

Secondary organic aerosol formation through aqueous phase photooxidation of aromatic compounds

Zoran Kitanovski¹, Irena Grgić¹, Alen Čusak² and Magda Claeys³

¹Laboratory for Analytical Chemistry, National Institute of Chemistry, SI-1000 Ljubljana, Slovenia

²EN-FIST Center of Excellence, SI-1000 Ljubljana, Slovenia

³Department of Pharmaceutical Sciences, University of Antwerp, BE-2610 Antwerp, Belgium

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Presenting author email: irena.grgic@ki.si

Secondary organic aerosol (SOA) formed through the gas-phase oxidation of volatile organic compounds (VOCs) and further gas-to-particle partitioning cannot explain the gap between atmospheric observations and model predictions of organic aerosols (Heald *et al.*, 2005). However, there is growing evidence that reactions in atmospheric waters may represent an additional and important source of SOA (Lim *et al.*, 2010). Formation of low-volatility products in the aqueous phase has been observed during reactions of carbonyl and monoaromatic compounds found in the atmosphere (Ervens *et al.*, 2011; Sun *et al.*, 2010).

Monoaromatic compounds can be considered as a proxy for anthropogenic and biomass burning emissions. Methyl-nitrocatechols have been identified as an important class of SOA compounds from biomass burning and proposed as suitable tracers (Iinuma *et al.*, 2010; Kitanovski *et al.*, 2012). In addition to nitrocatechols, other nitro-aromatics were determined in urban winter aerosols (Fig. 1), and constitute nearly 1% of the organic carbon (Kitanovski *et al.*, 2012). A noticeable unknown peak consistent with a nitroguaiacol isomer was also detected in the latter study.

In the present study, the formation of SOA through aqueous-phase photooxidation (and nitration) of guaiacol (2-methoxyphenol), known to be emitted upon biomass burning, was studied. The main objectives were to chemical characterize the low-volatility products and examine their possible presence in ambient aerosols.

The aqueous phase reactions were performed in a thermostated reactor under well-defined experimental conditions. A solution of guaiacol was exposed to simulated sunlight (Xenon lamp, 300 W) in the presence of H₂O₂ (source of OH radicals) and NO₂⁻. After isolation of the main reaction products by solid-phase extraction (SPE), their chemical structures were elucidated. To this aim, the SPE extract was first subjected to semi-preparative liquid chromatography, after which the main products were fractionated and isolated. Nuclear magnetic resonance spectroscopy (NMR) and liquid chromatography/negative ion electrospray ionization tandem mass spectrometry (LC/(-)ESI-MS/MS) were used for structural elucidation.

The main products of guaiacol photooxidation and nitration are two nitroguaiacols (4-nitroguaiacol, 4NG; and 6-nitroguaiacol, 6NG) and one dinitroguaiacol

(4,6-dinitroguaiacol, 4,6DNG). In addition, several minor phenolic oxidation products and oligomers of guaiacol and nitroguaiacol were formed. Using the isolated compounds as standards, several guaiacol products were identified in ambient PM₁₀ from the city of Ljubljana (Slovenia) by means of LC/(-)ESI-MS/MS.

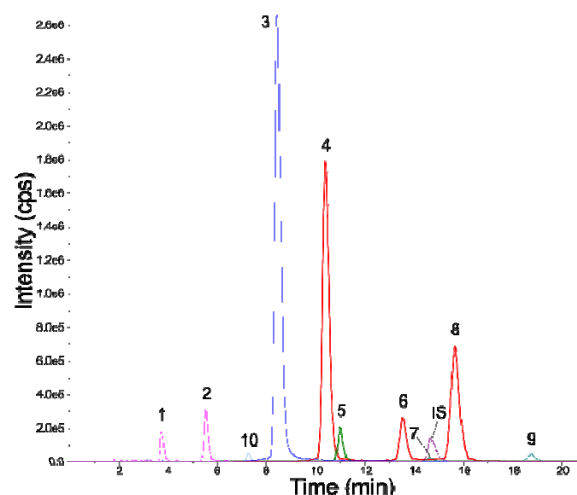


Figure 1. Selected reaction monitoring chromatograms for a winter sample (17/12/2010; PM₁₀ mass conc. = 60 µg m⁻³): 3NSA (1), 5NSA (2), 4NC (3), 4M5NC (4), 4NP (5), 3M6NC (6), 3M4NP (7), 3M5NC (8), 2M4NP (9), unknown nitroguaiacol (10), and picric acid (IS) (Kitanovski *et al.*, 2012).

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