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Detection of the high mass, gas phase oxidation products of trimethyl benzene, α-pinene and isoprene during aerosol chamber studies and their potential role in aerosol formation

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Many contemporary atmospheric problems are caused or exacerbated by the presence of aerosol particles; including reduction in local visibility, various human health problems (in the main pertaining to the respiratory system), perturbation of atmospheric chemistry and even climate change. Indeed the atmospheric aerosol is capable of altering both the direct radiative budget (through scattering of light) and indirect radiative budget (through propagation of cloud formation) of the Earth, thus having a major impact on global climate.

The Secondary Organic Aerosol (SOA) formed in the atmosphere following the oxidation of various volatile organic compounds (VOCs), constitute a large proportion of the total mass (as much as 90% in the urban atmosphere) and number concentration of organic aerosols (Kalberer *et al.*, *Science*, **303**, 1694–1662, 2004). The formation pathways and chemical composition of the SOA are not well characterised, however it has been proposed by Kalberer *et al.* (*Science*, **303**, 1694–1662, 2004) that polymerisation of the oxidation products of aromatic precursors plays a major role.

The University of Leicester Chemical Ionisation Reaction Time-of-Flight Mass Spectrometer (CIR-TOF-MS) took part in a joint measurement campaign at the Paul Scherrer Institute Aerosol Chamber, in order to explore the missing link between the gas and aerosol phases. Utilizing H_3O^+ ions to initiate proton transfer to the analyte species, the CIR-TOF-MS instrument was able to successfully capture in “real-time” (*ca.* 1 minute) the entire gas phase VOC/OVOC mass spectrum with sensitivities in the order of 0.1 count ppb^{-1} s^{-1}.

The aerosol chamber photo oxidation experiments were conducted for periods between 8 and 26 hours, with a single initial injection of a known SOA precursor with mixing ratios in the range 120 ppbV to 1.2 ppmV. The precursors were chosen to represent both anthropogenic and biogenic starting materials and included trimethyl benzene, α-pinene and isoprene.

This work constitutes a preliminary examination of the successful performance of the CIR-TOF-MS in monitoring the evolution of the gas phase oxidation products of the VOC, SOA precursors. Particular emphasis is placed on the successful detection of previously unseen high mass oxidation products present in the gas phase (up to m/z= 232) and the identification of possible dimers and trimers, which may constitute a link between the gas and aerosol phases *via* initiation of oligomer formation.