

Tip-Enhanced Raman Spectroscopy for characterizing SOA: a preliminary study

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The importance of characterizing composition and microstructure of aerosol particles is now well-established for inferring key properties of the aerosol such as hygroscopicity, the activity of cloud condensation, the reactivity, the optical properties, etc. [1]. Secondary Organic Aerosol particles (SOA) are formed through complex physico-chemical processes occurring in the atmosphere and leading to a complex chemical composition. The properties of atmospheric aerosols can be resolved at varying level of details including single particle level. Indeed, the composition and heterogeneity of a particle can be resolved with a degree of spatial resolution by single particle analytical methodology [1-3]. Tip-enhanced Raman spectroscopy (TERS), a combination of Raman spectroscopy and apertureless near-field scanning optical microscopy using a metallic tip which resonates with the local mode of the surface plasmon, can provide a high-sensitive and high-spatial-resolution optical analytical approach [4-5]. TERS is a technique that provides molecular information on the nanometre scale and may advantageously unravel chemical composition of SOA [6].

In this work we have investigated chemical composition of unique SOA particles using a bottom-illumination TERS instrument combining an atomic force microscope and a micro-Raman spectrometer. Aerosols were generated using a discharge flow reactor from heterogeneous OH-initiated oxidation of particulate-MBTCA on adapted substrates for TERS measurements. The optimization of analytical parameters to get both surface composition and topology of single particles in near-field mode are presented. The results are compared with those obtained with conventional Raman microspectrometry i.e. in far-field mode to discuss the relevance for characterizing SOA using TERS.

[1] Krieger *et al.* (2012) *Chem. Soc. Rev.* **41**, 6631-6662. [2] Mikhailov *et al.* (2009) *ACP* **9**, 9491-9522. [3] Morris *et al.* (2015) *Chem. Sci.* **6**, 3242-3247. [4] Bailo and Deckert, (2008) *Chem. Soc. Rev.* **37**, 921-930. [5] Zhang *et al.* (2016) *Anal. Chem.* 9328-9346 [6] Ofner *et al.*, *Anal. Chem.* **88** 9766-9772.