Atmospheric Environment 122 (2015) 571–576

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

Technical note

On a possible bias in elemental carbon measurements with the Sunset thermal/optical carbon analyser caused by unstable laser signal

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HIGHLIGHTS

- Unstable laser transmission signal in Sunset can lead to a bias in EC attribution.
- An instability of more than 10% around the split point leads to a substantial bias.
- An experiment checks the relevance of an instability during the cooling phase.
- Systematic monitoring of the laser transmission signal is strongly recommended.

ARTICLE INFO

Article history:
Received 12 June 2015
Received in revised form
29 September 2015
Accepted 30 September 2015
Available online 22 October 2015

Keywords:
Elemental carbon
Split point
Thermal optical method
Sunset
Unstable laser transmission signal

ABSTRACT

We present results that demonstrate a possible bias in the fractioning of total carbon (TC) into elemental carbon (EC) and organic carbon (OC) for measurements with the Sunset Laboratory Inc. Thermal/Optical Carbon Aerosol Analyser. The bias is caused by an unstable laser transmission signal. The transmission signal during the analysis of an instrument blank filter can give an indication of the possible bias. If the transmission signal around the OC/EC split point deviates from its initial value, the EC attribution is altered. In a sensitivity study, we show that for a deviation of 10% the EC content is substantially biased.

1. Introduction

Carbonaceous aerosol is often analysed with the Thermal/Optical Carbon Aerosol Analyser from Sunset Laboratory Inc., Tigard, OR (referred to as OC/EC analyser here), to determine organic carbon (OC) and elemental carbon (EC). These carbon fractions are differentiated on the basis of their thermal and chemical stability as described below.

A schematic view of the instrument is shown in Fig. 1. The OC/EC analyser consists in succession of a front oven, an oxidiser oven with manganese oxide, a methanator and a flame ionisation detector (FID).

The filter (Pallflex® Tissuquartz™) punch to be analysed is placed on a quartz boat, which can be freely positioned in the front oven. However, the boat should be always positioned at the same location to optimise the reproducibility. For analysis, the punch is stepwise heated according to a fixed analysis protocol, e.g. EUSAAR2 (Cavalli et al., 2010). The carbonaceous components on the filter will desorb through evaporation, pyrolysis and oxidation. After desorption, the carbon is absorbed in the carrier gas and transported to the oxidiser oven, where all components are oxidised to CO_2. In the methanator the carbon dioxide is reduced to methane, which is quantitatively measured with the FID. The output signal is thus directly related to the number of carbon atoms and is a mass metric.

The heating is performed in two cycles. In the first cycle, pure helium is used as carrier gas. The components measured in this cycle are counted as organic carbon. After the first heating cycle, the oven is cooled down and the carrier gas is switched to a mixture of

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http://dx.doi.org/10.1016/j.atmosenv.2015.09.076
1352-2310/

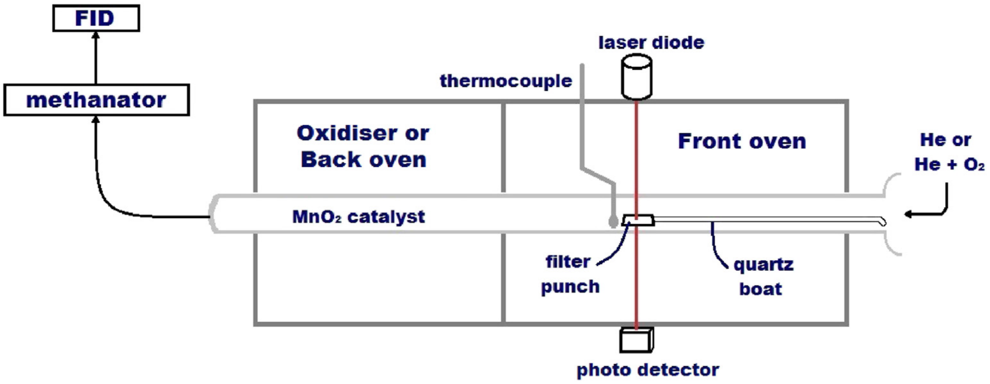

Fig. 1. Schematic view of the Sunset Laboratory OC/EC analyser.

helium and oxygen to create an oxidising atmosphere. The temperature is increased again and the refractory components that oxidise and volatilise in the second cycle are attributed to pyrolytic carbon and elemental carbon. After the oxygen cycle, a calibration cycle with a mixture of helium and methane as carrier gas is performed to calibrate the FID signal.

In the helium atmosphere, a fraction of OC pyrolyses and produces thermally stable, light absorbing material with the result that not all OC is desorbed in the first heating cycle and the filter becomes darker. In the second cycle, these components oxidise and must not be attributed to EC, because they constitute a part of OC. To correct for pyrolysis, transmission and reflection are measured continuously. Both laser signals, transmission and reflection, decrease in the helium cycle and increase again in the oxygen cycle. The point in the second cycle where the optical signal reaches its initial value is called the split point. The components that are measured in the part of the oxygen phase before the split point are called pyrolytic carbon. The pyrolytic carbon is counted as organic carbon. The OC/EC standardisation group of the European standardisation committee (CEN/TC265/WG35) [1]has decided that the laser transmission signal should be used for the correction. Therefore, we focus on the laser transmission signal in this technical note, which is referred to as laser signal.

Every day of analysis starts with a *clean oven* protocol to ensure that the oven does not contain any carbonaceous contamination. After the *clean oven* protocol, during which the last measured filter punch stays in the oven, the same filter punch is used for an instrument blank. For the blank, the same analysis protocol as for regular samples is used. In standard measurement protocols, only the carbon content of the instrument blank is taken into account. According to EC/OC CEN/TR 16243 (CEN, 2011) the OC and EC content of a laboratory blank filter has to be taken in account. However, as we will show in this technical note, it is also important to monitor the laser signal and oven temperature, which are recorded by the instrument. For a clean filter, the laser signal should be constant during the heating cycles. An unstable laser signal will not affect the total carbon counted, but it will change the partitioning between OC and EC. As we will further show, it is also important to monitor the laser signal during the cooling phase after the analysis is completed. An instability of the signal during this phase, which is not recorded by the instrument, can alter the initial laser signal of the next sample and therefore its split point.

2. Instrument performance and error estimate

2.1. Change in laser signal around the split point

We discuss measurements that were made after a factory repair (November 2014) of the oven due to its malfunction because of a misplaced thermocouple in the backoven. We do not think that this defect caused malfunction of the carbon analyser, because the front oven temperature control performed flawless. After the repair, the elemental carbon mass of a reference sample decreased on average by 26% with a shift in split point of 9 s, whereas the total carbon content did not differ significantly (see Table 1). Therefore, we investigated the possible cause of the EC mass change and observed different laser transmission signals for instrument blanks before and after the repair, see Fig. 2. The laser signal changed during an analysis, despite the fact that there was no apparent malfunction of any component of the instrument. We therefore cannot explain these different behaviours. If this behaviour of the laser signal was also present during sample analyses, the split is affected. After the repair, the laser was back at its initial signal later in time and thus a larger part of the evolving refractory carbon is counted as OC. To further investigate this issue, we explored if the change in transmission could explain the observed differences in EC and split time of the reference sample. The instrument blank data in Fig. 2 is not directly comparable to the data of our reference sample. The blanks followed the EUSAAR2 protocol, whereas the reference sample followed the NIOSH890 protocol (CEN, 2011) for comparison with former measurements on the same filter. Because we cannot compare the instrument blank data with the reference sample data, we will perform a sensitivity analysis on data from a field campaign.

Table 1
Comparison between the measurements before and after the repair including the standard deviations. All samples were taken from the same high volume sample which is used as reference sample. The reference sample was analysed with the NIOSH890 protocol (CEN, 2011).

	Before repair	After repair
Number of analyses	9	7
Split time (s)	552 ± 5	561 ± 2
EC mass (g/cm^2)	1.96 ± 0.14	1.45 ± 0.15
TC mass (g/cm^2)	26.3 ± 0.5	25.3 ± 0.6
EC/TC ratio	0.074 ± 0.005	0.057 ± 0.006

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[1] http://tinyurl.com/qzrpvr4.