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Time-of-flight aerosol mass spectrometry: Measuring gaseous iodine species after selective uptake in lab-generated aerosols

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Reactive iodine species play an important role in the marine atmospheric chemistry. Recent studies show that iodine containing compounds (e.g. I_2 and ICl) are involved in the tropospheric ozone depletion, the enrichment of iodine in marine aerosols and the formation of new particles in the marine boundary layer (MBL). Various laboratory and field measurements report that molecular iodine (I_2) and organoiodine compounds (e.g. CH_3I, CH_2I_2) are the most important precursors for reactive iodine in the MBL[1],[2]. However, the identification and quantification of reactive iodine containing compounds are still analytical challenges. Here, we present a new application of the time-of-flight aerosol mass spectrometer (ToF-AMS) for the quantification of gaseous I_2 and ICl in real-time.

Time-of-flight aerosol mass spectrometry enables the real-time analysis of the particle size, the particle mass and the chemical composition of non-refractory aerosols[3]. The aerosol enters the ToF-AMS through a critical orifice of 100 μm inner diameter. An aerodynamic lens system focuses the particles in a size range of 50-600 nm as a narrow beam into the vacuum system. While most of the air is removed by a skimmer, the particle beam is transmitted into the particle-sizing chamber. After passing the particle-sizing chamber, the non-refractory particles are flash-vaporized on a heated tungsten surface (500-600 °C) and then ionized by electron impact. The generated ions are extracted by an orthogonal extractor into the time-of-flight mass spectrometer, where the time resolved particle mass detection is performed.

Since gaseous compounds are removed inside the ToF-AMS, a direct measurement of gaseous iodine species is not possible. Therefore gaseous iodine species have to be transferred from the gas phase to the particle phase before entering the ToF-AMS. For this purpose α-cyclodextrin (α-CD) particles were used as selective sampling probes for I_2 and 1,3,5-trimethoxybenzene (1,3,5-TMB) particles as selective sampling probes for ICl[4]. The selective uptake (i.e. derivatisation) was carried out in a reaction chamber that was placed in front of the ToF-AMS. Fine particles of the sampling probe material, which had been generated by an atomizer, were continuously introduced into the reaction chamber. Reactive iodine species were introduced into the chamber by a temperature controlled and nitrogen flushed test gas source that was based on an open tube diffusion technique. After exiting the reaction chamber the resultant aerosol was analysed by ToF-AMS in the positive ion mode.

α-CD has the capability to form an inclusion complex with I_2. Inclusion complex formation can be improved by addition of I^- and Br^-. The α-CD-I_2-complex showed a typical signal at m/z 253.8 in the mass spectrum, that can be used for the identification and quantification of I_2. ICl reacts with 1,3,5-TMB to form 1-iodo-2,4,6-TMB. The presence of ICl can be identified by the molecular ion of 1-iodo-2,4,6-TMB at m/z 294 in the mass spectrum.

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