Online Method for Size-Resolved Chemical Speciation of Nano-Particles

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Keywords: nano-particles, instrumentation, mass spectrometry, nucleation.
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The growth of aerosol particles originating from nucleation is an important atmospheric process. The availability of condensable vapors for this growth is a prerequisite for these particles to become cloud condensation nuclei (CCN). To determine the source and the mechanisms of the aerosol growth, the condensing vapors need to be chemically speciated. However, the chemical analysis of particles in the size range between 2 nm and 20 nm is an experimental challenge and there are only very few instruments which can perform such an analysis under atmospherically relevant conditions. The TD-CIMS (Thermal Desorption Chemical Ionisation Mass Spectrometer, Voisin et al. (2003)) is a unique instrument which is capable performing such measurements online and has already given important insights into some atmospheric processes leading to aerosol growth (e.g. Smith at al. (2010)). However, further studies are necessary, especially with respect to other environments and different particle sizes.

In this study, a new instrument is introduced which allows the size-resolved identification of the chemical composition of particles in the size range below 20 nm. The TD-DMA (Thermal Desorption Differential Mobility Analyzer) collects particles on a substrate and transfers them into the gas phase so that they can be analyzed with a mass spectrometer. The particles first pass through a DMA unit, so that only those with a selected size can reach the substrate. The substrate currently consists of a stainless steel wire to which HV can be applied in order to precipitate the particles. Once enough particles are collected, the substrate can be moved into the sample inlet of a chemical ionization mass spectrometer (CIMS). In this mode of operation the CIMS inlet line is flushed with ultrapure nitrogen and the wire is heated by electrical current which evaporates the particles into the clean carrier gas. This procedure ensures that on the one hand, only the particulate constituents will be analyzed and on the other hand they can reach concentrations which are high enough for chemical speciation.

The advantages of the TD-DMA are as follows: (1) The analysis is performed online. (2) The collection of particles is carried out size-resolved, as particles with different sizes likely have different chemical compositions. (3) The collection and evaporation unit is compact and can in principle be combined with different analyzing instruments. (4) The measurement time required for the particle evaporation is small compared to the overall measurement time. However, during the collection period the mass spectrometer can be used to measure the gas phase composition of the sample air. This feature allows obtaining a full picture of the processes occuring in the gas as well as the particulate phase with one single mass spectrometer.

Lab experiments with a tandem DMA setup have shown that the maximum transmission of the DMA unit is between 45% for 5 nm (see figure 1) and 60% for 15 nm. It could also be demonstrated that close to 100% of the size selected particles can be precipitated onto the substrate. Sulphuric acid particles 15 nm in diameter were successfully collected and subsequently evaporated in the inlet of a CIMS which showed signals characteristic for sulphuric acid.

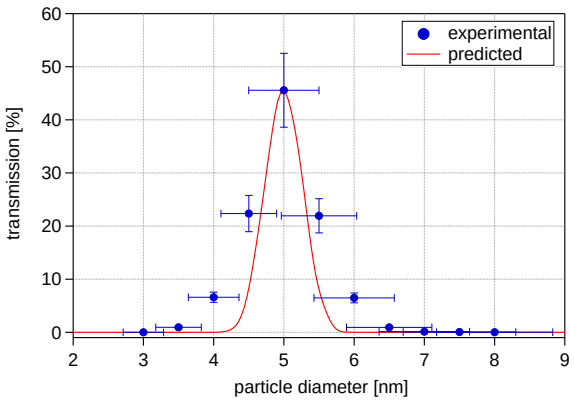

Figure 1: Experimental (blue) and predicted (red) transmission curve for particles with a diameter of 5 nm

The operational principle and the setup of the TD-DMA will be presented in detail. Results on the characterisation of the DMA transmission as well as first quantitative tests with respect to the collection and evaporation of different aerosol species will be discussed.

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