SEALED GLASS TUBE COMBUSTION OF µg-SIZED AEROSOL SAMPLES

J Genberg • N Perron • M Olsson • K Stenström[1]

Department of Physics, Division of Nuclear Physics, Lund University.

ABSTRACT. It is important to evaluate each step in radiocarbon analysis to ensure that the whole process is as efficient and accurate as possible. Aerosol filter samples contain a myriad of carbonaceous compounds with varying resistance to oxidation. Complete combustion of the sample is thus of great importance to ensure that the graphitized sample is representative of the original filter sample. We have evaluated sealed tube combustion of µg-sized aerosol samples using different types and amounts of reagents. Successful analysis of aerosol samples as small as 20 µg C was possible following small changes to our standard on-line method. The sealed tube combustion method performs well for standard samples containing 11 µg C.

INTRODUCTION

Already in the 1950s, radiocarbon was used as a tracer for modern and fossil carbon in carbonaceous aerosol particles (Clayton et al. 1955). In recent years, the technique has been used in several studies as aerosols have been afforded more attention because of their impact on health and climate (e.g. Szidat et al. 2004; Gelencsér et al. 2007; May et al. 2009; Genberg et al. 2011). The information provided by ^{14}C analysis of aerosol particles is valuable in aerosol source apportionment, which is important for aerosol model validation. Since the nuclear signature of the carbonaceous particles is unaffected by chemical processes in the atmosphere, ^{14}C is an almost perfect tracer for sources emitting modern carbon, e.g. the combustion of biofuels. However, the sampling time of the aerosol sample should be short (preferably a day or less to ensure good temporal resolution), which means that the amount of carbon collected is very small. An aerosol sample collected with a low-volume sampler for 1 day at the rural background site of Vavihill in southern Sweden may contain only 70 µg C. Several other analyses, besides ^{14}C measurements, may be conducted using the same filter. It is therefore vital for us to be able to handle µg-sized samples for accelerator mass spectrometry (AMS) analyses.

We have therefore developed a graphitization method capable of handling µg-sized samples as small as 25 µg C (Genberg et al. 2010). That method is based on on-line combustion and has worked satisfactorily. It has, however, resulted in debris in the valves closest to the combustion tubes. Aerosol filter samples are complex matrices containing impurities such as sulfur, nitrogen, chlorine, and metals. Since these compounds can have negative effects on sample purification and graphitization, they should not be spread in the graphitization system. We have therefore adapted and further developed a method of combusting samples in sealed glass tubes, rather than on-line, to minimize their potential effects on graphitization compared to the on-line combustion. Sealed glass tube combustion has also made our samples preparation more effective.

Carbonaceous particles are present in the atmosphere in numerous forms that vary in their resistance to oxidation, and it is important that all the carbon in the filter sample is combusted into CO_2. Buchanan and Corcoran (1959) presented a method using a mixture of copper oxide and manganese dioxide as oxidants for sealed glass tube combustion. Vandeputte et al. (1996) conducted a thorough study on combustion at lower temperatures in sealed Pyrex® glass tubes and found that manganese oxide was required for a satisfactory result. Endo et al. (2004) presented a method for the combustion of aerosol samples on which our method is based. They found that significantly higher amounts

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[1] Corresponding author. Email: kristina.stenstrom@nuclear.lu.se.

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of reagents (copper oxide, copper metal, and silver) were necessary for successful combustion of aerosol samples compared to other samples. However, their study was conducted on sample sizes of 1 mg C. To be able to analyze the small amounts of carbon collected in a few days' aerosol sampling, it was thus necessary to further develop the method for µg-sized samples.

In this study, we have investigated several factors to determine the optimal condition for the combustion of aerosol filter samples in sealed glass tubes. The factors investigated were the type and amount of reagent and the gas transfer system. We have also conducted experiments to validate the method for masses down to 11 µg C.

MATERIALS AND METHODS

The oxidative agent used was copper oxide in the form of rods (0.65 × 6 mm) or powder (Merck, pro analysi). They were cleaned immediately prior to use by flame-combustion in oxygen and vacuum. Iron powder (Merck, pro analysi, 10 µm) was used as the reduction catalyst, and magnesium perchlorate (Merck, $Mg(ClO_4)_2$ 1–4 mm) was used as a water trap. The silver was silver wool (Merck, for elemental analysis). The copper metal was produced by reducing the copper oxide rods in hydrogen gas (Air Liquide, 99.998%) at 500 °C. All glassware (quartz) was rinsed in water and heated at 950 °C in air for at least 2 hr.

Standards were prepared from reference materials IAEA C6, IAEA C7, and OxI, using OxI as primary standard. Background samples consisted of combusted CO_2 from a CO_2 bottle (AGA, 99.99%), acetanilide (Merck, pro analysi), and potassium phthalate (Merck, pro analysi). Aerosol samples were obtained on filters (Pall Tissuquartz™ 2500 QAT-UP) by sampling air from the roof of the Physics Department in Lund, southern Sweden, with a high volume sampler. Sample 1 was collected during early spring 2012 and filter 2 was sampled in late summer the same year. The total carbon content of the samples was determined by a carbon analyzer (DRI thermo optical analyzer 2001).

Combustion and Graphitization

On-line combustion was carried out as described by Genberg et al. (2010). Briefly, the sample was placed in a quartz tube with ~1-g copper oxide rods. The tube was evacuated and the sample was combusted by an open LPG (liquefied petroleum gas) flame. This combustion technique has shown to produce the same yield for aerosol filter samples as the carbon analyzer.

Sealed tube combustion was conducted in a similar way. The sample was placed in a quartz tube (180 mm long, 3/8″) together with the oxidative agent. In some cases, silver wool or copper metal was used to bind impurities. The tube was evacuated and sealed using a hydrogen/oxygen flame. The tube was placed in a muffle furnace and combusted for 10 hr at 900 °C and then left to cool in the oven. The tube was placed in a tube-cracker, which was evacuated and the tube was cracked open in vacuum to retrieve the CO_2.

Regardless of the combustion method, the CO_2 formed was cryogenically purified and converted into solid graphite by hydrogen gas over an iron catalyst at 600 °C, as described previously (Genberg et al. 2010). The carbon was quantified by measuring the pressure change and hydrogen (3 times the measured amount carbon) was added as reduction agent. Our new method differs from that described by Genberg et al. (2010) in the manner in which the graphite is stored before being used as targets for AMS measurements. In our new method, the reaction tubes are sealed with a Swagelok® cap after being filled with argon gas before being pressed. The pressed graphite targets were stored in argon gas to minimize contamination.

The graphite was analyzed at the Lund University Single Stage Accelerator Mass Spectrometer (SSAMS; Skog 2007) and the calculations were carried out using the matching size method (Santos et al. 2007). All ^{14}C data are presented as the fraction of modern carbon ($F^{14}C$) in accordance with Reimer et al. (2004).

Evaluation of the Physical Form of Copper Oxide

In the method described by Endo et al. (2004), copper oxide was used as the oxidative agent during the combustion. However, they did not report the physical form of the copper oxide. In the present study, 2 types of copper oxidants were used: copper oxide rods and copper oxide powder. Powder was added in an attempt to increase the contact area between the oxidant and the particles on the filter, although problems with high background have been found previously (Genberg et al. 2010). Small grains have been shown to increase the yield for pure substances as well as more complex matrices (Vandeputte et al. 1996). Rods were chosen since we have used them previously for the online combustion of small samples and they have proven reliable and produced low background. According to Vandeputte et al. (1996), rods render a lower carbon yield compared to powder.

Evaluation of the Amount of Silver and Copper

As mentioned above, aerosol samples are complex matrices containing contaminants such as sulfur that can affect the graphitization process. In order to remove the impurities, Endo et al. (2004) used both silver (100 mg) and copper metal (500 mg) in the combustion of a 1-mg C sample. In the present study, newly manufactured copper was cleaned by heating in vacuum while silver was used directly from the jar. Roughly 500 mg copper and 0, 10, or 30 mg of silver wool was added to the combustion tube.

RESULTS AND DISCUSSION

Background Due to Reagents

The amount of carbon reacted to CO_2 during combustion of the pure reagents varied considerably. The form of copper oxide (rods or powder) had the greatest effect on the amount of condensable gases detected after combustion, as reported by Genberg et al. (2010). Combustion of copper oxide powder produced condensable gases equivalent to ~1.5 μg C for every 100 mg of copper oxide used (100–800 mg copper oxide). Combustion of rods, on the other hand, produced condensable gases equivalent to ~2 μg C, independent of the amount of copper oxide between 400 and 1000 mg.

Silver wool did not contribute to any barometrically measurable condensable gases. For background samples (CO_2 gas, acetanilide, and potassium phthalate), there was a tendency towards slightly higher ^{14}C levels when silver was added to the combustion, which corresponded to 25 ng modern carbon per mg silver. For OxI standards, the silver wool in the combustion tube had no effect on the ^{14}C results, implying that the contamination is mainly modern. Copper metal, on the other hand, caused high and variable amounts of condensable gases. Copper was therefore not used to study graphitization performance or in the AMS measurement.

$F^{14}C$ values for background samples of acetanilide (prepared with 800 mg of copper oxide rods and 10 mg of silver wool) during the small-sample analyses are shown in Figure 1. The results seem to correspond to a constant background of $F^{14}C \approx 0.005$ and a modern contamination of ~0.4 μg C. The smaller samples are more affected by the modern contamination whereas the larger samples are more affected by the constant background. Due to the difficulties in accurately measuring small amounts of the solid sample material, some background samples and samples, especially the small ones, had to be divided after combustion. Splitting CO_2 prior to graphitization has proven to yield the same results as samples produced from individual aliquots of background samples or standards (Pearson et al. 1998; Santos et al. 2007). The results presented here confirm those results if a constant background is considered.

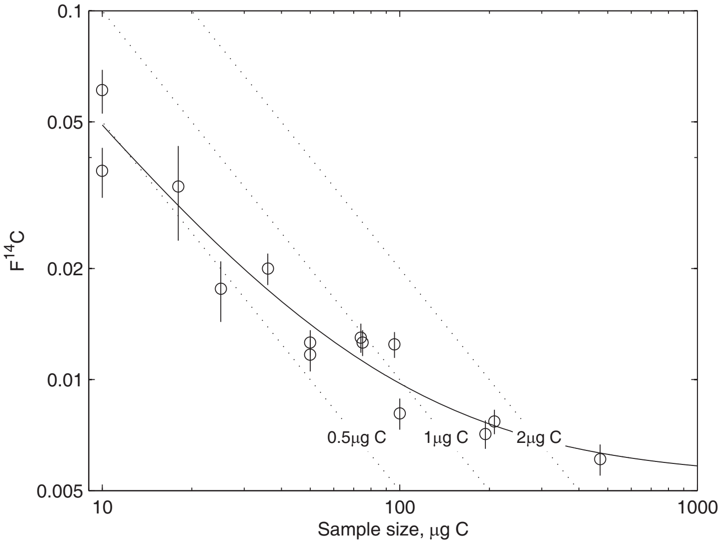

Figure 1 $F^{14}C$ obtained from AMS analyzes for background samples made from acetanilide ranging from 10 to 500 μg C. The data is not background-corrected. The dotted lines correspond to modern contamination of 0.5, 1, and 2 μg C. The solid line is the fit corresponding to a constant background of $F^{14}C = 0.0054$ and a modern contamination of 0.44 μg C. All background samples were prepared with 800 mg of copper oxide rods and 10 mg of silver.

Evaluation of Gas Transfer

One of the greatest challenges we encountered during this study was transferring the CO_2 from the tube-crackers to the reduction reactors when handling aerosol filter samples. The CO_2 was cryogenically transferred from the tube cracker to the reference cell through 1/4″ and 3/8″ tubing (between 60 and 100 cm) for quantification and then back to the reduction reactor (see Genberg et al. 2010). This method has proven satisfactory for other samples such as blood serum and atherosclerotic plaques as well as standards such as sugar, oxalic acid, and charcoal (Georgiadou et al. 2013). However, this method led to considerable variation in the yield for aerosol samples. The yield could however be increased by freezing the gases in the reference cell and, after 30 min of freezing, the yield was the same as for the on-line samples. This shows that the combustion of aerosol filter samples produces residual gases that must be removed to ensure efficient purification.

However, 30 min of freezing for each sample transfer would be time consuming. The problem was solved by treating the samples similarly to the online combustion samples. A small glass tube was mounted at the bottom of the tube-cracker unit (Figure 2). Condensable gases were frozen in the glass tube and residual gases were removed by evacuating the cracker. The remaining gas could thereafter be transferred quantitatively to the reference reactor with only seconds of freezing time required. This procedure gave the same yield for the samples combusted in sealed glass tubes compared to the on-line technique.

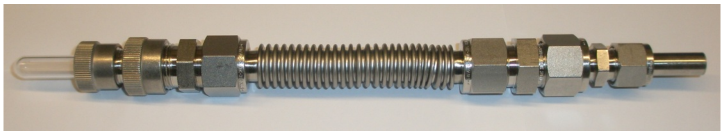

Figure 2 The modified cracker with a glass tube at the bottom where gases can be condensed during the first purification step.

Yield and Graphitization

For aerosol filter samples, 100 and 400 mg of copper oxide powder gave more than 10% lower yields than 800 mg, which means that more than 400 mg of copper oxide is needed for complete combustion. Copper oxide rods gave comparable yields independent of the amount of rods used (between 400 and 1600 mg), and the yield was the same as for on-line combustion and the carbon analyzer. The addition of silver wool (10 mg) may have had a positive effect on the yield from aerosol filter samples, but the effect was not statistically significant ($p = 0.1$).

Only samples combusted using copper oxide rods as oxidizer were used for graphitization due to the high background resulting from the necessary amounts of copper oxide powder. The yield and speed of graphitization were independent of whether silver was used in the combustion or not for both aerosol filter samples and standards. The $F^{14}C$ values for standards were also unaffected by the presence of silver during combustion. The use of silver thus appears to be unnecessary for successful combustion and graphitization. However, because of the possible increased yield we added 10 mg of silver to the combustion since it does not negatively influence the process. The small increase in background by the silver is considered acceptable.

Standards and the Small-Sample Study

The analysis of standards (IAEA C6 and IAEA C7) showed that the present method using sealed glass tube combustion is capable of reproducing nominal values of samples of reference materials containing 11 µg C (Figure 3a,b). The uncertainties in the measurements are similar to those obtained with on-line combustion.

^{14}C measurements of samples on aerosol filters show the complexity of the matrix compared to pure substances. For sample sizes of 50 µg C and above, the results are consistent (Figure 3c). The filter sample with 25 µg C was lost due to a broken glass tube and the 11-µg C sample showed strong divergence compared with the other samples. This large difference is probably due to the small sample size, but could also be influenced by variations in the sample. Filter 1 was fully used after these analyses; therefore, the analysis could not be repeated using the same filter. The second filter analyzed showed similar $F^{14}C$ values for all sample sizes ranging from 200 to 11 µg C (Figure 3d).

CONCLUSION

We have shown that small aerosol samples can be successfully combusted in sealed glass tubes with only minor changes to our online combustion technique. The protocol we developed involves combusting aerosol samples with 800 mg of copper oxide rods and 10 mg of silver wool in sealed glass tubes at 900 °C for 10 hr followed by slow cooling to room temperature.

Cryogenic purification of CO_2 formed by combustion of aerosol samples involving gas transfer over long distances in the graphitization system is possible but time consuming due to the presence of residual gases. This problem can be solved by carrying out the first purification stage in a smaller volume by modifying the tube-cracker.

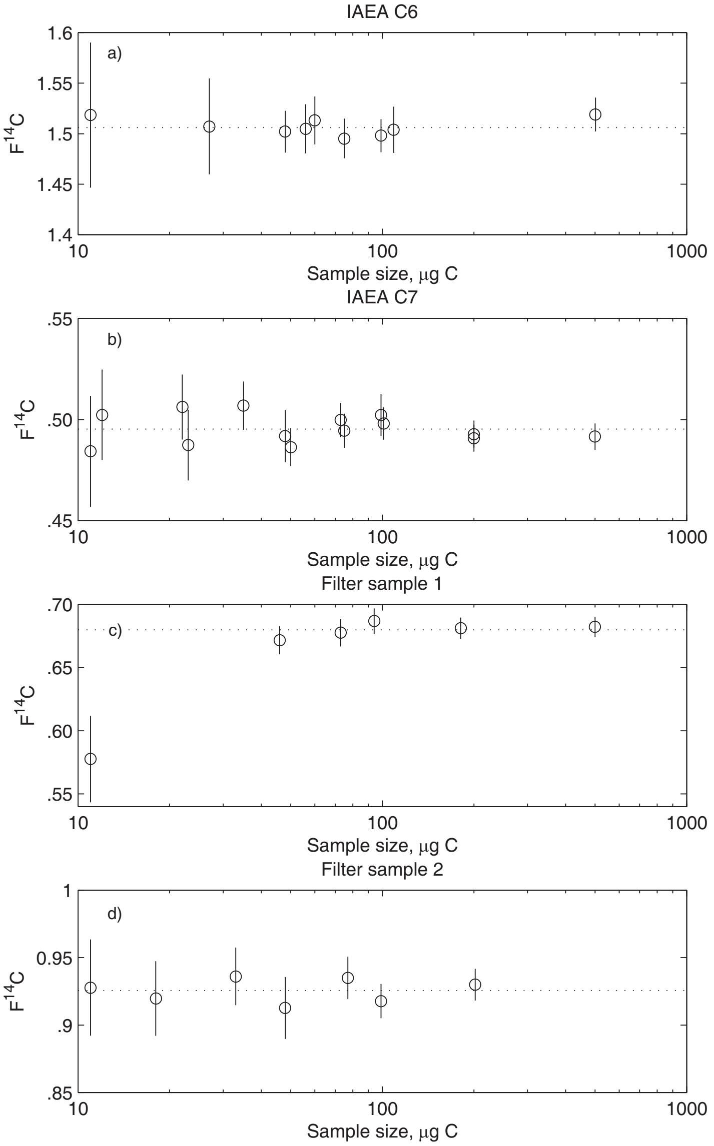

Figure 3 AMS results from standards calculated using the matching size method and OxI as primary standard: IAEA C6 (a); IAEA C7 (b); and filter samples (c and d). The dotted line corresponds to the nominal value in (a) and (b), the mean of the 5 largest samples in (c), and the mean of all samples in (d). Error bars show 1.96 standard deviations from the AMS measurement.

This method proved accurate for standards containing 11 µg C, but problems were encountered with the smallest aerosol filter samples. Results from the analysis of very small aerosol samples cannot always be relied upon due to the uncertainty as to whether the samples are representative or not. If analyses are performed on small parts of the filter area, the filters must be homogeneously loaded during sampling. If large filter areas with low loading are used, corrections must be made carefully with field blank filters. Although the AMS technique itself provides accurate measurements of µg-sized samples, samples that are too small should, if possible, be avoided when measuring ^{14}C in aerosol samples. Samples containing 50 µg C are routinely measured at our laboratory and we feel confident that the method presented in this paper is reliable for aerosol samples at least as small as 20 µg C.

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