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Atmospheric Measurement Techniques
Discussions

Interactive comment on "Clues for a standardised thermal-optical protocol for the assessment of organic and elemental carbon within ambient air particulate matter" *by* L. Chiappini et al.

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A wide range of OC-EC results have been reported in several inter-comparison studies before this paper. These studies compared different thermal/optical protocols, but however, very few of them clarified the quality assurance/quality control (QA/QC) process in performing these analyses and how well each protocol was actually implemented. Temperature calibration discussed in this paper is one great example. Without temperature calibration, the so-called "XXX protocol analysis" can differ from the desired temperature program up to several tens degrees (e.g., Chow et al., 2005a; Phuah et al., 2009). Trace oxygen level in the inert helium (He) atmosphere is important, too, but

few of the protocols specify the oxygen threshold, and as a result, it is hard to argue that two laboratories are actually performing the same protocol.

Among QA/QC the inadequacy in characterizing laser stability and signal/noise ratio (SNR) may be the most critical and yet commonly ignored factor causing diverse OC/EC splits. Temperature and oxygen, though changing the thermograms, generally have minor effects on OC/EC split if optical adjustments are implemented correctly (Chow et al., 2007). Every thermal/optical protocol implies stable laser baselines (i.e., flat reflectance and/or transmittance lines) throughout a blank analysis. A decreasing (or increasing) laser baseline (variability up to 10%) as shown in this study should never pass the QA/QC since it certainly alters the split point. Such drifts usually result from thermal expansion of oven components and highly depend on the design/maintenance of an analyzer. Besides protocol, the type of analyzer used for Fig 6 (as well as Fig. 3-4) needs be specified.

Although adjusting the potentiometer of photodiode changes the apparent reflectance (R) and transmittance (T), it does not change the SNR of R and T measurements. The detection range of R and T depends on the laser intensity, transfer loss, noises, and sensitivity of photodiode (again instrument-specific). Particularly for T, charring cannot be detected for very dark samples with statistically "zero" T at the beginning of analysis, which leads to delay of laser split point and negative bias of EC. In other cases split points were triggered by random noises leading to positive bias of EC (Chow et al., 2005b). Oven soiling increases the transfer loss of laser signal for some type of analyzers, decreases their SNR, and worsens their T detection limits. This explains Fig. 7, i.e., the higher the loading, the more below the T detection range and more underestimate of EC. The T detection range (in attenuation [ATN] based on SNR) of all carbon analyzers used in this study should be somehow quantified and compared, and only data with initial T well within all the detection ranges can be valid for inter-comparison.

In page 10239, the authors state that "when all the results are given in transmittance, no laboratory distinguish itself from the others". In page 10242, however, they conclude that overall uncertainty for EC (T) concentrations among the 5 laboratories is 29%! This seems contradictory and calls for reevaluation of the statistical analysis.

In page 10245, the influence of BrC and SOA on OC-EC analysis could simply be that they generates more charring than other organic compounds due to high polarity (Yu et al., 2002). Light absorption by BrC at 630-660 nm is small but much larger by charring.

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