

Real time chemical characterisation of aerosols via ATOFMS and ToF-AMS during REPARTEE I

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The advent of techniques of particle mass spectrometry offers great insights into the source apportionment and atmospheric chemistry of aerosols. The aerosol time-of-flight mass spectrometer (ATOFMS) offered by TSI provides information on a polydisperse aerosol, acquiring precise aerodynamic diameter ($\pm 1\%$) within the range 0.3 to 3 micrometres and individual particle positive and negative mass spectral data in real time. The AMS (Aerodyne Research, Inc.) provides online, real time measurements of the mass of non-refractory components of aerosol particles as function of their size. ATOFMS is capable of single particle analysis, whilst AMS requires the collection of an ensemble of particles to obtain sufficient sample for analysis. However, the AMS can quantify the size resolved organic carbon, sulphate, ammonium and nitrate mass loadings of aerosol in the size range between 60 and 600 nm. The data shown herein were collected at Regents Park (London-October 2006) during the REPARTEE I project. The general overview of the findings of the two particle mass spectrometers will be presented elsewhere. Herein, three main key findings will be presented.

1. The ATOFMS classified two types of nitrate-containing particles; one being formed locally, the other regionally transported from continental Europe. Local nitrate was formed at nighttime. AMS nitrate mass loading and ATOFMS total nitrate containing particles showed a very good correlation. The ATOFMS showed that the LRT nitrate particle type exhibits a diurnal temporal variation, evaporating during the day due to the higher temperature. However, the core of the LRT nitrate containing particles is still detected during the day and is composed mainly of elemental carbon and sulphate with a size distributions shifted towards smaller particles.

2. A fog event was monitored with state-of-the-art real-time aerosol mass spectrometers in an urban background location in London (England) during the REPARTEE-I experiment. Specific particle types rich in hydroxymethanesulphonate (HMS) were found only during the fog event. Formation of inorganic and organic secondary aerosol was observed as soon as fog was detected and

two different mechanisms are suggested to be responsible for the production of two different types of aerosol. Nitrate aerosol is produced in the liquid phase within fog droplets. Contrary to previous studies, the formation of HULIS was observed on interstitial particles but not in evaporated fog droplets, suggesting heterogeneous formation mechanisms depending on parameters other than the water content and not fully understood. Not only are secondary aerosol constituents produced during the fog event, but the primary aerosol is observed to be processed by the fog event, dramatically changing its chemical properties.

3. The application of the ART-2a neural network algorithm to the ATOFMS data characterized a specific particle type (rich in secondary organic aerosol and polycyclic aromatic compounds; SOA-PAH). The temporal trend of this particle type presented a strong weekday-weekend variation, suggesting a strong link with traffic emissions. Comparisons with several other measurements taken during the REPARTEE-I (including positive matrix factorization (PMF) analysis of the AMS data) excluded local primary anthropogenic sources. ATOFMS single particle mass spectra revealed a strong component of oxidized organic carbon, associated with PAH signals and flavonoids. This particle type was internally mixed with strong acidic sulphate species, but not with nitrate. Moreover, this particle type was found peaking only during the warmest part of the day (11.00-14.00) and is therefore thought to be influenced by photochemical reactions in the particle phase. The SOA-PAH particle type, rich in flavonoids, could suggest a mechanism for production of secondary organic aerosol from gas-phase reactions of PAH.

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