In situ Raman microspectroscopic analysis of soot samples with different OC content: Structural changes during oxidation

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Aerosol particulate matter generated by combustion sources (soot) can have a significant influence on atmospheric chemistry, Earth's climate and human health. Due to complex morphology, composition and structure of soot particles their properties (e.g., hydrophilicity) as well as their impact on the environment are not well understood. Ambient aerosols, in particular combustion derived aerosols are often characterized by their content of elemental carbon (EC) and organic carbon (OC), which are determined by thermo-optical methods. However, it is not clear whether different OC content in soot is related to the differences in soot structure and their changes during the oxidation.

The methods available for the characterization of the molecular and crystalline structures of soot are high-resolution transmission electron microscopy (HRTEM), X-ray photoelectron spectroscopy (XPS), X-ray absorption near edge structure (XANES), Infrared (IR) spectroscopy and Raman microspectroscopy (RM) (Ivleva *et al.* 2007). RM, which is based on the effect of inelastic light scattering, enables the nondestructive chemical analysis with the spatial resolution down to 1 µm. This method provides us not only with the information on the soot structure (including disordered graphitic and amorphous carbon) and associated reactivity (Schmid *et al.* 2011), but also allows us to characterize inorganic compounds in soot samples (e.g., metal oxides or salts), which can significantly enhance the soot reactivity and drastically decrease the EC/OC ratio (Bladt *et al.* 2014). Furthermore, by the combination of Raman microscope with e.g. oxidation setup *in situ* RM measurements can be performed.

In this presentation we focus on *in situ* RM analysis of structural changes occurring in soot with different OC content, and compare the RM data with the results of IR, XPS and XANES studies. We applied RM (LabRAM, HORIBA, λ_0 = 633 nm) in combination with the Linkam THMS600 heating stage for investigation of oxidation of soot with OC content of 5 % (Set-point 1, SP 1), 30 % (SP 2) and 80 % (SP 3) in air. Samples were produced with mini CAST burner, OC/EC was measured by a thermo-optical method, Sunset Lab (IMPROVE protocol) (Chow *et al.* 1993).

RM analysis of untreated samples revealed the differences in structure of soot with various OC content. We found the highest ID/IG ratio for SP 1 (typical for soot with higher structural order & EC content) and identified signatures from organic compounds (e.g., C–O str.) in the region ca. 1200 cm^{-1}. During the oxidation up to 500 °C no significant changes were detected for soot with low OC content (SP 1, Figure 1). In contrast, the narrowing of D band and increasing of ID/IG ratio were revealed for soot with high OC content (e.g., SP 3, Figure 1), indicating the combustion of organic substances and structural ordering of these soot samples.

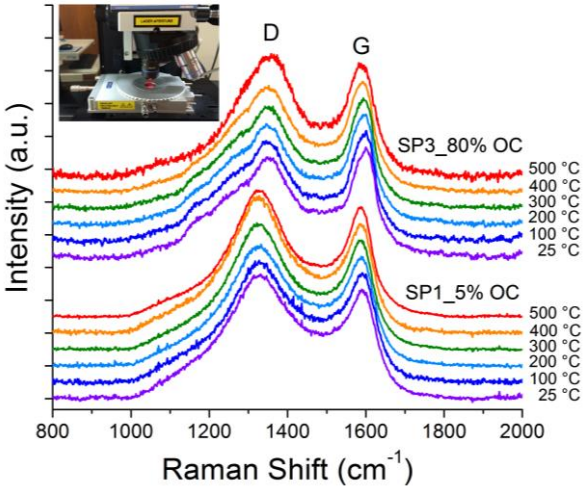

Figure 1. Raman spectra of soot samples with different OC content during oxidation. Insert: photo of setup for *in situ* RM measurements.

RM results in combination with IR, XPS and XANES data should help us to get better insight into complex composition and structure of soot samples, and improve on understanding of soot properties (e.g., reactivity and hygroscopicity), which vary significantly for soot samples with different OC content.

Bladt, H., Ivleva, N.P. and Niessner, R. (2014) *J. Aerosol Sci.* **70**, 26-35.

Chow, J.C., Watson, J. G., Pritchett, L. C., Pierson, W. R., Frazier, C. A. and Purcell, R. G. (1993) *Atmos. Environ. A-Gen.* **27**, 1185-1201.

Ivleva, N.P., McKeon, U., Niessner, R. and Pöschl, U. (2007) *Aerosol Sci. Tech.* 41, 655-671.

Schmid, J., Grob, B., Niessner, R. and Ivleva, N.P. (2011) *Anal. Chem.* **83**, 1173-1179.