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# Sulphuric Acid Measurements by CIMS – Uncertainties and Consistency between Various Data Sets

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Sulfuric acid is one of the key components in new particle formation in the atmosphere. Nucleation rate and the number concentration of freshly nucleated particles are both observed to strongly depend on sulfuric acid concentration. Though some advances have been achieved, measurement of gas phase sulfuric acid is still challenging due to extremely low concentrations of typically below some $10^7$ molecules $cm^{-3}$, the stickiness to surfaces, the tendency to form molecule- and molecule-ion-clusters and difficulties in calibration. Measurements are performed exclusively by chemical ionization mass spectrometry (CIMS) with the substantial drawback that no independent method to validate the CIMS-$H_2SO_4$ measurements is available. Direct calibration is hardly possible since gaseous concentrations of $H_2SO_4$ in the range of ambient concentrations, e.g. $<10^7$ molecules $cm^{-3}$, cannot be reliably provided and controlled. Thus, CIMS needs indirect calibration. In the method developed by Eisele and co-workers at NCAR, Boulder, CO, photolysis of ambient water vapor is used to yield OH radicals, which are then titrated by excess $SO_2$ to yield $H_2SO_4$ at the intake of the CIMS sampling tube. With carefully selected instrumental set-up and for “clean” atmospheric conditions it is justified to assume a quantitative conversion of OH to $H_2SO_4$ and the same calibration factor can be used for OH radical and $H_2SO_4$ measurements. Uncertainties arise from several factors with major contributions from the photochemical generation of OH, gas phase chemical impacts until to the conversion to $H_2SO_4$, and the formation of sulfuric acid clusters with other gas phase molecules which potentially affect the chemical ionization by nitrate ions, and the subsequent detection in the mass spectrometer. The uncertainties typically sum up to 30-60% (95% confidence) and will be discussed in more detail. Using chemical balance equations, the consistency of $H_2SO_4$ measurements for various data sets with respect to different instruments, different regions and chemical regimes will be presented. This presentation will focus on results obtained by Hohenpeissenberg Meteorological Observatory and University of Helsinki and further refer to data from previous studies going back to 1998.