation (2).

$$\phi = \frac{F^{14}C_m - F^{14}C_S}{F^{14}C_x - F^{14}C_S} \cdot \frac{m_S}{m_x} \tag{2}$$

To determine ϕ for our new setup, an OxII standard (100 μg C) was measured followed by two NaOAc standards (50 μg C each). The measured $F^{14}C$ of OxII and the first NaOAc correspond to $F^{14}C_x$ and $F^{14}C_m$, respectively. We assume that the second NaOAc is not affected by any cross contamination from the OxII run and therefore represents $F^{14}C_S$. This procedure was repeated four times yielding a cross contamination factor of $\phi = 0.25 \pm 0.07\%$ (Table S1). This value is in good agreement with the cross contamination of $\phi = 0.2 \pm 0.1\%$ determined for the EA-AMS setup in the same lab

(Salazar et al. 2015). We assume that the slightly higher cross contamination factor for the wet oxidation setup was caused by the flushing procedure, as the needle sequentially enters the vials containing the liquid samples before the oxidizer is added. Analogous to the constant contamination, we suggest to also reassess the cross contamination factor periodically.

Optimizations

The method updates described in this work were implemented to reduce contamination levels observed when using the original setup (Rauber et al. 2023). Moreover, some simplifications have been included. First, sodium persulfate was introduced as an oxidizing agent instead of potassium persulfate, as its higher solubility reduced needle clogging during flushing and sampling and simplified sample handling. Second, all needles used for the acidification, oxidation, flushing, and sampling are equipped with a side port contrary to the previously used front-port needles. These non-coring needles were introduced to minimize pieces of septa entering the vial during septum piercing steps. As the septum itself can be oxidized once in contact with the solution (see section Contaminations from Carbon-based Materials), a needle with side port reduces this source of potential contamination. Finally, we developed a glass-sintered needle to reduce sample losses while simultaneously avoiding potential contamination arising from the oxidation of carbon-based glues. The adjustable length of the new needle additionally allows the efficient flushing of smaller samples (as low as 2 mL). The implementation of the new needle reduced the amounts of water in the carrier gas substantially (up to ∼0.3 mL per sample) compared to the preceding setup using a non-sealed needle (Rauber et al. 2023). The previously used gas wash bottle (25 mL) is therefore not needed anymore and was removed. Due to this dislodged high-volume water trap within the gas line, CO_2 peaks arising from the sampling from the vial headspace are less prone to broaden. The narrower peak shape of CO_2 simplifies its trapping for subsequent AMS measurement.

Contamination from carbon-based materials

The determination of contamination amounts and isotopic signature as described above is time consuming and blocks the AMS instrument from measuring other samples. Hence, the implementation of the LI-850 turned out to be pivotal, because it allows to perform fast offline (i.e., without AMS) assessments of blank levels. On this basis, several variations on the wet chemical oxidation protocol have been investigated with respect to their impact on the blank amount. A summary of the results is shown in Table 1. The largest response was detected when adding shredded pieces of septa, either from the Exetainer® cap or from the cap of the vial being used to prepare the oxidizer solution, or when adding pieces of a dried two-component adhesive, similar to what is used to seal the commercially available sampling needles. All three materials appear to be prone to oxidation and therefore may lead to substantial additional contamination. Other changes, like varying the volume of water, acid or oxidizer resulted in only minor effects on the amount of contamination. Skipping the acidification steps, i.e. the removal of carbonates, or the pre-oxidation to remove impurities from the oxidizer also affected the background level only negligibly. Freshly baking out Exetainer® vials (5 hr, 500°C) and their caps (5 hr, 80°C) immediately before use may lead to modest improvements, but we opted against this approach as leak testing the vials prior to use would have to be skipped leading to the risk of sample loss due to leaking vials.

Consequently, minimizing contact of the oxidative solution with septa and glue is key to achieve low blank levels. Our newly designed glass-sintered needle allows us to completely avoid any carbon-based glue in the system. However, the Exetainer® vial septum is an indispensable part of the whole procedure. Using a front-port needle, pieces of septa have been punched and remained in the sample solution, visible to the naked eye. The measurement of Exetainer® septum pieces with an EA coupled to an AMS (Salazar et al. 2015) revealed a $F^{14}C$ of 0.0116 ± 0.0025 ($F^{14}C$ for Araldite® was measured to

Table 1. *Effect of different changes in the wet chemical oxidation protocol on the contamination level. Deviation refers to the normal protocol as described in the Methods section, i.e. 3 min of flushing, 5 mL of water, 0.5 mL of 8.5% H_3PO_4, 0.25 mL of 10% sodium persulfate solution*

Change in protocol	Change in contamination level [µg C]
Solvent volume	
Reduced water volume to 2 mL	–0.19
Increased water volume to 8 mL	+0.02
Preparation steps	
Freshly baked Exetainer® vial	–0.42
Freshly baked Exetainer® vial & cap	–0.52
No acidification before flushing	+0.08
Reduced 8.5% H_3PO_4 volume to 0.25 mL	–0.14
Increased 8.5% H_3PO_4 volume to 1 mL	+0.40
Increased flushing time to 10 minutes	–0.20
Oxidizer	
Used potassium persulfate as oxidizer	+0.42
No pre-oxidation of oxidizer solution	+0.17
Reduced 10% oxidizer volume to 0.1 mL	–0.02
Increased 10% oxidizer volume to 0.5 mL	+0.36
Additional extraneous carbon sources	
Added pieces of Exetainer® septum (~0.01 g)	+2.78
Added pieces of septum from oxidation vial (~0.02 g)	+51.0
Added pieces of glue (Araldite®) (~0.05 g)	+200.5

be 0.0566 ± 0.0030). This is in agreement with our ^{14}C-depleted values determined for the contamination and supports the assumption that this material is the main source of contamination. Further optimization of the needle by using a non-coring side port successfully lowered the background from 1.03 ± 0.06 µg C (front port) to 0.56 ± 0.05 µg C (side port) as measured offline with the LI-850.

Temperature influence on contamination

To further understand the sources and processes affecting contamination levels in our workflow, we investigated the influence of the high oxidation temperature on the degree of contamination. We detected a substantial increase in contamination with time when keeping the heating block of the CHS at 75°C (oxidation temperature) for longer periods of time. The results indicate a large increase of contamination over time at higher temperatures by 0.089 µg C/hr, while in samples kept at room temperature (20°C) the contamination increased by 0.016 µg C/hr (Figure 3). Hence, the oxidation time at high temperatures needs to be optimized to ensure (i) that samples are fully oxidized, and (ii) samples are not exposed to high temperature for too long to minimize contamination. Moreover, as the contamination appears to increase over time regardless of the storage temperature, samples should be prepared close to the measurement (ideally within 24 hr) or, if this is not possible, storage of the samples in a fridge or freezer until analysis is recommended. Exetainer® vial septa were tested to be gas-tight at these temperatures (Table S2). We assume that the increase of contamination can be ascribed to oxidation processes within the Exetainer® vial over time. Higher reaction rates at higher temperatures in combination with larger amounts of vapor containing oxidizer and potentially interacting with the surface of the septum may be responsible for the detected temperature dependency. Further evidence that the contamination evolves mainly from the oxidation of any carbon-containing material within the system becomes apparent when the CO_2 amount is detected while different components of the chemical
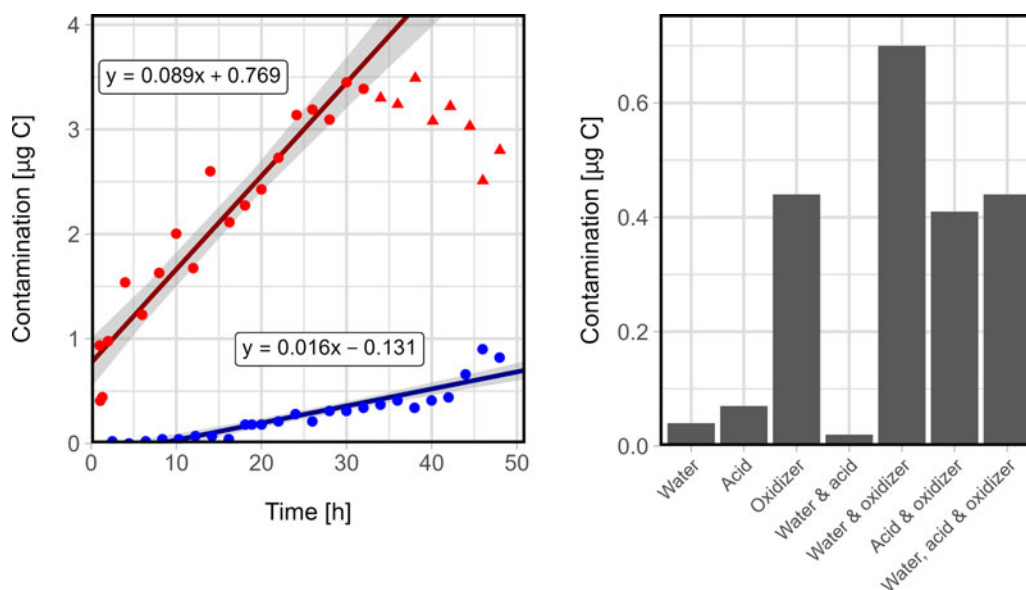
Figure 3. *Left: Linear fit for the time dependency of the contamination level at room temperature (blue) and 75°C (red). At 75°C, the contamination seems to reach a maximum level after ~30 hr of oxidation and scatters around a mean value of 3.1 ± 0.3 μg C afterwards. The last 8 values (triangles) are therefore not included for the linear fit. Right: Contamination level after ~1 h at 75°C dependent on the mixture of components (water, acid, oxidizer) added to the vial. Samples are treated according to the above-mentioned wet chemical oxidation protocol by just skipping the not listed components.*

wet oxidation procedure are skipped. While water and acid seem not to trigger high backgrounds, the presence of the oxidizer leads to a distinct increase of the contamination level (Figure 3). Thus, the presence of the oxidizer in combination with the temperature is the most critical factor to control contamination levels. This also means that the measurement of DIC is less sensitive in this regard, as no oxidizer is used for this procedure. The highest value was obtained in an experiment where the acidification step was skipped and oxidant was directly added to the water sample. We assume that in this case, carbonates contained in water increased the background due to the absence of the acid before the flushing step.

In order to optimize the oxidation time at 75°C, several Exetainer® vials were spiked with OxII standard (50 μg C each) and measured with the LI-850 applying different time lags with regard to the moment when the oxidizer was added. We infer that the oxidation process takes ~15–30 minutes to complete. Based on this result we fixed the oxidation time to 1 hr to ensure that all samples, which are normally not much larger than ~50 μg C for a ^{14}C measurement, are completely oxidized. Nevertheless, it is recommended to adapt the oxidation time based on the environmental samples and their quantity to be measured. For larger samples, 1 hr of oxidation may not be sufficient anymore. Furthermore, the oxidation time has also shown to be dependent on the specific compounds to be oxidized. The NaOAc standard for instance appears to have consistently longer oxidation times compared to the OxII standard. To mimic an environmental sample and therefore a more complex mixture of compounds, an atmospheric particulate matter standard (Urban Dust, Standard Reference Material 1649a, National Institute of Standards and Technology, Gaithersburg, MD, USA) was examined regarding its oxidation time and complete oxidation in less than 1 hr was confirmed (Figure S2). Nonetheless, as the exact composition of environmental samples is usually unknown and may strongly vary, it is advisable to adjust the sample amount and oxidation time based on some pre-tests. This guarantees optimal conditions for complete oxidation of the sample, while simultaneously retaining low blanks. While

higher temperatures would also favor shorter oxidation times, this may also lead to more leaks from the vial caps (Rauber et al. 2023). Furthermore, the Exetainer® supplier recommends to not heat them much above 70°C.

Needle assessment

The glass-sintered needle has several advantages when measuring the radiocarbon content of WSOC samples. First of all, the use of carbon-based glues to seal the space between the inner and outer capillary can be circumvented. That is of particular importance when working under the chemically harsh conditions of wet chemical oxidation with a mixture of acid and oxidizer. Glue has shown to react under these conditions and release CO_2, increasing contamination (Table 1). Furthermore, the oxidizing conditions likely affect long-term stability of the glue and may lead to needle leakage after a while. Soda lime glass is chemically inert and therefore less problematic in this regard. Secondly, the sintered needle allows easy adaptation of needle length to the requirements of the measurement. Our laboratory now uses a length of 120 mm, which allows us to flush very small liquid samples (∼2 mL) efficiently. Another optimization concerns the side port, which minimizes coring of the septum while the needle is entering the vials. As pieces of septa stemming from needle piercing have shown to produce CO_2 in the oxidative environment during sample preparation (Table 1), this step is crucial in terms of reaching low contamination levels. Finally, our custom-made glass-sintered needle is a low-cost solution, as materials are much cheaper than the available standard needles for treating carbonate samples, which partly arises from the fact that labor costs are not incurred.

A blank assessment on the needle sealant type was performed to reveal the effect of the replacement of carbon-based glue by soda lime glass. The constant contamination was ascertained according to the method by Hanke et al. (2017). With our equipment, we were not able to construct a glued needle with a side port. Therefore, the two investigated needles were both constructed with a front port for better comparability. The determined constant contamination for the glued needle (1.00 ± 0.20 µg C, $F^{14}C = 0.30 ± 0.06$) was within uncertainties as high as the one for the glass-sintered needle (0.95 ± 0.19 µg C, $F^{14}C = 0.21 ± 0.04$). Consequently, the effect of using soda lime glass instead of glue is only secondary and glued needles may still be a suitable option for wet chemical oxidation in some cases. The higher contamination values measured in this experiment compared to the final contamination assessment of the setup (i.e., 0.62 ± 0.12 µg C with an $F^{14}C$ of 0.19 ± 0.04; see Figure 2) are in good agreement with abovementioned increase of contamination that is observed when using a needle with a front port instead of a side port.

Intercomparison with TOC analyzer

The intercomparison of measured carbon amounts between our optimized setup and a commercial TOC analyzer shows good agreement (Figure 4). High correlation ($R^2 = 0.988$) and a slope close to 1 indicate a high comparability between the two methods. Therefore, we conclude that our new setup constitutes a significant improvement compared to the previous one, where quantification occurred with the pressure gauge of the GIS and suffered from high uncertainties, especially for small samples (Figure S3). While there is good agreement between the TOC analyzer and our new wet oxidation setup, it is unclear what caused the offset of 0.553 µg C/mL between the two measurement principles. The sucrose concentrations measured with the LI-850 (5.13 µg C/mL and 5.32 µg C/mL) disclose a modest overestimation of the real concentration (5.09 µg C/mL) but still giving a high accuracy. On the other hand, the TOC analyzer (4.89 µg C/mL and 4.79 µg C/mL) rather underestimated the sucrose concentration. We assume that such minor deviations were caused by the day-dependent calibration of the instruments.
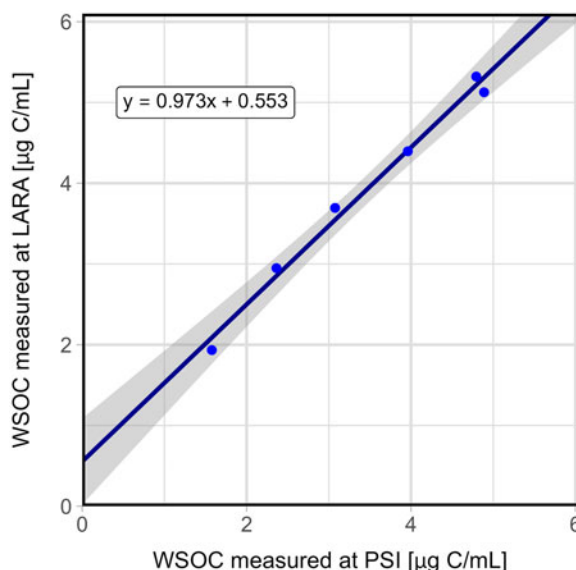
Figure 4. Comparison of identical samples measured with the herein described optimized setup installed at LARA and a commercially available TOC analyzer installed at PSI.

Conclusion and outlook

The radiocarbon analysis of WSOC in environmental samples is a powerful tool with a wide range of applications. Compared to other methods, wet chemical oxidation stands out with a high sample throughput, low blanks and the ability of measuring small samples (5–100 µg C). Here we present a setup for wet chemical oxidation as implemented at LARA at the University of Bern, which addresses optimizations in quantification and contamination levels. The precision and accuracy of WSOC quantification was clearly improved by the implementation of an NDIR CO_2 detector as confirmed by an intercomparison with a commercial TOC analyzer. Furthermore, the NDIR turned out to be a potent device for quick blank assessments and enables the confirmation of constant contamination conditions on a daily basis. This is deciding in quality control as the determination of constant contamination levels with the AMS is time consuming and can therefore be performed only sporadically. Extensive blank assessments on the system revealed that the oxidizer as well as the oxidation time at elevated temperatures are the critical parameters to reach and maintain low blank levels. The development of a glass-sintered non-coring needle minimized any carbon containing components being prone to oxidation and therefore releasing contaminating CO_2. This in combination with an optimized oxidation time was the key to reach a low contamination level of 0.62 ± 0.12 µg C.

Future work may focus on testing alternatives to the currently used Exetainer® septa. Alternatives should be free of carbon or less prone to oxidation to further lower the procedural blank, while preserving the excellent impermeability for gases as the presently used septa. Additional reduction of the contaminating background could also be reached by sample dependent optimization of oxidation time and oxidizer amount, as these optimal parameters may strongly vary dependent on the environmental material to be analyzed.

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Competing interest declaration. We declare that none of the authors has any competing interests.

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