

Quantitative single particle mass spectrometry with the Aerodyne aerosol mass spectrometer: development of a new classification algorithm and application to field data

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Single particle mass spectrometry using laser desorption / ionization instruments is well established; however, this method is typically not capable of providing quantitative information about the chemical composition of the individual particles. Efficient single particle mass spectrometry using the Aerodyne aerosol mass spectrometer (AMS) has become possible with the introduction of the light scattering probe by Cross *et al* (2009). Here, the particles are flash vaporized on a hot surface and ionized by electron impact ionization. This method provides reproducible fragmentation patterns of individual chemical species, and therefore enables quantification of different, non-refractory chemical compounds within the single particles (diameters ~300 - 1000 nm).

So far, published cluster algorithms like principal component analysis (Cross *et al*, 2009) or k-means clustering (Liu *et al*, 2012) have been used for the analysis of AMS single particle data. In these studies quantitative information on the content of different aerosol species has been acquired separately by using the same procedures as applied to AMS ensemble mass spectra. No unambiguous method was used yet to both quantify the contents of organic and inorganic species and to identify and separate different organic species within single particles.

Here, we present the development, laboratory validation, and field application of a new method for AMS single particle analysis, which provides both quantitative information about the contents of different organic and inorganic species within single particles and classification of particles into different particle types.

In a first step the single particle mass spectra are compared to reference mass spectra for typical particle components (i.e., NH_4NO_3 , $(\text{NH}_4)_2\text{SO}_4$, glucose as biomass (burning) proxy, oleic acid as cooking proxy, oxygenated organic aerosol OOA from ambient measurements, and gasoline engine exhaust). To obtain quantitative information on the content of these components in the particles, the corresponding mass spectra are subtracted proportionately from the single particle mass spectra. Depending on the components found in every single particle it is assigned to a certain particle type. This approach allows an unambiguous detection of different species within the single particle mass spectra, and, unlike clustering algorithms, does not depend on the specific dataset analyzed.

In laboratory measurements this method was tested and validated. Species in laboratory-generated single particle mass spectra are reasonably well

identified and separated, as long as sufficient signal is available.

The new single particle analysis method was applied successfully to AMS data acquired during field measurements which took place in July 2009 in Paris within the MEGAPOLI project. About 90% out of ~26,000 single particle mass spectra have successfully been classified according to their composition (Fig. 1). Particles originating from primary emissions (i.e. cooking and traffic) are found to be externally mixed with internally mixed particles of OOA, nitrate and sulphate. Only for a small fraction of particles, mixtures of different organic species or organics other than OOA with inorganics were found (“mixed organics” in Fig. 1).

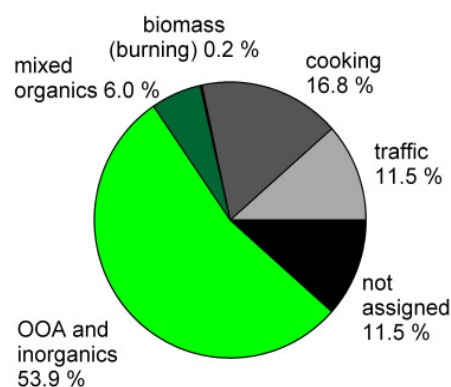


Figure 1. Classification of the AMS single particle mass spectra acquired during the MEGAPOLI campaign.

Comparison of averaged single particle composition with results from ensemble measurements showed good agreement. In addition to direct information about aerosol mixing state and consequently potential particle sources, this method provides valuable data on absolute concentrations of certain species within individual particles and their temporal variations.

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