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Evaluation of a 2-step thermal method for separating organic and elemental carbon for radiocarbon analysis

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Abstract

We thoroughly characterized a system for thermal separation of organic carbon (OC) and elemental carbon (EC) for subsequent radiocarbon analysis. Different organic compounds as well as ambient aerosol filter samples were introduced into an oven system and combusted to CO_2 in pure O_2. The main objective was to test which combustion times and temperatures are best suited to separate OC and EC. The final separation step for OC was combustion at 360 °C for 15 min. Combustion at this temperature proved enough to remove several organic test substances from the filter (including high molecular weight humic acid) but did not remove substantial amounts of EC. For isolation of EC, OC first needs to be completely removed from the filter. This was achieved by water extraction of the filter, followed by combustion of the water insoluble OC at 360 °C and combustion at an intermediate temperature step of 2 min at 450 °C. This last step removed the most refractory OC together with some EC. Finally, the remaining EC was combusted to CO_2 at 650 °C. The recovery of black carbon after the intermediate 450 °C step was approximately 80 %. Several tests provided strong evidence that OC was removed efficiently during the intermediate temperature step: (i) brown carbon, indicative of refractory OC, was removed; (ii) the fraction modern of EC did not decrease significantly if the temperature of the intermediate step was further increased. Based on tests with various organic compounds, we estimated that charred organic carbon could contribute 4–8 % to an elemental carbon sample that was isolated according to our method.

1 Introduction

Radiocarbon (^{14}C) measurements allow to distinguish fossil from contemporary carbon sources of carbonaceous aerosol and have therefore become an important method of source apportionment (e.g., Currie, 2000; Szidat et al., 2006, 2009; Gelencser et al., 2007; Schichtel et al., 2008; Minguillon et al., 2011; El Haddad et al., 2011; Genberg et al., 2011; Gilardoni et al., 2011; Glasius et al., 2011; Dusek et al., 2013). This method exploits the fact that the radioactive carbon isotope ^{14}C is not present in fossil fuels, whereas it is present at a typical contemporary level in carbonaceous material that derives from living biomass. The contemporary ^{14}C level is maintained by the production of ^{14}C from the absorption of thermal neutrons, generated by cosmic ray showers, by N_2, mainly in the upper troposphere and stratosphere. The produced ^{14}C is quickly oxidized via CO to $^{14}CO_2$, which is taken up by the biosphere. Therefore a characteristic $^{14}C/^{12}C$ ratio is established for the biosphere, which is closely linked to the atmospheric $^{14}C/^{12}C$ ratio (Levin et al., 2010). In organic material that does not exchange CO_2 with the atmosphere (e.g. fossil fuel), the ^{14}C isotope decays with the characteristic halflife of 5730 yr (Godwin, 1962).

The $^{14}C/^{12}C$ ratio of a sample is always reported relative to a standard of oxalic acid, whose activity is related to the activity of the biosphere under natural circumstances in the year 1950. We report our ^{14}C data as fraction modern ($F^{14}C$), following the nomenclature of (Reimer et al., 2004),

$$F^{14}\mathrm{C} = \frac{\frac{^{14}\mathrm{C}}{^{12}\mathrm{C}}(\mathrm{sample})}{\frac{^{14}\mathrm{C}}{^{12}\mathrm{C}}(1950)}. \tag{1}$$

The $^{14}C/^{12}C$ ratio of the sample and the standard are both corrected for machine background and normalized for fractionation to $\delta^{13}C = -25$ ‰. The standard is not corrected for decay since the year 1950.

The main sources of carbonaceous aerosol, fossil fuel burning, formation of biogenic secondary organic aerosol (SOA), and biomass burning, have distinct $F^{14}C$ values. In fossil fuels, which have been buried for much longer periods than the ^{14}C half-life, all ^{14}C has decayed and $F^{14}C$ is therefore 0. $F^{14}C$ of the current atmospheric or living biospheric carbon would ideally be around 1. However, atmospheric ^{14}C levels have been altered by anthropogenic processes, in particular by the nuclear bomb tests in the 1960's and emission of fossil CO_2, which does not contain ^{14}C. Nuclear bomb testing almost doubled the ^{14}C levels in the atmosphere, but since the stop of the bomb tests F^{14}C of atmospheric CO_2 has decreased steadily and is currently estimated at $F^{14}\mathrm{C} \sim 1.04$ (Levin et al., 2010). As a consequence, primary and secondary particles from biogenic origin have $F^{14}\mathrm{C} \sim 1.04$. Wood combustion is characterized by a variable F^{14}C, depending on the age and origin of the wood, since most of the wood burned today was fixed during the elevated ^{14}C levels following the nuclear bomb tests. Estimates based on tree growth models (e.g., Lewis et al., 2004; Mohn et al., 2008) give a range from 1.08 to 1.30 for biomass burning aerosols (Szidat et al., 2006, 2007, 2009; Minguillon et al., 2011; El Haddad et al., 2011; Genberg et al., 2011; Gilardoni et al., 2011).

The carbonaceous aerosol is often operationally subdivided in carbon fractions that comprise classes of carbonaceous material with similar properties. One of the most common sub-divisions aims to separate organic carbon from more refractory carbon components that are usually combustion derived and often referred to as soot, elemental, or black carbon. Organic carbon is assumed to consist primarily of individual organic molecules that are not or only weakly light absorbing and cover a great range of volatilities. On the other hand, a universal definition of elemental carbon, black carbon or soot is not agreed on in the literature and what is meant by these terms is often dependent on the analytical method or the context of the research (e.g. Petzold et al., 2013). This ambiguity is mostly caused by the fact that a clear distinction between organic and elemental carbon does not exist, but rather a continuous transition through more and more complex aromatic structures (e.g., Pöschl et al., 2006; Hammes et al., 2007). These include tars, chars, amorphous-like carbon consisting of randomly oriented poly-aromatic layers (e.g., Gustafsson et al., 2001) and finally carbon nano-spheres, which are thermally most refractory and strongly light absorbing (e.g. Ishiguro et al., 1997). These carbon fractions show gradually lower H/C and O/C ratios (e.g. Hammes et al., 2007), higher thermal refractivity and generally increasing light absorption. Petzold et al. (2013) suggest the use of the term "EC", with respect to the refractory component determined by thermal(-optical) methods. However, since the thermal method we use in this work is not a standard method, we will use the general term RC for refractory carbon isolated with our method and reserve the term EC for standard thermal-optical analysis.

Despite a lack of a clear separation between organic and refractory carbon, the division into refractory and organic carbon is still useful for source apportionment. The thermally refractory carbon in aerosols is more likely to be combustion-derived, even if some of the less refractory parts of the EC continuum, such as chars, are included. If the separation of organic carbon (OC) and refractory carbon (RC) is pragmatically set at a point in the EC continuum that includes only refractory combustion derived carbon into RC, performing ^{14}C analysis on RC and OC separately can help distinguish biomass burning and fossil fuel sources of aerosol carbon. Since RC does not contain any secondary carbon, which usually has a strong contribution from modern sources, RC usually has a lower F^{14}C than OC in most ambient samples.

The main challenge remains to isolate combustion-derived RC as completely as possible from organic material for ^{14}C analysis. The most common solutions for isolating RC (e.g. Szidat et al., 2004; Zhang et al., 2012; Bernadoni et al., 2013) are based on the thermal method by Cachier et al. (1989). In these methods, organic material is volatilized and oxidized to CO_2 during a low temperature step (S1) in pure oxygen. Then one or more intermediate steps, possibly in different atmospheres, are used to remove the most refractory OC together with the less refractory part of the EC continuum. In this work we used one intermediate step in pure oxygen (S2). Finally, a high temperature step (S3) in pure oxygen is used to oxidize the most refractory carbon to CO_2. The CO_2 isolated in step S1 is assumed to be representative of organic carbon (OC). The remaining material burnt in step S3 will be called “extracted refractory carbon” (RC_e) in this work.

In practice there are several artifacts that can lead to incomplete separation of OC and RC: (1) refractory organic material remaining after S1 and S2, for example biological particles; (2) charring and pyrolysis of organic compounds during S1 and S2, which produce material that is inseparable from the char and elemental carbon that was contained in the particles originally; (3) premature loss of refractory carbon during steps S1 and S2 through catalytic reactions. The first two mechanisms transfer organic material into the extracted refractory carbon, and therefore usually bias $F^{14}C_{(RC_e)}$ towards high values. Premature loss of RC results in a lower yield of RC, which might make ^{14}C analysis difficult. Since soot from burning biomass seems to be slightly less refractory than soot from fossil fuel burning, it is more easily lost in step S2, which will affect the source apportionment of RC (e.g., Han et al., 2007; Song et al., 2012; Zhang et al., 2012).

The goal of this research is to thoroughly evaluate a separation method for OC and EC based on the THEODORE method that was first proposed by Szidat et al. (2004). Our method was developed roughly in parallel with two other recently published methods (Zhang et al., 2012; Bernadoni et al., 2013) and used to analyze a large set of aerosol filter samples collected in the Netherlands. The evaluation of the current method will be also be compared to these two other methodological studies.

2 Materials and methods

2.1 System description

The system used for thermal separation of OC and EC at IMAU is shown in Fig. 1. It can be divided into two subsystems: (1) the extraction line where the combustion of the aerosol samples and the CO_2 formation occurs and (2) the CO_2 purification line, where the carbon dioxide is collected, purified and stored. These two parts are separated by a needle valve (D) that regulates the flow through the reaction tube (usually 30–50 mL min^{-1}). The needle valve keeps the pressure in the extraction line high, at roughly 1150 mbar, whereas the pressure in the second part is kept below 20 mbar, in order to prevent condensation of O_2 in the cryogenic traps.

The first part of the system, the reaction tube, is made from quartz glass and surrounded by three ovens (C). The tube can be opened and a movable sample holder can be inserted. This filter holder can be moved either into the first or the second oven. The first oven is kept at a temperature below 400 °C and used for OC combustion. The second oven is used for RC combustion. In the third oven, remaining incomplete combustion products are oxidized to CO_2 over a platinum catalyst at 650 °C.

The reaction tube is connected to two gas lines that provide pure helium (He) or oxygen (O_2). The first is an inactive gas used to clean the system before sample extraction, whereas O_2 is introduced for the combustion reaction and CO_2 formation. Before reaching the reaction tube, these gases are purified. For flushing of the extraction tube these gases can be directed by valve E directly to the vacuum pump. In this setting of valve E the CO_2 purification line is disconnected from the extraction line.

For collection of a CO_2 sample, valve E is switched and the gases are directed via valve F to the first cryogenic trap (1) and further via valve G to the glass line and vacuum pump. The cryogenic trap is cooled with liquid nitrogen and CO_2 and other gases with sufficiently low vapor pressure are collected, whereas O_2 and gases with higher vapor pressures are pumped away. At the end of the collection process, valve E is switched to disconnect the purification line from the extraction line and trap 1 is warmed to release the collected CO_2. By switching valve F the released CO_2 is flushed with He through the Cu reduction oven to remove traces of NO_x. The water trap after the reduction oven is cooled to −70 °C using a dry ice-ethanol mixture. The CO_2 is collected in cryogenic trap 2. After closing of valve F and evacuation of the purification line, the CO_2 can be released from this trap into the glass line. The glass line consists of different components: a flask containing phosphorous pentoxide (P_2O_5) to remove any remaining traces of H_2O vapor, a calibrated volume with pressure sensor for a manometric determination of the amount of CO_2, and sample tubes where the CO_2 is stored until the ^{14}C analysis.

2.2 Measurement protocol

Before an experiment is started, a sample is inserted into a movable filter holder and placed in the reaction tube. After flushing with He and O_2 the sample is introduced into one of the ovens. For total carbon (TC) combustion the filter piece is directly inserted into oven 2 and heated to 650 °C for 15 min. The organic carbon (OC) combustion is done in oven 1, usually at 340 °C or 360 °C for 15 min, but a range of possible parameters is evaluated in this work. After this step, RC is isolated. The protocol for the RC isolation is the main focus of this work and will be discussed in detail in Sect. 3.

2.3 Preparation of test filters

We performed experiments using known chemical substances to evaluate various aspects of the OC and RC separation. We used organic compounds and mixtures that represent typical components of the ambient organic aerosol: Glucose (alpha-D-Glucose, anhydrous, 96 %, Aldrich), Humic acid (Aldrich), a hydrocarbon standard mix (AccuStandard DRH-002S-R1), a fatty acid methyl ester (FAME) mix (Suppelco47885-U), and a non-volatile organic acid standard mix (Suppelco 46985-U). The exact composition of the organic mixtures is given in Tables 2–4. These organic compounds were applied to pre-heated quartz fiber filters of the same type that is used for collection of ambient aerosol samples. Small amounts (50–500 µL) of the three liquid organic mixes were directly pipetted onto the filter. The filters were analyzed after a short drying to evaporate the solvent (chloroform). Glucose was applied as an aqueous solution (50–100 µL) and the filter was dried before analysis over silica gel for several hours. In some experiments a commercial *carbon black* (Elftex 125, Cabot Corporation) was used as a surrogate for RC. The carbon black was pre-heated to 650 °C in air (not O_2) for 2 h to remove adsorbed organic material and a suspension of 0.2 g of carbon black in 100 mL of a 20 : 80 % ethanol – deionized water mixture was prepared. 200 mL of this suspension was applied to the filters, which were then dried over silica gel for 24 h.

2.4 ^{14}C measurements

The CO_2 collected from the combustion of various aerosol fractions was sent to the Centre for Isotope Research (CIO) at the University of Groningen for graphitization and AMS measurement. There CO_2 was reduced to graphite on a porous iron pellet (de Rooij et al., 2010) at a temperature of 600 °C in the presence of hydrogen gas at a molecular ratio of H_2/CO_2 of 2.5. The water vapor formed during the reaction was cryogenically removed using Peltier cooling elements. The graphitization yield is usually virtually 100 % for samples larger than 30 µg. The iron pellet was pressed into a 1.5 mm target holder, which was introduced into the AMS system for subsequent measurement.

The high-throughput AMS system (van der Plicht et al., 2000) is dedicated to ^{14}C analysis, and measures simultaneously $^{13}C/^{12}C$ and $^{14}C/^{12}C$ ratios. Sample batches are usually analyzed together with varying amounts of reference materials ranging from 50–500 µgC. Two reference materials with known ^{14}C content are used: the HOxII standard ($F^{14}C = 1.3406$) and graphite derived from a ^{14}C free CO_2 gas ($F^{14}C = 0$). Contamination during the graphitization and AMS measurement causes deviations of the measured $F^{14}C$ values from the nominal values. The magnitude of these deviations can be used to quantify the contamination with modern ($F^{14}C = 1$) and fossil carbon ($F^{14}C = 0$), which in turn are used for correcting the sample values (de Rooi et al., 2010). The modern carbon contamination is between 0.15 and 0.35 µgC, and the fossil carbon contamination is typically around 1 µgC (Prokopiou, 2010).

2.5 Filter handling

Ambient aerosol samples were collected on Whatman quartz fiber filters (QMA 1851-150) using a high volume sampler (Digitel, DHA-80). Before loading, the filters were pre-heated at 800 °C for several hours, then wrapped in pre-heated (500 °C) aluminum foil and stored in sealed polyethylene bags at −18 °C until use. Then the filters were placed into the high volume sampler in a filter holder that was pre-cleaned with ethanol. After sampling the filter was removed from the sampler immediately, wrapped again in clean aluminum foil and stored at −18 °C in a sealed plastic bag until analysis. During the transport to and from the field site (approximately 1 h) the filters were kept at ambient temperature. Blank filters used to determine the contamination introduced during handling and storage were treated exactly like the sample filters, except that they were kept in the high volume sampler for one minute only without switching on the sampler.

For analysis circular pieces with a diameter of 3 cm were cut from the filter. The tweezers and cutter were cleaned in acetone followed by ethanol and let dry for at least 10 min before handling the filters. For the separation of refractory carbon the water soluble carbon was removed from the filter pieces by soaking the pieces in MilliQ water overnight (14 mL of water/filter piece) and drying them for 24 h over silica gel. A small fraction of insoluble aerosol material can be lost during the water extraction but this should have little influence on the ^{14}C content of the refractory carbon.

3 Tests of the OC-RC separation method

3.1 Contamination from filter handling and thermal separation

3.1.1 Test procedure

Since organic material is ubiquitously present in the environment, it is virtually impossible to measure small carbon samples without introducing contamination. If the quartz fiber filters on which the aerosols are sampled or the filter holder are exposed to ambient air they quickly adsorb volatile organic carbon. Any contact with tools or surfaces increases the contamination despite pre-cleaning. Therefore, the contamination that cannot be eliminated by our filter handling protocol has to be quantified as accurately as possible and subtracted from the carbon concentration of our samples.

We assessed the contamination introduced by the thermal separation system in two ways. The first way is to directly introduce a pre-cleaned filter piece (7.07 cm^2) into the analytical system and measure the amount of CO_2 after all the extraction steps detailed in Sects. 2.1 and 2.2. A second, indirect way of inferring the contamination is by combusting standard materials with known ^{14}C content and measuring the deviation from the expected values. Two standard materials (see 2.4) a HOxII standard and a ^{14}C free graphite powder were put directly onto the sample holder and combusted at 650 °C for 15 min. Figure 2 shows that F^{14}C measured on anthracite samples deviates from the nominal value of 0 because of contamination during the extraction. As the contamination adds a roughly constant amount of C to each extraction, the experimentally determined F^{14}C of small amounts of standard material deviates more strongly from the nominal value than for larger amounts. The actual contamination can be parameterized as a sum of two components: a modern contamination (M_{mc}) with $F^{14}\mathrm{C}_{(\mathrm{mc})} = 1$ and a fossil contamination (M_{fc}) with $F^{14}\mathrm{C}_{(\mathrm{fc})} = 0$. Then the experimentally determined mass (M_{m}) after subjecting the standard material to combustion and purification can be written as:

$$M_{\mathrm{m}} = M_{\mathrm{st}} + M_{\mathrm{mc}} + M_{\mathrm{fc}}, \tag{2}$$

where M_{st} is the carbon mass of the standard that was introduced into the ovens. This parameterization has a physical foundation, since contamination with aged, partially decayed ^{14}C sources is rare in a laboratory environment and most sources of contamination are either modern carbon or fossil fuel derived. From the F^{14}C values measured in small standard samples we can calculate the mass of modern contamination by a simple mass balance equation:

$$M_{\mathrm{m}} \cdot F^{14}\mathrm{C}_{(\mathrm{m})} = M_{\mathrm{st}} \cdot F^{14}\mathrm{C}_{(\mathrm{st})} + M_{\mathrm{mc}} \cdot F^{14}\mathrm{C}_{(\mathrm{mc})} + M_{\mathrm{fc}} \cdot F^{14}\mathrm{C}_{(\mathrm{fc})}, \tag{3}$$

where M_{m} is the experimentally determined carbon mass, $F^{14}\mathrm{C}_{(\mathrm{m})}$ the experimentally determined fraction modern, and $F^{14}\mathrm{C}_{(\mathrm{st})}$ the nominal fraction modern of the standard material.

Substituting $F^{14}\mathrm{C}_{(\mathrm{st})} = 0$ for the anthracite standard and considering that $F^{14}\mathrm{C}_{(\mathrm{fc})} = 0$ and $F^{14}\mathrm{C}_{(\mathrm{mc})} = 1$, this equation allows to estimate the mass of modern contamination $M_{\mathrm{mc}} = F^{14}\mathrm{C}_{(\mathrm{m})} \cdot M_{\mathrm{m}}$. Once the modern contamination is known, M_{fc} can be derived from measurements of the HOxII standard by substituting $F^{14}\mathrm{C}_{(\mathrm{st})} = 1.3406$, $F^{14}\mathrm{C}_{(\mathrm{fc})} = 0$ in

Eq. (3) and combining with Eq. (2):

$$M_{\mathrm{fc}} = ((1.3406 - F^{14}\mathrm{C}_{(\mathrm{m})}) \cdot M_{\mathrm{m}} - (1 - F^{14}\mathrm{C}_{(\mathrm{m})}) \cdot M_{\mathrm{mc}})/1.3406 \tag{4}$$

3.1.2 Results

The direct determination of the contamination from blank filter analysis yields usually around 1–2 µg of carbon/sample for organic carbon (OC) and extracted refractory carbon ($\mathrm{RC_e}$), which includes all the contamination introduced by filter cutting and handling. This contamination is not increased by subjecting a clean filter to the water extraction procedure, described in Sect. 2.2. Field blank filters yield on average the same amount of OC and a slightly higher amount of $\mathrm{RC_e}$ of 2 µg C sample^{-1}. The latter does not depend strongly on the filter area used. For a typical filter piece of 3 cm in diameter this amounts to approximately (0.35 ± 0.15) µg C cm^{-2} for OC. For $\mathrm{RC_e}$ extraction 2–3 filter pieces are usually analyzed to collect enough material for ^{14}C analysis and therefore the contamination of $\mathrm{RC_e}$ is approximately 0.1 and 0.2 µg C cm^{-2} for three and two filter pieces, respectively.

The organic fraction of one field blank filter was analyzed for ^{14}C by pooling several extracts of the same filter. This fraction had $F^{14}\mathrm{C}_{(\mathrm{OC,blank})} = (79.7 \pm 1.5)\,\%$, which is close to typical ambient $F^{14}\mathrm{C}_{(\mathrm{OC})}$ values. The ^{14}C content of $\mathrm{RC_e}$ was analyzed by pooling $\mathrm{CO_2}$ extracted from 5 different blanks that for test purposes were kept in the filter stacks of the sampler not for one minute but for varying amounts of time up to several days without being exposed to the air stream. The time in the sampler had no effect on $\mathrm{RC_e}$ concentrations, which indicates that $\mathrm{RC_e}$ on the blank filter is only introduced by filter handling and thermal extraction. The $F^{14}\mathrm{C}_{(\mathrm{RC_e,blank})}$ for these 5 samples is (54.3 ± 1.4) %, which is significantly higher than typical values of $F^{14}\mathrm{C}_{(\mathrm{RC_e,blank})}$ from ambient aerosol samples (e.g., Szidat et al., 2006). The blank correction will therefore shift $F^{14}\mathrm{C}_{(\mathrm{RC_e})}$ to lower values.

Twelve independent measurements of the anthracite standard throughout the time period 2010–2013 yielded an average modern contamination M_{mc} of (1.95 ± 0.85) µg C per extraction, excluding one outlier of 6 µg. However, an improved cleaning method for the reaction tube used from 2011 onwards resulted in a lower M_{mc} to (1.38 ± 0.20) µg C per extraction for the 5 standards measured in this time period from 2011–2013. The fossil contamination is on average (1.45 ± 0.21) µg C per extraction for 12 samples between 2011–2013 and is not influenced by the change in cleaning procedure of the reaction tube.

Figure 3 compares the modern and fossil contamination, and the handling blank converted to $\mu\mathrm{g\,cm^{-2}}$ for a typical filter piece of $7.07\,\mathrm{cm^2}$ for OC and TC. For EC the range for 1–3 filter pieces is given. The sum of M_{fc} and M_{mc} is slightly lower than the total carbon handling blank. The blanks are also compared to a filter sample with a carbon mass concentration in the lower range of typical filter samples used for radiocarbon analysis in our group. For samples with a total carbon concentration $\gtrsim 20\,\mu\mathrm{g\,cm^{-2}}$, the amount of carbon on a blank filter is less than 5 % of the carbon amount on a typical ambient filter. Therefore, the blank correction does not introduce large uncertainties to the data.

3.1.3 Discussion

The contamination introduced by the filter handling and analysis is reasonable compared to expected sample size. The contamination is on the order of $1\,\mu\mathrm{g\,extraction^{-1}}$ for OC and RC and probably difficult to reduce even further without special clean room facilities. The sum of M_{fc} and M_{mc}, which is more indicative of the contamination introduced by the thermal extraction system, is lower than the total carbon handling blank. Figure 2 indicates that contamination from filter handling contributes roughly 1/3 to the total blank.

3.2 Loss of elemental carbon at OC combustion temperatures

3.2.1 Test procedure

Several studies show that when heating different kinds of soot in He-O_2 mixtures or air, a small mass loss can start already at fairly low temperatures of around 300 °C (e.g. Sharma et al., 2012; Su et al., 2004). To test for loss of RC at temperatures that are typically used to combust OC we used commercial carbon black samples (Elftex), which is often regarded as an appropriate surrogate for diesel soot (e.g. Yezerets, 2005, and references therein). The carbon black was applied to quartz fiber filters as described in Sect. 2.3. Before analysis, the filters were heated at 100 °C in oxygen to remove any ethanol that might have adsorbed on the filter during the application of the carbon black suspension. The filters were then exposed to 340 °C in pure O_2 for up to two hours and the amount of CO_2 evolved during this time was determined manometrically. Blank filters spiked with only deionized water and ethanol were analyzed in the same way and the carbon amount found on the blank filter (around 1 $\mu g\,cm^{-2}$) was subtracted from all analyzed filters.

3.2.2 Results

Figure 4 shows the loss of carbon black material at 340 °C in O_2 as a function of oxidation time for two types of quartz fiber filters, namely circular Whatman QMA 1851-150 (Filter 2) as used for the ambient samples in this study, compared with a square Whatman QMA No: 1851-865 (Filter 1), which was already several years old. The loss of carbon black increases linearly with oxidation time and the rate is roughly half for filter 2. Impurities in the filter material can catalyze the loss of soot and this example shows that the quartz fiber filter material itself can make a difference in the rate of oxidation of soot. On filter type 1, which was used in all subsequent studies with this system, approximately 1.5 h are necessary to oxidize 10 % of the carbon black at 340 °C. Considering that the filter is only heated for 15 min for OC determination, the loss of carbon

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black in this time period is less than 3 %. In ambient aerosol the concentration of RC is usually significantly smaller than the concentration of OC. Assuming that typically 20–30 % of total carbon consists of RC the contribution of prematurely evolved RC to the extracted OC should be below 1 %, if carbon black is a suitable model for atmospheric RC.

3.2.3 Discussion

Several studies (e.g., Sharma et al., 2012; Han et al., 2007) show that most carbon black samples are somewhat more thermally refractory than diesel soot, which in turn seems to be more refractory than soot from wood burning, at least with respect to the thermal-chemical oxidation method (Song et al., 2012). Therefore, the carbon black experiments can give a reasonable estimate for the loss of more refractory types of soot, but it must be kept in mind that some types of soot or char can be less refractory than carbon black. However, it is reasonable to assume that even for less refractory types of soot the contribution of prematurely evolved RC to the OC sample will not exceed a few percent.

This is supported by indirect evidence gained by combustion of an ambient filter sample at increasing temperatures of 300, 320, 340, 360, and 380 °C (not shown). If prematurely oxidized RC significantly contributed to the OC that is combusted at these temperatures, this contribution should increase at higher temperatures. This would cause a decrease of $F^{14}C_{(OC)}$ with oven temperature, since the $F^{14}C_{(RC)}$ is usually considerably smaller than $F^{14}C_{(OC)}$. Even though the amount of extracted OC increased with oven temperature and was 30 % higher at 380 °C than at 300 °C, $F^{14}C_{(OC)}$ remained at 80.9 ± 1.3 %, independent of the oven temperature. A similar result was found by Szidat et al. (2004), who also concluded that the influence of prematurely evolved RC on $F^{14}C_{(OC)}$ is negligible.

3.3 Charring of organic test compounds

3.3.1 Test procedure

Charring of organic compounds during thermal desorption is often monitored by optical methods, such as a laser beam, to detect an increase in the light absorption through a filter. This is especially useful when the heating of a filter occurs in an inert gas, where charring is substantial and loss of EC is negligible. When combusting a filter in pure O_2, charring is significantly reduced. A small loss of EC could partially offset the small increase in light absorption caused by charring. It can therefore be difficult to conclusively quantify charring by optical methods, especially on highly loaded filters such as often used for ^{14}C analysis.

We therefore used representative organic test materials described in Sect. 2.3 to investigate their charring characteristics directly. The test compounds were applied to pre-cleaned quartz fiber filters. The filters were introduced into oven 1 at 340 °C for 15 min and the amount of evolved CO_2 was determined manometrically. The combustion step at 340 °C was repeated a second time to verify that all OC was oxidized during the first combustion step. Then the filter was introduced into oven 2 at 650 °C and the evolved CO_2 was measured. Since only organic and no refractory carbon was present on the filter originally, the CO_2 measured at 650 °C originates from the char that was formed during the combustion of the organic test material.

3.3.2 Results

Figure 5 shows that charring is small for all investigated compounds during flash heating in O_2. Less than 2 % of glucose, of humic acid, of the hydrocarbon standard mix, and of the fatty acid methyl ester (FAME) mix is found as refractory carbon after the first OC combustion step. Charring is slightly higher for organic acids, of which 3.5 % are found as refractory carbon. However, these are normally only a small fraction of the total organic carbon in ambient aerosols. Moreover, they are largely removed by water extraction of the filter prior to RC analysis. In general, our results imply that 1–2 % of the water insoluble OC is found as RC_e. Even this small amount can have a measurable effect on $F^{14}C_{(RC_e)}$, because RC_e constitutes usually a small fraction of TC. Assuming that elemental carbon is around 20 % of total carbon, then around 5 % of the analyzed RC_e can be charred organic carbon. Depending on the $F^{14}C_{(OC)}$ this could cause an overestimation of $F^{14}C_{(RC)}$ by up to 5 %.

3.3.3 Discussion

Removal of organic carbon by flash heating in O_2 was originally developed to minimize the charring artifact (Cachier et al., 1989) and from our tests it is clear that this approach is very successful for water insoluble compounds, but less successful for water soluble carbon. WSOC usually also accounts for the majority of charring during heating under inert atmospheres (e.g., Yang et al., 2002). Zhang et al. (2012) used laser transmission measurements to monitor charring during the OC combustion steps. They combusted the water extract of an ambient aerosol sample, which showed even higher charring than the organic acids investigated in this work. However, for water extracted ambient samples they also concluded that the contribution from charred OC to the extracted RC can be reduced to below 5 % for ambient samples. This indicates that the water insoluble test compounds chosen for our charring test are representative of the ambient water insoluble aerosol. This makes them a useful substitute for evaluating charring in OC-EC separation systems that lack optical monitoring. Cachier et al. (1989) found a higher percentage of charred humic acids remaining on the filter (∼ 30 %) and somewhat higher amounts of charred glucose (∼ 10 % for filter loadings comparable to our work). The reason for this difference is not clear.

3.4 Tests with ambient filters

3.4.1 Test procedure

During the charring tests we found that, except for a small charred fraction, all organic test compounds used in this study were removed after combustion at 340 °C for 15 min in pure O_2, even high molecular weight humic acid. However, the continuous transition from OC to the most refractory carbon in form of elemental carbon nano-spheres in ambient aerosols is difficult to capture using simple test compounds. Therefore ambient samples are also used to test the efficiency of separating OC and RC in ambient aerosols.

The extraction methods usually utilize a practical compromise by excluding compounds with intermediate refractivity from the analysis. A short intermediate step S2 in O_2 at higher temperature should remove a mixture of the most refractory organic material and less refractory elemental carbon from the filter (e.g. Szidat et al., 2006; Zhang et al., 2012). However, the use of too harsh oxidation methods that allow only the most refractory part of RC to be recovered have the disadvantage that biomass burning soot is likely selectively lost. Biomass burning soot is less refractory than soot from liquid fuels (e.g., Song et al., 2012; Zhang et al., 2012) and has been found to evolve together with chars during thermal treatments rather than with diesel soot. Selective removal of biomass burning soot thus artificially decreases $F^{14}C_{(RC_e)}$ which leads to an underestimate of the fraction modern of RC.

We therefore investigate how different choices of parameters for extraction step S2 (with temperature for S1 remaining constant at 340 °C) affect (1) the recovery of RC and (2) the efficiency of OC removal. A water-extracted filter was kept in the first oven for 15 min for OC combustion (S1). Then it was introduced into the second oven at a higher temperature T2 for 1–3 min and the CO_2 that evolved during this extraction step was pumped away. Then the filter was taken out of the oven system, while the CO_2 resulting from the combustion step S1 was purified and processed. For the last step the filter was introduced into oven 2 at 650 °C and RC_e was measured.

The complete removal of OC is difficult to assess directly. However, two indirect estimates are used that can indicate the extent of OC removal. First, refractory OC is often associated with highly polymeric, char- or tar-like substances. These substances are often subsumed under the name “brown carbon” (BrC), which is characterized by its light absorption properties (e.g., Andreae and Gelencser, 2006; Poeschl, 1996). The recovery of RC was estimated by comparing the light absorption of a water extracted filter piece to the absorption of a filter piece after organic carbon was removed during S1 and S2. Absorption was measured using an integrating sphere photometer (Hitzenberger et al., 1996; Wonaschütz et al., 2008). BC and BrC concentrations were determined by measuring the light absorption of the filter pieces at 3 different wavelengths. BrC is distinguished from BC by exploiting the different wavelength dependence of light absorption following Wonaschütz et al. (2008). If brown carbon is removed after S1 and S2, this gives a good indication that the extraction protocol was effective in removing most refractory OC.

A second method is to measure the mass and F^{14}C of the refractory carbon $\mathrm{RC_e}$ as a function of increasing temperature and/or duration of step S2. If a decrease in recovered mass is associated with a strong decrease in $F^{14}\mathrm{C}_{(\mathrm{RC_e})}$, this can be an indication that fairly “modern” organic material is still being removed when the temperature of step S2 is increased.

3.4.2 Results

The effect of the duration and temperature of S2 on the recovery of black carbon are shown in Fig. 6. A duration of S2 of 1 min causes loss of black carbon that does not exceed 20 %. There is little change in black carbon content between a filter that has been exposed to 450 °C and 500 °C for 1 min, which suggests that 1 min of heating might not be enough for the filter temperature to fully reach 500 °C. When the duration of S2 is increased to two minutes an increase in temperature from 400 °C to 450 °C causes little extra loss of BC. The amount of BC remaining after S2 of 450 °C is very similar for exposure times of 1 min and 2 min, suggesting that little additional BC is removed by increasing the oxidation time. However, raising the temperature further to 500 °C strongly decreases the recovered BC to around 60 %. If the duration of S2 is increased to 3 min, then the recovery at 400 °C and 450 °C decreases by only 8 % and remains comparable, whereas the recovery at 500 °C decreases sharply to 50 %. This indicates that a temperature 500 °C is too high, since substantial amounts of BC are removed. A time step of 1 min is likely too short for the filter to reach the desired temperature, therefore a step of 2 min was tried for further experiments.

$F^{14}C_{(RC)}$ of filter CA18 was measured as function of S2 temperature with S2 duration of 2 min. Figure 7a shows that the amount of remaining RC_e (black bars) decreases only slightly if the S2 temperature is raised from 400 °C to 450 °C, but only 50 % of the original RC remains after 2 min at 500 °C. $F^{14}C_{(RC_e)}$ (grey bars) remains virtually unchanged for S2 temperatures of 400 °C and 450 °C and then decreases from 0.36 to 0.31 once the S2 temperature is raised to 500 °C. $F^{14}C$ of the material removed by each successive temperature increase can be calculated according to the mass balance:

$$F^{14}C_{(2-1)} = (F^{14}C_{(RC1)} \cdot M_{RC}(T_1) - F^{14}C_{(RC2)} \cdot M_{RC}(T_2))/(M_{RC}(T_1) - M_{RC}(T_2)), \qquad (5)$$

where $F^{14}C_{(2-1)}$ is the fraction modern of the material that was removed by raising S2 temperature from T_1 to T_2; $F^{14}C_{(RC1)}$, $F^{14}C_{(RC2)}$ are the fraction modern of the refractory carbon recovered after T_1 and T_2; $M_{RC}(T_1)$ and $M_{RC}(T_2)$ are the mass of the refractory carbon recovered after T_1 and T_2. These are shown in Fig. 7a as patterned bars. It is obvious that the removed carbon has a similar fraction modern as the RC_e itself, which suggests that the largest amount of organic carbon was removed already at S2 of 400 °C and the higher temperature steps remove mainly RC. The slight decrease in $F^{14}C$ with increasing S2 temperature results more likely from differential oxidation of biomass burning EC and fossil fuel EC, than from remaining organic carbon. If organic carbon was left in the sample a larger decrease in $F^{14}C_{(RC)}$ between 400 °C and 450 °C would be expected than at a temperature that is high enough to burn significant amounts of black carbon.

Figure 7b shows similar results for a 1 min S2 time step. Filter CA2 was used for these experiments, since not enough material was left of filter CA18 for further tests. An increase in temperature of S2 from 400 °C to 500 °C does not cause a strong decrease in the recovered RC. A similar trend was observed for the black carbon concentrations shown in Fig. 6. This supports our conclusion that the filter itself probably does not reach 500 °C within 1 min. However, even though not much extra material is removed during 1 min at 500 °C, the fraction modern of the recovered RC decreases significantly. Following mass balance Eq. (6), F^{14}C of the carbon removed by raising T to 500 °C is 0.67, very close to the F^{14}C of water insoluble organic carbon of filter CA2 (0.62). This shows that a time period of 1 min for the intermediate step S2 is probably not sufficient to remove all organic carbon from the filter.

The final decision was to use a S2 temperature step of 2 min at 450 °C, because this combines reasonable BC recovery rates with removal of most refractory OC. The removal of brown carbon by this temperature protocol was tested on 4 ambient filter samples. Two of the samples had marine air mass origin, whereas the other two had continental air mass origin. The extraction parameters for removing OC were 15 min at $T_1 = 360$ °C for S1 and 2 min at $T_2 = 450$ °C for S2.

The two samples with marine air mass origin contain little water insoluble brown carbon (Table 1), whereas the continental samples contain significant amounts. After OC removal the brown carbon is below detection level for all test filters, which is further indication for satisfactory removal of the organic fraction. The recovery of BC is approximately 80 % for three of the filters, which is close to the target value for which the S2 step was chosen. However, for filter CA21 the recovery is slightly above 100 %. Filter CA21 was sampled for a week during fairly high aerosol concentrations and has therefore a very high aerosol loading (TC = 219 μg cm^{-2}). It is possible that the saturation of the integrating sphere method is reached and a small loss of BC cannot be detected. However, is also possible that 2 min at 450 °C are not enough to remove such large amounts of OC that is coating the BC. However, since all the brown carbon is nevertheless removed, this does not seem very likely. Alternatively, a fairly high amount of brown carbon that is relatively susceptible to charring could produce measurable amounts of black carbon during S1 and S2. The $F^{14}\mathrm{C}_{(\mathrm{RC_e})}$ values of filter samples with a BC recovery of ~ 1 should be treated with caution, and possibly the extraction procedure should be repeated either with higher temperature or longer duration of S2.

3.4.3 Discussion

The amount and F^{14}C as well as optical properties of $\mathrm{RC_e}$ suggest that an S2 time removal step of 2 min around 450 °C is a good choice for separating organic and refractory carbon. Two other methods published in the literature (Zhang et al., 2012; Bernardoni et al., 2013) use a similar approach but different combustion temperatures and atmospheres. Each is evaluated with different methods, but some main conclusions are similar. The black carbon recovery by the presented method (~ 80 %) is similar to the one reported for the Swiss S4 protocol (Zhang et al., 2012) and slightly higher than in the method proposed by Bernardoni et al. (2013). The contamination of $\mathrm{RC_e}$ with charged OC is estimated to be $< 5\,\%$ in this work and Zhang et al. (2012). This similar performance in different test procedures gives additional confidence in these methods.

The method presented in this work does not use a He step, which the other methods find necessary to remove a non light absorbing carbon fraction that co-evolves with BC in O_2 up to very high temperatures. At present it is not clear whether this carbon fraction is truly organic, such as pollen or other refractory bio-polymers or whether it might be elemental carbon that is potentially not so strongly light absorbing, such as the more amorphously oriented carbon layers seen by Gustafsson et al. (2001).

A future inter-comparison of these three and also other methods (e.g., Zencak et al., 2007; Heal et al., 2011) would shed more light on the issue how strongly the differences in the extraction protocols affect $F^{14}\mathrm{C}_{(\mathrm{RC_e})}$. Such an inter-comparison has been done for organic and total carbon (Szidat et al., 2013), but only very limited data on RC were available at that time.

4 Conclusions

We tested a thermal method designed to separate organic and combustion derived refractory carbon for radiocarbon analysis of aerosol samples. For OC extraction the sample is combusted in pure oxygen at 360 °C for 15 min. For RC extraction a water-extracted filter sample is first subjected to 360 °C for 15 min, followed by a 2 min intermediate combustion step at 450 °C to completely remove OC. After OC removal RC is extracted at 650 °C for 15 min.

The recovery of RC after the OC removal steps was quantified by measuring the recovery of black carbon (BC) using an optical method. The BC recovery was around 80 %, which is comparable to two similar methods (Zhang et al., 2012; Bernardoni et al., 2013). The effectiveness of the OC removal steps are strongly supported by the successful removal of brown carbon in 4 ambient test samples and by the removal of several organic test compounds, including high molecular weight humic acid.

Charring of water insoluble organic test materials was found to be minor. Less than 2 % of the organic test compounds were found as RC after the OC combustion step. From this we estimate that around 5 % of RC could originate from charred OC. This is in close agreement with Zhang et al. (2012), who estimated charring of ambient samples using optical methods.

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Table 1. Brown carbon (BrC) and black carbon (BC) detected in 4 ambient filter samples before OC removal and after OC removal (OC rem.) using S1 at 360 °C for 15 min and S2 at 450 °C for 2 min in pure oxygen. mar – filter with back trajectories starting over the ocean, cont – filter with back trajectories starting over the land.

sample	BrC $\mu g\,cm^{-2}$	BrC (OC rem.) $\mu g\,cm^{-2}$	BC $\mu g\,cm^{-2}$	BC (OC rem.) $\mu g\,cm^{-2}$	BC recovery %	$F^{14}C$ (RC_e)
CA30 – mar	3.81	bdl*	13.21	11.08	84	13.6
CA59 – mar	bdl*	bdl*	2.80	2.21	79	10.4
CA85 – cont	21.54	bdl*	15.04	11.86	79	29.7
CA21 – cont	15.62	bdl*	11.71	12.63	108	39.3

* bdl: below detection limit $< 2\,\mu g\,cm^{-2}$.

Table 2. The following calibration solutions were used for the tests of aerosol charring: (1) ACCU standard (DRH-008S-R2): selected hydrocarbons in chloroform. The concentration of each chemical compound is at stated next to the compound in μg mL^{-1}.

n-Hexane	600
n-Heptane	600
n-Octane	800
n-Nonane	800
n-Decane	1200
n-Undecane	1200
n-Dodecane	1200
n-Tetradecane	1200
n-Hexadecane	1000
n-Octadecane	500
n-Eicosane	200
n-Tetracosane	200
n-Octacosane	100
n-Dotriacontane	100
n-Hexatriacontane	100
n-Tetracontane	100
n-Tetratetracontane	100

Table 3. (2) Supelco FAME (Fatty Methyl Ester) standard mix. This standard contains the following compounds in a total concentration of 10 mg mL^{-1}. The weight percentage of each individual compound is given next to the compound.

Cis 13,16 Docosadienoic acid methyl ester	2 wt. %
cis 4,7,10,13,16,19 Docosahexaenoic acid methyl ester	2 wt. %
cis 11,14 Eicosadienoic acid methyl ester	2 wt. %
cis 5,8,11,14,17 Eicosapentaenoic acid methyl ester	2 wt. %
cis 8,11,14 Eicosatrienoic acid methyl ester	2 wt. %
cis 11,14,17 Eicosatrienoic acid methyl ester	2 wt. %
cis 11 Eicosenoic acid methyl ester	2 wt. %
Methyl cis – 10 heptadecenoate	2 wt. %
Methyl hexanoate	4 wt. %
Methyl γlinolenate	2 wt. %
Methyl arachidate	4 wt. %
Methyl arachidonate	2 wt. %
Methyl behenate	4 wt. %
Methyl butyrate	4 wt. %
Methyl decanoate	4 wt. %
Methyl dodecanoate	4 wt. %
Methyl elaidate	2 wt. %
Methyl erucate	2 wt. %
Methyl heneicosanoate	2 wt. %
Methyl heptadecanoate	2 wt. %
Methyl linoleate	2 wt. %
Methyl linolelaidate	2 wt. %
Methyl linolenate	2 wt. %
Methyl myristate	4 wt. %
Methyl myristoleate	2 wt. %
Methyl oleate	4 wt. %
Methyl octanoate	4 wt. %
Methyl palmitate	6 wt. %
Methyl palmitoleate	2 wt. %
Methyl pentadecanoate	2 wt. %
Methyl cis10pentadecenoate	2 wt. %
Methyl stearate	4 wt. %
Methyl tricosanoate	2 wt. %
Methyl tetracosanoate	4 wt. %
Methyl tridecanoate	2 wt. %
Methyl undecanoate	2 wt. %
Methyl cis15tetracosenoate	2 wt. %

Table 4. (3) Nonvolatile organic acid standard mix. Solvent = water, concentration of each compound is given next to the compound in µg mL^{-1}.

Pyruvic acid	800
Lactic acid	900
Oxalacetic acid	660
Oxalic acid	450
Methyl malonic acid	590
Malonic acid	520
Fumaric acid	580
Succinic acid	590

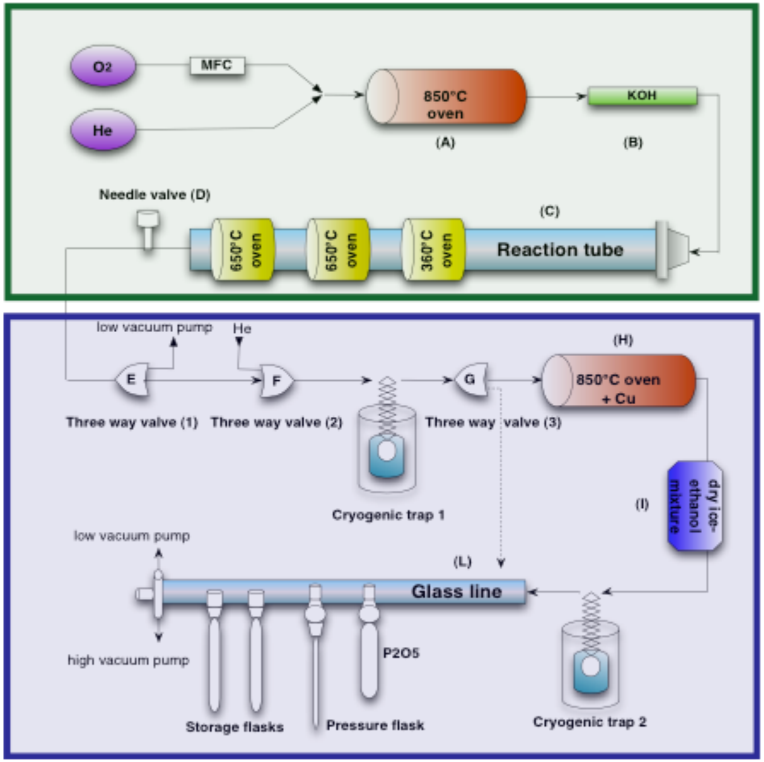

Fig. 1. The EC–OC separation system consists of two sub-systems: (1) the extraction tube (green box), where organic and elemental carbon are oxidized to CO_2 and (2) the purification line (blue box), where CO_2 is collected and separated from interfering gases. By switching three-way valve E to the low vacuum pump the purification line can be separated from the extraction tube.

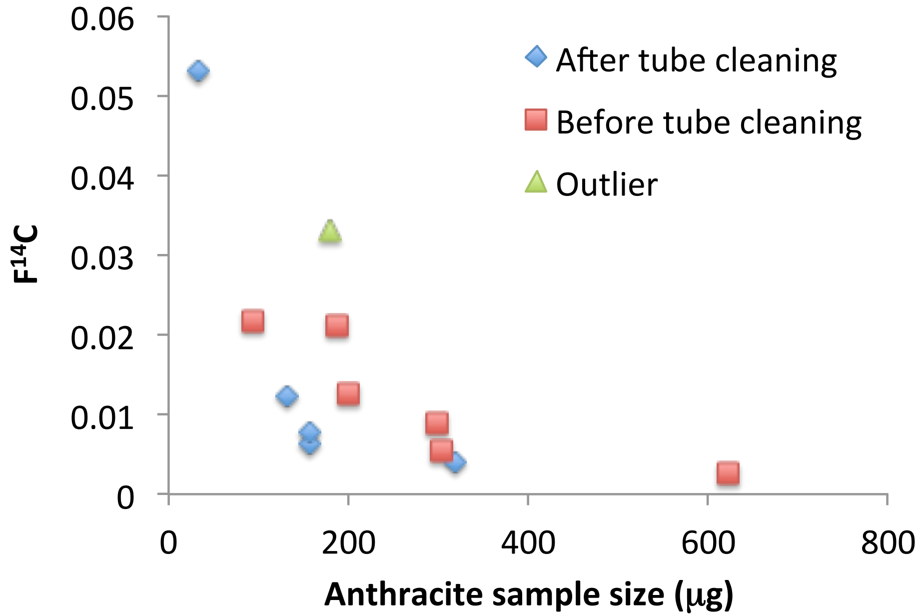

Fig. 2. The experimentally determined $F^{14}C$ of the anthracite standard (nominal $F^{14}C = 0$) as a function of sample size. The blue diamonds correspond to samples measured after a new protocol for cleaning the reaction tube was introduced, the red squares before the new protocol. An outlier is shown in green.

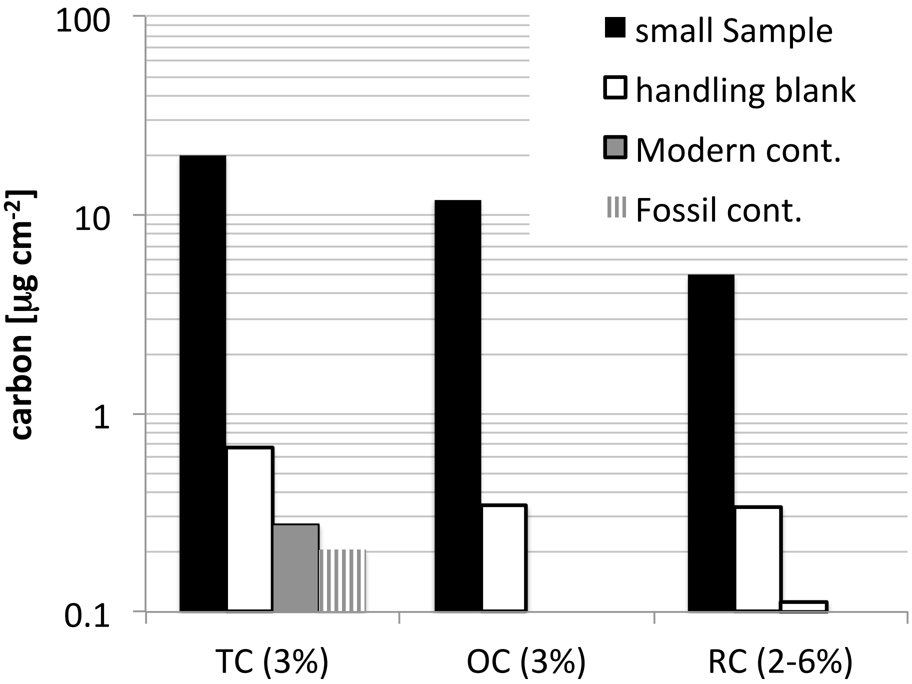

Fig. 3. The carbon concentration found on a typical lightly loaded filter sample compared with the directly measured handling blank (white bars), and the average modern and fossil contamination derived from analysis of anthracite and HoxII standards. The modern and fossil contamination could only be determined for total carbon. The two white bars for RC give an upper and lower limit of the handling blank, depending on the number of filter pieces used in the extraction.

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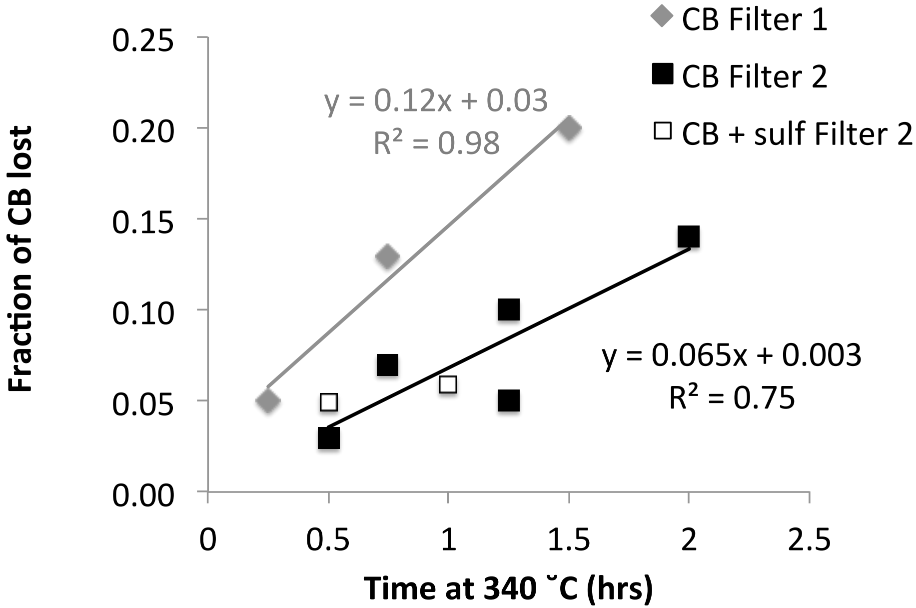


Fig. 4. Fraction of carbon black (CB) that was lost at 340 °C in pure oxygen as a function of oxidation time for two different filter types from the same manufacturer (Filter 1: Whatman QMA 1851-865 and Filter 2: Whatman QMA 1851-150). The open squares correspond to carbon black coated with ammonium sulfate.

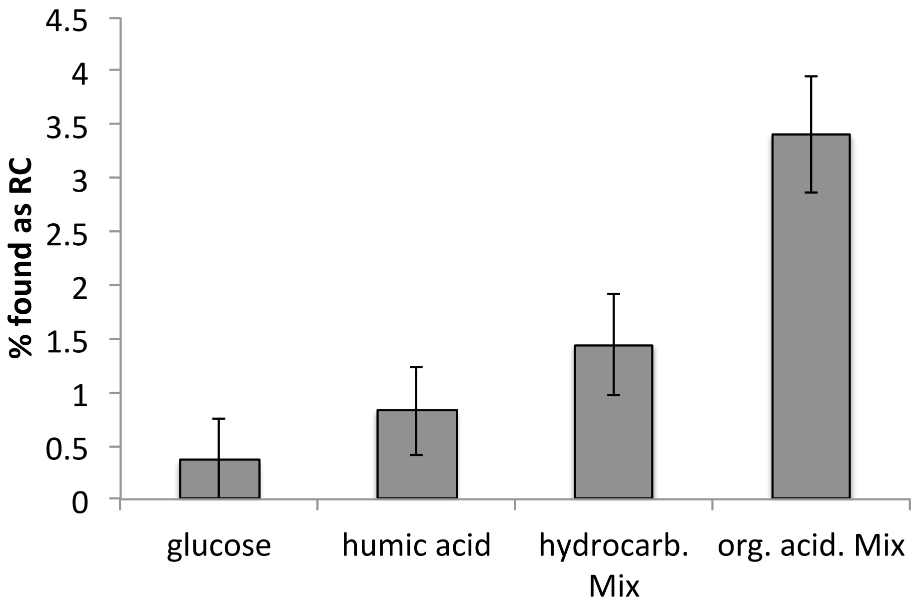


Fig. 5. Charring of several test compounds given as % of the substance found as RC after heating at 340 °C for 15 min in pure oxygen. See the Tables 2–4 for a description of the hydrocarbon and organic acid mixes.

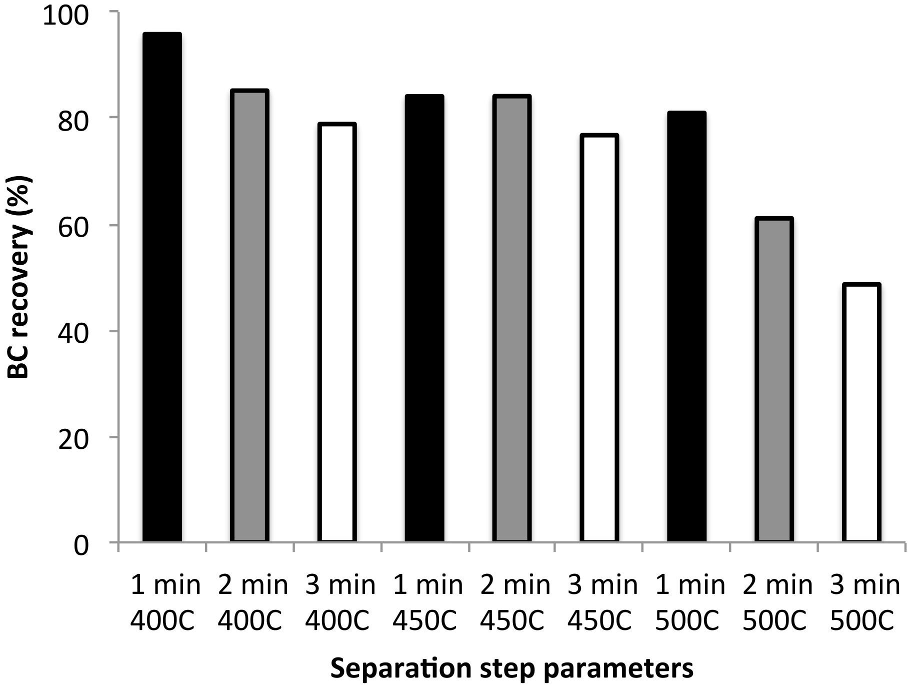
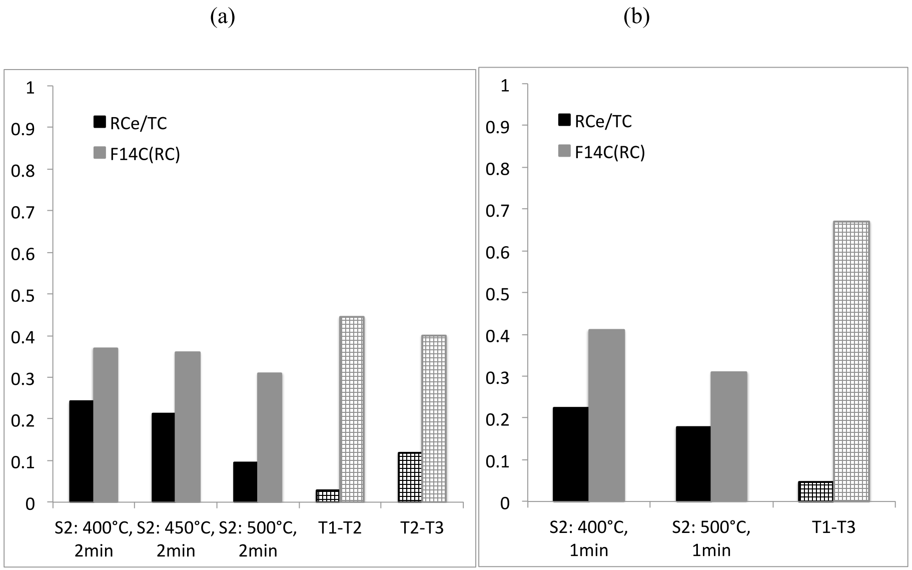


Fig. 6. Black carbon recovery as a function of duration and temperature of separation step S2.


(a)

(b)

Fig. 7. Fraction modern and mass fraction (RC_e/TC)of the extracted refractory carbon (RC_e) remaining after a separation step S1 (15 min at 360 °C) and S2. The duration and temperature of separation S2 are given on the x-axis. The difference in RC_e/TC and $F^{14}C$ (RC_e) found after extraction step S2 at lower and higher temperature are given as shaded bars.