

## TOWARDS ON-LINE $^{14}\text{C}$ ANALYSIS OF CARBONACEOUS AEROSOL FRACTIONS

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**ABSTRACT.** Atmospheric carbonaceous aerosol is traditionally divided into organic carbon (OC) and elemental carbon (EC). Their respective carbon amounts are usually analyzed by means of an OC/EC analyzer and their fossil and non-fossil origins can be determined by radiocarbon analysis, which has proven to be a powerful tool for carbonaceous aerosol source apportionment. Thus far, separation of OC and EC has been performed off-line by manual and time-consuming techniques. We present an on-line system that couples a commercial OC/EC analyzer with the gas ion source of the accelerator mass spectrometer (AMS) MICADAS and its  $\text{CO}_2$  feeding system. The performance achieved with reference materials and blanks are discussed to demonstrate the potential of this coupling for source apportionment of atmospheric carbonaceous particulate matter.

### INTRODUCTION

The widespread atmospheric relevance of carbonaceous aerosol has been increasingly recognized in the last 20 yr. Indeed, not only does it constitute one of the most significant mass fractions of the atmospheric particulate matter (PM), but also represents a decisive and yet insufficiently characterized actor in the global climate (IPCC 2007), as well as a threat to human health (Highwood and Kinnersley 2006; Mauderly and Chow 2008).

Since PM encompasses a wide range of carbon-containing compounds that exhibit very different physical and chemical properties, identifying and studying them all has proven unrealistic (Turpin et al. 2000). Therefore, the picture has been conventionally simplified by dividing the total carbon (TC) of the carbonaceous particulate matter into 2 subfractions: organic carbon (OC) made of lighter, weakly refractory and non-light-absorbing compounds, and elemental carbon (EC) consisting of strongly refractory, light-absorbing, highly polymerized compounds (Pöschl 2005). While EC is mainly emitted as a primary product of combustion processes, OC stems from combustion, industrial, biological, or geological processes when formed primarily (Pöschl 2005) or can result as a secondary product from the condensation of low-vapor compounds produced during the photo-oxidation of volatile organic compounds (Hallquist et al. 2009).

Although this classification is widely acknowledged, the boundary between OC and EC is artificial and highly method-dependent (Schmid et al. 2001; ten Brink et al. 2004). The thermal methods aiming at measuring OC and EC concentrations rely on the difference of refractivity of both fractions and apply stepwise temperature programs to atmospheric quartz-fiber filter samples in order to liberate and quantify carbonaceous fractions of increasing refractivity. With these techniques, OC is removed from the filter and analyzed at lower temperature followed by the EC determination at higher temperature. However, OC can undergo a partial pyrolysis to form EC during heating. To correct for that charring artifact that leads to overestimated EC concentrations, thermo-optical methods monitor the optical behavior of the analyzed filter to identify the point at which the filter transmittance (Birch and Cary 1996) or reflectance (Chow et al. 1993) gets back to its initial value, defining as EC the carbon evolved after this “split point.” Since this optical correction is valid only if pyro-

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lyzed OC and EC present the same light absorption coefficients (Yang and Yu 2002), optimized temperature programs have been proposed, either to minimize charring (Cavalli et al. 2009) or to reach equivalent apparent absorption cross-sections for EC and pyrolyzed OC (Conny et al. 2009). Today, the thermo-optical approach is widely used to quantify the subfractions of the carbonaceous aerosol and thus to gain an insight into their sources.

Analyzing the radiocarbon content of OC and EC allows for a refined source apportionment. As an internal marker,  $^{14}\text{C}$  enables a direct discrimination between the non-fossil and fossil contributors of carbonaceous fractions. Since OC and EC do not originate from the same processes, they often show very different  $^{14}\text{C}$  signatures (Szidat et al. 2004a, 2006, 2007; Szidat 2009). So far, the methods used to fully separate OC and EC for  $^{14}\text{C}$ -based source apportionment have relied on rather time-consuming techniques, thus allowing only manual and off-line  $^{14}\text{C}$  measurements (Szidat et al. 2004b). A thermo-optical, “split-point”-based method for EC isolation and subsequent  $^{14}\text{C}$  analysis was proposed by Currie and Kessler (2005), and presented minimized, but not totally suppressed, charring-induced EC contamination. A new separation method using a thermo-optical OC/EC analyzer in pure oxygen is currently under development to circumvent that charring issue and achieve in a single run the physical separation of OC and EC and their direct recovery as  $\text{CO}_2$  for later off-line  $^{14}\text{C}$  measurements.

On-line measurements, however, can provide faster and more convenient  $^{14}\text{C}$  analysis. They are enabled by the use of gas ion sources, which have paved an interesting way for direct measurements of  $\text{CO}_2$  (Bronk Ramsey et al. 2004; Ruff et al. 2007) through the coupling between a combustion device and an accelerator mass spectrometer (AMS). Thus, couplings of gas chromatography with AMS (GC-AMS) (Bronk Ramsey et al. 2004), or of an elemental analyzer with AMS (EA-AMS) (Uhl et al. 2004; Ruff et al. 2010a) have been achieved. In the latter, the total combustion in an EA allows for measurements of TC and possibly of EC, provided that the filters have undergone an OC-removing pretreatment. However, because it is operating at a single, high temperature, this instrument does not enable a gradual desorption of selective carbonaceous fractions, which is necessary for OC analysis. Consequently, the direct coupling between an OC/EC analyzer and an AMS appears as the most convenient way to separate and quantify carbonaceous fractions and perform their direct  $^{14}\text{C}$  analysis.

In this work, we present the first coupling of a commercial, automatic thermo-optical OC/EC analyzer with the small AMS system MICADAS (Synal et al. 2004, 2007) equipped with a gas ion source (Ruff et al. 2007). On the basis of reference materials and blanks analyses, we discuss the validity of the system and its potential for source apportionment of atmospheric carbonaceous aerosol.

## **MATERIALS AND METHODS**

### **OC/EC Analyzer**

We used a thermo-optical OC/EC analyzer (RT 3080, Sunset Laboratory Inc, USA) (Bae et al. 2004). In that device, the carbon released from a heated atmospheric filter goes through a  $\text{MnO}_2$  bed heated to  $850\text{ }^\circ\text{C}$  to be oxidized to  $\text{CO}_2$ . It is then detected and quantified by a NDIR detector before being released to the ambient air. In the presented system, we adjusted the gas flow parameters of the OC/EC analyzer to run it at  $65\text{ mL/min}$  of pure  $\text{O}_2$ , anticipating the use of a thermal method that we are currently developing. The temperature program controlling the instrument was set to one step at  $760\text{ }^\circ\text{C}$  for  $170\text{ s}$  to achieve a quick and total combustion of the pure reference compounds used to validate the system.

### Gas Interface

The coupling between the OC/EC analyzer and the AMS gas ion source relied on the gas interface developed by Ruff et al. (2010a) for an online EA-AMS system. The gas transfer was based on a zeolite trap that adsorbed the  $\text{CO}_2$  coming from the OC/EC analyzer, thus isolating it from the high oxygen stream. As described in Ruff et al. (2010a), the trap consists of a metal holder filled with X13 sodium aluminosilicate, i.e. a X-structured zeolite molecular sieve showing a high affinity for polar molecules such as  $\text{CO}_2$ . However, with a diameter of 6 mm, a length of 3 cm, and a mesh of 10 Å, the volume of this trap was more than twice as that used in the EA-AMS coupling. This was meant to avoid any  $\text{CO}_2$  breakthrough in the  $\text{O}_2$  stream from the OC/EC analyzer, an issue that was not critical for the EA running with a He stream. A heating coil (Watlow, USA) wrapped around the trap was used to heat it up in about 40 s from room temperature to 480 °C. Most  $\text{CO}_2$  was actually observed to be desorbed between 300 and 350 °C, but heating more enabled a quicker desorption process. A K-type temperature sensor (Watlow, USA) fixed on the surface of the trap and connected to a temperature controller (Omron, Japan) ensured the temperature regulation.

The trap could be alternately connected via a 6-port valve to the combustion instrument (here, the OC/EC analyzer) or to a gas-tight syringe (Hamilton, USA) acting as an adjustable  $\text{CO}_2$  reservoir and connected with the gas ion source of the MICADAS (Ruff et al. 2007). The interface was run semi-automatically by a LabVIEW program (National Instrument Corporation, USA).

### OC/EC-AMS Coupling

To remove any water liable to affect the quality of the  $^{14}\text{C}$  measurements, a glass tube filled with  $\text{Mg}(\text{ClO}_4)_2$  powder (p.a., Fluka, Switzerland) was installed between the OC/EC analyzer outlet and the gas interface to act as a water trap. Figure 1 shows the final setup. When connected to the interface, the OC/EC analyzer exhibited a back pressure of about 240 hPa in the “trap loading” phase (Figure 1a), whereas the normal operating back pressure ( $\sim 70$  hPa) was observed during the “venting” (Figure 1b). This setup resulted in higher amounts of carbon measured than actually introduced. Therefore, we installed a 3-way valve upstream of the interface to direct the instrument exhaust either to the interface during the “trap loading” phase or to an outlet equipped with a metering valve, which was manually adjusted to keep the back pressure constant at  $\sim 240$  hPa. The OC/EC analyzer was recalibrated at that pressure by analyzing known amounts of sucrose solution.

### Sample Preparation

Under a flow box, reference materials were dissolved in ultrapure water to give carbon concentrations in the range of  $2 \text{ g L}^{-1}$ : IAEA C7 and C8 (Le Clercq et al. 1998), fossil acetanilide (p.a., Merck, Germany), and NIST Ox-II (SRM 4990C). Five to 10  $\mu\text{L}$  of solution were dropped on  $2\text{-cm}^2$  punches from a prebaked (800 °C for 8 hr) binder-free quartz-fiber filter (MK 360, Munktell, Sweden) using a 10- $\mu\text{L}$  syringe (Hamilton, USA). Blank filters were also prepared by dropping 10  $\mu\text{L}$  of ultrapure water on similar filter punches. The prepared samples were then left to dry in a laminar flow box for about 1 hr before being wrapped in aluminum foil and small air-tight plastic bags and stored in the freezer ( $-18$  °C) until analysis.

### Analysis Procedure

$^{14}\text{C}$  analyses were performed as follows: a sample filter punch (16 mm diameter, i.e.  $2 \text{ cm}^2$ ) was inserted into the OC/EC analyzer and a new run was started immediately. The analyzer was first purged with pure  $\text{O}_2$  for 2 min to avoid contamination resulting from the air introduced in the system. Some 20 s after starting the analysis phase (i.e. shortly before some  $\text{CO}_2$  was detected by the

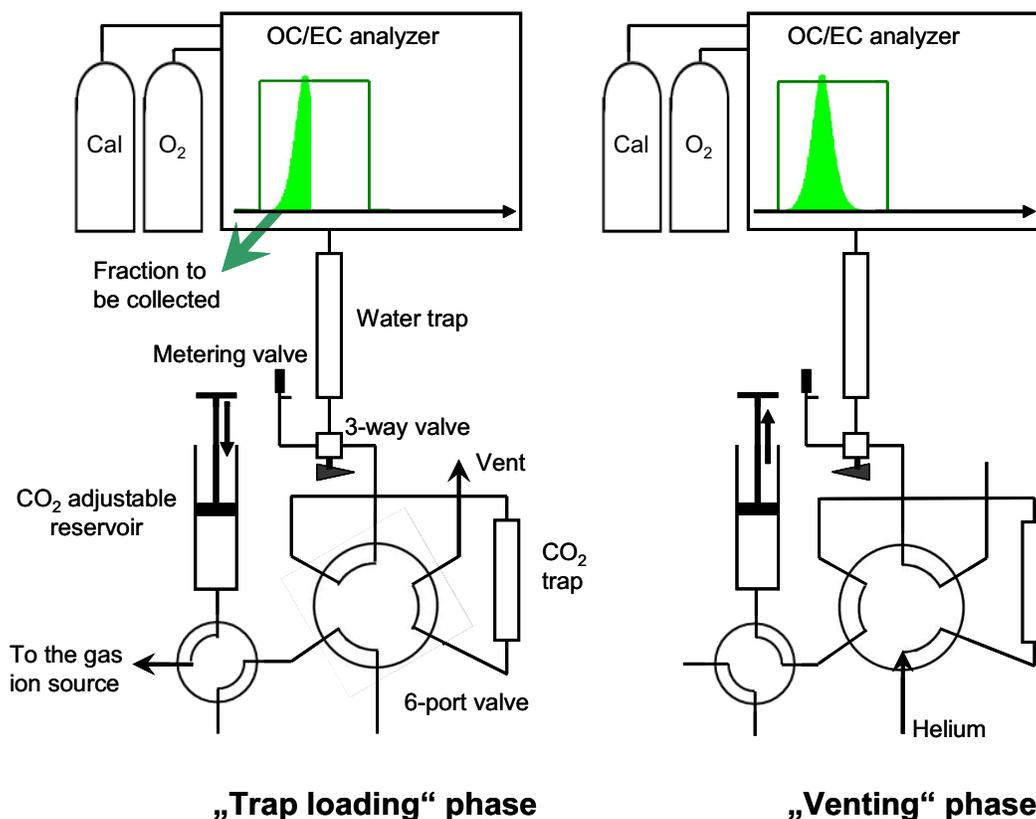


Figure 1 Coupling system between the thermo-optical analyzer and the gas interface. a) Trapping of the CO<sub>2</sub> from the wanted fraction. In the meantime, the CO<sub>2</sub> from the former run is injected to the ion source. b) Transfer of the trapped CO<sub>2</sub> to the adjustable reservoir.

NDIR detector of the OC/EC analyzer), the 6-port and 3-way valves were simultaneously switched to the “trap loading” position (Figure 1a) to direct the OC/EC analyzer exhaust towards the CO<sub>2</sub> trap. At the same time, the target was changed on the AMS and presputtered with the cesium beam to remove carbon contaminants on its surface (Ruff et al. 2007). A sequence was also started from the LabVIEW panel to clean the syringe that serves as an adjustable CO<sub>2</sub> reservoir. After 2.5 min, when 96 to 99% of the CO<sub>2</sub> peak was detected, both valves were switched back to the “venting” position. The trapped CO<sub>2</sub> was desorbed by increasing the trap temperature to 480 °C and flushed with a He flow of about 100 μL min<sup>-1</sup> into the CO<sub>2</sub> reservoir (Figure 1b). The reservoir size was adjusted to the carbon amount and a suitable volume of He was added to obtain a concentration of 5% CO<sub>2</sub> in He. The actual AMS measurement was then started by pressing the gas mixture through a capillary into the gas ion source (Ruff et al. 2007) at a regular speed of ~1 μg carbon per minute. Meanwhile, the trap was cleaned at 550 °C by several He flush/vacuum cycles and finally cooled down (Ruff et al. 2010a).

NIST Ox-I standards (SRM 4990) as well as fossil CO<sub>2</sub> sealed in gas ampoules were also regularly measured as references, using the ampoule cracker system that is connected to the gas interface (Ruff et al. 2010b).

## RESULTS AND DISCUSSION

## First Measurements

The setup of the first on-line coupling between an automatic thermo-optical OC/EC analyzer and the MICADAS worked successfully. This setup shows that the existing gas ion source (Ruff et al. 2007) and gas interface using a zeolite trap (Ruff et al. 2010a) can be adapted to different combustion devices for on-line  $^{14}\text{C}$  analyses. In Table 1, the measurements of different standard materials for the validation of the system quality are presented in chronological order. The uncorrected  $^{14}\text{C}$  values result from a reduction procedure of the AMS raw data, as presented in Wacker et al. (2010). They were further corrected for a blank contribution, as described below, to yield the corrected  $^{14}\text{C}$  results. After this correction, all but 2 of the  $^{14}\text{C}$  signatures agree within the 1- $\sigma$  range with the nominal values. Ox-II mean of means lay outside the 1- $\sigma$  interval, but did not differ significantly from the nominal value. In order to exclude any systematic errors, the purity of the Ox-II solution was checked independently: 20  $\mu\text{L}$  (containing 40  $\mu\text{g}$  carbon) of the solution were combusted in the THEODORE device (Szidat et al. 2004b); the resulting  $\text{CO}_2$  was sealed in a glass ampoule and analyzed using the cracker system described in Ruff et al. (2010b). That measurement demonstrated that no contamination stemmed from the solution.

Table 1 First measurements of reference materials with the coupling system using C7, C8 (IAEA), Ox-II (NIST), and fossil acetanilide. Results are given in chronological order. A blank contribution of 2.0  $\mu\text{g}$  carbon and 54 pMC with 20% uncertainties for both parameters was considered for determination of the corrected data.

	Mass ( $\mu\text{g C}$ )	$\Delta^{13}\text{C}$ (‰)	Uncorrected $^{14}\text{C}$ pMC	Corrected $^{14}\text{C}$ pMC
<b>C7</b>	17.5	-15.3	$50.6 \pm 1.4$	$50.2 \pm 2.1$
	17.0	-15.3	$50.7 \pm 1.4$	$50.3 \pm 2.1$
	17.6	-19.4	$52.0 \pm 1.5$	$51.8 \pm 2.1$
	18.0	-15.7	$50.0 \pm 1.5$	$49.6 \pm 2.1$
Mean of means		-16.4		$50.5 \pm 1.0$
Nominal		-14.5		49.54
<b>C8</b>	12.5	-16.4	$20.3 \pm 1.3$	$13.9 \pm 3.0$
	12.2	-18.5	$22.2 \pm 1.4$	$16.0 \pm 3.0$
	12.0	-15.7	$21.4 \pm 1.8$	$15.0 \pm 3.4$
Mean of means		-16.8		$15.0 \pm 1.8$
Nominal		-18.3		15.01
<b>Fossil acetanilide</b>	8.9	-29.8	$12.4 \pm 1.2$	$0.4 \pm 4.7$
	15.0	-32.2	$7.3 \pm 0.7$	$0.2 \pm 2.5$
	20.1	-31.4	$5.5 \pm 0.5$	$0.2 \pm 1.8$
Mean of means		-31.1		$0.2 \pm 1.4$
Nominal		Not known		0
<b>Ox-II</b>	18.2	-25.4	$120.6 \pm 3.7$	$128.9 \pm 4.8$
	17.7	-16.6	$122.5 \pm 2.8$	$131.2 \pm 4.0$
	17.3	-17.6	$123.6 \pm 2.8$	$132.8 \pm 4.0$
Mean of means		-19.8		$131.1 \pm 2.4$
Nominal		-17.8		134.07

### Blank Contributions

Analysis of an individual filter blank prepared similarly to the reference materials led to a mass of  $2.0 \pm 0.3 \mu\text{g}$  carbon. Moreover,  $^{14}\text{C}$  measurement of 8 pooled blank filter punches stacked together at the front of the OC/EC instrument quartz insert yielded a value of  $54 \pm 3 \text{ pMC}$ . The carbon mass per punch was found to be substantially lower than for the single filter. We interpret this to be due to an incomplete combustion of the carbonaceous material on the pooled filters, due to their inhomogeneous heating in the quartz insert. We assumed that the recovered carbon was representative for the total carbon content of the set of punches. Therefore, we corrected our  $^{14}\text{C}$  measurements considering a blank contribution of  $2.0 \mu\text{g}$  carbon at  $54 \text{ pMC}$  with 20% uncertainties for both parameters. That contamination resulted probably from the adsorption of volatile organic compounds on the quartz fibers of the punches during their drying under the flow box. To check the importance of that artifact, we conducted a series of carbon measurements in which we placed a quartz filter punch at the front of the OC/EC instrument quartz insert, baked it out by running a blank analysis, and dropped a reference solution on the purified punch right before analysis. Combustions with ultra-pure water gave a blank carbon amount of about  $0.8 \pm 0.1 \mu\text{g}$  carbon, regardless of the injected volume. We did not perform any  $^{14}\text{C}$  blank analysis because too much water would have been required to get a satisfying amount of carbon. However, this series of analyses showed that the blank contributions may be reduced substantially in future applications.

### Cross-Contamination

In Table 1, the  $\Delta^{13}\text{C}$  and raw  $^{14}\text{C}$  signatures of the first sample in the acetanilide and Ox-II series reveal a cross-contamination from the previous run. It amounted to up to about  $0.5 \mu\text{g}$  carbon, suggesting that part of the carbon may remain in the system. Adsorption of  $\text{CO}_2$  on the zeolite trap despite the trap cleaning procedure may be one source of cross-contamination, as already mentioned by Ruff et al. (2010a). As that earlier work revealed substantially lower carbon amounts than what we observed here, other parts of our system may have contributed to the cross-contamination as well. Therefore, improving the cleaning procedure will be necessary in our case.

### Ion Currents

During the measurements,  $^{12}\text{C}^+$  currents on the high-energy side of the AMS amounted to  $0.7 \pm 0.1 \mu\text{A}$ . This tends to be somewhat lower than what was achieved by coupling the same gas ion source with an elemental analyzer (Ruff et al. 2010a), where currents of  $0.9\text{--}1.1 \mu\text{A}$  were obtained.

### CONCLUSION AND OUTLOOK

We exploited the flexibility of an AMS equipped with a gas ion source and a gas interface to successfully achieve the first coupling between the MICADAS and a commercial OC/EC analyzer. First on-line  $^{14}\text{C}$  measurements of reference materials were performed and proved to be satisfying, although some contamination issues suggested that the system cleaning procedure can be further optimized. Future investigation will focus on adapting the thermal program of the OC/EC analyzer to real atmospheric filters in order to achieve on-line  $^{14}\text{C}$  measurements of OC and EC, thus fostering the potential of  $^{14}\text{C}$  for source apportionment of carbonaceous aerosol.

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