Differences and analogies of structural changes of CAST soot and atmospheric aerosol samples during thermal-optical analyses

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Elemental Carbon (EC), Black Carbon (BC) and Organic Carbon (OC) are important components of the atmospheric aerosol because of their climatic and health effects. However, the correct determination of these components is not trivial. Results of different measurement techniques show differences by factors up to nine especially in the presence of Brown Carbon (BrC) (e.g. Reisinger et al., 2008; Hitzenberger et al., 2006; Wonaschütz et al., 2009).

During thermal-optical analyses of EC and OC, samples are heated stepwise first in an inert (He), then in an oxidizing (He+O₂) atmosphere. The pyrolysis of the samples during the inert mode is corrected for optically, but uncertainties in the OC/EC split remain (Cheng et al., 2012). BrC and other water soluble organic carbons (WSOCs) are thought to bias the results of thermal-optical measurement techniques due to their high potential to pyrolyze during the inert heating procedure. Also the presence of certain metal salts influences the pyrolyzation of OC (Wang et al. 2010). Although there is consent about the confounding role of pyrolyzation, the concrete structural reorganizations of the material during thermal-optical analyses are not fully understood.

In the present study structural changes of soot produced with a miniCAST generator (Jing Technologies) as well as of atmospheric aerosol samples during two thermal-optical measurement protocols (NIOSH870, Birch and Cary, 1996 and EUSAAR2, Cavalli et al., 2010) are investigated. EC and OC are determined for all samples with a dual-optics OC/EC analyzer (Sunset Instruments Inc.), which is also used as an oven for the preparation of the heated samples. The heated samples are analyzed with Raman Spectroscopy, which is sensitive to the bonding types and the degree of structural ordering (i.e. the amount of aromatic rings) in carbonaceous materials (Ferrari and Robertson, 2000). The content of BrC is measured with the Integrating Sphere method (Wonaschütz et al., 2009) and back trajectories are calculated with HYSPLIT for the atmospheric aerosol samples.

Both, atmospheric aerosol samples and CAST samples, with a high amount of BrC show changes in the Raman spectra during the heating process in the OC/EC instrument. The extent of the changes, however, is different for the two measurement protocols. The increase of structural ordering due to heating is slightly less pronounced for the EUSAAR2 protocol with a lower maximum temperature in the inert phase.