Development of a dual-wavelength thermo-optical transmittance analyser: characterization and first results

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Carbonaceous aerosol (CA) plays an important role in many different issues ranging from human health to global climate change. It mainly consists of organic carbon (OC) and elemental carbon (EC) although a minor fraction of carbonate carbon could be also present. Thermal-optical methods (TOT/TOR) are presently the most widespread approach to OC/EC speciation. Despite their popularity, there is still a disagreement among the results, especially for what concerns EC as different thermal protocols can be used. In fact, the pyrolysis occurring during the analysis can heavily affect OC/EC separation, depending on PM composition in addition to the used protocol. The main hypothesis at the basis of the technique relies on the optical properties of EC and OC: while EC is strongly light absorbing, OC is generally transparent in the visible range. However, a fraction of light-absorbing OC exists: the Brown Carbon (BrC) (Andreae and Gelencsér, 2006). The presence in the sample of BrC can shift the split point since it is slightly absorbing also @ 635nm, the typical laser wavelength used in this technique (Chen et al., 2015).

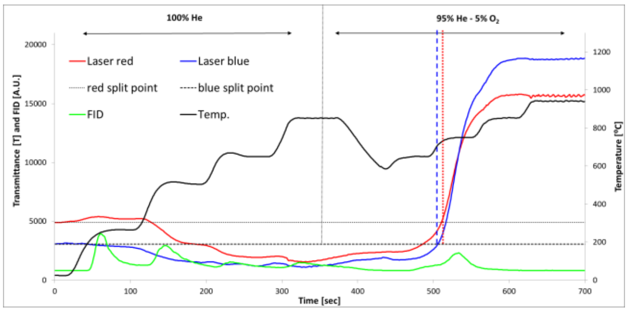

Figure 1: TOT analysis performed with both 635 and 405 nm lasers showing the identification of two distinct split points (and consequently of two different EC and OC repartitions).

At the Physics Department of the University of Genoa, a Sunset EC/OC analyser unit has been modified in order to monitor the optical transmittance during the thermo-optical analysis at two different wavelengths: 635 nm (the original wavelength of the instrument) and 405 nm (Fig.1). The additional use of the 405 nm transmittance measurement provides valuable information about the composition of the sample as well as on the pyrolytic carbon formation, both able to affect the instrumental "split point" (i.e. the moment of the analysis in which the laser transmittance is back to its starting value, thus defining EC/OC separation).

We present here the new instrument set-up, providing its full characterization with "synthetic" samples (i.e. mixtures of sucrose, graphitic carbon, and pure scattering particles). Moreover, we show also the results obtained analysing at 2-λ - with both NIOSH and EUSAAR_2 protocols - real PM samples collected in very different conditions (i.e. summer-winter) and sites (ranging from urban to rural/mountain).

Furthermore, we have recently introduced a new possibility, based on the apportionment of the absorption coefficient (b_{abs}) of particle-loaded filters, for correcting the thermo-optical analysis of PM samples (Massabò et al, 2016), an example in Fig.2. The apportionment is based on the optical analysis performed by the Multi-Wavelength Absorbance Analyser (MWAA), an instrument developed at the Physics Department of the University of Genoa (Massabò et al., 2015). The apportionment method uses the information gathered at five different wavelengths in a renewed and upgraded version of the approach usually referred to as Aethalometer model (Sandradewi et al., 2008).

We present here also the results of the thermo-optical analysis correction (Massabò et al., 2016) applied to the dual-λ analysis, which lead to a better homogeneity between the results obtained with different thermal protocols.

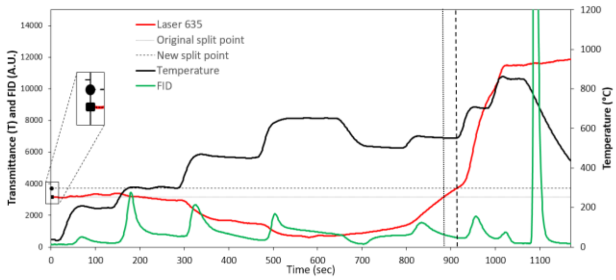

Figure 2: Example thermogram showing the original split point –square dot (i.e. non-corrected for BrC presence)- and the new split point – round dot (i.e. corrected for BrC presence). The new split point is rightmost of the original one leading to a new EC/OC separation.

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