

Sulphur speciation in marine submicron aerosol particles using *on-line* thermal-desorption aerosol mass spectrometry

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Atmospheric aerosol particles are known to have significant impact on both the earth's climate and human health. Therefore extended knowledge on the composition of ambient aerosol particles and on generation and transformation processes associated with such particles are imperatively needed in order to assess the effects of ambient aerosols. A modern analytical tool that is increasingly used to investigate the composition of aerosol particles with high temporal resolution is *on-line* aerosol mass spectrometry.

In this study the applicability of this technique to the identification and quantification of sulphur species in marine aerosol particles was investigated using an Aerodyne Research, Inc. Aerosol Mass Spectrometer (AMS) in laboratory and field experiments. The Aerodyne AMS samples ambient aerosol particles in a size range from about 60 nm up to 700 nm and focuses them onto a vaporizer, heated to 600 °C using an aerodynamic lens assembly. Non-refractory aerosol components flash-evaporate, and the generated vapour is electron impact ionized and subsequently analysed using a high resolution time-of-flight mass spectrometer. The resulting mass spectra can be used to determine mass concentrations and species-resolved particle size distributions of non-refractory aerosol components.

Since no physical separation of different species is performed prior to the mass spectrometric analysis, the identification and quantification of individual compounds within the aerosol has to be done by mathematically separating the mass spectrometric information. In order to identify and separate different sulphur-containing aerosol species known to exist in the marine atmosphere – namely sulphate, elemental sulphur, methanesulphonic acid (MSA), dimethyl sulphonyde (DMSO), and dimethyl sulphone (DMSO₂) – laboratory measurements were performed to determine the standard fragmentation patterns of these species under the measurement conditions of the Aerodyne AMS.

Within the standard fragmentation patterns individual marker peaks containing a sulphur atom, but not being shared by different components, have been identified and consequently used to determine each species' contributions to the overall mass spectra. By applying a specially designed peak fitting algorithm to the high-resolution spectra and corrections for fragment intensities the quantification of the individual sulphur-containing species in ambient aerosol spectra is possible. This extraction and quantification procedure was then applied to ambient aerosol data collected during a cruise in the Southern Atlantic Ocean, determining the concentrations of these species with high temporal resolution for the first time.

In addition to these field results, a discussion on the limitations of this method for speciation of sulphur compounds and other non-refractory aerosol species using *on-line* aerosol mass spectrometry will be provided.