

DEVELOPMENT OF GRAPHITIZATION OF μg -SIZED SAMPLES AT LUND UNIVERSITY

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ABSTRACT. To be able to successfully measure radiocarbon with accelerator mass spectrometry (AMS) in atmospheric aerosol samples, graphitization of small sample sizes ($< 50 \mu\text{g}$ carbon) must provide reproducible results. At Lund University, a graphitization line optimized for small samples has been constructed. Attention has been given to minimize the reduction reactor volume and each reactor is equipped with a very small pressure transducer that enables constant monitoring of the reaction. Samples as small as $25 \mu\text{g}$ of carbon have been successfully analyzed, and the mass detection limit of the system has probably not been reached.

INTRODUCTION

Lund University employs a single stage accelerator mass spectrometry (SSAMS) facility, which operates at 250 kV (Skog 2007; Skog et al. 2009). Measurements are made for studies in archaeology, geology, biomedicine, and environmental science. Some environmental samples consist of aerosol samples, which are analyzed to determine the fossil impact on atmospheric aerosol mass. Aerosol particles affect our health and are estimated to be responsible for 800,000 deaths annually, mainly due to lung diseases (WHO 2002). Aerosol particles also affect the climate by scattering and absorbing sunlight and influencing cloud formation (Solomon et al. 2007). These properties result in aerosols having a net cooling effect on our climate, but the uncertainty of the effect is large.

A substantial fraction of the aerosol mass is carbon-containing substances called carbonaceous aerosol. Carbonaceous aerosol may roughly be regarded to originate from 3 sources: combustion of fossil fuels, biomass burning, and biogenic sources. The fossil fuel is ^{14}C -free due to its old age, while biomass and biogenic aerosols have recent ^{14}C content. Measuring ^{14}C in an aerosol sample may therefore distinguish between fossil and contemporary carbon, which is valuable in understanding the origin of ambient aerosols.

To further enhance the source apportionment, the carbonaceous particles may be separated into fractions. The most common separation technique is to utilize the thermal stability of different fractions. In this manner, the carbon is separated into operationally defined organic carbon (OC) and elemental carbon (EC) fractions (e.g. Chow et al. 1993; Birch and Cary 1996). EC is of great importance to the Earth's climate since it is dark and absorbs sunlight and thus heats the atmosphere, contributing to global warming (Solomon et al. 2007). OC, which is the major fraction of the carbonaceous aerosol, may be involved in cloud formation and have a cooling potential. Aerosol in background air in southern Sweden contains about $1.5 \mu\text{g C}/\text{m}^3$ during summer, which yields small samples of carbon if a high time resolution is required, unless a high-volume sampler is used. One week of sampling at the EUSAAR (European Supersites for Atmospheric Aerosol Research) background station Vavilhäll ($56^{\circ}1'N$, $13^{\circ}9'E$; 172 m asl) without a high-volume sampler yields $\sim 500 \mu\text{g C}$, which after separation may result in $50 \mu\text{g C}$ or less left for graphitization. To handle these small amounts required, graphitization lines optimized for small sample sizes have been developed at numerous laboratories (e.g. Hua et al. 2001; Santos et al. 2007) based on CO_2 reduction using H_2 and Fe as catalyst, providing reproducible samples down to $2 \mu\text{g C}$ (Santos et al. 2007). Measurement of such small samples will result in a decreased precision compared to larger samples. However, for source apportion-

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ment studies, this will still yield sufficient results, since other parts of the studies are connected to larger uncertainties. One example is the ^{14}C content in biomass (see Lewis et al. 2004).

METHODS

Graphitization Line Structure

The original graphitization line for μg -sized samples was constructed in 2005 and updated in autumn of 2008. The structure (Figure 1) consists of 6 separate reduction reactors with individual combustion tubes for on-line combustion. The combustion tubes may be replaced by vessels containing collected CO_2 or tube crackers (if using sealed-tube combustion). The reduction reactor part of the line is constructed from 1/4" steel tubing, while the back part consists of 3/8" tubing to facilitate pumping. Gas bottles of CO_2 , H_2 , Ar, and O_2 are connected to the line and all gas flows, except O_2 , can be adjusted by a needle valve. The line is equipped with 10 pressure measurement devices: 1 in each reduction reactors, 2 by the vacuum pumps, 1 at the back line, and the final one is fitted in a reference cell of known volume (far left in Figure 1). A Pfeiffer oil-free diaphragm pump (MVP 015-2) and a Pfeiffer turbomolecular pump station (TSH 071, which contains 1 turbo pump and 1 diaphragm backing pump) are used as low- and high-vacuum pumps. A cold trap placed in liquid nitrogen is located before the pumps to further improve the vacuum. The pressure obtained at the high-vacuum side is $<2 \times 10^{-7}$ mbar.

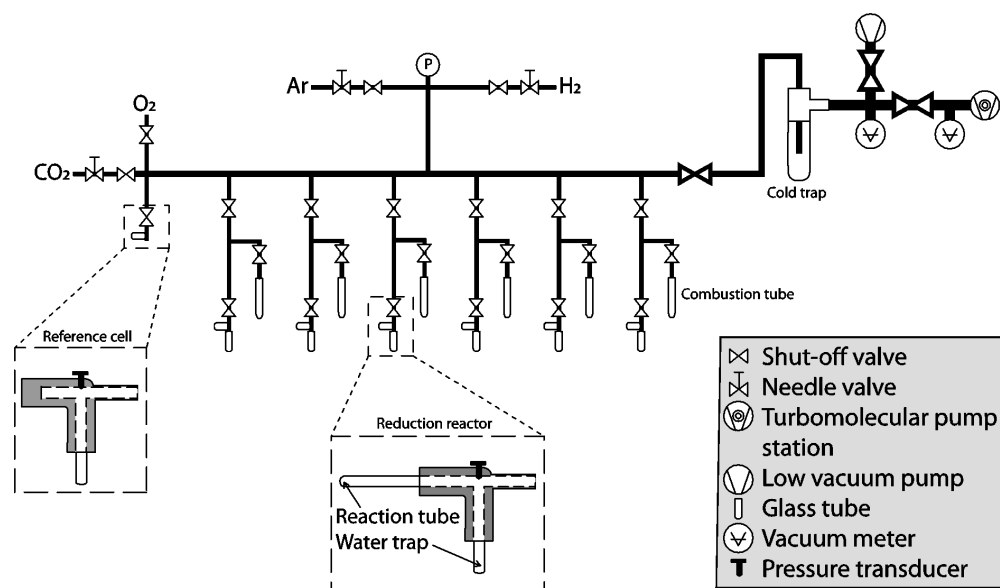


Figure 1 Schematic of the graphitization line. Reduction reactors are constructed from modified Swagelok[®] elbows.

The reduction reactors are produced from modified Swagelok[®] 1/4" elbows (SS-400-9). Two holes (1/4" and 3 mm) are drilled in each elbow (see Figure 1). A 19-mm long, 1/4" steel tube is welded at the 1/4" hole to connect the elbow to the valve. The pressure transducer is glued into the 3-mm hole (see below). The reaction tube and the water trap tube are 1/4" OD quartz tubes, 45 and 30 mm long fitted with Swagelok Teflon[®] ferrules. Teflon has proven to reduce outgassing at high temperatures compared to Viton[®] O-rings (Steier et al. 2006). The internal volume of the reactor is about 1.8 cm³, which corresponds to a pressure change of 1.1 mbar/ μg C at 20 °C. The reference cell is constructed in the same manner but has a Swagelok steel plug (SS-400-P) instead of a reaction tube,

resulting in a volume of 1.3 cm^3 . The reference cell is used if quantitative sample measurement is required and may also be useful when small amounts of H_2 are to be added. After mounting the quartz tubes, the reactor is evacuated and closed to check that all fittings are properly tightened. The pressure must be constant for at least 20 min before any sample preparation can begin.

Pressure Transducers

The first reduction reactors were equipped with Honeywell Micro Switch™ pressure transducers (142PC3OA), also used by Hua et al. (2001). These have been replaced due to leakage through the transducers. The updated reactors were therefore constructed with Fujikura pressure transducers (XFGM-6 100KP GWSR) fitted with Varian Torr Seal low-vapor-pressure epoxy (Varian Part #9530001). The pressure is monitored in all 6 reactors and in the reference cell at the back line simultaneously by an ADC-11 terminal block mounted on an USB ADC-11/12 data logger. Pico Log 5.20.3 software is used to gather and handle the data. Apart from the advantage of simultaneous measurement, the results are saved and may be used in sample evaluation.

The XFGM-6 pressure transducer has proven to be heat sensitive, which causes a fluctuating baseline while combusting the samples and putting the oven on the reaction tubes. To avoid this, aluminium sheets are fitted around the transducers (tape on the inside to avoid short-circuits) and an aluminium plate is positioned between the oven and transducer.

Materials

Merck pro analysi $0.65 \times 6 \text{ mm}$ copper oxide is used as oxidative agent during sample combustion. The copper oxide is precleaned by baking in air for 2 hr at $500 \text{ }^\circ\text{C}$. Merck copper oxide powder, pro analysi, has also been used. The iron used is Merck $10\text{-}\mu\text{m}$ pro analysi and as water trap magnesium perchlorate, Merck $\text{Mg}(\text{ClO}_4)_2$, 1–4 mm, is used. All glassware is quartz and baked after cleaning for 2 hr at $950 \text{ }^\circ\text{C}$ in air.

Solid Sample Preparation

The CuO is initially cleaned once more to fully remove all carbonaceous contaminants. Approximately 1 g of precleaned CuO is placed in a $3/8''$ quartz tube (length 80 mm) and the tube is evacuated. Oxygen is added and the tube is heated by an open LPG (liquefied petroleum gas) flame until glowing. The tube is once more evacuated and the CuO is heated towards high vacuum. After cooling in vacuum, CuO is immediately mixed with the sample in the same quartz tube and fitted onto the vacuum line.

The sample is combusted by an open flame in vacuum and the formed CO_2 is initially frozen in the combustion tube with LN_2 . Uncondensed gases are removed by the pump. The CO_2 is subsequently transferred to the reaction reactor while the combustion tube is cooled by an ethanol slush ($-60 \text{ }^\circ\text{C}$) to trap water formed during combustion. When the transfer is complete, any remaining gases are removed while the CO_2 is frozen in the water trap of the reduction reactor (Figure 1). If quantification of the sample size is needed, the formed gas the CO_2 is transferred to the reference cell and the pressure change is recorded. The CO_2 is finally transferred back to the reduction reactor, where the pressure of CO_2 ($p\text{CO}_2$) is measured at room temperature after thawing the gas. The CO_2 is frozen in the water trap of the reduction reactor once more and H_2 is added (3 times the CO_2 pressure). The heated oven is put on the reaction tube and graphite is formed on 2 mg of iron catalyst at $600 \text{ }^\circ\text{C}$.

When the reaction is complete (indicated by no pressure change), the remaining H_2 is removed and the tube is cooled to room temperature and filled with argon gas. The individual reaction tubes are

wrapped in aluminium foil and placed in plastic tubes. The plastic tubes are subsequently filled with argon gas and sealed while awaiting target pressing. The samples are analyzed at Lund University SSAMS facility (Skog 2007; Skog et al. 2009).

Background samples are prepared from ^{14}C -free CO_2 in the same manner as the other samples. The CO_2 is transferred into the combustion tube (containing pretreated CuO) prior to combustion. An alternative combustion technique, using O_2 instead of CuO , has been tested to further simplify the sample preparation. Another test carried out was adding CuO powder to enhance physical contact between CuO and the sample. Both these practices were rejected due to unsatisfying results (see below).

RESULTS AND DISCUSSION

Graphitization

Samples ranging in size from 15 to 500 $\mu\text{g C}$ were in most cases graphitized within 1 hr at 600 $^\circ\text{C}$. The measured pressure during a typical reduction reaction is presented in Figure 2, which demonstrates the quick reactions. Santos et al. (2007) showed that a temperature of 450 $^\circ\text{C}$ was superior to 550 $^\circ\text{C}$ for small samples. The samples in this study showed a prolonged graphitization time when a temperature of 450 $^\circ\text{C}$ was used and some samples only reached a reduction yield of 30% at the lower temperature after 1 hr. The yield was calculated as described in Hua et al. (2001). The smallest sample in this study is 25 $\mu\text{g C}$. At this sample size, temperature does not influence isotopic fractionation during the graphitization, according to the study by Santos et al. (2007).

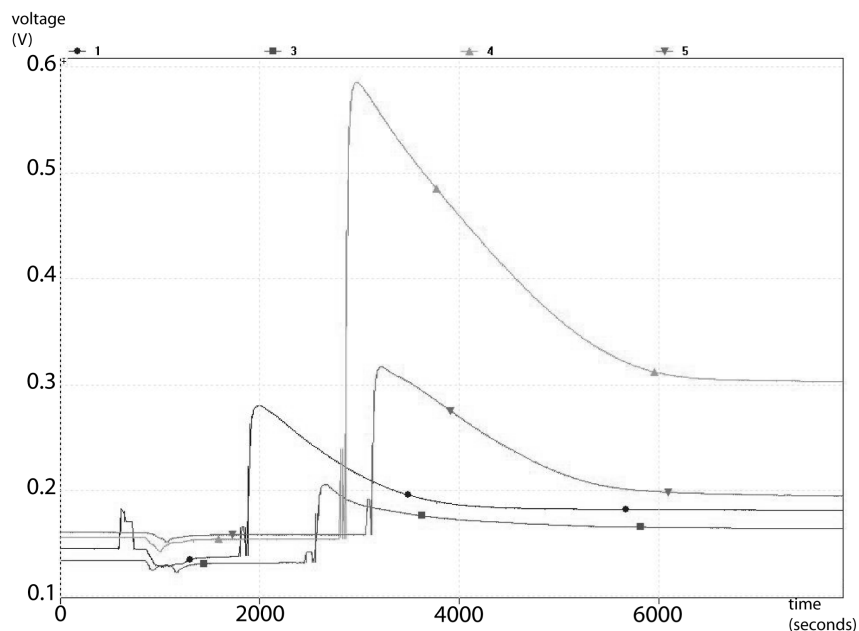


Figure 2 Pressure change measured as voltage during typical graphitization process. A voltage offset of 0.1 V corresponds to a pressure change of roughly 100 mbar. Pressure change is almost zero within 1 hr demonstrating a quick reaction. Line 1 (circles) is $\sim 20 \mu\text{g C}$, line 3 (squares) is $\sim 10 \mu\text{g C}$, line 4 (upward triangles) is $\sim 80 \mu\text{g C}$, and line 5 (downward triangles) is $\sim 30 \mu\text{g C}$. The pressure before the reaction is vacuum and the vacuum signal differs between the reactors from 135 to 160 mV. The noise at 1000 seconds is due to sample combustion.

The initial CO_2 pressures in the reduction reactor (p_{CO_2}) were measured at room temperature, while the total pressure drops during graphitization (dp) were measured with the ovens on at an elevated temperature. This caused the ratio between the pressure drop and initial CO_2 gas (dp/p_{CO_2}) to end up between 3.3 and 3.4 for all sample sizes from 25 to 500 μg C. This was not entirely due to the fact that pressure is proportional to absolute temperature of the gas, but it can also be attributed to the heat sensitivity of the pressure transducers. This effect can be avoided by measuring p_{CO_2} and dp at the same temperature. The use of this protocol gives a dp/p_{CO_2} value close to 3, which suggests a complete reduction. If the effect was due to oxygen released from the heating of CuO reaching the reactor, the effect would be mass dependent and less significant for larger samples.

Alternative Preparation

Some alternative methods for sample preparation have been investigated but rejected due to insufficient quality of the results. To avoid the cleaning of CuO and repeated exposure of the combustion tube to the atmosphere, we investigated if sample combustion in pure oxygen would be suitable for our application. Oxygen condenses at 90 K and we assumed it might remain in the CO_2/O_2 mixture when cryogenically separated with LN_2 (77 K). However, the oxygen is easily removed by the pump since the vapor pressure of oxygen at 77 K is ~ 0.2 bar. Two separate expansions towards vacuum are sufficient to recover clean CO_2 from a CO_2/O_2 mixture taken directly from the gas bottles. About 0.4 bar of O_2 provides ~ 0.1 μmole of O_2 in our combustion tubes, which would theoretically be enough to fully combust 0.1 μmole or 1.2 mg of pure carbon. The problem, however, emerged with graphitization when samples combusted by O_2 resulted in a slower and incomplete reduction reaction, indicating an incomplete combustion. An increasing number of the samples did not commence graphitization, which is crucial since unique atmospheric samples sometimes only supply carbon for 1 graphitization.

CuO powder (~ 200 mg, cleaned in the same manner as the CuO needles) released gas, which could not be removed cryogenically, equivalent to 6 μg C as CO_2 when combusted. This effect is not observed even with uncleaned CuO needles. The matter was not fully examined, but it seemed like the powder adsorbed carbonaceous gases from the air during the short exposure time.

AMS Results

The $^{14}\text{C}/^{12}\text{C}$ ratio was converted to pMC by using IAEA C6 as primary standard and combusted ^{14}C -free CO_2 as background. The CO_2 background samples were combusted with CuO in the same manner as the solid samples to acquire realistic background values. Samples of a secondary standard (normally IAEA C7) were used to verify the calibration. For samples measured at 1 specific run, the background had to be estimated since the measured background showed an unreasonably high value. The elevated ^{14}C level seemed to be associated only with the background sample, and not with the standards. The background used at this particular run was estimated in order to fit both the primary and secondary standard, and it was similar to backgrounds measured at other runs. Both primary standard and background are approximately the same size as the sample to avoid the effect of declining pMC values shown in Brown and Southon (1997) and Hua et al. (2004) (Santos et al. 2007). We do not take into account the additional mass of either modern or dead carbon but only the additional ^{14}C counts. Results from measurements of IAEA C7 and C8, measured at 4 different runs, are within the uncertainty of the consensus value (Figure 3). The uncertainty of the measurement is increasing with smaller samples due to less counting statistics. The fact that the additional mass of carbon from the background can be successfully disregarded may be due to the thorough cleaning of the oxidizing agents.

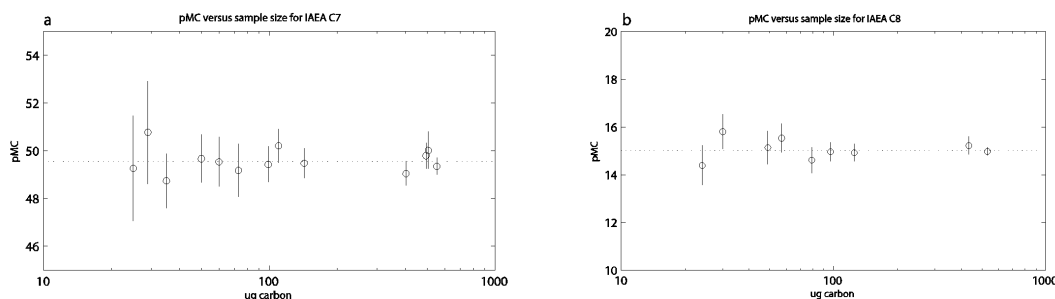


Figure 3 Measured pMC values of IAEA C7 (a) and IAEA C8 (b). IAEA C6 is used as primary standard and combusted ^{14}C -free CO_2 is used as background. Some samples are derived from fixed background values. Error bars show 1σ and the dashed lines are the consensus values of C7 (pMC = 49.53) and C8 (pMC = 15.01).

CONCLUSION

The new graphitization line was constructed with focus on minimizing the reduction reactor volume, and an internal volume of $\sim 1.8\text{ cm}^3$ has been achieved. The reactions in the small-volume reactors are complete within 1 hr, which enables quick sample turnover. Samples as small as $25\text{ }\mu\text{g}$ have been graphitized using this graphitization line with reproducible results. The pMC values of the standards are within uncertainty of consensus values when samples are normalized and background corrected with standards and background samples whose size are approximately the same.

OUTLOOK

To further minimize the volume of the reference cell, the 90° elbow (SS-400-9) can be replaced by another elbow with a tube already fitted (SS-400-2R-4), which would result in an internal volume of 1.06 cm^3 and 1 less joint with possible leakage. This will be undertaken in Lund in autumn 2009.

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