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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.

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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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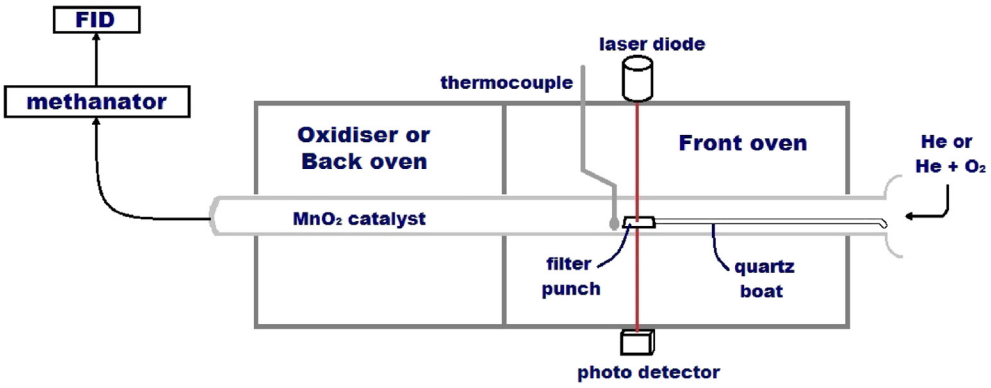

Fig. 1. Schematic view of the Sunset Laboratory OC/EC analyser.

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.

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

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

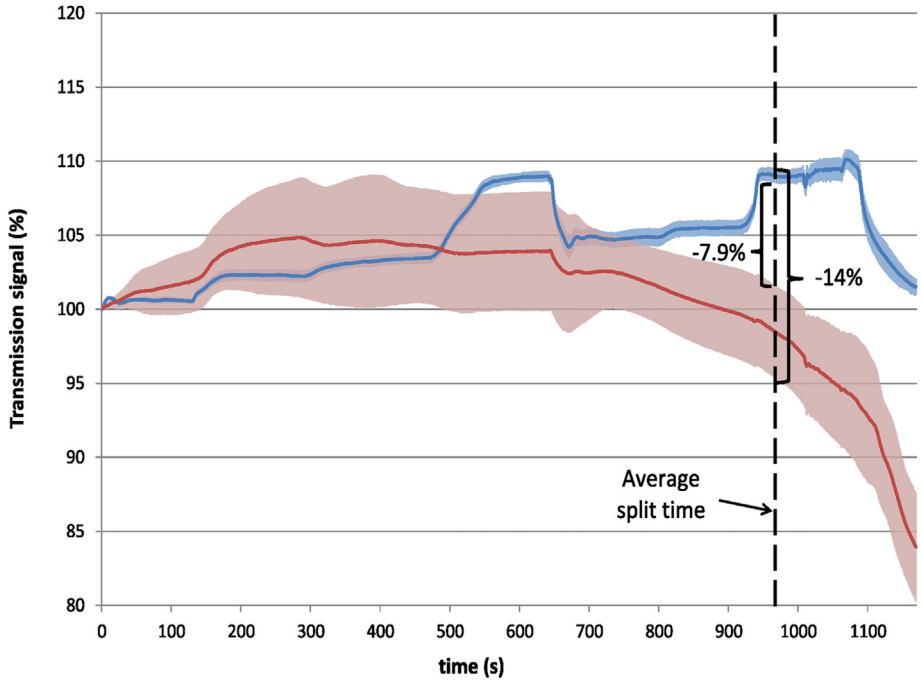

Fig. 2. Instrument blanks of the OC/EC analyser at TNO before (blue, $n = 11$) and after (red, $n = 39$) the repair in November 2014. The blanks are analysed using the EUSAAR2 protocol Cavalli et al. (2010). The full lines represent the averages and the shaded areas represents the standard deviation in the distribution of the different blanks. The values are normalised according to Eq. 1 (see Sect. 3). (For interpretation of the references to colour in this figure caption, the reader is referred to the web version of this article.)

2.2. Sensitivity analysis

From 2nd September until the 15th of October 2014 a field campaign was conducted at the Cabauw Experimental Site of Atmospheric Research (CESAR observatory[2]) in the Netherlands. As part of the campaign samples were collected and analysed for their carbonaceous composition following the EUSAAR2 protocol. The analysis took place after the repair. Based on 80 analysed samples from the field campaign, we determined the average time of the split point to calculate the influence of a change in transmission signal around the split point on the EC attribution. The split point was on average at 964 s, with a standard deviation of 23 s. By comparing the instrument blank data before and after the repair at the average split point (Fig. 2), we see that the difference between before and after the repair ranges from −7.9% to −14%. As measure for sensitivity, we calculate the resulting impact on EC for a 10% uncertainty in laser signal at the split point.

For all 80 samples, we determined the average 'slope' at the split point. The average slope is the increase in laser signal per second expressed as a percentage of the transmission value at that time. In the Cabauw samples, the increase of the laser signal at the split point was on average 3% per second. A significant (>10%) deviation of the laser signal around the split point thus leads to a shift in split point of 3–4 s.

For the same samples, we have integrated the FID signal between the split and 4 s earlier and between the split and 4 s later. The integrated FID signal gives the amount of EC evolving in the time interval (ΔEC). For a shift backward in time $\Delta EC = 0.30$ g cm^{-2} (14%) and for the shift forward in time $\Delta EC = 0.34$ g cm^{-2} (16%). A deviation of the laser signal of 10% thus substantially impacts on the EC attribution. This sensitivity study with realistic laser signal variations, confirms that laser instability is a possible source for the observed shift in split time and EC attribution for the reference sample.

2.3. Case study: the influence of an unstable laser signal on EC

To further investigate the potential bias in EC and to confirm the results of the sensitivity calculations, we work out an example based on filter samples analysed in 2014, both before and after the repair, with the analyser at TNO. For 16 selected, different samples we use the laser transmission signals of their respective blanks analyses to calculate the potential impact on split time. The filters considered here were sampled at the sites Barcelona (BCN, Spain), Cabauw (CAB, the Netherlands), Duisburg (DUI, Germany) and Ispra (IPR, Italy). For each site one sample with low TC, one with high EC, one with high OC and one with moderate values has been selected. The following approach, which we used in our case study, can also be used as a correction of the split point. We have matched every sample to the instrument blank of the same measurement day. In the instrument blank's raw data, we have marked the split point of the analysed filter according to the manufacturer's software. For this instrument blank, the difference in transmission (ΔTr) is determined between the laser signal at the marked split point and the laser signal averaged over the first 60 s of the protocol (the averaged initial transmission). We now assume that the so-obtained relative change in laser transmission signal during blank analysis also occurs during sample analysis with the same protocol. This relative change was applied to the sample's laser signal by multiplying the laser signal values around the original split with the relative change. By comparing the new laser signal with its initial value, we have determined a 'corrected split point'. By setting a manual split at the corrected split point we calculated the corrected EC values and the difference in EC between the 'normal split' and 'corrected split' (ΔEC).

The approach used above can thus be seen as a suggestion for a correction of the split point. The stepwise correction scheme is here

[2] http://www.cesar-observatory.nl/.

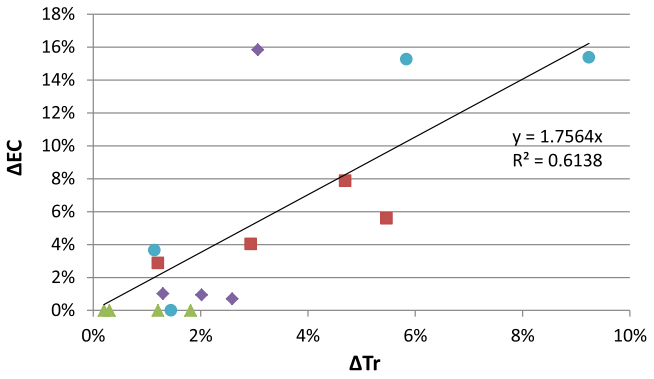

Fig. 3. The absolute bias in EC caused by an unstable laser signal around the OC/EC split point expressed as a percentage. The bias is calculated as an example for 16 samples taken from BCN (red squares), CAB (blue circles), DUI (green triangles) and IPR (purple diamonds). The results are plotted against the absolute value of ΔTr. (For interpretation of the references to colour in this figure caption, the reader is referred to the web version of this article.)

summarised:

1. Take an analysis of a sample and the blank analysis of the same day.
2. Mark the split point as calculated from the sample by the manufacturer's software in the blank analysis and compare laser signal at this point to the initial laser signal.
3. Calculate the relative change (=laser signal at split/initial laser signal).
4. Correct the laser signal around the original split point by multiplying with the relative change.
5. Compare corrected laser signal to the initial value (uncorrected) and determine the new split point.
6. Calculate OC and EC content by manually setting the new split point.

The results of this case study are shown in Fig. 3. The bias in EC is strongly correlated with the relative change in laser transmission signal ($R^2 = 0.61$). The slope between the relative change in transmission and the relative change in EC is 1.76, which means that the relative change in EC is larger than the relative change in transmission.

2.4. Change in laser signal during cooling phase

A remarkable feature of the transmission instability in our instrument, is its strong decrease during the final cooling phase. At the end of the protocol, the laser signal was, on average, 16% lower than its initial value. After the measurement protocol we still observed a continued decrease of the laser signal with respect to the initial signal. To illustrate this, we have added a cooling phase to the standard analysis protocol. With this adapted protocol, we have analysed a blank filter. The laser signal and front oven temperature of this blank analysis are shown in Fig. 4. The end of the regular protocol is marked with a dashed line and the end of the calibration, at which the OC/EC analyser normally stops recording, is marked with a solid line. By extending the recording time, we can see the behaviour after the normal protocol, which otherwise is overlooked very easily or not even noted at all. In the figure, we see that the laser signal decreases even further after the regular recording period. The temperature decreases to 40 °C and stays at that temperature for 10–15 min, during which the laser signal increases again. Only after 10–15 min the temperature suddenly drops to 35 °C and the laser transmission signal is stable and back at its initial value.

According to the manufacturer, a new measurement can be started at a temperature below 75 °C. We assume that an analyst starts replacing the sample at 75 °C and that the replacement of the sample and purging of the oven, which takes place before every measurement, take 2 min. The initial laser signal of the next sample, averaged over the first 120 s of the protocol, is then 17% lower than the initial signal of the first sample. By comparing the bias in

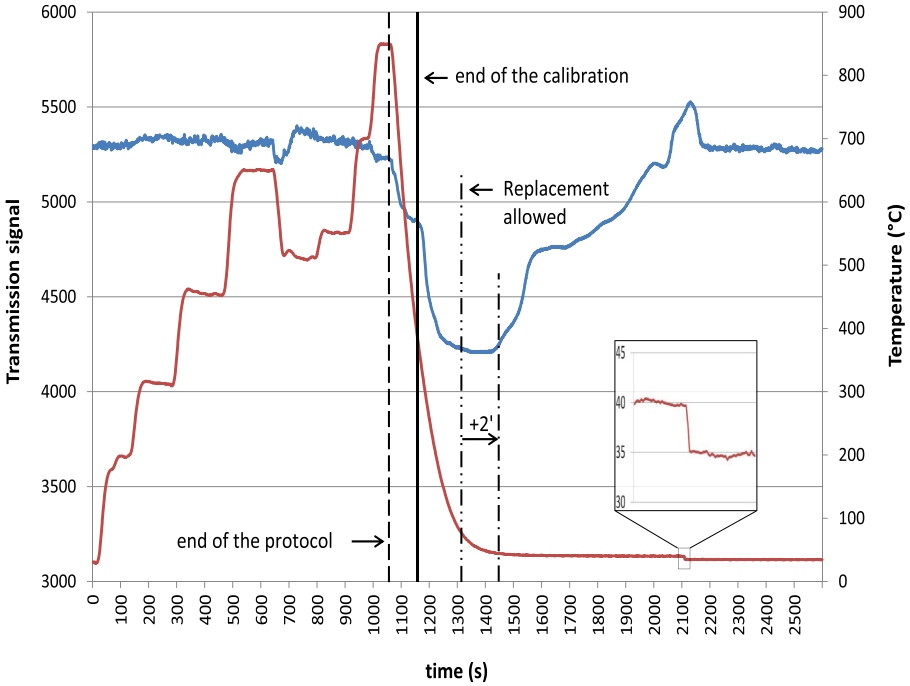

Fig. 4. Transmission signal (blue) and temperature (red) of an instrument blank, including the cooling phase. (For interpretation of the references to colour in this figure caption, the reader is referred to the web version of this article.)

Table 2
Comparison between the measurements with cold start and warm start including the standard deviations.

	Cold start	Warm start
Starting temperature (°C)	30.3 ± 0.2	38.4 ± 0.2
Split time (s)	965.3 ± 1.7	959.3 ± 1.5
EC mass (g/cm^2)	2.60 ± 0.18	3.12 ± 0.19
TC mass (g/cm^2)	14.35 ± 0.14	14.30 ± 0.14
EC/TC ratio	0.181 ± 0.013	0.218 ± 0.011

laser signal with the slope at the split point, as calculated above, we calculate a shift in split of 5.7 s, which results in a significant bias in EC attribution.

The shift caused by the reduced transmission at the end of the protocol results in an earlier split point, and therefore partially compensates the shift caused by the unstable laser signal as discussed before, which leads to a later split point.

To investigate the influence of the instability during the cooling phase, we analysed eight punches of one filter sample. Four of the punches are analysed with a so called warm start. The warm start means that the punch is directly placed into the oven when the software gave the notification that it was safe to replace the sample (below 75 °C). The time between two measurements was kept as short as possible. The other four punches are analysed with the so called cold start. For the cold start we only started a new analysis if the front oven temperature dropped below 35 °C. The results of this experiment are shown in Table 2. The initial temperature is taken directly from the raw data and averaged over the four punches. The other data are calculated with the calculation software of the manufacturer and also averaged over the four punches.

The split point in the warm start measurements is shifted 6 s, on average. This is in agreement with our calculation above, where we showed that the change of laser signal in the cooling phase causes a shift in split point of 5.7 s. The shift leads to a significant bias ($p < 0.01$) in EC attribution to the total carbon mass of 0.52 g cm^{-1}.

3. Broader perspective

The study presented in this technical note is a case study that only concerns one instrument. To investigate if similar problems occur in other Sunset instruments, several European institutes provided us with their instrument blank data. We have received instrument blank data from RUG (University of Groningen, the Netherlands), IUTA (Institute of Energy and Environmental Technology, Duisburg, Germany) and CSIC (Spanish National Research Council, Institute of Environmental Assessment and Water Research (IDAEA), Barcelona, Spain) and compared to our own data. The received blank data were normalised and averaged over a certain period of time.

The normalisation is done according to

$$Tr^{\mathrm{norm}}(t) = \frac{Tr^{\mathrm{raw}}(t)}{Tr^{\mathrm{raw}}(t=0)} \times 100\% \quad (1)$$

where $Tr^{\mathrm{norm}}(t)$ is the normalised laser transmission value at time t, $Tr^{\mathrm{raw}}(t)$ is the laser transmission value in the raw data at time t and t is the time in the analysis protocol in seconds ($t = 0$ corresponds to

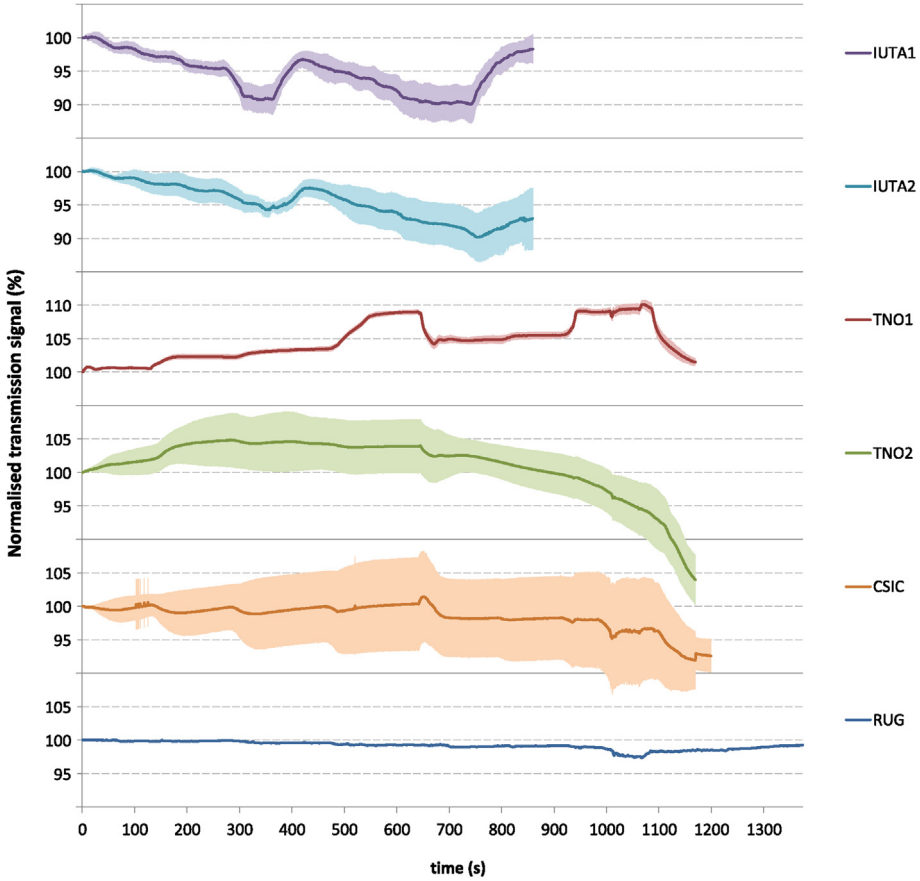

Fig. 5. The normalised transmission signal for instrument blanks of different institutes. The curves are normalised according to Eq. 1. The shaded area represents the standard deviation in the distribution.

the first data point). The normalisation is done in such a way that the transmission is expressed as a percentage of the transmission at the first data point.

The normalised blanks are plotted in Fig. 5. The shaded area is the standard deviation in the distribution of blanks. Most blank runs followed the EUSAAR2 protocol, except the blanks of IUTA, which followed the NIOSH protocol. Both runs with cold and warm start are included, no separation between these two 'types' is made. For both TNO and IUTA, we have separated the blanks in two periods, 1 and 2 respectively. At TNO the separation is chosen at the repair discussed in Sect. 1 and the separation for the IUTA blanks is chosen at a change of the oven. From RUG only one blank is available so that no range given for this curve.

In Fig. 5, we can see that the laser signals behave different under the influence of heating of the oven. The transmission signal of RUG is the most stable. Based on the data shown in Fig. 5, a bias due to a unstable laser signal around the split point is likely for CSIC and IUTA. However, at the end of the protocol, the deviation from the initial value is not as much as for TNO2. Further intercomparison studies could clarify if split time corrections such as described in Sect. 2.3 could improve the accuracy of EC measurements. An experiment as described in Sect. 2.4 could further clarify whether an unstable laser signal at the end of the protocol and/or in the cooling phase affects the measured EC masses.

4. Conclusions

We investigated the stability of the laser transmission signal and its influence on the EC results measured with the Sunset Laboratory Inc. Thermal/Optical Carbon Aerosol Analyser. In a sensitivity analysis, we demonstrated that a deviation of 10% of the laser signal around the OC/EC split point can lead to substantial change of EC concentrations. The case study (Sect. 2.3) confirms this substantial bias. Further, we found significant difference in EC concentration caused by unstable laser signal during cooling phase of the instrument. The analysis of the instrument blank data from several European institutes suggests that the deviation of EC results due to unstable laser signal might be a more common problem among users of the Sunset laboratory instrument. That is why we strongly recommend a systematic monitoring of the laser signal during an instrument blank analysis and during cooling phase of the instrument after the measurement.

Acknowledgements

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