



First results on the real-time analysis of laboratory produced SOA, using a new resonance-enhanced multiphoton ionisation aerosol mass spectrometer.

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Organic aerosols (OA) can contribute to 20-50% of the total fine aerosol mass in continental mid-latitudes (Putaud et al., 2004) and up to 90% in tropical highly forested areas or urban areas (Andreae et al., 1997). OA are thus ubiquitous constituents of the atmospheric aerosol (see for example Murphy et al., 1998). They can be separated in primary organic aerosols (POA) and secondary organic aerosols (SOA). SOA generally constitute 10 to 20% of the total OA at the Earth's surface (Chung and Seinfeld, 2002). Generally, SOA are formed by atmospheric oxidation of volatile organic compounds (VOCs), emitted into the atmosphere leading to the formation of low-volatility, chemically more functionalised, oxidation products. These compounds can condense on pre-existing particles.

Anthropogenic VOCs such as alkanes, alkenes, and carbonyls represent a significant fraction of the organic gas-phase in the urban atmosphere. These compounds can form anthropogenic SOA (ASOA) when undergoing oxidation. It has been generally accepted that hydrocarbons possessing six or more carbon atoms can act as SOA precursors (Grosjean and Seinfeld, 1989). Several measurement techniques are used today to analyse atmospheric aerosols, including off-line and on-line techniques, for example laser vapourisation/ionisation mass spectrometers (Prather et al., 1994 ; Gard et al., 1997). These instruments are employed to characterise SOA particles formed by photooxidation or ozonolysis experiments in smog chambers (Bahreini et al., 2005 ; Gross et al., 2006).

We will present first results on the real-time analysis of laboratory produced SOA formed from ozonolysis of anthropogenic VOCs (indene, methylstyrene, o-xylene), using a newly built Resonance-Enhanced Multiphoton Ionisation (REMPI) aerosol mass spectrometer. This instrument is meant to be a new, versatile instrument open to the French and European community : aerosols are focused into the ion source of a time-of-flight mass spectrometer (TOFMS) using an aerodynamic lens. They are optically detected and sized (d_{ae}) when crossing two continuous laser beams (403 nm). The instrument can be operated in two modes in the future: 1) A single particle mode where the scattering signals are used to trigger an IR and an UV laser for vaporisation and ionisation of single particles inside the ion source of the TOF-MS, in temporarily separated steps. In this mode, the chemical composition of the particle will be determined as a function of the number size distribution. Variation of the IR laser pulse energy will permit to analyse specifically their surface composition. 2) The second mode is a thermal desorption mode where the TOF-MS will work at a regular repetition rate and particles will be constantly vaporized using a cartridge heater placed near the ion source. The resulting vapor plume will be ionised by a pulsed KrF excimer laser (248 nm). REMPI at this wavelength permits to detect, with high sensitivity, aromatic degradation products in the condensed phase in real time.

References :

Andreae, M.O. and Crutzen P.J., Atmospheric aerosols : Biogeochemical sources and role in atmospheric chemistry, *Science* 276, 1052-1058, 1997.

Bahreini, R., Keywood, M. D., Ng, N. L., Varutbangkul, V., Gao, S., Flagan, R. C., Seinfeld, J. H., Worsnop, D. R., and Jimenez, J. L., Measurements of secondary organic aerosol from oxidation of cycloalkenes, Terpenes, and m-xylene using an aerodyne aerosol mass spectrometer, *Environ. Sci. Technol.* 39(15), 5674–5688, 2005.

Chung, S.H., and Seinfeld, J.H., Globale distribution and climate forcing of carbonaceous aerosols, *J. Geophys Res.* 107(D19), 4407, doi:10.1029/2001JD001397, 2002.

Gard, E., Mayer, J.E., Morrical, B.D., Dienes, T., Fergenson, D.P. and Prather, K., Real-time analysis of individual atmospheric aerosol particles : Design and performance of a portable ATOFMS, *Anal. Chem.* 69, 4083-4091, 1997.

Grosjean, D., Seinfeld, J.H., Parameterization of the formation potential of secondary organic aerosols, *Atmos. Environ.* 23, 1733-1747, 1989.

Gross, D. S., Gälli, M. E., Kalberer, M., Prevot, A. S. H., Dommen, J., Alfarra, M. R., Duplissy, J., Gaeggeler, K., Gascho, A., Metzger, A., and Baltensperger, U., Real time measurement of oligomeric species in secondary organic aerosol with the aerosol time-of-flight mass spectrometer, *Anal. Chem.* 78(7), 2130–2137, 2006.

Murphy, D.M., Thomson, D.S., and Mahoney, T.M.J., In situ measurement of organic, meteoritic material, mercury and other elements in aerosols at 5 to 19 kilometers, *Science* 282, 1664-4669, 1998.

Prather, K.A., Nordmeyer, T., and Salt, K., Real-time characterization of individual aerosol using time-of-flight mass spectrometry, *Anal. Chem.* 66, 1403-1407, 1994.

Putaud, J. P., Raes, F., Van Dingenen, R., Brüggemann, E., Facchini, M. C., Decesari, S., Fuzzi, S., Gehrig, R., Hüglin, C., Laj, P., Lorbeer, G., Maenhaut, W., Mihalopoulos, N., Müller, K., Querol, X., Rodriguez, S., Schneider, J., Spindler, G., ten Brink, H., Tørseth, K., and Wiedensohler, A., A European aerosol phenomenology 2: chemical characteristics of particulate matter at kerbside, urban, rural and background sites in Europe, *Atmos. Environ.* 38, 2579–2595, 2004.