Measuring and modelling of aerosol chemical composition for the SANA intensive field campaigns
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Abstract
During the intensive field campaign SANA 2 in August/September 1991, measurements of aerosol particles and related gases have been performed. The accumulation mode particles showed a diurnal cycle of their chemical composition due to the diurnal cycles of the temperature and relative humidity. Nitrate appeared in the accumulation mode particles in dependence on the temperature. During morning sampling periods with easterly winds, potassium has been detected in accumulation mode particles which was supposed to be externally mixed with sulfate. Model calculations showed different pH-values and different mass fractions of volatile compounds in the potassium and the sulfate particles.

1 Introduction
The interaction of aerosol particles with related trace gases has already been mentioned by Wigand [1] in 1913. Aerosol particles which contain hygroscopic compounds take up water with increasing relative humidity. In addition to water, also trace gases like ammonia and nitric acid can condense on aerosol particles in dependence on their concentrations and on the temperature and relative humidity. These gases can react chemically with the particulate material. Experiments e.g. by Harrison & Pio [2] and Willison et al. [3] have shown a loss of chloride due to reactions of sea salt particles with H₂SO₄ and HNO₃ or their precursor gases. The equilibrium of gas phase nitric acid and ammonia with particles consisting of sulfate, nitrate and ammonia has been described e.g. by Saxena et al. [4]. However, experiments (e.g. Sheridan et al. [5]) have shown the presence of a so called "external mixture", i.e. particles of the same size have different chemical compositions.

A model has been developed, which permits the computation of equilibria be-
between the gas phase and particles of different sizes and chemical compositions. During the SANA 2 experiment, the gas phase species \( \text{NH}_3 \) and \( \text{HNO}_3 \) as well as the temperature and relative humidity have been measured in addition to the aerosol particles (Seidl et al. [6]). So the measurements offered a good data base for the initialization of model calculations, which demonstrate the interaction of externally mixed particles with the gas phase.

2 Results of field measurements

The aerosol particles have been sampled by a 5 stage impactor. The aerodynamic cut-off radii of the stages 1 to 5 were 0.02 \( \mu \text{m} \), 0.07 \( \mu \text{m} \), 0.245 \( \mu \text{m} \), 0.86 \( \mu \text{m} \) and 3.0 \( \mu \text{m} \). The gases \( \text{NH}_3 \) and \( \text{HNO}_3 \) have been sampled on filter packs. In general 3 impactor samples and 7 to 8 filter samples have been taken per day. The black carbon concentration has been measured by an aethalometer. The detailed sampling and analytical procedures are described by Brunnemann et al. [7]. In the following, mainly the results concerning sulfate, nitrate and potassium will be presented. The discussion will be limited to the accumulation mode particles, which can be assumed to be in equilibrium with the gas phase considering the timescale of the four hours impactor sampling period. Wexler & Seinfeld [8] have shown, that particles smaller than 1 \( \mu \text{m} \) radius can get into equilibrium within this time. In general, 1 \( \mu \text{m} \) radius can be regarded as an upper limit for the accumulation mode. The actual radius of the accumulation mode particles depends on the relative humidity, which will be shown in section 2.2 for sulfate and potassium particles.

2.1 Gas - particle phase distribution of nitrate

In the accumulation mode particles, sulfate, nitrate and ammonium were the major ions with regard to the equivalent concentrations. Consequently, nitrate could only be present as ammonium nitrate. This is a rather unstable compound which dissociates with increasing temperature (Stelson & Seinfeld [9]). This dissociation was observed during the field measurements (Seidl et al. [6]). During the morning sampling period, nitrate was mainly observed in the accumulation mode particles. During the noon and evening sampling periods, the accumulation mode particles contained only little nitrate, and in the gas phase the \( \text{HNO}_3 \) concentration was higher than in the morning (Fig. 1). This gas - particle phase distribution was found to be a function of the temperature. Below approximately 15\(^\circ\text{C}\), most nitrate was in the particulate phase, and above approximately 20\(^\circ\text{C}\), most nitrate was in the gas phase. Then, the particles in the accumulation mode consisted mainly of ammonium and sulfate (and small mass concentrations of other ions, which have been close to the detection limit). This gas - particle phase distribution of nitrate is not a specific quantity like the dissociation constant of ammonium nitrate but depends also on the total mass concentration of nitrate and on the relative humidity. It also requires a total mass concentration of ammonium which is sufficient to form ammonium nitrate. So the observed rela-
Figure 1: Concentrations of ions for the three impactor sampling periods on Sep. 3, 1991 in Melpitz. The concentrations of the respective ions are drawn from the base line, no stacked bars are used in this figure.
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Figure 2: Concentration of black carbon (BC) as function of the potassium (K) concentration. The black carbon concentration has been determined by an aethalometer.

The size distribution of potassium was different to the size distribution of sulfate but similar to that of nitrate (Fig. 1). Therefore, one can assume the sulfate and potassium particles to be externally mixed. As initial guess for the model simulations, potassium is taken as potassium nitrate due to the similar size distri-
Figure 3: Aerodynamic mass mean radii of sulfate and potassium as function of the relative humidity.

...bution of nitrate (see below).

The assumption of an external mixture is also supported, when one looks at the mass mean radii of sulfate and potassium as function of the relative humidity (Fig 3). The mass mean radius of sulfate shows an increase with the relative humidity, beginning at humidities above 60%. The mass mean radius of potassium shows nearly no increase with the relative humidity except for cases above 90%.

3 Model Simulations

An aerosol model has been developed, which describes individual particle classes within a closed box. Particles in a class have fixed masses of non-volatile compounds (e.g. sulfate or metal ions) and a fixed number concentration. The particles take up volatile compounds, e.g. nitrate, in thermodynamic equilibrium with the gas phase. So every particle class can have a different chemical composition. For humid particles with a liquid phase, the activity coefficients of the ions are calculated by the Pitzer theory (Clegg & Brimblecombe [11]). The deliquescence relative humidity is calculated as a function of the temperature for 25 electrolytes. For the other electrolytes, fixed deliquescence relative humidities are taken. No supersaturated salt solutions are modeled. To consider the curvature of the droplet surfaces, the Kelvin correction is applied on the partial pressures of the trace gases for humid particles. The surface tension is calculated in dependence on the concentration of the electrolyte solution.
Figure 4: Results of model calculations for three cases similar to conditions on Sep. 3, 1991. Case 1 represents noon conditions, Case 2 morning conditions. In Case 3, the relative humidity is set to 97%. \( r_o \) = dry radius, \( r \) = radius, \( w \) = mass of liquid water of the particles.
This model has been applied to analyze the SANA measurement data. Model calculations have been done with initial values derived from measurements on Sep. 3, 1991. Three size classes of ammonium sulfate (S) and potassium nitrate (K) particles, respectively, are used to initialize the model. Three cases with different temperatures and relative humidities are considered: Case 1 represents the noon measurement period and Case 2 the morning measurement period. For Case 3, the same temperature as for Case 2 is taken, but the relative humidity was set to 97% (Fig. 4). The total (gas and particle phase) mass concentrations of NH₃, HNO₃ and HCl are the same for all cases.

For the noon conditions (Case 1), all particles are in a dry state. For the morning conditions (Case 2), the S particles are above their deliquescence point. Then these particles are electrolyte solution droplets. The gases NH₃, HNO₃ and HCl dissolve in these droplets. The K particles are still in the dry state. At a temperature of 10°C, potassium nitrate particles dissolve at approximately 96% relative humidity (depending on their size due to the Kelvin correction). Therefore, the relative humidity was set to 97% in Case 3. Otherwise, the same initial conditions as in Case 2 were taken. At 97% relative humidity, also the K particles are dissolved. The model results show higher pH-values for the K than for the S particles. Consequently, higher mass fractions of nitrate and chloride are found in the K particles. Ammonium, which dissolves preferentially in particles with low pH-values, has higher mass fractions in the S particles. Also as solution droplets in equilibrium with the gas phase, the sulfate particles consist mainly of ammonium sulfate and the potassium particles mainly of potassium nitrate. Other ions have only minor mass fractions. The higher pH-values of the potassium particles may have an effect on chemical reactions in the liquid phase.

4 Conclusions

The measurements demonstrated the gas - particle phase interactions for the accumulation mode particles. The SANA measurements were especially suitable for this purpose, because an almost complete set of information on trace gases and meteorological conditions was obtained in addition to the aerosol measurements. The model calculations supported the supposition of an external mixture of ammonium sulfate and potassium nitrate particles. Different deliquescence humidities and pH-values of these two particles types have an effect on the chemical reactions in the particles which possibly affect also the gas phase atmospheric chemistry.

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References


