

Chemical modification of particles containing peroxides due to mixing with particles containing ammonium iodide detected by aerosol mass spectrometry

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Atmospheric aerosols have an important impact on climate and human health. They interact directly or indirectly as cloud condensation nuclei with radiation and can deeply enter the breathing system. To understand the toxicity, the mechanism of forming, aging and interacting with the ambient gas phase species and radiation, the chemical composition has to be determined (Pöschl, 2005).

Organic peroxides are formed by ozonolysis or by OH-radical reaction of volatile organic compounds. Autoxidation leads to highly oxidized multifunctional molecules with several (hydro-) peroxygroups. It is suggested that they have an important role at the nucleation of new particles (Mentel *et al.*, 2015). Peroxides in the particle phase can be analyzed offline by iodometric-spectrometry (Docherty *et al.*, 2005).

In this project an online technique to detect peroxides in aerosol particles was developed using a combination of iodometry and aerosol mass spectrometry. For this, particles containing hydrogen peroxide H_2O_2 and ammonium sulfate $(\text{NH}_4)_2\text{SO}_4$ were mixed with particles containing ammonium iodide NH_4I and α -cyclodextrin (α -CD) in a flow tube reactor (figure.1). Due to coagulation of these particles internally mixed particles are formed. NH_4I reacts with H_2O_2 forming iodine which is complexed by α -CD and detected by the High-resolution time-of-flight aerosol mass spectrometer of Aerodyne Research Inc. which delivers mass spectra of bulk aerosol particles with a time resolution of several seconds and particle size distribution in a range of 35 nm to 1.5 μm (De Carlo *et al.*, 2006). The particles were generated by pneumatic atomization of solutions containing 0.1 g/L $(\text{NH}_4)_2\text{SO}_4$ and different concentrations of H_2O_2 and another solution containing 0.2 g/L NH_4I , 0.07 g/L α -CD and some drops of acetic acid.

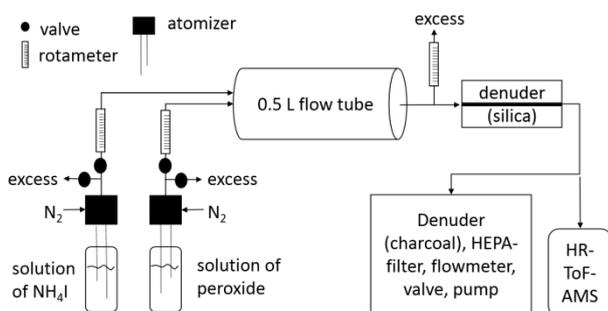


Figure 1. Schematic set up.

It was observed that pure NH_4I produces the ions I^+ , HI^+ and I_2^+ in the ion source (electron impact) of the mass spectrometer, making it difficult to follow the reaction only by the time series of I_2^+ . Since the EI-ionization of a pure compound provides reproducible mass spectra with a constant ratio between the forming fragment ions, it can be assumed that a certain mixture of two compounds as NH_4I and I_2 produce a reproducible superposition of the mass spectra as well. So a change in the ratio of the concentrations of NH_4I and I_2 in the particle leads to a change in the ratio of the concentration of the detected ions I^+ (m/z 127), HI^+ (m/z 128) and I_2^+ (m/z 254) (figure 2).

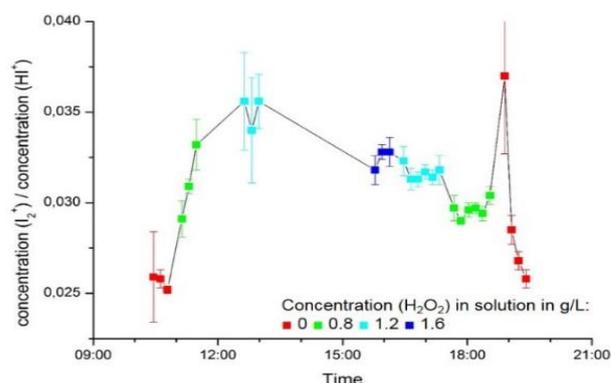


Figure 2. Time Series of I_2^+/HI^+ -ratio. The colors indicate the concentration of H_2O_2 in solution. Red: 0, green: 0.8 g/L, cyan: 1.2 g/L and blue: 1.6 g/L.

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