Analysis of structural changes of two different CAST soots during a thermal-optical measurement procedure

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Carbonaceous material contributes a large amount to atmospheric aerosols and has strong climatic and health effects. Reliable measurement techniques for Elemental Carbon (EC), Black Carbon (BC) and Organic Carbon (OC) therefore are essential. Measurements, however, still suffer from method specific differences with 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).

Thermal-optical measurement techniques are widely used for the separation of EC and OC and based on the differing thermal stability of both components: The sample is heated stepwise, first in an inert (He) atmosphere, then in an oxidizing ($He+O_2$) atmosphere. The pyrolysis of the sample in the He-phase is corrected for optically but uncertainties in the OC/EC split remain (Cheng et al. 2012). Knowledge about the concrete structural reorganizations of the material during the heating process could therefore improve the understanding of this bias.

In the present study, structural reorganizations of carbonaceous material during the heating process were investigated using Raman microscopy, transmission electron microscopy (TEM) and UV-Vis spectroscopy. The content of BrC in the sample was analyzed with the integrating sphere method (Wonaschütz et al. 2009).

A miniCAST soot generator was operated under two different combustion conditions in order to generate samples with a high amount of BrC (here referred to as ‘brown’ sample), and a low amount of BrC (referred to as ‘black’ sample).

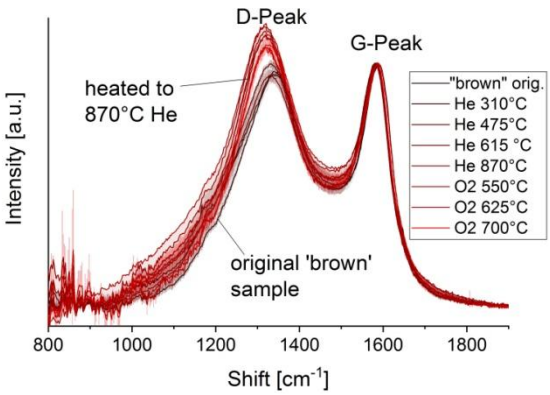

Figure 1: Raman spectra of the 'brown' sample heated to different temperature steps of the NIOSH870 protocol

The original samples were analysed with a dual-optics ECOC analyser (Sunset Instruments Inc.) which was also used for the preparation of the heated samples. Heated samples according to each temperature step of the NIOSH870 (Birch and Cary, 1996) protocol were analyzed with Raman spectroscopy (Fig.1) and UV-Vis spectroscopy. Selected samples were additionally analyzed with TEM.

All measurement techniques show an increase of ordering of the material in the ‘brown’ sample due to heating but no significant changes for the ‘black’ sample. The Raman spectra are fitted with five curves according to Sadezky et al. (2005) (Fig.2) and suggest – in combination with an interpretation by Ferrari and Robertson (2000) – an increasing amount of polyaromatic rings in the sample. The evaluation of the electron diffraction patterns shows an increase of the crystallite sizes from 1.6 nm to 2 nm when the ‘brown’ sample is heated to 870°C in He.

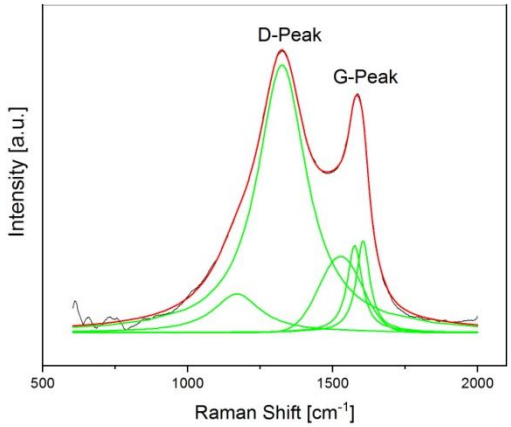

Figure 2: Raman spectrum with curve fit according to Sadezky et al. (2005)

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