

Treatment of small samples of particulate organic carbon (POC) for radiocarbon dating of ice

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Abstract

A filtration method for radiocarbon determination on particulate organic carbon (POC) in glacier ice is explored at VERA (Vienna Environmental Research Accelerator). Previous work on true samples has shown that laboratory contamination is the limiting factor. By systematic investigations on the origin of carbon contamination, we were able to reduce the background significantly. In two first measurements using artificially produced clean ice a blank level as low as 1.3 $\mu\text{gC}/\text{kg}$ ice could be achieved. These results were obtained by a simplified combustion scheme using valve-sealed vials. The combustion yield for organic materials was found to be 80% with a very low background typically below 1 μgC . Outliers turned out to be the main obstacle when dealing with such minute carbon amounts.
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1. Introduction

The fundamental limit of radiocarbon determination on small samples will finally be imposed by counting statistics. Assuming an overall detection efficiency of 5%, a statistical uncertainty of 1% is possible for modern samples as small as 4 μgC . However, experience at other laboratories [1–6] and at VERA [7–9] show that presently technical difficulties of sample processing and laboratory contamination are the limiting factors.

Our present interest in small radiocarbon samples was spawned by first measurements on ice samples obtained from the ablation zone of the Gorner–Glacier (Monte Rosa massif, Swiss Alps) at VERA which are reported in [9]. These samples cannot be dated adequately by common

stratigraphic tools. Radiocarbon dating offers an alternative method, though various analytical challenges must be overcome in order to obtain useful results. Particulate organic carbon (POC) is present as aerosols trapped inside the ice matrix, but only in minute amounts (typically less than 100 $\mu\text{g}/\text{kg}$, but varying strongly). It is technically distinguished from DOC (dissolved organic carbon) as the fraction which is retained by a pore filter of typically 0.4 μm pore size. The quartz fiber filters which we use in this work have no well defined pore size, so our procedure does not completely respect the definition of POC, which is, however, irrelevant for dating applications. Additionally, for pre-industrial atmospheric POC there is no need to separate the major POC fractions like e.g. organic carbon and elemental carbon (OC and EC, see e.g. [10] for recent aerosol), since we expect that both fractions are useful for dating the ice formation.

The first measurements on Gorner–Glacier ice showed a surprisingly large scatter in the pMC values, and the

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average process blank was 6.8 μgC . The present paper focuses on the systematic investigations carried out since then to understand and reduce laboratory contamination, and covers aspects of small ^{14}C samples which are independent from ice samples. Earlier experiments already presented in [9] are quoted where required for a complete picture.

The second goal of the present work was speeding up sample preparation (especially the combustion step), since fast turn-around is required for systematic investigations and iterative optimizing.

2. Methods

The procedure still follows the outline given in [9]. The ice sample is put into a vessel which is closed hermetically, and the melt water is filtrated by N_2 overpressure onto a quartz filter. The filter is combusted in a closed quartz vial using copper oxide. The resultant CO_2 is catalytically reduced to graphite which is measured for ^{14}C content in our AMS system VERA.

Contamination can be introduced into the sample in every step of the procedure. Particle contamination may occur during drilling of the ice sample. In the laboratory, it may be due to insufficient cleaning of the melting vessel, it may be present on the quartz filter before filtration, or be introduced via rinsing liquids (see below). Soluble compounds are not expected to contribute to the contamination in these first steps. During combustion, carbon contamination may be present on the sample vial, or in the copper oxide used. During the graphitization process cross contamination may occur, or carbon may be present in the iron catalyst. In these later steps, outgassing from vacuum pumps or seals may contribute. The prepared carbon may adsorb volatile carbon from laboratory air. Throughout the process, whenever the sample is exposed to laboratory air, dust may enter. In the ion source of the AMS system, cross contamination and organic compounds in the residual gas can introduce background.

Some routine measures against contamination were adopted without further questioning. The filters, quartz vials and copper oxide are heated at 950 $^\circ\text{C}$ for 4 h to remove any carbon, and temporarily stored in saturated H_2O atmosphere. To avoid contamination with laboratory dust, all handling of ice samples, filters and other sensitive materials takes place inside a laminar flow box (class 100).

3. Particle contamination during filtration

The melting apparatus for ice samples is already described in [9]. Ice samples of up to 1.5 kg are melted inside a double-walled glass vessel by using warm water flowing through the double walls, at a rate of ~ 1 kg/h. Filtration is done under over-pressure with clean N_2 . To ensure that no POC sticks to the melting vessel pre-filtered (quartz filter plus membrane filter) 1 M HCl is used to rinse the vessel following sample processing and filtering. This

HCl is then filtered onto the sample filter and serves the dual purpose of both increasing the extraction of POC from the sample, and acidifying particulate inorganic carbon. Rinsing is repeated twice using ~ 50 mL of clean (pre-filtered) double-distilled H_2O (DDH $_2\text{O}$). Different ways of removing carbonates have been tried over the course of the development of the experimental procedure (e.g. exposure to HCl vapors). In-situ HCl rinsing in place takes less time and the filter is handled less, thus reducing the possibility of contamination with laboratory dust or adhesion of volatile carbon compounds.

Our first approach to get an idea of the particle contamination during filtration is inspection and particle counting under a microscope. Results are obtained within less than one hour after the filtration. Due to their flat surface, membrane filters are suited for particle counting (Osmonics Magna polycarbonate (PCTE) filters, 0.22 μm pore size). Different amounts of DDH $_2\text{O}$ – between a few drops and 250 ml – were filtered in the melting apparatus. The whole area of the filter was studied under the microscope. Using an ocular meter, the particles registered were roughly split up into three fractions: below 1 μm in diameter, 1–3 μm , and larger particles – the latter were measured individually. The total mass deposited was estimated from the size and number of the deposited particles, assuming a density of 2 g/cm^3 . This is only a semi-quantitative method which we could not validate against any independent measurement of particle mass: weighing the net contamination on the filters failed due to the small mass ($\sim \mu\text{g}$). However, we think that the results obtained allow some conclusions. For the three filters inspected we found that the main contribution to the visible mass comes from few (typically less than 5) large particles, which outweigh the summed mass of the smaller fractions. The deposition statistics for such a small number of relevant particles suggests that the reproducibility of the contamination mass is probably low and outliers have to be expected.

A quantitative method of assessing the carbon contamination are manometric measurements of CO_2 after combustion. The procedures are the same as for AMS target preparation, and are described later in this paper.

Quartz fiber filters (Sartorius QMF, 85 g/m^2 , binder-free, 25 mm) are used for filtration of the ice samples. If diameters smaller than 25 mm are used, they are punched out before baking. These filters have no defined cut-off size, but for sampling of aerosols from air, the manufacturer quotes a retention of 99.999% for 0.3 μm particle size. The filters are heated at 950 $^\circ\text{C}$ for 4 h to remove any carbon, and temporarily stored in saturated H_2O atmosphere.

In order to assess the background introduced by the quartz filters, we combusted a total of 15 pre-heated, moistened quartz filters of 8 and 10 mm diameter. 9 filters yielded less than 1 μgC . Three more filters gave between 1 and 2 μg , but for one of these a strongly increased amount of non-condensable gases (at 77 K) was detected in the quartz vial after combustion. This indicates leakage, thus a supposed contamination of this filter might have

escaped. There exist, however, three outliers (4.0, 4.5 and 6.2 μgC) for which no obvious problems were noted. Noticeably, two of these (and one filter very close to 2 μg) were prepared the same day early on in our experiments, when the procedure was not established, and longer waiting times occurred. If the three outliers are rejected, the average blank value is 0.9 μgC , with a standard deviation of 0.6 μgC .

The influence of the delay between baking of the filters and processing is shown in Fig. 1. Three filters of 25 mm diameter were stored for extended time periods, and compared against a control set processed at the day of baking. These larger filters show a higher background already at the beginning (average 2.4 μgC , standard deviation 0.6 μgC). The contamination increases by 0.6 μgC per day to a saturation level of 6.5 μgC . Naturally, this behavior depends on the storing conditions. A similar filter exposed for 5 days in the running laminar flow box yielded 20 μgC .

In [9] we observed a process blank of 6.8 μgC for filters of 8 mm diameter. Since then, we have removed two possible sources of background: firstly, the tube fittings of the melting pot had a hidden dead volume which likely stored particles from previously measured samples. Thus, part of the carbon observed in process blanks was probably cross contamination. The affected fitting was modified. Additionally, we discovered that the Viton seal of the melting vessel had disintegrated under repeated HNO_3 exposure which had been used for cleaning the vessel prior to use. Particles of this seal have probably contaminated the melt water. We now have changed to a Teflon seal.

For the glacier samples presented in [9] the process blanks were determined by performing the filtration procedure without ice sample, i.e. by filtering the rinsing liquids alone. Ideally, a process blank which is characteristic of the entire procedure should employ a particle-free ice sample. First attempts to produce such an ice blank have failed – measurements yielded between 5.4 and 28.0 $\mu\text{gC/kg}$. Therefore, a systematic study was performed.

Disposable PET bottles (1.5 L, from commercial mineral water) serve as moulds for the ice samples. Their shape

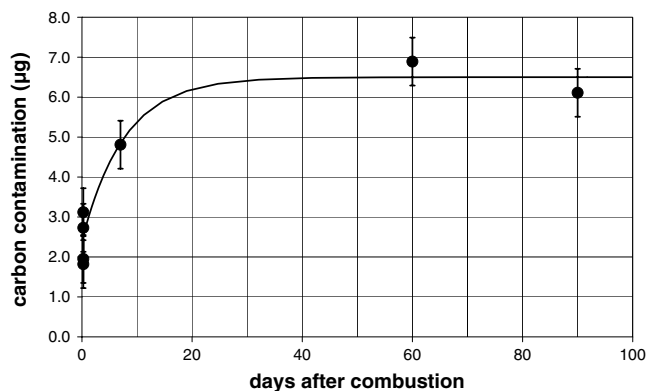


Fig. 1. Degradation of baked quartz filters by carbon uptake during storage.

resembles a piece of a drill core and fits perfectly into our melting vessel. Different from glass, they do not crack during freezing, and they can be cut open and stripped easily for removal of the ice. We compared rinsing with a laboratory detergent (Mucosol, Merz + Co), with diluted NH_3 , and with DDH_2O for cleaning, but found no significant difference. A total of six bottles were filled with filtered DDH_2O and immediately pushed out again through a sample filter. The carbon masses found for these water blanks lie between 0.4 and 2.7 μgC . The very same bottles were reused when producing artificial clean ice by freezing the filled water bottles.

Two of these artificial ice samples have been processed so far, by filtrating them in a similar way to a regular ice sample. Combustion and manometric measurement of the CO_2 gave a value of $1.3 \pm 0.3 \mu\text{gC}$ for both samples.

4. Combustion

The measurement of μg amounts of carbon dioxide is possible with our graphitization apparatus [9] with a reactor volume of $2.6 \pm 0.2 \text{ cm}^3$ (1 mbar CO_2 corresponds to 1.3 μgC). In our regular procedure, the samples are combusted for four hours inside evacuated, flame sealed quartz vials. Evacuation time and oven cool down duration extend the total time needed to about nine hours. For systematic investigations, where the proceedings depend on the outcome of the previous experiments, the turn-around time is crucial. A faster (and simpler) method was necessary. Instead of flame-sealing, the quartz vials are now closed with a valve (Swagelok, Type SS-4P4T).

Possible sources of contamination in this step are carbon in or on the copper oxide and, special to our procedure, degassing of the valve seals, and leakage of ambient carbon compounds through the valve. The yield may be degraded by incomplete combustion due to too short duration or too low temperature, by CO_2 escaping through a leaking valve, or if sample material evaporates and condensates inside the valve which has to remain at room temperature.

The sample is placed at the bottom of a quartz vial (200 mm length, 6 mm outer/4 mm inner diameter), which is then filled with copper oxide about half way up. During evacuation of the vial, we observed that copper oxide particles were blown into the valve, causing leakage. Thus, the vials are now closed by quartz filters of 6 mm diameter placed inside the valve fitting. During evacuation, the sample is heated to $\sim 110^\circ\text{C}$ until the pressure in the vacuum system close to the vial drops to 10^{-3} mbar (measured with a Convectron gauge). This is mainly required to remove water if the sample is a wet quartz filter, and takes 10 to 15 min. We have not yet investigated whether this preheating removes volatile laboratory contamination or leads to sample losses by evaporation.

The closed, evacuated vial is inserted into a vertical tube oven set to 850°C , while the valve is cooled by a fan. For the first five minutes, the bottom end of the vial sticks out through a small hole in the base plate of the oven. The

copper oxide is brought to combustion temperature, while the sample is still cold. The sample is then pulled into the center of the oven. By heating the copper oxide before the sample is heated, we ensure that even volatile carbon compounds are oxidized because vapors have to pass through the pre-heated copper oxide. Elongated evacuation times and the detection of non-condensable gases after combustion are indications for leakage of the valve or the fitting.

Copper oxide was already identified as a possible source of contamination at other laboratories (see [6] and references therein). We chose it as the first target for our investigations, before the combustion with valve-sealed vials was available. Eleven samples containing between 100 and 1000 mg copper oxide were combusted in flame-sealed vials for four hours at 950 °C. We observed that the resulting CO₂ pressure was low or consistent with 0 mbar, and it showed no trend with the amount of copper oxide. Thus, we conclude that the copper oxide contributes only negligibly to the carbon contamination. We tried a radiocarbon determination only for one sample which gave a pMC of 50 ± 5 . However, due to the low CO₂ pressure we cannot be sure whether the carbon measured in the AMS really originates from the copper oxide.

Since time saving was a main objective of the new method, we have limited the combustion time to about 1 h. Together with the lower temperature, this might lead to incomplete combustion. Known amounts of three different carbon compounds have been processed to study the CO₂ yield: polyethylene terephthalate (PET), sucrose and graphite. Compact pieces (graphite splinters, sugar grains, cuts of PET) were used, since they are easier to weigh and handle. Additionally, they are expected to burn slower than dispersed material, so we expect to obtain a lower limit for the efficiency. The materials were inserted into vials already containing a moistened quartz filter to simulate realistic conditions. For two PET samples and one sucrose sample (0.8, 3.5 and 1.0 mgC, respectively) we observed a CO₂ yield of $(79 \pm 1)\%$. This yield is sufficient for our purposes. In contrast to that, the yields for graphite were significantly lower and not reproducible. For five samples between 0.17 and 0.43 mgC, the yields varied between 4% and 53%.

Despite the uncertainty introduced by the low combustion efficiency for graphite, we used this method in the later part of our investigation on laboratory contamination.

5. Graphitization

Our small-sample graphitization unit [9] is based on the method described by Vogel et al. [11]. The combined background introduced by graphitization and AMS measurement was already determined in [9] as 0.5 µgC on average, but with large scatter. Background may enter in the graphitization process via the iron catalyst and through cross-contamination between samples. We have investigated the contribution of the iron catalyst used (Merck,

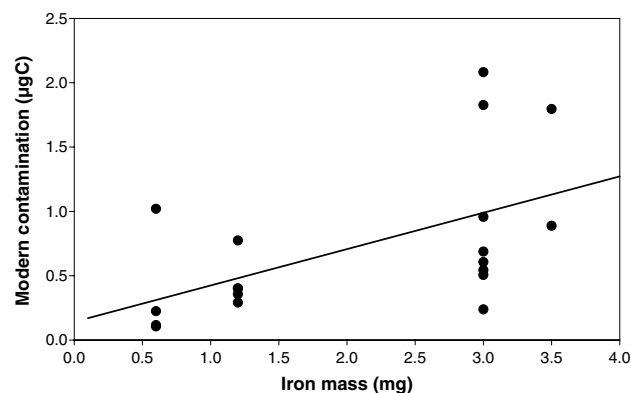


Fig. 2. Contamination with modern carbon versus amount of iron catalyst used for the graphitization reaction. The contamination was calculated from the pMC measured for “dead” CO₂ by assuming 100 pMC of the contaminant. The trend indicates a contribution from the iron.

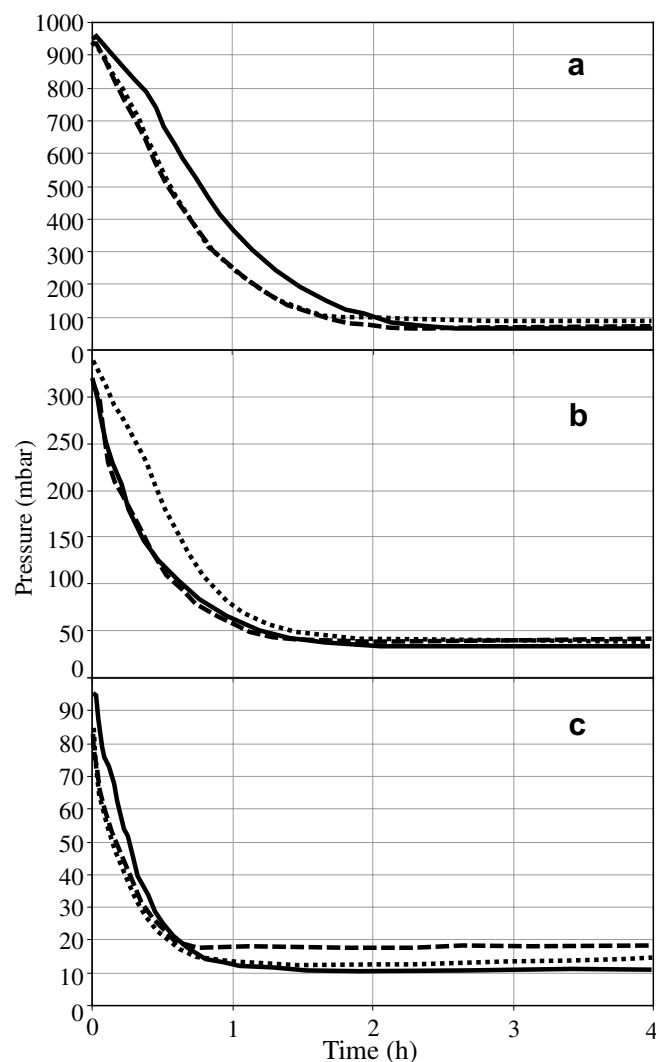


Fig. 3. Pressure versus time curves of the graphitization of different amounts of CO₂ and iron catalyst. (a): 400 µgC, (b): 130 µgC, (c): 40 µgC. Solid lines: 0.6 mg Fe, dashed lines: 1.2 mg Fe, dotted lines: 3.0 mg Fe. The reaction rate depends on the amount of CO₂ (1 mbar CO₂ = 1.3 µgC), but not on the iron used.

grain size 10 μm , produced by reduction) systematically. The CO_2 used is commercially available (Linde, purity >99.9993 vol%), obtained from a Hungarian mineral spring and is free of ^{14}C [12]. The graphite samples were measured for ^{14}C with AMS. The results are shown in Fig. 2. Despite the significant scatter of the data points, there is a significant correlation between the amount of iron used and the contamination with modern carbon. On average, the 9 samples containing less than 2 mg Fe yielded $0.4 \pm 0.1 \mu\text{g}$ modern C, whereas the 11 samples above 2 mg Fe yielded $0.9 \pm 0.2 \mu\text{g}$ modern C (the uncertainties of the average values was estimated from the standard deviations, which are 0.3 and 0.7 μg modern C, respectively).

Presently, the reaction is terminated after a pre-selected time interval by the control computer, by switching off the ovens and by pumping off the H_2 (and any residual sample CO_2). To assess the time required and to minimize it, we have systematically investigated the dependence of the amounts of iron catalyst and sample CO_2 on the duration of the reaction (Fig. 3). Interestingly, varying the amount of iron from 0.6 to 3.0 mg does not influence the reaction rate, which on the other hand depends significantly on the amount of CO_2 (varied from 30 to 300 mbar). All reactions lasted less than 3 h, so we decided to automatically terminate the reactions after 4 h.

6. Conclusions and outlook

Contamination can enter at every stage of processing ice samples. Systematic investigations allow to assess its sources and help to minimize their effect.

Freshly baked quartz filters take up ambient carbon quickly, thus it is best practice to use them the same day. For the combustion of unused, wetted quartz filters, a blank of $0.9 \pm 0.6 \mu\text{gC}$ is achieved. However, several outliers with much higher contamination (several μg) still impose a problem. Such outliers can be the result of unnoticed faults in the processing, but are also inherent to the nature of particulate contamination which is not a quasi-continuous, reproducible process, but dominated by a few large particles. For two artificial ice blank samples processed with the complete filtration procedure, a background of 1.3 ± 0.3 was measured, which is only insignificantly higher than obtained for unused filters. This is significant progress compared to our background of $6.8 \mu\text{gC}$ reported in [9]. Investigations on the influence of the iron catalyst used show that a part of the background of typically $0.5 \mu\text{gC}$ in graphitization and AMS measure-

ment can be attributed to the iron catalyst used, so a reduction of the amount or an improved pretreatment procedure is desirable. This will be the next goal for systematic investigations.

Whether the reduced background can improve the precision of ^{14}C dating of ice will be investigated by new measurements on samples from Gorner–Glacier. If an insufficient reproducibility of the results is observed again, it can be no longer attributed to laboratory contamination, but should be interpreted as a true inhomogeneity of the age of the POC.

Flame sealing requires some skill and imposes a hurdle for personnel with little experience (like students employed for only a few measurements) or little practice (like scientists preparing only a handful of samples per year). Sample combustion in valve-sealed vials was found to be significantly simpler, and can be done in much shorter time. For organic compounds tested, the combustion yield was high, only compact graphite grains could not be combusted sufficiently within 1 h. Longer combustion duration and higher temperatures can probably raise this efficiency, allowing us to apply this method also for true samples.

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