HYGROSCOPIC PROPERTIES OF AEROSOLS. INVESTIGATIONS OF PARTICLES FROM JET ENGINES AND THE REMOTE TROPOSPHERE

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Summary

Hygroscopic properties (i.e. the ability to take up water) of aerosol particles play a crucial role for potential impacts of atmospheric aerosols on e.g. atmospheric visibility, radiative forcing, cloud formation and with that also on the earth climate. After emission, aerosol particles experience continuous modification by atmospheric aging processes, usually leading to an increase of particle hygroscopicity and to a reduction of differences between individual particles. This study focussed on the characterisation of hygroscopic properties of different aerosol types, including a fresh jet engine combustion aerosol, a continental-rural aerosol at the background station K-puszta, Hungary, and an aged free tropospheric (FT) aerosol at the Swiss high-alpine research station Jungfraujoch (JFJ, 3580 m asl).

Hygroscopic growth factors (diameter at a specific RH divided by the dry diameter) of ambient aerosol particles as a function of relative humidity (RH) are commonly measured with a hygroscopicity tandem differential mobility analyser (H-TDMA). A new low-temperature H-TDMA was developed enabling measurements in the temperature range \(-20 \degree C \leq T \leq 30 \degree C\) for the first time, since the annual mean temperature at the JFJ station is below 0 \degree C. It is crucial to determine properties of atmospheric aerosols at ambient temperatures in order to prevent artefacts due to evaporation or condensation of volatile compounds.

The instrument was extensively tested in laboratory experiments at \(T = 20 \degree C\) and \(-10 \degree C\) with \((\text{NH}_4)_2\text{SO}_4\), NaCl, and NaNO\(_3\), which are typical inorganic aerosol constituents. The instrument proved, as shown with theoretically calculated growth curves, to measure hygroscopic growth factors with high accuracy and high time resolution. Field measurements were conducted in winter, when mainly FT air masses are encountered at the JFJ station. Properties of particles with dry diameters \(D_0 = 50, 100,\) and \(250 \text{ nm}\) were measured at around ambient temperature \((-10 \degree C\). Observed hygroscopic growth factors were almost as high as for pure \((\text{NH}_4)_2\text{SO}_4\) and nearly independent of their initial dry size, indicating that the FT aerosol consisted mainly of water-soluble and distinctly hygroscopic substances. An important parameter regarding the direct radiative forcing caused by aerosols is the mixing state of light absorbing and light scattering material. The JFJ aerosol was characterised by nearly monomodal growth distributions, which means that the particles were to a large extent internally mixed in the investigated size range. Furthermore, continuous water uptake over the whole RH range was observed instead of a gradual deliquescence, indicating that the particles remained at least partially liquid even at low RH (10\%). A possible reason for the absence of ef\(f\)l orescence is the complex mixture of inorganic salts and probably many organic species, but this effect should be addressed in further studies.

The influence of fuel sulphur content (FSC) and operating conditions on hygroscopic properties and cloud condensation nuclei (CCN) activity of combustion particles emitted by a jet engine combustor was investigated with a H-TDMA and a CCN counter, respectively. The combustor was operated with low, medium, and high FSC, and older and more modern operating conditions at high altitude cruise were simulated. These measurements revealed that the FSC has a strong influence on particle hygroscopicity and CCN activity, while the effect of investigated operating conditions was unclear. The combustion particles were not hygroscopic at low FSC but sufficiently hydrophilic to be activated as CCN if the supersaturation exceeded the critical value for Kelvin activation. The particles were distinctly more hygroscopic at medium and high FSC level, which is attributed to an increasing amount of sulphuric acid adsorbed on the soot particles. Increasing activation ratios and decreasing activation diameters with increasing FSC, detected at a fixed supersaturation, showed that this hygroscopic growth enables the particles to overcome the Kelvin barrier at lower supersaturation. Potential impacts of particulate aircraft emission on
Cirrus cloudiness are hence expected to increase with increasing FSC. The link between hygroscopic growth and CCN activity was confirmed by a semiempirical model approach, which was successfully used to predict FSC dependent CCN concentrations from measured growth factors.

The continental-rural aerosol from K-puszta was investigated to assess the contribution of water-soluble organic matter (WSOM) to hygroscopic water uptake. Water-soluble matter (WSM), on average composed of 47 wt % inorganic salts and 53 wt % WSOM, was extracted from fine aerosol (PM$_{1.5}$) samples. Solid phase extraction was, in a second step, used to isolate a major fraction (~70 wt %) of WSOM (so-called isolated organic matter ISOM, less hydrophilic) from inorganic salts and remaining most hydrophilic organic matter. This approach allowed a hygroscopicity closure for atmospheric WSM and the investigation of a major fraction of atmospheric WSOM in pure form to be conducted for the first time. WSM and ISOM were extensively chemically characterised and hygroscopic properties were determined by means of the H-TDMA technique. The hygroscopicity of ISOM was comparable to secondary organic aerosol obtained in smog chamber experiments, but lower than that of highly soluble organic acids and inorganic salts, and higher than that of aquatic reference humic and fulvic acids, which were investigated for comparison. Deliquescence of initially dry ISOM was observed at moderate RH values between 30 and 60%. A hygroscopicity closure for K-puszta WSM was performed using inorganic composition data, measured hygroscopicity of pure ISOM, and a presumed hygroscopicity for the small non-isolated WSOM fraction. Good agreement was obtained with an average difference of ~8% between modelled and measured WSM water uptake at 90% RH. The contribution of WSOM to particulate water at 90% RH was, according to experiments and model prediction, on average 29%. This is less than the contribution of WSOM to WSM mass, but still a considerable amount. The relative importance of the isolated and non-isolated WSOM fractions is probably comparable, and therefore one should aim for a supplementary method enabling the isolation of the remaining most hydrophilic WSOM fraction towards an improved understanding of the whole WSOM.
Zusammenfassung

Hygroskopische Eigenschaften (d.h. die Fähigkeit zur Wasseraufnahme) von Aerosolpartikeln spielen eine wichtige Rolle in Bezug auf mögliche Auswirkungen atmosphärischer Aerosole auf atmosphärische Sichtweiten, Strahlungsantrieb, Wolkenbildung und damit auch auf das Klima der Erde. Aerosolpartikel erfahren nach ihrer Emission ständige Veränderungen durch Alterungsprozesse, die in der Regel zu verstärkter Hygroskopizität und zu einer Verringerung der Unterschiede zwischen den einzelnen Partikeln führen. Das Ziel dieser Studie war die Charakterisierung der hygroskopischen Eigenschaften verschiedener Aerosoltypen, vom frischen Verbrennungsaerosol eines Düsentriebwerkes über ein kontinental-ländliches Hintergrund aerosol von K-puszta (Ungarn) bis zu einem gealterten Aerosol bei der hochalpinen Forschungsstation Jungfraujoch (JFJ, 3580 m.ü.M.).

Hygroskopische Wachstumsfaktoren (HWF, Durchmesser bei einer bestimmten Luftfeuchtigkeit dividiert durch den Trockendurchmesser) von Umgebungsaerosolen als Funktion der relativen Luftfeuchtigkeit (RL) werden üblicherweise mit einem "hygroscopicity tandem differential mobility analyser" (H-TDMA) gemessen. Weil die Jahresdurchschnittstemperatur auf dem JFJ unter 0 °C liegt, wurde ein neuer H-TDMA für tiefe Temperaturen entwickelt, der erstmals im Temperaturbereich $-20^\circ C \leq T \leq 30^\circ C$ messen kann. Es ist wichtig, die Eigenschaften von Aerosolen bei Umgebungsbedingungen zu bestimmen, um Artefakte durch Verdampfung oder Kondensation von flüchtigen Verbindungen zu verhindern.

Das Instrument wurde mit den typischen anorganischen Aerosolkomponenten (NH₄)₂SO₄, NaCl, and NaNO₃ bei den Temperaturen $T = 20^\circ C$ und $-10^\circ C$ ausführlich getestet. Der Vergleich mit theoretisch berechneten Wachstumskurven zeigte, dass das neue Instrument HWF mit einer hohen Genauigkeit und Zeitauflösung messen kann. Feldmessungen auf dem JFJ wurden im Winter durchgeführt, wenn die Station meistens in der freien Troposphäre (FT) liegt. Dabei wurden die HWF von Partikeln mit den Trockendurchmessern $D_0 = 50, 100$ und 250 nm etwa bei Umgebungstemperatur ($-10^\circ C$) bestimmt. Die gemessenen Werte waren praktisch unabhängig vom ursprünglichen Trockendurchmesser und beinahe so gross wie für reines (NH₄)₂SO₄, was darauf hinweist, dass das Aerosol der FT vorwiegend aus wasserlöslichen und stark hygroskopischen Verbindungen besteht. Der Mischungszustand von Licht absorbierendem und streuendem Material ist ein wichtiger Parameter für den direkten Strahlungsantrieb durch Aerosole. Das JFJ Aerosol war durch nahezu monomodale Wachstumsverteilungen charakterisiert, was bedeutet, dass die Partikel im untersuchten Größebereich weitgehend intern gemischt waren. Ausserdem wurde, an Stelle einer stufenweisen Deliqueszenz, eine kontinuierliche Wasseraufnahme über den ganzen Feuchtigkeitsbereich beobachtet, was darauf hinweist, dass die Partikel auch bei tiefer RL (10%) mindestens teilweise flüssig bleiben. Ein möglicher Grund für das Ausbleiben der Effloreszenz ist die komplexe Zusammensetzung aus anorganischen Salzen und höchstwahrscheinlich vielen organischen Verbindungen. Dieser Effekt sollte in weiteren Studien genauer untersucht werden.

Der Einfluss vom Schwefelgehalt des verwendeten Treibstoffs (STS) und vom Betriebszustand der Düsentriebwerksbrennkammer auf die hygroskopischen Eigenschaften der Verbrennungspartikel und deren Eignung als Wolkenkondensationskeime (CCN) wurde mit einem H-TDMA und einem CCN-Zähler untersucht. Die Brennkammer wurde mit Treibstoff unterschiedlichen Schwefelgehaltes betrieben und es wurden frühere sowie moderne Flugbedingungen simuliert. Diese Messungen zeigten, dass der STS einen starken Einfluss auf die Partikel eigenschaften hat, während die Auswirkungen unterschiedlicher Betriebsbedingungen unklar sind. Bei tiefem STS waren die Verbrennungspartikel nicht hygroskopisch, aber doch ausreichend hydrophil, um als CCN aktiviert zu werden, wenn...
die Übersättigung den kritischen Wert für Kelvinaktivierung überstieg. Ein erhöhter STS wirkte sich mit einer deutlichen Zunahme der HWF aus, was mit einer zunehmend dicken Schicht von adsorbierter Schwefelsäure erklärt wird. Das hygroskopische Wachstum ermöglicht den Partikeln, die Kelvin-Barriere bei tieferen Übersättigungen zu überwinden, was sich in einer Abnahme der gemessenen kritischen Aktivierungsdurchmesser bei einer konstanten Übersättigung äusserte. Allfällige Auswirkungen auf die Zirrusbewölkung sind daher verstärkt bei hohem STS zu erwarten. Der Zusammenhang zwischen hygroskopischem Wachstum und CCN-Aktivierung wurde durch semiempirische Modellrechnungen bestätigt, die eine gute Vorhersage der CCN-Konzentrationen auf Grund der beobachteten Hygroskopizität erlaubten.

Das kontinental-ländliche Aerosol von K-puszta wurde mit dem Ziel untersucht, den Einfluss der wasserlöslichen organischen Substanzen (WSOM) auf die HWF zu bestimmen. Dazu wurden aus Proben der feinen Aerosolfraction (PM$_{1.5}$) die wasserlöslichen Substanzen (WSM), im Mittel aus 47% anorganischen Salzen und 53% WSOM zusammengesetzt, extrahiert. Anschliessend wurde ein Grossteil (~70%) der WSOM, die sogenannten isolierten organischen Substanzen (ISOM, weniger hydrophil), von den anorganischen Salzen und den verbleibenden stark hydrophilen organischen Substanzen getrennt. Dieser neuartige experimentelle Ansatz ermöglichte eine Hygroskopizitäts schliessung für die WSM und die erstmalige Untersuchung der HWF eines Hauptteils der WSOM in reiner Form. WSM und ISOM wurden chemisch charakterisiert und ein H-TDMA wurde zur Messung der HWF verwendet. Die HWF von ISOM waren vergleichbar mit denen von sekundären organischen Aerosolen in Smogkammer- Experimenten, aber geringer als diejenigen von stark hygroskopischen organischen Säuren und anorganischen Salzen. Deliqueszenz wurde zwischen 30 und 60% RL beobachtet. Die anorganische Zusammensetzung, die gemessenen HWF von ISOM und ein mutmasslicher Wert für die HWF der nicht isolierten WSOM Fraktion wurden für die Hygroskopizitäts schliessung verwendet. Die Übereinstimmung zwischen gemessenen und vorhergesagten HWF für die WSM war gut, wobei die letzteren Werte etwas tiefer lagen. Auf Grund der Messungen und der Modellrechnungen wurde geschätzt, dass die WSM im Mittel für etwa 29% der Wasseraufnahme bei 90% RL verantwortlich sind, was ein beträchtlicher aber geringerer Beitrag ist als derjenige zur Masse der WSM. Weil die Beiträge der ISOM und der restlichen nicht isolierten WSOM Fraktion wahrscheinlich vergleichbar sind, sollte zwecks vollständiger Charakterisierung eine Methode entwickelt werden, welche die Isolierung der noch verbleibenden WSOM Fraktion in reiner Form ermöglicht.
1. Introduction

1.1 Atmospheric Aerosol

“Response of a deciduous forest to the Mount Pinatubo eruption: enhanced photosynthesis”. What is the link between a volcanic eruption and enhanced photosynthesis rates of plants as suggested in this recent publication by Gu et al. (2003)? – It is light scattering by aerosol particles.

The injection of large amounts of SO$_2$ into the stratosphere by the tremendous eruption of Mount Pinatubo in 1991 resulted in enhanced sulphate aerosol concentrations (Baran and Foot, 1994; Herber et al., 1996) in the aftermath of this volcanic event. Scattering of incident solar radiation by this aerosol layer reduced the global solar radiation (sum of direct and diffuse radiation), but it increased the diffuse solar radiation at the earth surface. Since the radiation use efficiency of plant canopies is higher for diffuse than for direct beam radiation (Gu et al., 2002), the altered radiation had a positive effect on photosynthesis rates. Gu et al. (2003) estimated the photosynthetic response of a hardwood forest (Harvard Forest, Massachusetts) to be of the order of +23% in 1992 and +8% 1993 on cloudless conditions. On a global scale this additional carbon sink is suggested to be at least partially responsible (Farquhar and Roderick, 2003) for the observed decline of growth rate of atmospheric CO$_2$ concentration (see Fig. 1.1), that followed the Mount Pinatubo eruption (Conway et al., 1994; Jones and Cox, 2001). The example discussed above illustrates how complex interactions between aerosols and atmospheric processes typically are.

![Figure 1.1](image)

**Figure 1.1:** Interannual changes in atmospheric CO$_2$ concentrations with the influence of anthropogenic emissions and ENSO cycle (El Niño Southern Oscillation) removed, leaving the component due to climate forcing of volcanic eruptions. Adapted from Jones and Cox (2001).

An aerosol is defined as a suspension of fine solid or liquid particles in a gas, covering the size range from a few nanometres to tens of micrometres. Atmospheric aerosols may be directly emitted as particles (primary aerosol) or formed in the atmosphere by gas-to-particle conversion processes (secondary aerosol). They are typically composed of inorganic salts, crustal elements, and carbonaceous material comprising elemental carbon (EC) and organic carbon (OC) (Heintzenberg, 1989). Aerosol sources include both natural
and anthropogenic emissions. Natural contributions arise from e.g. sea spray, dust storms, biogenic emissions and volcanic eruptions, while anthropogenic contributions arise from e.g. combustion processes, SO$_2$ emissions (→ secondary sulphate aerosol), and biomass burning.

An anthropogenic increase of atmospheric aerosol burdens has many effects on the environment. The most readily perceived impact is visibility degradation (Charlson 1969; Sloane and White, 1986; Hand et al., 2002; Watson, 2002). Everyone is familiar with large atmospheric visibility ranges on very dry days (e.g. “Föhn” days in the Swiss alps), where light scattering by aerosol particles is small due to the absence of particulate water. Adverse health effects were reported in numerous epidemiological and laboratory studies (e.g. Dockery et al., 1993; Donaldson et al., 1998). Health effects are typically less apparent, except for the severe smoke incident in London in 1952, which immediately caused thousands of deaths (Brimblecombe, 1987). Aerosols also affect the earth climate via their so-called direct and indirect radiative effects (Charlson, 1992; Schwartz, 1996). In an equilibrium state the average net radiative flux at the top of the atmosphere is zero. A change in either the solar radiation or infrared radiation changes the net radiative flux. The corresponding imbalance is called “radiative forcing”. Direct radiative forcing by aerosols arises from scattering and absorption of solar and infrared radiation (Li and Kou, 1998; Haywood et al., 2001; Loeb and Kato, 2002). Indirect radiative forcing by aerosols is broadly defined as the overall process by which aerosols perturb the earth-atmosphere radiation balance by modulation of cloud albedo and cloud amount. Aerosol particles acting as cloud condensation nuclei (CCN) or ice nuclei (IN) may alter cloud droplet or ice crystal number concentration and mean sizes (Twomey, 1974), thereby causing changes of cloud optical properties (Kuang and Yung, 2000; Nakajima et al., 2001) and cloud formation and precipitation efficiency (Rosenfeld 1999; Rosenfeld 2000).

Hygroscopic water uptake of atmospheric particles is of particular importance for all abovementioned effects, mainly because of increased particle sizes under high relative humidity (RH) conditions. Light scattering cross section and airway deposition efficiency strongly depend on particle size. CCN activity and hence potential aerosol cloud interactions are larger for hygroscopic particles, because hygroscopic growth enables them to overcome the Kelvin barrier at lower supersaturation (see below). Lifetimes of atmospheric particles are also linked with CCN activity since wet deposition is the major pathway of aerosol removal apart from dry deposition. Besides atmospheric relevance, hygroscopic growth is a crucial point in many aerosol measurement applications, simply because water condensation or evaporation alters many aerosol physical properties (e.g. size, mass, and optical properties) as soon as the instruments are not operated at ambient RH.

1.2 Theory of Hygroscopic Growth

The hygroscopic growth factor $g$ of an aerosol particle is here defined as

$$ g(RH) = \frac{D(RH)}{D_0} $$

(1.1)

where $D_0$ and $D(RH)$ are equilibrium particle diameters at dry conditions and at the prevailing RH, respectively. Other common definitions with respect to applied experimental techniques (see section 1.3.1) are mass growth factors or optical scattering growth factors.

The Köhler theory describes the hygroscopic growth of soluble particles in humid air (Köhler, 1921; Köhler, 1936). A brief overview of classical Köhler theory and models for nonideal and mixed solution behaviour is given here. Further details about the thermodynamics of atmospheric aerosols may be found in Pruppacher and Klett (1997) or...
Seinfeld and Pandis (1998). The following equations are cited from these books unless mentioned otherwise.

### 1.2.1 Raoult’s Law (Ideal Solutions)

The equilibrium water vapour pressure $e_w$ over pure water (flat surface) is only a function of temperature. RH is defined as the ratio between the actual partial pressure $e$ of water in the air and the saturation vapour pressure $e_{w}$ at this specific temperature:

$$ RH = \frac{e}{e_w} \quad (1.2) $$

The equilibrium vapour pressure over an aqueous solution $e_{sol}$ is always smaller than $e_w$. The vapour pressure depression over an ideal aqueous solution is a linear function of the solute concentration (Raoult’s law):

$$ \frac{e_{sol}}{e_w} = x_w \quad (1.3) $$

whereas the mole fraction $x_w$ of water is defined as

$$ x_w = \frac{n_w}{n_w + \sum n_i} \quad (1.4) $$

and $n_w$ and $n_i$ are the number of moles of water molecules and solute molecules/ions, respectively. The summation in the denominator of eq 1.4 goes over all solute species/ions. For ideal solutions in equilibrium with the gas phase it follows directly from eq 1.3 and the definition of RH (eq 1.2) that

$$ RH = x_w \quad (1.5) $$

In the absence of clouds, water vapour is generally available in excess compared to liquid phase water, i.e. atmospheric conditions determine the RH and the solution concentration of liquid aerosol particles equilibrates by condensation or evaporation of water. Concentration and growth factor of a solution droplet are causally connected (see eq 6.4). Equation 1.5 shows hence that basically the solute effect (eq 1.3) is responsible for the hygroscopic growth of soluble aerosol particles, and that the equilibrium particle growth factor depends on the RH, but not on the absolute water vapour partial pressure.

### 1.2.2 Nonideal and Mixed Solutions

An aqueous solution, in general, approaches ideality as it becomes more and more dilute ($x_w$ close to unity). This condition is, according to eq 1.5, only fulfilled at high RH. Concentrated aerosol droplets at low RH deviate significantly from ideality. This deviation from ideality is usually described by introducing activity coefficients. The modified Raoult’s law for nonideal solutions is then

$$ \frac{e_{sol}}{e_w} = \gamma_w x_w \quad (1.6) $$
1. Introduction

where $\gamma_w$ is the activity coefficient of water. The water activity $a_w$ is defined as the product of $\gamma_w$ and $x_w$, and it is equivalent to the effective equilibrium RH over a solution. Concentration and temperature dependent water activities of mixed electrolyte solutions are often described with semiempirical approaches like the Pitzer-Simonson-Clegg model in which ion interactions are used to describe the solution nonideality (Pitzer, 1991; Clegg et al., 1992). Model parameters for inorganic systems of atmospheric importance are given by e.g. the aerosol-inorganic-models AIM2 I–III (Carslaw et al., 1995; Massucci et al., 1999; Clegg et al., 1998a; Clegg et al., 1998b), which are also available on the Web (http://mae.ucdavis.edu/wexler/aim.html).

The organic aerosol fraction consists, unlike the inorganic constituents, of hundreds of different species, which have diverse chemical structures and possess quite different properties. Water activities of mixed organic solutions are hence often described by group contribution methods (GCM) like the UNIFAC (UNIQUAC Functional Group Activity Coefficients Model, where UNIQUAC stands for Universal Quasi-Chemical) approach. GCMs use functional groups instead of molecules as the interacting entities, and are hence often applied in order to reduce to about 20 groups the number of parameters needed to describe hundreds of organic species (Fredenslund et al., 1977). UNIFAC has been shown to be effective in predicting the properties of mixtures in various applications (Gmehling, 1995), and it has been tested and adapted for organics of atmospheric importance (Saxena and Hildemann, 1997; Peng et al., 2001; Choi and Chan, 2002b).

First models for the phase equilibrium of mixed inorganic/organic systems of atmospheric importance have recently been developed by (Clegg et al., 2001; Ming and Russell, 2002; Russell and Ming, 2002). These models apply Pitzer’s approach to electrolytes and the UNIFAC approach to organics, whereas possible interactions between inorganic ions and organics are considered by additional terms in the UNIFAC approach. However, only limited experimental data of such mixtures is so far available in order to determine and validate model parameters.

Hygroscopic growth factor of mixed particles ($g_{\text{mixed}}$) can also be estimated from volume fractions $\varepsilon_i$ of individual compounds in the mixed particle and their respective growth factors $g_i$ in pure form:

$$g_{\text{mixed}} = \left( \sum_i \varepsilon_i g_i \right)^{1/3}$$

Equation 1.7 is equivalent to the Zdanovskii-Stokes-Robinson relation (ZSR relation) (Zdanovskii, 1948; Stokes and Robinson, 1966; Chen et al., 1973) including the approximation that there are no interactions between the different solutes, i.e. that the total water uptake of the mixed particle is equal to the total amount of water associated with the corresponding amounts of individual species in pure form. The effect of an insoluble core on the hygroscopic growth of a particle can also be described with eq 1.7 and $g_{\text{insoluble}} \equiv 1$. ZSR predictions are typically less accurate than more sophisticated semiempirical approaches, but this method is an adequate approximation if experimental data of specific mixtures are not available or if computing speed is a limiting factor. However, the accuracy of ZSR predictions can be improved by introducing interaction parameters (Kirgintsev and Luk’yanov, 1966). This concept was recently evaluated by Clegg et al. (2003) for some inorganic, organic, and inorganic/organic mixtures of atmospheric importance.

1.2.3 Kelvin Effect

A key aspect of aqueous aerosols is their curved surface since the equilibrium vapour pressure over a curved surface $e_d$ is always larger than the corresponding vapour pressure
over the same solution with a flat surface $e_{sol}$. The relative vapour pressure increase $S_{Kelvin}$ over a droplet of diameter $D$ is given by the Kelvin equation:

$$S_{Kelvin} = \frac{e_{d}}{e_{sol}} = \exp \left( \frac{4M_u \sigma_{sol}}{RT \rho_u D} \right)$$ \hspace{1cm} (1.8)

where $M_u$ is the molar mass and $\rho_u$ is the density of water, $\sigma_{sol}$ is the surface tension of the solution, $R$ is the ideal gas constant, and $T$ is the temperature. The Kelvin effect is caused by the size dependence of the additional Gibbs free energy associated with the droplet surface.

### 1.2.4 Köhler Equation

The complete Köhler equation for nonideal solution droplets is obtained by combination of the modified Raoult’s law (eq 1.6) and the Kelvin equation (eq 1.8):

$$\text{RH} = \frac{e_{d}}{e_{u}} = \gamma_u x_u S_{Kelvin} = \gamma_u x_u \exp \left( \frac{4M_u \sigma_{sol}}{RT \rho_u D} \right)$$ \hspace{1cm} (1.9)

The equilibrium RH in eq 1.9 is an implicit function of $D$, since all concentration dependent parameters $\gamma_u$, $x_u$, and $\sigma_{sol}$ depend on the growth factor $D/D_0$. For ideal solutions ($\gamma_u \rightarrow 1$), the Köhler equation simplifies to:

$$\text{RH} = x_u \exp \left( \frac{4M_u \sigma_{sol}}{RT \rho_u D} \right)$$ \hspace{1cm} (1.10)

Apart from neglecting nonideal behaviour, eq 1.10 is valid over the whole RH range. In literature, eq 1.10 is usually further simplified to (details in Seinfeld and Pandis, 1998):

$$\ln(\text{RH}) = \frac{4M_u \sigma_u}{RT \rho_u D} - \frac{6M_u \sum n_i}{\pi \rho_u D^3}$$ \hspace{1cm} (1.11)

where $\sigma_u$ is the surface tension of pure water. However, additional approximations included in eq 1.11 are only valid for dilute solutions, hence restricting eq 1.11 to conditions around 100% RH. Nevertheless, it is an illustrative representation of the Köhler equation, and it is also suitable to determine the critical supersaturation $RH_{crit}$ and the critical growth factor $g_{crit}$ for cloud droplet activation.

The equilibrium RH as a function of particle diameter and growth factor (Köhler theory, eq 1.9) as well as the isolated contributions of the Raoult effect (eq 1.6) and the Kelvin effect (eq 1.8) are illustrated in Fig. 1.2 with the example of an ammonium sulphate particle of initial dry diameter $D_0 = 100$ nm. The Raoult term is always <100%, and the Kelvin term is always >100%. Solute concentration and droplet surface curvature decrease with increasing growth factor (diameter), and consequently both, Raoult and Kelvin term, converge to 100%. The Raoult and Kelvin terms are, on a logarithmic RH scale, approximately proportional to the inverse volume (~$D^{-3}$) and the inverse diameter (~$D^{-1}$), respectively (see eq 1.11). The Köhler curve which is the product of the Raoult and Kelvin terms, is hence dominated by the Raoult term at small growth factors (low RH), and by the Kelvin term at large growth factors (high RH). The equilibrium RH is <100% for sufficiently small growth factors, reaches a maximum $RH_{crit}$ >100% at $g = g_{crit}$, and converges to 100% at larger growth factors. The equilibrium is stable (instable) if the
Gradient of the Köhler curve is positive (negative). Solution droplets are hence stable as long as the RH remains <RH_{crit}, but they act as CCN if the RH and the growth factor reach the critical values RH_{crit} and g_{crit}, respectively, i.e. they undergo unlimited growth until their water uptake depletes the water vapour concentration. Both, RH_{crit} and g_{crit}, depend on the chemical composition and initial dry diameter of the particle.

![Köhler theory](image)

**Figure 1.2:** Köhler theory. Critical RH and growth factor for cloud droplet activation are marked by RH_{crit} and g_{crit}, respectively.

### 1.2.5 Deliquescence and Efflorescence

The Köhler theory (eq 1.9) describes the behaviour of liquid solution droplets. Many inorganic salts and some organic species form solid crystals at sufficiently low RH. The RH where a solid particle dissolves (deliquescence RH, DRH), is determined by thermodynamics, whereas the RH where crystallisation of a liquid droplet occurs (efflorescence RH, ERH) depends on nucleation kinetics. This results in a hysteresis, i.e. a RH range where both solid crystals and liquid droplets may exist, depending on the particles RH history. Fig. 1.3 shows the same Köhler curve as Fig. 1.2, but now including the hysteresis effect and with exchanged abscissa and ordinate. A solid particle does practically not change its size under increasing RH conditions until the DRH is reached and the particle dissolves. The DRH is equal to the RH where the equilibrium size according to Köhler theory corresponds to a saturated solution droplet. Reversible growth along the Köhler curve by condensation or evaporation of water vapour is observed in the range DRH < RH < RH_{crit} under increasing or decreasing RH conditions. Once being in the liquid state, the particles may exist as metastable solution droplets in the range DRH > RH > ERH. The ERH is given by the solute supersaturation at which crystallisation starts. Crystallisation may also occur at RH > ERH, triggered by e.g. insoluble impurities acting as nucleation sites. A particle is activated as a cloud droplet if RH_{crit} and g_{crit} are exceeded.
1.2 Theory of Hygroscopic Growth

Figure 1.3: Hysteresis of ammonium sulphate particles. Dissolution and crystallisation occur at deliquescence RH (DRH) and efflorescence RH (ERH), respectively. $RH_{crit}$ and $g_{crit}$ mark critical RH and growth factor for cloud droplet activation, respectively.

1.3 Measurement of Hygroscopic Properties

1.3.1 Growth Factors Under Subsaturated RH Conditions

A large variety of experimental techniques, each with its specific advantages and handicaps, are used to measure the hygroscopic growth of aerosol particles. These techniques base on the detection of the effect of water absorption on particle mass, optical properties, or diameter.

Mass growth factor measurements are either conducted with the electrodynamic balance technique (EDB; Tang et al., 1986; Liang and Chan, 1997), where a single particle is levitated in an electromagnetic field under controlled RH conditions, or by mass determination of humidity controlled filter or impactor samples, where the sample mass is determined by gravimetry (Hänel, 1976; McInnes et al., 1996; Hitzenberger et al., 1997), absorption of beta particles using the beta gauge method (Speer et al., 1997, Speer et al., 2003), elemental analysis using thermal conductivity detection (EA-TCD; Lee and Hsu, 1998), gas chromatography using thermal conductivity detection (GC-TCD; Lee and Chang, 2002), or a tapered element oscillating microbalance (TEOM; Rogers et al., 1998; Allan, 1998). Stanier et al. (2003) recently developed the dry-ambient aerosol size spectrometer (DAASS), which measures aerosol number size distributions of atmospheric aerosols at dry and ambient conditions, in order to assess the amount of aerosol water at atmospheric conditions from the difference of integrated volumes.

Humidity controlled nephelometry (Rood et al., 1985; Rood et al., 1987, Dougle et al., 1998; ten Brink et al., 2000) or dual-nephelometry (McInnes et al., 1998) are used to determine light scattering growth factors, where the ratio of integrated light scattering between humid and dry conditions is determined sequentially with a single nephelometer or in parallel with a pair of instruments, respectively. FTIR-spectroscopy has been used to determine deliquescence and efflorescence properties of aerosol particles as a function of temperature via infrared absorption spectra (Onasch et al., 1999).
Diameter growth factors can be indirectly determined using a RH controlled optical particle counter (OPC, Hand et al., 2000; Ames et al., 2000), where Mie theory, assuming spherical particles, is used to derive particle sizes from scattering intensities. Direct measurement of diameter growth factors is conducted by the hygroscopicity tandem differential mobility analyser (H-TDMA) technique (Liu et al., 1978; Rader and McMurry, 1986). A H-TDMA is the main instrument used for the studies conducted in this work (chapters 2–4 and 6). A schematic illustration of the H-TDMA measurement principle is given in Fig. 1.4, more technical details can be found in chapter 2 and Fig. 2.1.

An H-TDMA, designed to measure hygroscopic growth factors $g$ of aerosol particles, consists basically of two differential mobility analysers (DMA) operated in series. A DMA (Whitby and Clark, 1966; Knutson and Whitby, 1975) is a contact free particle size spectrometer enabling the isolation of a monodisperse fraction from a charged polydisperse aerosol. Particles are selected with respect to their electrical mobility, and hence their electrical mobility equivalent diameter is defined as the diameter of a singly charged spherical particle with equal drift velocity in an electric field. Particles entering a H-TDMA are first dried and then fed into a diffusion charger ($^{85}$Kr) to achieve charge equilibrium, before a monodisperse fraction of this dry polydisperse aerosol is selected in a first DMA (DMA 1). Resulting dry monodisperse particles of known size (dry diameter $D_0$) are then exposed to high RH in the RH-conditioner, inducing particle growth by condensation of water. A two-step humidification process may alternatively be used to simulate different RH histories in order to detect the hysteresis behaviour (see section 1.2.5) under increasing and decreasing RH conditions. The diameter $D(RH)$ after equilibration at high RH conditions is finally determined by scanning the whole size range with a second DMA (DMA 2) and a condensation particle counter (CPC). Growth factors obtained with a H-TDMA are generally mean values representative of the whole selected aerosol fraction. Additional information can be obtained from changes of the standard deviation of the monodisperse fraction during growth. The example illustrated in Fig. 1.4 represents an aerosol with homogeneous hygroscopic properties, i.e. all particles of the selected size undergo equal hygroscopic growths and the standard deviation of the monodisperse distribution remains hence unchanged. Fresh ambient aerosols are often external mixtures with different hygroscopic growth factors of individual particles. Such aerosols are characterised by an increasing standard deviation during hygroscopic growth or even by separation of the initially monodisperse fraction into more and less hygroscopic modes (e.g. Zhang et al., 1993).

The H-TDMA technique is suitable to investigate hygroscopic properties of laboratory generated or ambient aerosols in the range $RH < \sim 95\%$ with a high time resolution and a high accuracy in terms of electrical mobility diameter growth factors. Restrictions of this technique are the applicable size range (typically $D_0 < \sim 300$ nm for high RH investigations), and the fact that volume or mass growth factors deduced from mobility diameter growth factors are affected by uncertainties of varying particle shape and solution density during growth.

### 1.3.2 Activation Under Supersaturated RH Conditions

Solution droplets are in stable equilibrium at $RH < 100\%$ due to the Raoult effect. The Kelvin effect causes particles to remain in stable equilibrium also under supersaturated RH conditions as long as $S < S_{crit}$ ($S = RH − 1$), but the particles become activated as cloud droplets as soon as the supersaturation exceeds $S_{crit}$ (see section 1.2.4). $S_{crit}$ depends on dry particle size and chemical composition. CCN spectra of aerosols, i.e. the CCN concentration as a function of $S$ in the supersaturation range of atmospheric importance ($0.01\% < S < 1\%$) are measured with so-called CCN counters (CCNC). The most commonly used CCNC types are based on the thermal gradient diffusion chamber method.
1.3 Measurement of Hygroscopic Properties

(Wieland, 1956; Twomey, 1963). A review of currently used static and continuous flow thermal gradient diffusion type CCNCs is given by Nenes et al. (2001), and the specific instrument used in this study (chapter 5) is described in detail in Giebl et al. (2002).

Figure 1.4: H-TDMA measurement principle.

Figure 1.5 illustrates the basic operation principle of thermal gradient CCNCs. Two wetted plates are maintained at different temperatures ($T_{hot} = 16 \, ^{\circ}C$ and $T_{cold} = 20 \, ^{\circ}C$ in this example). Diffusion of water vapour and heat from the hot to the cold plate leads to linear effective water vapour pressure $e_{eff}$ and temperature gradients, respectively (Fig. 1.5a). The saturation water vapour pressure $e_w$ profile is not linear due to the convexity of $e_w$ as a function of temperature. $e_w$ is smaller than $e_{eff}$ at any position between the plates with a maximum difference close to the centre line. The resulting supersaturation profile, i.e. $S = e_{eff} / e_w - 1$ is shown in Fig. 1.5b. Highest supersaturation develops in the centre range indicated by horizontal dotted lines. Particles activated at this supersaturation are optically counted, and CCN spectra of an aerosol are obtained by variation of the supersaturation via the applied temperature gradient.

Other CCNC techniques include isothermal haze chambers (IHC), diffusion tubes, and expansion-type Kelvin spectrometers. The indirect detection of CCN spectra in IHCs (Fitzgerald et al., 1981) bases on the optical detection of droplet sizes at $RH = 100\%$ and the unique relation between droplet equilibrium diameter at $RH = 100\%$ and critical supersaturation $S_{crit}$ (Laktionov, 1972). Diffusion tube type CCNCs consist of a heated, wetted tube with a steady aerosol flow (Leaitch and Megaw, 1982). The aerosol along the centre line is exposed to supersaturation since water vapour diffuses faster than heat. More details about IHCs and diffusion tubes are discussed in McMurry (2000). Holländer et al. (2002) recently developed an expansion-type CCNC. This instrument utilizes the effect that expansion induced cooling of initially saturated air leads to supersaturated conditions.
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Figure 1.5: Thermal gradient CCN counter. Profiles of a) saturation water vapour pressure, effective water vapour pressure, temperature, and b) supersaturation.

1.4 Motivation

Hygroscopic properties of atmospheric aerosols are of particular importance regarding their impacts on e.g. the earth climate (see above). The large variety of different sources for particulate matter leads to fresh particles with distinctly different properties. After their formation or emission, particles experience continuous modification by atmospheric aging processes like e.g. coagulation, condensational growth and chemical processing. Such aging processes usually lead to increasing particle hygroscopicity and to a reduction of differences between individual particles.

The general topic of this thesis was the characterisation of hygroscopic properties of different aerosol types. An aged free tropospheric aerosol at the high-alpine research station Jungfraujoch was investigated by means of a new low-temperature H-TDMA specially designed for that purpose (chapters 2 and 3). The studies presented in chapters 4 and 5 focussed on the characterisation of jet engine combustion particles, representing a specific aerosol source in the upper troposphere and lowermost stratosphere (UTLS). The aim of the last study (chapter 6) was to determine the influence of secondary organic matter on the hygroscopic properties of a continental-rural aerosol encountered at the background station K-puszta, Hungary.

1.4.1 Hygroscopicity Measurements at Low Temperatures

Estimates of global and annual mean radiative forcing due to a number of agents are shown in Fig. 1.6 (IPCC, 2001). The dominant positive forcing, caused by increased greenhouse gas concentrations (mainly CO₂ and CH₄), is relatively well understood. Aerosol effects on the radiative balance are by contrast only poorly quantified. Direct forcing by aerosols is split into contributions by the different components sulphate aerosol, fossil fuel burning,
1.4 Motivation

biomass burning and mineral dust. The sign of the direct forcing may be positive or negative depending on whether light absorption or scattering dominates, whereas the transition between positive and negative net effects depends also on the surface albedo below the aerosol layer. The tropospheric aerosol indirect effect, i.e. changes of cloud albedo and amount induced by aerosol particles acting as CCN or IN, is suspected to cause a substantial negative forcing due to enhanced reflection of incoming shortwave solar radiation, but not even a best estimate value can be given to date. The sum of direct and indirect aerosol radiative forcing may partially offset the greenhouse gas forcing in terms of global and annual mean values. However, spatial distributions of aerosols are inhomogeneous and also variable in time in contrast to well-mixed greenhouse gases. Hygroscopic growth as a function of RH is one of the key parameters of atmospheric aerosols needed for an improved quantification of aerosol direct and indirect effects (IPCC, 2001), illustrated by some examples below.

![Figure 1.6: Global and annual mean radiative forcing due to a number of agents for the period from pre-industrial (1750) to present (~2000). The height of the rectangular bar denotes a central or best estimate value while its absence denotes no best estimate is possible. The vertical lines indicate estimates of the uncertainty ranges. (IPCC, 2001).](image)

Aerosol parameters and other atmospheric quantities are monitored at the Swiss high-alpine research station Jungfraujoch (JFJ, 46°33'N 7°98'E, 3580 m asl) in the framework of the Global Atmosphere Watch (GAW) programme. In winter the JFJ station is mostly located in the free troposphere, but it is often influenced by the planetary boundary layer through thermally driven aerosol transport in the afternoon of summer days. Mean ambient temperature at the JFJ is −1 °C in summer and −14 °C in winter. Outdoor air samples heated to indoor temperature are hence completely dried up (RH < 10%) even if ambient RH is high. This results in a size reduction of the aerosol particles due to evaporation of water. In addition, volatile inorganic (ammonium nitrate) and organic compounds, present in the particulate phase at low temperatures, may partition mainly to the gas phase.
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Figure 1.7 shows a snapshot of number size distributions simultaneously measured outdoors (ambient measurements) and indoors (dry measurements) (Nessler et al., 2003). The size distribution “dry measurements, corrected for RH = 67%” was obtained by multiplication of dry particle diameters with hygroscopic growth factors at 67% RH obtained from H-TDMA measurements (Weingartner et al., 2002; chapter 2 of this study). The good agreement between ambient and corrected indoor size distribution clearly suggests that in this particular case the difference between outdoor and indoor measurement was only a result of water evaporation. However, Fig. 1.8 shows a different snapshot from the same day, where the ambient and corrected indoor size distributions agree only in the size range $D > 100$ nm. Particle concentrations in the range $D < 100$ nm are smaller for the corrected indoor measurement, indicating that in this particular case small volatile particles, present under ambient conditions, evaporated during heating to indoor conditions.

**Figure 1.7**: Snapshot of ambient, dry and corrected dry number size distributions (one-hour average) simultaneously measured at the Swiss high-alpine research station Jungfraujoch in February 2000 (one-hour average). In this particular case, ambient and dry size distributions differ only by a shift in particle size caused by hygroscopic growth at high RH. Adapted from Nessler et al. (2003).

**Figure 1.8**: Snapshot of ambient, dry and corrected dry number size distributions (one-hour average) simultaneously measured at the Swiss high-alpine research station Jungfraujoch in February 2000 (one-hour average). In this particular case, ambient and dry size distributions differ by a shift in particle size caused by hygroscopic growth at high RH, but also in the total number concentration caused by evaporation of volatile particles (size range $<100$ nm) under dry, warm conditions. Adapted from Nessler et al. (2003).
The effects discussed above clearly show the need of aerosol measurements under ambient conditions whenever possible. A new low-temperature H-TDMA working in the temperature range from −20 °C to 30 °C was hence designed and characterised in order to conduct hygroscopicity measurements at the JFJ at ambient temperatures and to investigate model aerosols in laboratory experiments at temperatures typically encountered in the lower free troposphere.

1.4.2 Jet Engine Combustion Particles

Most particulate emissions of air traffic occur in the UTLS (Petzold et al., 1999), where residence times of pollutants are longer compared to the lower troposphere and may hence have a relatively larger impact on the earth climate. Figure 1.9 shows estimates of annual and global mean radiative forcing caused by aircraft emission in a) 1992, and b) predictions for 2050 (IPCC Special Report, 1999). The global mean forcing induced by aircraft in 1992 of ~0.05 W m\(^{-2}\) is small compared to the influence of e.g. greenhouse gases (see Fig. 1.6), but the local impact in regions with high air traffic density (Europe, North Atlantic flight corridor, North America) may be an order of magnitude larger (Minnis et al., 1999). Furthermore, potential impacts are expected to increase in future due to the large growth rates of air traffic. The pattern of aircraft induced forcings predicted for 2050 looks quite similar to 1992, but absolute values are about a factor of four larger (note different ordinate scales).

![Figure 1.9: Radiative forcing from subsonic aircraft in a) 1992 and b) predicted for 2050. The level of scientific understanding for each contribution is indicated below the bar charts. (IPCC Special Report, 1999).](image)

The most readily perceived impact of particulate and water vapour emissions by aircraft is the formation of condensation trails, so-called contrails, which consist of ice particles. The conditions for contrail formation, described by the Schmidt-Appleman criterion, are well understood (Schmidt, 1941; Appleman, 1953; Schumann, 2000; Schumann et al., 2000). Contrails form only if the exhaust plume RH exceeds saturation with respect to liquid water during dilution with entrained background air. However, the processes leading to ice particle formation in aircraft contrails are still not fully understood. The fact, that water vapour saturation with respect to liquid water is required indicates that neither heterogeneous ice nucleation nor immersion freezing induced by the exhaust particles, which might both occur in the range above saturation with respect to ice, are dominant. The remaining two options are either direct homogeneous freezing of water-soluble coatings
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existing on the exhaust particles, or homogeneous freezing of liquid droplets after preceding CCN activation of exhaust particles. In the relevant temperature range these two processes occur theoretically just below (Koop et al., 2000) or just above liquid water saturation, respectively, and may hence not be distinguished by verification of the Schmidt-Appleman criterion.

The critical ambient temperature below which contrails form depends, according to the Schmidt-Appleman criterion, mainly on the overall aircraft efficiency and ambient RH, but it has also been shown that an increased fuel sulphur content (FSC) results in a slightly increased threshold temperature for contrail formation (Schumann et al., 2002). Contrails are persistent in ice-supersaturated air, but they evaporate within a short time in ice-subsaturated air. The radiative forcing by line shaped contrails (bars “Contrails” in Fig. 1.9) is fairly well quantified since the fractional coverage of cloud free regions with line shaped contrails and contrail optical properties may be retrieved from satellite data (Minnis et al., 1999; Ponater et al., 2002; Meyer et al., 2002). Unlike low-level clouds, contrails cause a positive net effect on the radiation balance, because the effect on the outgoing longwave radiation dominates for these optically thin clouds.

A large fraction of cloud free regions in the UTLS are supersaturated with respect to ice (Gierens et al., 1999). Particulate aircraft emissions are also suspected to affect cirrus cloudiness in these regions via different mechanisms. Persistent contrails may transform into cirrus clouds (“contrail-cirrus”) induced by continued ice crystal growth and contrail spreading by wind shear (Jensen et al., 1998). Aircraft exhaust providing potential nucleation sites for cloud droplet or ice particle formation may alter naturally occurring cirrus clouds (Ström and Ohlssen, 1998) or even induce cirrus formation under conditions where no natural cirrus clouds would have formed (Gierens, 2003). These effects on cirrus cloudiness are only poorly quantified till now (see also Fig. 1.9), but there are a couple of studies indicating correlations between aircraft emissions and cirrus cloudiness.

Figure 1.10: Vertical profile of the fraction of data points where crystals contain a concentration of absorbing material $\delta > 0.01 \, \mu g \, m^{-3}$ (line), and the annual use of aviation fuel for the year 1990 (NASA) averaged over an area between 7°E–14°E and 46°N–52°N (diamonds). (Ström and Ohlssen, 1998).

Increased UTLS particle concentrations in regions with high air traffic density have been reported by Schlager et al. (1997) and Hofmann et al. (1998). Ström and Ohlssen (1998)
observed a clear correlation between vertical profiles of aircraft fuel consumption and data points with high concentrations of absorbing particulate matter (Fig. 1.10), indicating a significant contribution of aircraft to UTLS concentration of absorbing particulate matter. Furthermore, they observed an increasing fraction of activated ice particles compared to totally available particles with increasing concentrations of absorbing material, suggesting a link between aircraft emissions and ice particle concentrations in cirrus clouds. Differences in cirrus cloud cover trends between regions with high air traffic density and adjacent regions with low air traffic density suggest a positive correlation between air traffic and cirrus occurrence (Boucher 1999; Minnis et al., 2001; Nakanishi et al., 2001; Zerefos et al., 2003). An example is given in Fig. 1.11 (Zerefos et al., 2003), where the longitudinal distribution of cirrus trends from 1984–1986 to 1994–1996 is correlated with aircraft fuel consumption in 1992.

**Figure 1.11:** a) Longitudinal distribution of the percentage changes of cirrus cloud cover and their standard errors (black line) from 1984/1985/1986 to 1994/1995/1996 and of the total fuel consumption (grey line) in 1992 during the wintertime (DJFM), over heavy air traffic locations (35°N–55°N). b) Same as (a) but for low air traffic locations (5°N–25°N). Values on the abscissa correspond to 36 equal regions of 10° longitude, from west to east, on which cirrus cloud data have been averaged for the two latitudinal belts. R is the correlation coefficient between the two lines. (Zerefos et al., 2003).

Hygroscopic properties and CCN activity of jet engine combustion particles are important parameters for an improved understanding and quantification of the
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The abovementioned impacts of aviation on climate. Investigations conducted in this study (chapter 4 and 5) were part of the EU project PartEmis (measurement and prediction of emissions of aerosols and gaseous precursors from gas turbine engines) (Wilson et al., 2003; Petzold et al., 2003). The overall goal of the PartEmis project was an improved understanding of the formation of carbonaceous aerosol and gaseous aerosol precursors, with a focus on the influence of combustor operating conditions, fuel sulphur content (FSC), and turbine section on these processes and particle properties.

1.4.3 Organic Aerosol

Atmospheric aerosols often contain a large fraction of organic compounds. Mean aerosol composition observed at three European background sites belonging to the GAW network are shown in Fig. 1.12 (Krivácsy et al., 2001). The marine aerosol at Mace Head is seen to be dominated by sea salt, whereas the high-alpine aerosol at Jungfraujoch and the continental-rural aerosol at K-puszta comprise ~50–60 wt % organic matter. About two thirds of this organic matter has been found to be water-soluble. Water-soluble organic matter (WSOM) may be responsible for a considerable amount of particulate water (Ansari and Pandis, 2000), and it may also play an important role in the droplet nucleation process (Facchini et al., 1999). Particulate water that cannot be explained with the water uptake of the inorganic aerosol fraction is commonly defined as excess water. A clear correlation between organic mass fraction of the total mass and excess water has been found during the Southeastern Aerosol and Visibility Study (SEAVS) in 1995 conducted at a rural site in the Smoky Mountains (see Fig. 1.13) (Dick et al., 2000).

![Figure 1.12](image-url)

**Figure 1.12:** Share of the mass concentrations of inorganic ions, black carbon (BC), water-soluble organic matter (WSOM) and water-insoluble organic matter (WINSOM) at three European background sites. Standard deviation values referring to the natural variation of the components are shown in parenthesis. Adapted from Krivácsy et al. (2001).

Water-soluble organic matter is composed of hundreds of individual species (Saxena and Hildemann, 1996), where each contributes only a small fraction towards total mass of WSOM. This vast number of organic species complicates quantification of particulate water associated with WSOM. Approaches previously applied in laboratory and field experiments towards this aim include:

i) Investigation of pure surrogate organic species and of their mixtures with other organic or inorganic substances (Na et al., 1995; Cruz and Pandis, 2000; Lightstone et al., 2000; Peng et al., 2001; Peng and Chan, 2001; Prenni et al., 2001; Choi and Chan, 2002a,b; Marcolli et al., 2003; Hämeri et al., 2002). Such experiments provide input data for semiempirical thermodynamic models describing organic or mixed inorganic/organic systems (see section 1.2.2).
ii) Investigation of secondary organic aerosol in smog chamber experiments (Virkkula et al., 1999; Cocker III et al., 2001a; Cocker III et al., 2001b; Saathoff et al., 2003). In this approach, secondary organic aerosol is obtained by (photo-)chemical oxidation of typical gaseous precursors, leading to low vapour pressure oxidation products which condense on existing particles or form new particles after reaching a critical supersaturation.

iii) Investigation of chemical composition and hygroscopic growth factors of atmospheric aerosols. Excess water, i.e. the difference between particulate water measured and the amount predicted for the inorganic fraction only, is then attributed to WSOM (Saxena et al., 1995; Swietlicki et al., 1999; Dick et al., 2000; Speer et al., 2003).

A new approach to investigate the effect of WSOM on hygroscopic growth of atmospheric aerosol was used in this study (chapter 6). Water-soluble matter (WSM) was first extracted from atmospheric fine aerosol. In a second step, solid phase extraction (SPE), recently adapted by Varga et al. (2001), was used to isolate a major fraction of WSOM (~70 wt %) from WSM. Both WSM and isolated organic matter were chemically characterised (Galambos et al., 2003), and hygroscopic properties were determined (chapter 6). This approach allowed measurements of hygroscopic properties of a major fraction of atmospheric WSOM in pure bulk form to be conducted for the first time. Furthermore, hygroscopic growth factors of the isolated organic matter in combination with growth factors calculated for the inorganic fraction enabled to perform a hygroscopicity closure for the WSM and with that to assess the influence of the organic fraction on the hygroscopic growth of atmospheric aerosol.

![Figure 1.13: Excess water (\(v_{\text{wt}} - v_{\text{wi}}\)) at 85% RH as a function of the organic fraction of the total mass (SEAVS study in 1995 at a rural site in the Smoky Mountains). The dimensionless water volume \(v_{\text{wt}}\) is defined as the ratio of water volume to dry particle volume and the indices \(t\) and \(i\) indicate the total particulate water and the water amount associated with inorganic compounds, respectively. The density of organic compounds is assumed to be 1.4 g cm\(^{-3}\). (Dick et al., 2000).](image-url)
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2. New Low-Temperature H-TDMA

Hygroscopicity of aerosol particles at low temperatures. 1. New low-temperature H-TDMA instrument: Setup and first applications

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Abstract. A hygroscopicity tandem differential mobility analyzer (H-TDMA) is described that allows a fast and accurate determination of the water uptake by submicrometer aerosol particles at temperatures below 0 °C. To avoid volatilization of semivolatile particles, the humidification works without heating the gas stream, and the gas-phase composition is not changed during the analysis. The applied scanning mobility analysis allows a fast and accurate measurement of the humidogram, but care has to be taken with too high scanning velocities leading to artifacts in the particle size measurement. During a field campaign at a high-alpine site (Jungfraujoch, 3580 m above sea level), humidograms of free tropospheric particles were measured at \( T = -10 \) °C. The hygroscopic growth of these particles was characterized by monomodal growth distributions, which means that in the observed size range (dry particle diameters \( D_0 = 50–250 \) nm) the free tropospheric aerosol was to a large extent internally mixed. No distinct deliquescence was observed, indicating that the multicomponent aerosol particles are present in a liquid state even at a low relative humidity (RH) <10%. At RH 85%, average hygroscopic growth factors of 1.44, 1.49, and 1.53 were measured for \( D_0 = 50, 100, \) and 250 nm. The estimated soluble volume fraction of the particles in the observed size range was found to be 0.79, 0.86, and 0.91, respectively.

2.1 Introduction

The hygroscopic properties of the atmospheric aerosol play a crucial role in air quality, acid deposition, biochemical cycles, visibility reduction, and formation of clouds and precipitation. In recent years, the impact of aerosol particles on climate change has been recognized. While the combined positive climate forcing of the greenhouse gases can be fairly well estimated, the complexity of the aerosol-cloud-climate system makes the negative forcing due to atmospheric aerosols the largest current source of uncertainty in predictions of the future global climate (IPCC, 2001). The atmospheric aerosol affects the earth’s radiation balance in two ways, directly and indirectly. Aerosol particles influence the climate directly by absorbing as well as reflecting the incoming short-wave solar radiation back to space. This capability is strongly dependent on the particle size, which is itself a function of the relative humidity (RH). It is well-known that, in the presence of water vapor, the size of an aerosol particle may increase by 1.1–2.5 times as compared to its original “dry” size over the RH range of 30–95%, depending on aerosol composition.

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(Kasten, 1969; Hänel, 1976; Fitzgerald et al., 1982). The number size distribution and the hygroscopic properties of the aerosol also determine which fraction of aerosol particles can act as cloud condensation nuclei (CCN) and thus contribute to the indirect aerosol effect. This effect refers to the fact that an increased number of cloud droplets may alter the microphysical properties of clouds (Twomey, 1977).

The response of aerosol particles to changes in RH can be measured with a variety of instruments. The water content as a function of RH may be obtained either by weighing a bulk aerosol sample (Hitzenberger et al., 1997), by an elemental analyzer (Lee and Hsu, 2000), by the Karl Fischer method (Ohta et al., 1998), or by determining the growth factor of aerosol particles under enhanced RH conditions. The latter is possible by means of the single-particle levitation technique (Tang and Munkelwitz, 1993; Tang and Munkelwitz 1994; Tang 1997) or a hygroscopicity tandem differential mobility analyzer (H-TDMA) (Liu et al., 1978; Rader and McMurry, 1986).

In the field, hygroscopicity measurements are commonly performed using humidity-controlled nephelometry (Dougle et al., 1998) or by means of a H-TDMA. The latter technique has been used at a number of sites around the globe (Sekigawa, 1983; McMurry and Stolzenburg, 1989; Covert and Heinzenberg, 1993; Svenningsson et al., 1997; Zhang et al., 1993; Berg et al., 1998; Swietlicki et al., 1999; Swietlicki et al., 2000; Cocker et al., 2001; Baltensperger et al., 2002). Most of these measurements have been performed in the planetary boundary layer, and it was often found that the submicrometer aerosol particles were characterized by two or more modes of hygroscopic growth rather than a broad distribution of growth. This means that, near sources, the aerosol is in many cases externally mixed regarding its hygroscopic properties.

All of these measurements have been performed at room temperature (20–30 °C), which may differ from ambient temperature. However, the gas temperature may significantly influence the partitioning of components between the particulate and the gas phases and thus change the hygroscopic behavior of particles. The organic fraction of particulate matter in both rural and urban areas is a complex mixture of many compounds. Recent studies have shown that organic material may considerably alter the hygroscopic properties of aerosol particles (Cruz and Pandis, 2000). Saxena et al. (1995) used H-TDMA and impactor data from the Grand Canyon and Los Angeles in the United States and concluded that organic material from freshly produced aerosol particles hindered hygroscopic growth, while organic species in particles found in aged air masses seemed to increase growth. Semivolatile inorganic compounds are also important. Ammonium nitrate losses during sampling have been reported in numerous studies. Russell et al. (1983) estimated that at temperatures greater than 30 °C most nitrate will be in the gas phase as nitric acid (HNO₃), while at temperatures lower than 15 °C most nitrate is present in the particulate phase. The relative humidity and the concentration of ammonia and nitric acid gases also affect the equilibrium, but temperature is by far the most important variable.

The aerosol indirect effect occurs also in the middle and upper troposphere, i.e., in the −40 °C < T < 0 °C temperature range. If under these conditions the aerosol is heated to room temperature, nitrate or semivolatile organics may desorb from particles and considerably alter their hygroscopic properties. Therefore, at these altitudes, hygroscopic properties of aerosol particles have to be measured at ambient temperatures to prevent artifacts due to volatilization of semivolatile compounds. An ideal location to perform such studies is the high-alpine site Jungfraujoch (JFJ) at 3580 m above sea level (46.55°N, 7.98°E). It is situated on the northern side of the main central European alpine chain in Switzerland with ambient average temperatures of −1 °C in summer and −14 °C in winter and is perennially covered by snow. Since July 1995, the JFJ station has been conducting measurements under the Global Atmosphere Watch (GAW) program of the World Meteorological Organization (WMO). During the summer, JFJ is often influenced by the planetary boundary layer (PBL) through thermally driven aerosol transport in the afternoon,
2.1 Introduction

while at other times and seasons the site is mainly located in the free troposphere (FT) (Lugauer et al., 1998). Several studies on atmospheric aerosols have been previously conducted here (Baltensperger et al., 1997; Nyeki et al., 1998a,b; Weingartner et al., 1999; Lugauer et al., 2000; Zellweger et al., 2000), with most aerosol measurements being performed indoors at 20–30 °C.

In this work a new version of a H-TDMA is introduced that is capable of measuring the hygroscopic growth of aerosol particles at temperatures below 0 °C. The operating principle of the low-temperature H-TDMA is presented, and the advantages and limitations of the scanning mobility analysis are investigated. A measurement of the humidogram of (NH₄)₂SO₄ particles at 20 °C is then discussed, and field measurements at the high-alpine site JFJ are presented. The hygroscopicity of aerosol particles in the free troposphere was measured at this site at ambient temperatures (T = −10 °C) with high temporal resolution. In the second part of this work (Gysel et al., 2002), a detailed discussion of the hygroscopic properties of laboratory-generated (NH₄)₂SO₄, NaCl, and NaNO₃ particles at 20 and −10 °C and the agreement with theory is discussed.

2.2 Experimental Section

This instrument was designed to meet the following demands: (i) The hygroscopicity of particles with diameters between 20 and 250 nm can be determined in the temperature and RH ranges −20 °C < T < 30 °C and 10% < RH < 90% with an accuracy of 0.1 °C and <1.6%, respectively. (ii) The acquisition time of one size scan is <5 min. (iii) For a sufficiently high aerosol concentration, the change in particle mobility diameter is measured with an accuracy of <1%. (iv) The gas-phase composition is not changed during the measurement, and the humidifier works without changing the gas temperature. (v) The instrument is robust, suited for field experiments, and measurements can be conducted in stand-alone operation.

2.2.1 General Working Principle

Figure 2.1 shows the experimental setup of the low-temperature H-TDMA. All components and tubing that need to be held at constant temperature are located inside an isolated cylinder (stainless steel, volume = 20 L) and are submersed in a water/ethylene glycol bath. This bath is connected in a closed loop arrangement to a cooling/heating unit. The liquid is recycled once per minute, which ensures a temperature gradient ΔT < 0.1 °C at T = −10 °C inside the cylinder. The bath temperature determines the temperature at which the hygroscopic properties are measured.

First, the aerosol (flow rate: 0.3 L min⁻¹) enters a silica gel diffusion dryer designed for operation at low temperatures (T = −20 °C) to dry the sample to a frost point temperature of Tᵢ < −30 °C. This corresponds to a RH < 15% for T > −10 °C. If a lower RH is required, the aerosol can additionally be dried with a phosphorus pentoxide dryer. The dry aerosol is then charged with a diffusion charger (⁸⁵Kr) and fed into the main part of the H-TDMA where the measurement involves three steps. In a first differential mobility analyzer (DMA1), a narrow size range of the dry aerosol is selected. This monodisperse aerosol is conditioned to a well-defined higher RH and fed into a chamber with a residence time of 1 min. Although water vapor equilibration times are very short for pure submicrometer particles (milliseconds or shorter), the high residence time was chosen because it is known that organic films may impede the transfer of water across the particle surface and thus increase the characteristic time scale for water vapor to reach equilibrium with the particles (Saxena et al., 1995). The aerosol particle diameter at this new RH is then measured using a second DMA (DMA2) and a condensation particle counter (CPC). The DMAs are TSI 3071 types, where the HV connector was modified to allow submersed operation. To avoid any
heat bridges, the DMAs and all other critical parts have no thermally conducting contact to the cylinder walls. In the H-TDMA presented in this paper, a TSI 3022A CPC was used to count particles. However, using a different CPC (such as a TSI 3010 or 3760) would be an improvement to our system, since these CPCs have a higher flow rate leading to better counting statistics and to a smaller response time (see below). For the determination of hygroscopic growth factors ($D/D_0$), defined as the ratio of the humidified particles diameter ($D$) to the dry particle diameter ($D_0$), a precise measurement of $D$ as well as $D_0$ is required. Although $D_0$ can be calculated, in practice, $D_0$ is periodically measured simply by “switching off” the humidifier and thus lowering the RH in DMA2 to the low RH present in DMA1. The value of $D_0$ determined in this manner is used as the reference dry diameter for further calculations. This procedure increases the quality of the data because the low RH in DMA1 is checked and instrumental drifts in the diameter measurements are easily identified.

Figure 2.1: Sketch of the low-temperature H-TDMA. The main components are submersed in a water/ethylene glycol bath ensuring constant temperature.

2.2.2 Sheath Airflow System

The H-TDMA was designed to maintain the gas-phase composition by using recirculating air streams; however, one has to consider that the chemical composition of particles may have changed during the drying process in the diffusion drier. For example, NH$_4$NO$_3$ particles will to some extent volatilize in the diffusion drier when they are transferred from a humid to a dry environment. The reverse may occur in the humidifier when, for example, a sample with high HNO$_3$ gas-phase concentration is exposed to high RH leading to a
2.2 Experimental Section

transfer of nitric acid to the aerosol phase. Apart from the stability of the flows, operating the DMAs in a closed-loop arrangement also has the advantage of being relatively simple and robust. Great care has to be taken that the pumps are absolutely airtight. This is of great importance because a leak of, for example, 1% would cause a change in the aerosol flow of about 10%. Another critical point is that the pump works at a temperature of approximately 50 °C. Outgassing material from inside the pump (e.g., from rubber membranes or O-rings) may condense at lower temperature inside the H-TDMA and significantly change the aerosol and gas-phase composition. For the instrument presented in this paper, airtight pumps were used operating with Teflon membranes, thus avoiding any artifact by outgassing material. The sheath airflows (3.5 L min$^{-1}$) are controlled by critical orifices located in the excess air outlet of the DMAs. The critical operation of the orifices is guaranteed by monitoring the vacuum pressure with pressure sensors. The pulsation in the air exiting the pump is removed with a valve, which generates a slight overpressure of 200 mbar inside the pump.

After particle filtration, the sheath air is fed to a heat exchanger located inside the water/ethylene glycol bath. This exchanger was designed such that air with $T = 30 ^\circ$C is assimilated with $\Delta T < 0.1 ^\circ$C to a bath temperature of $-10 ^\circ$C. Care was taken in designing the exchanger of the second DMA such that no moisture is lost by condensation caused by the pressure increase in the heat exchanger.

2.2.3 RH Generation, Measurement, and Calibration

The dry and monodisperse aerosol exiting DMA1 is humidified by passing it through a vertically oriented Gore-Tex tube (0.6 cm i.d., 40 cm long). This tube is located inside another tube where a secondary air stream is circulating in counter flow direction (flow rate: approximately 3 L min$^{-1}$). Moisture can diffuse from this secondary flow through the Gore-Tex membrane into the aerosol stream. The secondary airflow circulates in a closed-loop arrangement and is branched up into a saturated and dry path. The RH is determined by the airflow ratio through these branches. This is realized with a PID controller that controls the pump power in both branches by comparing a set RH with that measured by a capacitive sensor (HP101A, Rotronic). To prevent an overshoot in RH, the saturator of the humidified branch is also located inside the water/ethylene glycol bath. This humidifier works without heating the aerosol and is able to generate RHs up to 90% even at temperatures below 0 °C.

The RH inside DMA2, which finally determines the measured particle size, is deduced from precise measurement of the bath and dew point temperature. The temperature is measured at the upper and lower part of the bath (i.e., at the entrance and exit of the DMA) by means of PT100 resistors. The dew point is monitored in the excess air of the DMA with two dew point sensors (model 2002 Dewprime, EdgeTech, and model 911 Dew-all, EG&G). Since the dew point temperature measurement depends on air pressure, care was taken to avoid a significant pressure drop between DMA2 and the sensors. The utilization of two dew point sensors increases the reliability, as malfunctioning of one instrument (such as contamination of the mirror surface) is easily detected by comparison.

The measured dew points are periodically checked with a separate calibration loop, where filtered air is saturated with water vapor at a certain bath temperature and fed into the dew point sensors. A heat exchanger before the saturator ensures that at low temperatures the air is saturated at the bath temperature. This allows an internal calibration of the dew point sensors by adjusting the measured dew point temperatures to the bath temperature measurements in the data acquisition program. With this procedure the bath and dew point temperature measurement is achieved with an accuracy of 0.15 °C for each value, which transforms to a RH accuracy of 1.1% at 90% for $T = 20 ^\circ$C and 1.6% at 90% for $T = -10 ^\circ$C.
2. New Low-Temperature H-TDMA

2.2.4 Measurement at $T < 0 \, ^\circ C$

The selected particle mobility diameter in the DMA is a function of gas temperature and pressure. The data analysis takes into account that the volumetric flows, the air viscosity, and the gas mean free path are temperature and pressure dependent.

For $T < 0 \, ^\circ C$, frost points are measured by the dew point sensors. These temperatures are converted in the data evaluation into dew points, and RH is always calculated with respect to liquid water unless otherwise mentioned.

Principally, $T < 0 \, ^\circ C$ measurements are conducted in a manner similar to those at $T = 20 \, ^\circ C$. The water in the humidifier and RH calibration circuit will freeze and fulfill their service by saturating the air with respect to ice. Experimental difficulties may arise if the secondary airflows of the humidifier freeze up, leading to a plugging of the airstreams. Such a freezing of the tubing occurs when the H-TDMA is cooled off to a lower working temperature and high RH is already present in the system. In such a case, one has to defrost and dry the whole system. At JFJ, the instrument was continuously operated during 4 weeks at $T = -10 \, ^\circ C$ and the hygroscopic growth was predominantly measured at RH 85%. A drop in performance of the humidifier was temporarily observed after 1 week of continuous operation at this high RH. We assign this to a plugging of pores with ice in the Gore-Tex material, reducing the permeability of the tube. In this situation, a simple reduction of the humidifier RH set point during a period of approximately 4 h often solved this problem – a procedure that was also used to check the reference dry diameter ($D_0$).

In this and the companion paper (Gysel et al., 2002), we will present measurements performed at $T < 0 \, ^\circ C$ in the field as well as in the laboratory. For all laboratory experiments, particles were generated, dried, charge-neutralized at room temperature ($T = 20 \, ^\circ C$), and cooled for the first time inside the H-TDMA. For the field measurement at JFJ, great care was taken to maintain the original aerosol composition. The sampling head, diffusion dryer, charger, and all tubing were kept at ambient temperature. The continuously monitored RH of the aerosol entering the H-TDMA was always <10%.

2.2.5 Process Control and Data Processing

Stand-alone operation is made possible by using a custom-written LabView program running on a personal computer. Analog-to-digital and digital-to-analog converters are used to monitor temperature and RH measurements as well as to change the applied DMA voltages and RH set points. The aerosol size spectra of humidified particles may be obtained by changing the voltage on DMA2 either in discrete steps or continuously. In the first method, also called differential mobility particles sizer (DMPS), a fixed voltage is applied, and after a certain waiting time, the particle number concentration exiting the DMA is measured. This method is often applied in H-TDMA analysis because it ensures high accuracy of the diameter measurement. The main disadvantage of this method is a low time resolution, which may cause problems with the measurement of rapidly changing particle size distributions (the overall scan time, a function of the number of size bins, is typically 15 min). In the second method, also called scanning mobility particle sizer (SMPS; Wang and Flagan, 1990; Endo et al., 1997), the applied voltage at the DMA center rod is continuously increased in magnitude, and the CPC signal is monitored with a sampling rate of 0.1 Hz. With this method, a scan with a high size resolution can be achieved within 60 s or less. At low number concentrations subsequent scans can be averaged to improve particle counting statistics. For both measuring methods, LabView subroutines were written and embedded in the main program. This allows different dry particle sizes to be measured and an optimal automatic adjustment of the scanned diameter ranges.
2.3 Results and Discussion

2.3.1 Comparison of Stepping and Scanning Mobility Analysis (DMPS vs SMPS)

First, the application of the SMPS routine in the present instrument will be discussed. We will show that care has to be taken with too short scan times resulting in high scanning velocities \((v_s)\). Since the applied voltage is increased exponentially with scanning time in most applications, we define \(v_s\) as the change in diameter on a logarithmic scale per time:

\[
v_s = \frac{d \log D}{dt}
\]

This definition results in nearly constant values of \(v_s\) over the scanned diameter range.

Figure 2.2 shows H-TDMA size spectra measured with the SMPS technique for different scanning velocities as well as a DMPS spectrum for comparison. \((\text{NH}_4)_2\text{SO}_4\) particles were produced by atomization of an aqueous solution and subsequent diffusion drying. The spectra were measured with DMA2, while the first DMA was operating at a fixed voltage selecting particles with \(D_0 = 101.5\) nm. To investigate the influence of the scanning velocity on the shape of the size spectra, the particles were not humidified (RH < 10% in the humidifier), and the measurement was performed at \(T = 20^\circ\text{C}\). The size spectra were fitted with log-normal size distributions:

\[
\frac{d N_c}{d \log D} = \text{constant} \exp \left( - \frac{\left( \log(D) - \log(D_m) \right)^2}{2\log^2(\sigma)} \right)
\]

where \(N_c\) is the count rate (in s\(^{-1}\)) of the CPC, \(D_m\) is the fitted modal diameter, and \(\sigma\) is the standard deviation.

A high agreement between DMPS and SMPS was found for low-scanning velocities; however, for \(v_s > 0.004\) s\(^{-1}\), the accuracy of the particle size measurement decreased significantly. The impairment of the resolution appeared in higher \(\sigma\) values and in larger count rates at larger diameters. These artifacts are mainly due to a smearing effect caused by the response time of the CPC and also depend on the flow rates as well as on the type of CPC (Russel et al., 1995). One can easily imagine that a fraction of particles is buffered before and inside the CPC, resulting in a retarded detection. For our H-TDMA configuration, the smearing effect is negligible since size spectra are generally taken in small diameter size ranges resulting in \(v_s < 0.002\) s\(^{-1}\). However, if the SMPS technique is applied for the rapid determination of the size distribution in a larger range, the smearing effect may become important (see below).

Besides this smearing effect, high-scanning velocities may also lead to another uncertainty: The absolute diameter measurement depends strongly on the delay time \((t_d)\), which is the average time the aerosol takes to travel from the sample extraction slot of the DMA to the point of detection in the CPC. This delay is taken into account by the SMPS software (by assuming plug flow), but an under- or overestimation of \(t_d\) will shift the measured size distribution either to larger or smaller diameters. The true diameters \(D_{true}\) are related to the measured diameters \(D_{meas}\) by

\[
D_{true} = D_{meas} 10^{\left( v_s \cdot \Delta t_d \right)}
\]

where \(\Delta t_d\) is the error in the delay time \(t_d\).
To determine the true $t_d$, the monodisperse size distributions in Fig. 2.2 were measured assuming a certain constant $t_d$ and were shifted laterally (by varying $\Delta t_d$) so that the average modal diameter agreed with the modal diameter measured in the stepping mode. The best agreement was found for $t_d = 3.4$ s.

The relative error in the measured diameters is given by

$$\frac{\Delta D}{D} = 10^{(\nu_{td})} - 1$$

Again, this shift increases significantly for high $v_s$. The correct determination of $t_d$ is of great importance if spectra are taken over a broad size range and with short scan times. For example, if spectra are taken in the diameter range of 16–630 nm with a scan time of 60 s (= default scan time of the commercially available SMPS software) the measurement will be performed with $v_s = 0.0266$ s$^{-1}$ and an error in $t_d$ of $\Delta t_d = 1$ s will translate into a relative error of $\Delta D/D = 6.3\%$. A calculation of higher moments (such as the volume size distribution) will result in a significant enlargement of this error.

The delay time error has a negligible effect on the H-TDMA results as long as relative size changes are deduced from the spectra, such as growth factors ($D/D_0$). This is due to the fact that, as long as the spectra are acquired with constant $v_s$, the measured diameters $D_{meas}$ are proportional to the true diameters $D_{true}$ (see eq 2.3).

![Figure 2.2](image.png)

**Figure 2.2:** Comparison of H-TDMA spectra measured under dry conditions with the DMPS and SMPS methods for different scanning velocities ($v_s$). The standard deviation ($\sigma$) and the modal diameter ($D_m$) of the spectra are deduced by fitting the measured data (symbols) with log-normal size distributions (lines, eq 2.2). The SMPS measurement was corrected with a “true” delay time of $t_d = 3.4$ s resulting in modal diameters that are fairly independent of the scanning velocity. For $v_s > 0.004$ s$^{-1}$, the impairment of the resolution appears in higher $\sigma$ values.
2.3 Results and Discussion

2.3.2 Measurement of Hysteresis Behavior of Particle Growth

Humidograms of various laboratory-generated aerosols at +20 and −10 °C as well as a comparison with theoretical calculations are presented in the following and are also discussed in our companion paper (Gysel et al., 2002). First, we will illustrate in detail how the RH-dependent growth of an aerosol is measured with the H-TDMA. Figure 2.3 shows a typical measurement of the humidogram of laboratory generated (NH₄)₂SO₄ particles. In this example, the H-TDMA operating temperature was set to 20 °C. The aerosol was again produced by atomization and subsequent drying of an aqueous solution, and DMA1 was operated at a fixed voltage to select $D_0 = 100$ nm particles. The hygroscopic growth of the particles is characterized by a strong increase in diameter at its deliquescence humidity DRH = 80%, which is due to the phase transition of particles changing from dry crystals to saturated solution droplets. We define DRH as the RH in the transition regime where the growth of the droplets reaches the growth of solution droplets. In this example, the phase transition is not a sharp function of RH. A distinct increase in particle size is already seen at RH < DRH and will be discussed in more detail below. Due to the hysteresis phenomenon, the particles that experienced RH > DRH may stay in a metastable state well below the deliquescence point, and their equilibrium size is described by the Köhler theory (Pruppacher and Klett, 1997). The dashed line in Fig. 2.3 is such a model which uses a semiempirical calculation of the water activity of (NH₄)₂SO₄ solutions (see Part 2 for more details).

**Figure 2.3:** Example of a humidogram of laboratory-generated $D_0 = 100$ nm (NH₄)₂SO₄ particles at $T = 20$ °C. Points are labeled according to increasing and decreasing RH conditions and different states of hygroscopic growth. The dotted line is a theoretical curve (see text).

Figure 2.4 exemplifies how this measurement was performed and how the different cases (increasing or decreasing RH scans) were determined. Figure 2.4a shows the temporal evolution of the RH measured just after the humidifier as well as the RH in DMA2. Since DMA2 is operated in a closed-loop arrangement, the RH inside this instrument shows a delayed response to a change of the humidifier RH set point. This circumstance is utilized to assess the development of the RH. When passing through the instrument, the aerosol experiences increasing RH when the humidifier RH set points are subsequently lowered, resulting in lower RH in the humidifier compared to DMA2. On the other hand, the aerosol experiences decreasing RH when the humidifier RH is suddenly increased, resulting in a higher RH in the humidifier.
Figure 2.4: Temporal evolution of the humidogram measurements presented in Fig. 2.3: a) RH before and inside DMA2, b) fitted modal diameters (points) and diameters of half-maximum (lines) giving an impression of the shape of the number size distribution, and c) standard deviation of the size spectra. Points are labeled according to decreasing (open symbols) and increasing (closed symbols) RH conditions. Vertical dotted lines delimit conditions leading to a different hygroscopic growth (see text).

Figure 2.4b shows the temporal evolution of the size distribution measured continuously by DMA2 using the SMPS technique (time resolution: 5 min; scanning velocity: $v_s = 0.0014 \text{ s}^{-1}$), which enabled 136 size spectra to be measured within 12 h. A monomodal shape was found for all measured size distributions, and the modal diameters, calculated by fitting the spectra with log-normal size distributions (eq 2.2), as well as the diameters of half-maximum are also indicated. The standard deviation ($\sigma$) of the fitted spectra is shown in Fig. 2.4c and depends on the measured modal diameters. It ranges from 1.053 to 1.060 for “dry” $D = 100$ nm particles and increases up to $\sigma = 1.070$ for $D = 150$ nm particles. A theoretical calculation has shown that the observed change in $\sigma$ can be explained by ~85% in magnitude with the size dependent width of the DMA2 transfer function. The remaining
15% are partially attributed to morphological inhomogenities within the monodisperse particle population.

Different symbols for the fitted modal diameter and for the standard deviations are used in Figs. 2.3 and 2.4 to distinguish between conditions of increasing and decreasing RH. The determined modal diameters together with the RH in DMA2 were used for plotting the corresponding humidogram (Fig. 2.3).

For pure NaCl and (NH$_4$)$_2$SO$_4$ particles, it was observed in many experiments that the phase transition at the deliquescence point is not a sharp function of RH. For these salts, it was found that the humidograms can be divided into three different states. In the following, this classification is exemplified on the basis of the (NH$_4$)$_2$SO$_4$ measurement, and the different states are indicated in Figs. 2.3 and 2.4.

**State a.** The particles in the H-TDMA are always exposed to RH < DRH, and the RH in DMA2 (which determines the final particle size) is <70%. This results in no hygroscopic growth, and the points are located on the lower (“dry”) hysteresis branch. In this range, a reduction of the mobility diameter is often observed and is interpreted as a restructuring of the particles. For the comparison of H-TDMA measurements with theoretical growth curves, the determination of the minimal diameter $D_{min}$ in this RH range is of great importance because $D_{min}$ relates more closely to the volume equivalent diameter of the dry particle (see Part 2 for more details).

**State b.** The aerosol experienced RH > DRH (either in the humidifier or in DMA2), and the RH in DMA2 is larger than the crystallization RH, which is 37% for pure (NH$_4$)$_2$SO$_4$ particles (Oatis et al., 1998). For this condition the points are located on the upper (wet) part of the hysteresis branch.

**State c.** The particles never experienced RH > DRH but the RH in DMA2 is > ~70%. There, as already mentioned, an increase of the particle size is observed for the lower hysteresis curve. This hygroscopic behavior was observed during several measurements although often a smaller gradual onset of deliquescence at RH < DRH was measured (see (NH$_4$)$_2$SO$_4$ measurements in companion paper; Gysel et al., 2002). Up to RH ~77%, this phenomenon is observed for decreasing or increasing RH, which is a strong indication that up to this value the growth is a reversible process and that the particles are present in the form of an internally mixed phase (liquid/solid). Note that near the DRH, at RH 78–79%, two points were measured that are characterized with a relatively broad growth distribution ($\sigma = 1.08$, see Fig. 2.4). Such a gradual onset of deliquescence was also observed in other laboratory studies for pure salt particles with a H-TDMA (Hämmeri et al., 2000) and with light scattering techniques (Dougle et al., 1998). Neubauer et al. (1998) used online laser desorption ionization spectrometry to access humidity effects on single aerosol particles and observed that at RH < DRH similar spectra to those of aqueous droplets were measured. They attributed this water uptake to defects such as cracks on the particles surface. Braun and Krieger (2001) used an electrodynamic balance and observed a “stable” mass increase at RH < DRH for micrometer sized pure NaCl particles. From the analysis of the particle light-scattering intensity fluctuation, they concluded that during deliquescence, water is taken up from the gas phase and forms an aqueous solution shell around the solid particle (Krieger and Braun, 2001).

### 2.3.3 Field Measurements

The Cloud and Aerosol Characterization Experiment (CLACE) was organized at the JFJ research station in Switzerland from February 2 to March 31, 2000 with the participation of eight Swiss, German, and Hungarian institutes. Besides the extensive measurement of aerosol number size distributions, optical properties, volatility, and chemical composition, the hygroscopicity of the particles was measured with two H-TDMA instruments. Our H-TDMA was operated at $T = -10$ °C while the other H-TDMA (Busch et al., 1994)
measured the hygroscopic properties at room temperature (25–30 °C). A comparison of both H-TDMA data sets combined with the data on aerosol volatility and chemical composition will yield detailed information about the nature of the particles and will be the subject of a future manuscript.

During the campaign, the hygroscopic growth of particles with $D_0 = 50, 100, \text{and } 250 \text{ nm}$ was continuously measured at a constant RH of 85% and at $T = -10 ^{\circ} \text{C}$. Most of the time, the station was located in the FT, and the shape of the humidified H-TDMA size spectra were preferentially characterized by a narrow monomodal growth distribution ($\sigma < 1.08$). This implies that the particles in the observed size range were to a large extent internally mixed regarding their hygroscopic properties and hence also chemically. This is in contrast to the behavior of continental polluted aerosols where the particles generally separate into a less and more hygroscopic group. Only during temporally limited periods where the station was influenced by local pollution (mainly due to construction work), bimodal distributions with a more and a less hygroscopic mode were found. The latter mode is clearly attributed to freshly emitted combustion particles emitted from heavy-duty diesel engines, which are known to have a hydrophobic behavior (Weingartner et al., 1997). During periods when the station was exposed to a dust plume from North Africa, $D_0 = 250 \text{ nm}$ particles often exhibited bimodal growth distributions. It was found that Saharan dust particles, which were to some extent also present in the submicrometer size range, were characterized by a low hygroscopicity.

During several episodes, the RH was lowered to measure the RH dependence of the growth factors at $T = -10 ^{\circ} \text{C}$. In this paper we will focus on two such events where the station was clearly located in the FT. Figure 2.5 shows humidograms measured on March 6 and 16, 2000. The data were acquired with a scanning velocity $v_s < 0.0016 \text{ s}^{-1}$ and with a time resolution of 5 min. After 3 scans (i.e., after 15 min) the applied DMA1 voltage was changed such that $D_0 = 50, 100, \text{and } 250 \text{ nm}$ particles were measured alternately with a high temporal resolution. The acquisition of all points in Fig. 2.5 with $20% < \text{RH} < 80%$ lasted only twice for 3 h. Therefore, these humidograms can be considered as a snapshot of current atmospheric conditions.

The relatively high scatter of the $D_0 = 250 \text{ nm}$ data is due to very low inlet concentrations: The average number size distribution over the time periods presented in Fig. 2.5 shows concentrations of $dN/d\log D = 92, 136, \text{and } 63 \text{ cm}^{-3}$ for $D_0 = 50, 100, \text{and } 250 \text{ nm}$, respectively. These measurements clearly show that with the applied SMPS technique data with a good quality and a high temporal resolution can be achieved even at very low number concentrations.

It is interesting to note that the humidograms are characterized by a continuous increase of $D/D_0$ as function of RH – no distinct deliquescence behavior is observed during these increasing RH scans. It is well-known that multicomponent aerosols may exhibit a hysteresis behavior different from pure salts, i.e., the deliquescence humidity DRH of mixed salts is always lower than the DRH of the individual salts in the particle (Tang and Munkelwitz, 1993). DRH is also considerably lowered by the presence of nitrate – a major ionic component found in JFJ samples. The RH of $<10%$ in the DMA1 was obviously not low enough to dry the particles completely, and we presume that the measured particles were always present in a liquid state in the H-TDMA. Since liquid particles are spherical, no shape correction was applied (see Gysel et al., 2002).

The solid line in Fig. 2.5 is an empirical model. The measured growth factors were fitted by the power law expression (Swietlicki et al., 2000):

$$ D/D_0 = (1 - \text{RH}/100\%)^\gamma $$

where the RH is given in percent. The only unknown parameter $\gamma$ was found to be $-0.191$, $-0.210$, and $-0.223$ for $D_0 = 50, 100, \text{and } 250 \text{ nm}$, respectively. This model fits the data.
2.3 Results and Discussion

well and can be used to extrapolate the hygroscopic growth to RH 90%, yielding $D/D_0 = 1.55, 1.62,$ and $1.67$ for $D_0 = 50, 100,$ and $250$ nm, respectively. In this campaign, the dry diameters $D_0$ were determined by a comparison of the output of DMA1 with DMA2 at RH $10\%$. If one assumes that the particles still contain some water at this RH, then these growth factors are underestimated. This error can be estimated by means of the empirical model. According to eq 2.5, the particles exhibit a hygroscopic growth of $D/D_0 \sim 1.02$ at RH $10\%$, which translates into an underestimation of measured growth factors by about $2\%$.

![Figure 2.5](image)

**Figure 2.5:** Humidograms of $D_0 = 50, 100,$ and $250$ nm particles measured at $T = -10^\circ C$ during increasing RH scans at the high-alpine site Jungfraujoch located in the free troposphere. The greater scatter for the $D_0 = 250$ nm particles is due to very low number concentrations. The data points were acquired with a temporal resolution of 5 min.

If one assumes that the particles are composed of an insoluble core with a hygroskopically inactive volume surrounded with soluble material, one can calculate the
soluble volume fraction ($\varepsilon$). Such an analysis has the advantage that the size-dependent Kelvin effect is accounted for, allowing comparison of the hygroscopicity of particles at different sizes in terms of their chemical composition. The hygroscopically inactive volume can be water insoluble (such as elemental carbon), but it may also consist of water-soluble compounds that do not contribute significantly to the hygroscopic growth of particles [e.g., high molecular weight organics such as humic acids as measured by Krivácsy et al. (2001) at JFJ]. Since (NH$_4$)$_2$SO$_4$ was found to be a major component (up to 40%) of the particulate mass at JFJ (Krivácsy et al., 2001), (NH$_4$)$_2$SO$_4$ was chosen as the soluble component in this model. According to Pitchford and McMurry (1994), for sufficiently soluble particles, $\varepsilon$ is given by

$$\varepsilon = \left( \frac{g_{\text{sol}}^3 - 1}{g_{\text{sol}}^3 - 1} \right)$$

(2.6)

where $g_e$ is the observed growth factor and $g_{\text{sol}}$ is the theoretical growth factor of a fully soluble (NH$_4$)$_2$SO$_4$ particle at $T = -10$ °C taken from Gysel et al. (2002). At RH 85%, $\varepsilon$ is found to be 0.79, 0.86, and 0.91 for $D_0 = 50, 100, \text{ and } 250 \text{ nm}$, respectively. If the above-mentioned underestimation in the growth factor is taken into account, $\varepsilon$ is increased to 0.86, 0.94, and 0.99 for $D_0 = 50, 100, \text{ and } 250 \text{ nm}$, respectively. It is interesting to note that $\varepsilon$ increases with increasing particle size. We attribute this to different particle formation processes. Weingartner et al. (1999) showed that especially during the colder seasons the smaller particles ($D < 20 \text{ nm}$) at JFJ are predominantely formed by (photo-) chemical reactions and may grow in size by gas-to-particle conversion whereas larger particles ($D > 100 \text{ nm}$) are advected by (long-range) transport to the station. However, the detailed mechanisms leading to the observed hygroscopic behavior remain to be elucidated.

The determined growth factors at RH 90% can be compared with H-TDMA measurements performed at other remote sites. Swietlicki et al. (2000) report H-TDMA measurements for $D < 50 \text{ nm}$ particles from Izaña, Tenerife (ES), at 2367 m above sea level. This station is influenced by the lower FT from time to time. At this site, bimodal growth spectra for $D_0 = 50 \text{ nm}$ were measured ($D/D_0 = 1.43$ and 1.62 for RH 90% and room temperature), which were attributed to a mixing of different air masses. It was supposed that the more hygroscopic particles probably originated from the marine boundary layer while the less hygroscopic mode was attributed to entrained particles from the lower FT. This is in contrast to our findings: In the FT at JFJ, particles were internally mixed with a higher growth factor (i.e. $D/D_0 = 1.55$ at RH 90% for $D_0 = 50 \text{ nm}$ and $T = -10 \text{ °C}$). The reasons for these differences are at present unknown. One possible reason could be a different chemical FT air mass composition.

A future analysis of the JFJ H-TDMA data sets will provide further information to solve the question to what extent the chemical composition and thus the hygroscopicity of particles will change when they are heated from ambient to laboratory temperature.

### 2.4 Acknowledgments

The financial support of Meteo Swiss (Global Atmosphere Watch) is highly appreciated. In addition, we thank the International Foundation High Altitude Research Stations Jungfraujoch and Gornergrat (HFSJG), who made it possible for us to carry out our experiments at the High Altitude Research Station at Jungfraujoch. We also thank Silvia Henning, Nicolas Bukowiecki, Stefan Nyeki, András Hoffer, Matthias Weller, and Sebastian Schmidt for assistance in field work.
2.5 Literature Cited


3. Hygroscopicity of Aerosol Particles at Low Temperatures

Hygroscopicity of aerosol particles at low temperatures.

2. Theoretical and experimental hygroscopic properties of laboratory generated aerosols

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Abstract. A Hygroscopicity Tandem Differential Mobility Analyzer (H-TDMA) system has been used to measure hygroscopic growth curves and deliquescence relative humidities (DRH) of laboratory generated (NH₄)₂SO₄, NaCl, and NaNO₃ particles at temperatures $T = 20 \, ^\circ C$ and $-10 \, ^\circ C$. Good agreement (better than 3.5%) between measured growth curves and Köhler theory was found using empirical temperature and concentration dependent values for water activity, solution density, and surface tension. The measured growth curves only experience a small temperature dependence in the observed temperature range. Therefore, to a first approximation, it is possible to neglect the temperature dependence of the water activity for theoretical calculations in the temperature range $-10 \, ^\circ C < T < 25 \, ^\circ C$. The small differences between experiment and theory, which were predominantly observed for NaCl particles, are probably caused by a small amount of water adsorbed on the “dry” crystals. It was also observed that these particles experience a significant restructuring at relative humidity RH $<$ DRH, which was also taken into account for a comparison with theoretical curves. If salt particles are used for instrument calibration, precautions regarding the dry particle diameter have to be taken.

3.1 Introduction

Atmospheric aerosols contain a large fraction of ionic species (Heintzenberg, 1989). Most of these species are hygroscopic by nature and exhibit the properties of deliquescence and efflorescence under atmospheric conditions. The hygroscopic properties are important factors affecting air quality, visibility degradation, radiation forcing, and climate change. The relative humidity (RH) dependence of light scattering is one of the parameters needed to estimate the direct climate forcing by aerosol particles (Schwartz, 1996; Charlson et al., 1992). The total scattering cross section of a particle is affected by hygroscopic particle growth particularly in two ways. On one hand the cross section of the particles increases, and on the other hand the Mie scattering efficiency of particles changes (Hegg, 1993). Thus, the dry particle size distribution and the hygroscopic growth factors of the particles in humid air must be known to model the humidity dependence of the light scattering of an aerosol. The growth factors of mixed salt solutions can be determined experimentally.

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Approximations from single salt data are possible, but precise predictions are still an open area of research. While a number of techniques are available (Tang and Munkelwitz, 1994; McMurry and Stolzenburg, 1989; Onasch et al., 1999), Hygroscopicity Tandem Differential Mobility Analyzer (H-TDMA) systems are usually used for the determination of the hygroscopic properties of aerosol particles in field experiments. If analysis is to be conducted in the free troposphere where typical temperatures are below 0 °C, then measurements should ideally be conducted under ambient conditions, as a change in temperature may significantly alter the particle composition. Therefore, a new H-TDMA system working in the temperature range from −20 °C to 30 °C was developed (Weingartner et al., 2002).

While part 1 (Weingartner et al., 2002) describes the system and presents first field measurements at \( T = -10 ^\circ C \), this paper compares experimental growth factors of different salts with theoretical values. The growth factors of laboratory generated single salt (e.g. NaCl or \((NH_4)_2SO_4\)) particles are often used for H-TDMA calibrations. It will be shown that a number of precautions have to be taken into account because the initial dry diameter of these salts may differ from the true volume equivalent diameter by two reasons, i.e., the nonspherical shape and the water content of the dry particles. To avoid this problem, the RH in our setup was determined and calibrated separately by a direct and highly accurate measurement.

In this study, the hygroscopic properties at different temperatures of laboratory generated single salt \((NH_4)_2SO_4\) (ammonium sulfate), NaCl (sodium chloride), and NaNO₃ (sodium nitrate) aerosols were investigated. These salts are common constituents of natural aerosols. Sulfates are a major fraction of the natural ionic aerosol fraction. NaCl is a constituent of maritime aerosols. NaNO₃ is formed by the reaction of sea salt with nitric acid from polluted air masses. Growth curves in humid air and the deliquescence relative humidity (DRH) of \( D_0 = 100 \) nm particles were measured at 20 °C and at −10 °C. In addition, the growth factors of \( D_0 = 50 \) and 100 nm particles at 90% RH with respect to liquid water (at 20 °C) or to ice (at −10 °C) were measured to verify the influence of the Kelvin effect. In this context the independent RH measurement allows a comparison of experimental data with theoretical values to be conducted.

### 3.2 Experimental Section

The growth factors of salt particles were measured with the H-TDMA system described in detail in part 1 (Weingartner et al., 2002). Briefly, a narrow size range of a polydisperse dry aerosol was selected with a first Differential Mobility Analyzer (DMA). This monodisperse aerosol was then humidified, and the resulting size of the wet particles was measured with a Scanning Mobility Particle Sizer (SMPS) consisting of a second DMA and a Condensation Particle Counter. To improve the growth factor measurement accuracy, the dry particle size exiting the first DMA was periodically checked with the second DMA. The RH was determined by measurement of the system temperature and sheath air dew point using dew point sensors. The measurement uncertainty of the RH depends to a first approximation only on the relative calibration difference between the temperature and the dew point, which is better than 0.2 °C.

Artificial aerosol particles were generated by atomization of about 0.02 wt % salt solutions ((NH₄)₂SO₄, purity >99.5%, Fluka; NaCl, >99.5%, Merck; NaNO₃, >99%, Merck) in deionized water (18 MΩ·cm, Millipore). The atomizer (TSI 3076 type) was operated with artificial air (80% N₂ >99.999%, 20% O₂ >99.995%). The solution droplets were dried in a custom-built diffusion dryer (residence time ~300 s).
3.3 Theory

3.3.1 Köhler Theory

The Köhler theory of the growth of aqueous solution droplets in humid air is described in detail in Pruppacher and Klett (1997). In the equilibrium state, the RH is equal to the ratio between the vapor pressure over the solution droplet $e_d$ and the saturation vapor pressure of water $e_w$.

\[
RH[\%] = 100 \frac{e_d}{e_w} \tag{3.1}
\]

The Köhler equation gives the relation between the droplet diameter $D$ and the equilibrium RH

\[
\frac{e_d}{e_w} = a_w S_{\text{Kelvin}} = a_w \exp \left( \frac{4M_w \sigma_{\text{sol}}}{RT \rho_w D} \right) \tag{3.2}
\]

where $a_w$ is the water activity, $S_{\text{Kelvin}}$ is the Kelvin correction factor, $M_w$ is the molar mass, and $\rho_w$ is the density of water, $\sigma_{\text{sol}}$ is the surface tension of the solution, $R$ is the ideal gas constant, and $T$ is the temperature. The vapor pressure over the solution droplet is influenced by the Kelvin and the solution effect. The Kelvin effect describes the increase of the vapor pressure over a curved surface relative to a flat surface. It appears in eq 3.2 as the factor $S_{\text{Kelvin}}$. Dissolved molecules or ions lead to a decrease of the vapor pressure over the solution relative to pure water. The equilibrium RH over a (flat) solution depends on the solute concentration and species and on the temperature, and it is defined as the water activity $a_w$. For diluted solutions the water activity can be approximated by the molar ratio of the water (Raoult’s law), but this approximation should not be applied for concentrated solutions (RH < 90%).

The growth factor $g$ of a spherical particle is defined as the ratio between the particle diameter $D$ in humid air and the volume equivalent diameter $D_0$ of the solid particle:

\[
g(RH) = \frac{D(RH)}{D_0} \tag{3.3}
\]

Theoretical growth factors can be calculated from the solution concentration $c_{\text{sol}}$ (in mass percent), the solution density $\rho_{\text{sol}}$ and the salt density $\rho_s$ by

\[
g \equiv \frac{D}{D_0} = \left( \frac{\rho_s}{c_{\text{sol}} \rho_{\text{sol}}} \right)^{(1/3)} \tag{3.4}
\]

With the water activity $a_w$, the surface tension $\sigma_{\text{sol}}$, and the volume equivalent diameter $D_0$, the equilibrium RH corresponding to this growth factor can be calculated for concentrated solutions (eq 3.2). The empirical values of solution density, water activity, and surface tension as a function of concentration and temperature used for the theoretical calculations are listed in the Appendix (section 3.6).
Below 0 °C the equilibrium vapor pressures over liquid water and ice are different. The Köhler theory (eq 3.2) is valid for liquid droplets at any temperature. For this reason RH always means the humidity relative to the saturation vapor pressure of liquid water if not otherwise stated.

### 3.3.2 Hysteresis Effect

The equilibrium size of salt particles in humid air often shows a hysteresis effect depending on their RH history. A solid particle exposed to increasing RH does not significantly change its size until the DRH is reached and a solution droplet is formed. At the DRH the equilibrium droplet size given by the Köhler equation (eq 3.2) corresponds to a saturated solution droplet. Because of the Kelvin effect, the DRH increases with decreasing particle diameter. A theoretical calculation of the DRH of NaCl particles as a function of the particle size (Cinkotai, 1971) shows that the influence of the Kelvin effect on the DRH can be neglected for particles larger than \( D_0 = 100 \) nm. A further increase of the RH leads to droplet growth in accordance with Köhler theory. Once in the liquid phase, the particle can exist in a metastable equilibrium state as a supersaturated solution droplet at a RH below the DRH. The efflorescence relative humidity (ERH) is given by the supersaturation at which crystallization takes place. Due to insoluble impurities, the crystallization can occur above the ERH.

### 3.4 Results

#### 3.4.1 Shape Correction and Restructuring Below DRH

Theoretical growth factors are calculated with the volume equivalent diameter \( D_0 \), while the H-TDMA measures the mobility diameter \( D_{mob} \), which is only equal to the volume equivalent diameter \( D_0 \) for spherical particles. It is well-known (Pruppacher and Klett, 1997) that dry \((NH_4)_2SO_4\) particles are virtually spherical, while dry NaCl particles are cubic. Therefore the measured mobility diameter \( D_{mob} \) of the dry NaCl particles must be shape corrected to get the volume equivalent diameter \( D_0 \). Because the solution droplets are always spherical, no shape correction is applied for droplets. The aerodynamic drag forces \( F_{drag} \) on nonspherical particles are described with a modified Stokes’ law (Willeke and Baron, 1993)

\[
F_{drag} = \frac{3\pi \eta v D_0 \chi}{C_c(D_0)}
\]  

where \( \eta \) is the gas viscosity, \( v \) is the velocity, \( \chi \) is the dynamic shape factor, and \( D_0 \) is the volume equivalent diameter of the particle. For spherical particles, \( \chi_{sphere} \) has per definition the value 1, while for cubic particles, \( \chi_{cube} \) is equal to 1.08 (Hinds, 1999). The Cunningham slip correction factor \( C_c \) is given in Hinds (1999)

\[
C_c = 1 + \frac{1}{PD} [15.60 + 7.00 \exp(-0.059PD)]
\]  

where \( P \) is the pressure in kPa and \( D \) the particle diameter in µm. The relation between the mobility diameter \( D_{mob} \) and the volume equivalent diameter \( D_0 \) of a cubic particle is

\[
f_{cube} = \frac{D_0}{D_{mob}} = \frac{1}{\chi_{cube} C_c(D_{mob})}
\]
For $D_0 = 100$ nm particles (at 980 mbar air pressure) eq 3.7 yields a correction factor of $f_{cube} = 0.96$, which is applied to the experimental mobility diameter $D_{mob}$ of the solid NaCl particles to obtain the volume equivalent diameter $D_0$.

Figure 3.1 shows the behavior of solid 100 nm NaCl particles below the DRH at $T = 20$ °C. The particle size decreases by up to 9% when the particles are brought from dry air (RH < 20%) to a RH just below the DRH of ~75%. One can imagine that the reduction of the electrical mobility diameter is caused by elimination of particle shape irregularities. The variations between different runs are most probably caused by small variations of the particle generation, such as solution concentration and diffusion dryer condition. Krieger and Braun (2001) studied deliquescence-efflorescence-cycles of NaCl particles in an electrodynamic trap. Repetitions of this cycle with the same particle showed that the optical properties of the newly formed solid particle changed with each repetition even under very similar conditions. This was attributed to variations in the morphology of the newly crystallized particle. The two points highlighted by the arrows had been exposed to RH above 50% in the humidifier before their size was measured at 20–30% RH. Thus they already experienced a certain restructuring resulting in a smaller size than found for other particles of the same run. This indicates that the restructuring process is to some extent irreversible.

![Figure 3.1: Restructuring of 100 nm NaCl particles at 20 °C below the deliquescence point. Arrows denote particles that were exposed to RH above 50% before their size was measured at 20–30% RH. Different symbols are given for different runs.](image)

A restructuring was observed for (NH$_4$)$_2$SO$_4$ particles as well, but the size reduction was always smaller than 2%. A comparison of all measurements of (NH$_4$)$_2$SO$_4$ particles indicates that the restructuring effect is less distinct for smaller particles and for lower temperatures.

In the following, the minimum solid particle diameter $D_{min}$ is chosen to calculate the dry particle volume equivalent diameter $D_0$, which is used as reference for the experimentally determined growth factors. This choice is justified by the fact that experimental growth...
factors relative to $D_{\text{min}}$ were always reproducible in contrast to growth factors relative to the particle diameter at RH < 20%.

3.4.2 Humidograms

Growth curves of laboratory generated $D_0 = 100$ nm $(\text{NH}_4)_2\text{SO}_4$, NaCl, and NaNO$_3$ particles in humid air were measured at 20 °C and −10 °C. Two to five measurement runs were made per salt and per temperature. The results are presented in Figs. 3.2–3.4. RH always denotes the humidity relative to liquid water. The measurement accuracy at 90% (20 °C) and at 81.7% RH (−10 °C) is indicated by the error bar in the charts. The experimental growth factors are sorted by “decreasing RH” and “increasing RH”. Increasing RH means that the particles have not been exposed to higher RH before, which allows the DRH to be measured. Decreasing RH means that the particles have been previously exposed to higher RH. Therefore, if these particles have (not) passed the DRH, these data points are solution droplets (solid particles) on the upper (lower) branch of the hysteresis curve. For further details, the reader is referred to part 1 (Weingartner et al., 2002). Both $(\text{NH}_4)_2\text{SO}_4$ and NaCl particles show the hysteresis effect in the growth curve. Starting at low RH, the dry salt particles do not change their size substantially (except for the restructuring described above) until they reach the DRH and a solution droplet is formed. The small particle growth just below the DRH is most probably caused by water adsorption on imperfection sites of the lattice and is discussed in part 1 (Weingartner et al., 2002).

A further increase of the RH leads to particle growth by condensation of water in accordance with Köhler theory. At decreasing RH, the droplets reduce their size by evaporation of water and can exist below the DRH as metastable supersaturated solutions. A further decrease of the RH down to the ERH leads to crystallization of the droplets. In the operational mode used for this experiment, the ERH was not measured. An upper limit for the ERH is given by the lowest data point on the upper branch of the hysteresis, but the difference to the real ERH depends arbitrarily on the measurement cycle. In addition to the experimental values, theoretical growth curves are plotted in Figs. 3.2–3.4. The curves “Theory” are calculated according to eq 3.2 using salt specific surface tension, solution density, and water activity values. The concentration and temperature dependence of these parameters is considered except for NaNO$_3$ where only water activity values for 25 °C were available (see Appendix, section 3.6). In general, the agreement between experiment and theory is very good. A detailed discussion for each salt is given below.

At temperatures below 0 °C the formation of ice particles has to be taken into account. Possible processes are the nucleation of ice on solid particles and the freezing of solution droplets. The first process cannot take place in the H-TDMA because the setup is designed such that air is never supersaturated relative to the saturation vapor pressure over ice. The second process depends on the freezing point depression due to the solute. The higher the RH, the more dilute the solution droplets and the lower the freezing point depression. For each temperature, there is a lower limit for the relative humidity $\text{RH}_{\text{crit}}$ where droplet freezing is theoretically possible. $\text{RH}_{\text{crit}}$ was calculated from empirical freezing point depressions (Lide, 1998) and theoretical growth factors (cf. Theory, section 3.3). It is found that $\text{RH}_{\text{crit}}$ is almost independent of temperature and salt species and has a value slightly higher (~0.8%) than 100% humidity relative to the ice phase. Therefore, freezing of solution droplets in the H-TDMA is not expected. This is in accordance with the experimental results, because the measured growth factors agree well with the liquid phase theory (Figs. 3.2b, 3.3b, and 3.4b).

3.4.3 $(\text{NH}_4)_2\text{SO}_4$

The experimental results for $D_0 = 100$ nm $(\text{NH}_4)_2\text{SO}_4$ particles at 20 °C are shown in Fig. 3.2a. The experimental growth factors agree well with the theoretical growth curve.
The particles show the hysteresis effect as described above. The deliquescence transition was observed at 80 ± 1.2% RH in good agreement with literature data of 79.9% (Onasch et al., 1999) and 80.3% (Tang and Munkelwitz, 1993), respectively.

The experimental results for $D_0 = 100$ nm (NH$_4$)$_2$SO$_4$ particles at −10 °C are shown in Fig. 3.2b. The experimental growth factors are 2% smaller than the theoretical values over the whole RH range. This is a relatively large difference compared to the experimental variations between the individual experimental runs. The deliquescence transition was observed at 82.5 ± 1.5% RH in agreement with literature data of 82.0% (Onasch et al., 1999) and 82.6% (Tang and Munkelwitz, 1993), indicating that the difference between experiment and theory is real. The constancy of the difference over the whole RH range suggests that the measured minimum diameter at $T = −10$ °C is 2% larger than the real volume equivalent diameter of the particle. This could be caused by remaining small particle shape irregularities at these low temperatures (see above).

The experimental growth factors of the investigated salt particles showed only weak temperature dependence. A theoretical sensitivity analysis was performed, and it was found that the Kelvin effect causes a growth factor reduction of 0.2–0.3% at −10 °C compared to 20 °C and that neglecting the temperature dependence of the water activity causes growth factor errors smaller than 2% at any RH. Therefore, it is a good approximation to use water activity values of 25 °C for the temperature range −10 °C < $T$ < 25 °C. This approximation has the advantage that the concentration dependence of the water activity can be described with a simple third- or fourth-order polynomial compared to the quite extensive semi-empirical water activity models.
3.4.4 NaCl

Solid NaCl particles are cubic, as already mentioned. Therefore, the measured mobility diameters of solid NaCl particles are multiplied by the correction factor $f_{\text{cube}} = 0.96$ to obtain the volume equivalent diameter (see above). The experimental results for $D_0 = 100$ nm NaCl particles at 20 °C are shown in Fig. 3.3a. The NaCl particles show deliquescence at DRH = 75 ± 1.2% at 20 °C in agreement with literature data of 75.4% (Tang and Munkelwitz, 1993). The experimental growth factors are 3.5% smaller than the theoretical values over the whole RH range (cf. curve “Theory”). The same difference between experimental and theoretical growth factors of $D_0 = 96$ nm NaCl particles at 20 °C was observed by Krämer et al. (2000) with a H-TDMA system. The curve “Theory fitted” was fitted to the experimental data by multiplication of the theoretical curve “Theory” with the constant factor 0.965. The excellent agreement of the curve “Theory fitted” with the experimental growth factors supports the assumption that the measured minimum diameter (including the cube correction) is still 3.5% larger than the volume equivalent diameter corresponding to the real amount of salt. Weis and Ewing (1999) measured the water content of 200 nm NaCl particles with infrared absorption spectroscopy. They observed that at RH = 25% NaCl particles contain water in pores and adsorbed on the surface, resulting in a H$_2$O to NaCl molar ratio of about 0.08. The 3.5% difference between experiment and theory observed in this study corresponds to a molar ratio of about 0.17. This is reasonable because in this study the particles are smaller, and the minimum diameter was measured at about 70% RH.

![Figure 3.3](image-url)

**Figure 3.3:** Growth factors of $D_0 = 100$ nm NaCl particles as a function of RH, for $T = 20$ °C (a) and $T = -10$ °C (b).
3.4 Results

The experimental results for $D_0 = 100$ nm NaCl particles at $-10^\circ$C are shown in Fig. 3.3b. The deliquescence transition takes place at $75 \pm 1.5\%$ and is in agreement with literature data of $76.1\%$ (Tang and Munkelwitz, 1993) within the measurement accuracy. Similar to the results at $20^\circ$C the experimental growth factors at $-10^\circ$C are $3.5\%$ smaller than the theoretical values over the whole RH range (cf. curve “Theory”).

Again, the amount of water adsorbed on the particles at RH < DRH reduces the hygroscopic growth factors and might even depend on the particle generation conditions. Therefore, care has to be taken when the hygroscopic growth of salt particles is used for the calibration of H-TDMA measurements, even when the minimum diameter just below the DRH is considered.

3.4.5 NaNO$_3$

Figure 3.4 shows that the NaNO$_3$ particles did not exhibit the deliquescence phenomenon in this experiment. The continuous growth of the particles indicates that they were present as solution droplets all the time. Literature data (Tang and Munkelwitz, 1994) report a hysteresis effect of NaNO$_3$ particles at $25^\circ$C with a DRH of $74.5\%$, and an ERH between $30\%$ and $0.05\%$. These measurements were made with the single-particle levitation technique, where lower RH values can be reached than with the diffusion dryer. The minimum RH in this experiment (about $6\%$ after the diffusion dryer) was obviously not low enough for the spontaneous crystallization of the NaNO$_3$ particles. Because of the missing crystallization, the NaNO$_3$ particles are in the liquid-phase already in the first DMA and have a diameter larger than the volume equivalent diameter of the solute NaNO$_3$. Thus, the droplet diameter measured at the minimal RH ($RH_{\text{min}}$) is divided by the theoretical growth factor $g(RH_{\text{min}})$ ($1.02$ at $20^\circ$C and $6\%$ RH and $1.05$ at $-10^\circ$C and $15\%$ RH, respectively) to deduce the volume equivalent diameter $D_0$.

![Figure 3.4: Growth factors of $D_0 = 100$ nm NaNO$_3$ particles as a function of RH, for $T = 20^\circ$C (a) and $T = -10^\circ$C (b).](image-url)
3. Hygroscopicity of Aerosol Particles at Low Temperatures

The results for \( D_0 = 100 \) nm NaNO\(_3\) particles at 20 °C and at −10 °C are shown in Fig. 3.4. The theoretical growth factors (cf. curves “Theory”) are calculated with empirical water activity values at 25 °C. Again, neglecting the temperature dependence of the water activity yields a good approximation (see above). As the NaNO\(_3\) particles do not show the hysteresis effect, there is no difference between the growth factors measured at increasing and decreasing RH. At both temperatures, the experimental results agree with the theory within the measurement accuracy.

3.4.6 Growth Factors

In addition to the growth curves of \( D_0 = 100 \) nm particles, some growth curves of \( D_0 = 50 \) nm particles were also measured but are not shown here, because the 50-nm particles showed qualitatively the same behavior as the 100-nm particles. Table 3.1 gives growth factors for the \( D_0 = 50 \) and 100 nm particles for 90% RH \((T = 20 \) °C\) and for 81.7% RH \((T = −10 \) °C\), respectively. The latter RH value is chosen, because 81.7% RH at −10 °C is equivalent to 90% humidity relative to ice. The cubic shape of NaCl particles and the growth factor of the NaNO\(_3\) particles in the first DMA (cf. Results for NaNO\(_3\)) are taken into account in the experimental values. The experimental growth factors \( g_{\text{exp}} \) measured in the RH range 90 ± 3% \((T = 20 \) °C\) and 81.7 ± 3% \((T = −10 \) °C\), respectively, were corrected to the desired relative humidity \( RH_{\text{des}} \) with theoretical growth factor values \( g_{\text{th}} \):

\[
g_{\text{exp}} \left( RH_{\text{des}} \right) = g_{\text{exp}} \left( RH_{\text{exp}} \right) \frac{g_{\text{th}} \left( RH_{\text{des}} \right)}{g_{\text{th}} \left( RH_{\text{exp}} \right)}
\]

(3.8)

### Table 3.1: Growth Factors of Salt Particles, Where \( g_{\text{exp}} \) Is the Experimental Growth Factor, \( \Delta g_{\text{exp}} \) Is the Absolute Measurement Uncertainty and \( g_{\text{th}} \) Is the Theoretical Growth Factor\(^a\)

<table>
<thead>
<tr>
<th>salt</th>
<th>( T ) [°C]</th>
<th>( RH ) [%]</th>
<th>( D_0 ) [nm]</th>
<th>( g_{\text{exp}} )</th>
<th>( \Delta g_{\text{exp}} )</th>
<th>( g_{\text{th}} )</th>
<th>( g_{\text{exp}} - g_{\text{th}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\text{NH}_4)_2\text{SO}_4)</td>
<td>20</td>
<td>90</td>
<td>100</td>
<td>1.68</td>
<td>0.05</td>
<td>1.69</td>
<td>−0.01</td>
</tr>
<tr>
<td>((\text{NH}_4)_2\text{SO}_4)</td>
<td>20</td>
<td>90</td>
<td>50</td>
<td>1.66</td>
<td>0.05</td>
<td>1.65</td>
<td>0.01</td>
</tr>
<tr>
<td>((\text{NH}_4)_2\text{SO}_4)</td>
<td>−10</td>
<td>81.7</td>
<td>100</td>
<td>1.46</td>
<td>0.03</td>
<td>1.49</td>
<td>−0.02</td>
</tr>
<tr>
<td>((\text{NH}_4)_2\text{SO}_4)</td>
<td>−10</td>
<td>81.7</td>
<td>50</td>
<td>1.42</td>
<td>0.03</td>
<td>1.46</td>
<td>−0.03</td>
</tr>
<tr>
<td>NaCl</td>
<td>20</td>
<td>90</td>
<td>100</td>
<td>2.29</td>
<td>0.08</td>
<td>2.35</td>
<td>−0.03</td>
</tr>
<tr>
<td>NaCl</td>
<td>20</td>
<td>90</td>
<td>50</td>
<td>2.30</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaCl</td>
<td>−10</td>
<td>81.7</td>
<td>100</td>
<td>1.92</td>
<td>0.04</td>
<td>2.00</td>
<td>−0.04</td>
</tr>
<tr>
<td>NaCl</td>
<td>−10</td>
<td>81.7</td>
<td>50</td>
<td>1.97</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaNO(_3)</td>
<td>20</td>
<td>90</td>
<td>100</td>
<td>1.91</td>
<td>0.08</td>
<td>1.94</td>
<td>−0.01</td>
</tr>
<tr>
<td>NaNO(_3)</td>
<td>20</td>
<td>90</td>
<td>50</td>
<td>1.86</td>
<td>0.08</td>
<td>1.88</td>
<td>−0.01</td>
</tr>
<tr>
<td>NaNO(_3)</td>
<td>−10</td>
<td>81.7</td>
<td>100</td>
<td>1.60</td>
<td>0.04</td>
<td>1.61</td>
<td>−0.01</td>
</tr>
<tr>
<td>NaNO(_3)</td>
<td>−10</td>
<td>81.7</td>
<td>50</td>
<td>1.55</td>
<td>0.04</td>
<td>1.59</td>
<td>−0.02</td>
</tr>
</tbody>
</table>

\(^a\)At −10 °C RH = 81.7% corresponds to 90% humidity relative to ice.

\(^b\)The cubic shape of the dry NaCl particles and the water content of the NaNO\(_3\) droplets in the first DMA are considered in the experimental growth factors.

In Table 3.1, \( \Delta g_{\text{exp}} \) is the absolute measurement uncertainty, while \( g_{\text{th}} \) is the theoretical growth factor. The experimental growth factors agree well with the theoretical values. As discussed above, the differences between theory and experiment for \((\text{NH}_4)_2\text{SO}_4\) and NaCl particles are probably caused by the water content of the dry particles. Due to the Kelvin
effect, the growth factors of the 50-nm particles are smaller than those of the 100-nm particles.

3.5 Acknowledgments

This work has been carried out with financial support from the Bundesamt für Bildung und Wissenschaft, BBW (PARTEMIS project). We thank Ulrich Pöschl and Lutz Krämer for helpful discussions and Peter Häberli for his help in experimental work.

3.6 Appendix

The Köhler theory (cf. section Theory) gives the relation between the RH and the equilibrium droplet diameter (eq 3.2). For the calculation of the theoretical growth curves, concentration and temperature dependent (semi-)empirical values of the solution density, surface tension, and water activity are needed. All functions and values needed for the calculation are listed in this section.

3.6.1 Solution Density

Densities of salt solutions $\rho_{\text{sol}}$ up to high supersaturation are reported in Tang (1997)

$$\rho_{\text{sol}}(T, x) = \rho_w(T) + \sum_i A_i x^i$$  \hspace{1cm} (A3.1)

where $x$ is the salt concentration in mass percent and $T$ is the temperature. The density $\rho_w$ of pure water is tabulated in Lide (1998), and the coefficients $A_i$ are listed in Table 3.2 (Tang, 1997).

Table 3.2: Coefficients for the Calculation of the Density of Salt Solutions (Tang, 1997)

<table>
<thead>
<tr>
<th>salt</th>
<th>$\text{(NH}_4\text{)}_2\text{SO}_4$</th>
<th>$\text{NaCl}$</th>
<th>$\text{NaNO}_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>mass percent range</td>
<td>0–78</td>
<td>0–45</td>
<td>0–98</td>
</tr>
<tr>
<td>$A_1$</td>
<td>5.92</td>
<td>7.41</td>
<td>6.512</td>
</tr>
<tr>
<td>$A_2$</td>
<td>$-5.036 \cdot 10^{-3}$</td>
<td>$-3.741 \cdot 10^{-2}$</td>
<td>$3.025 \cdot 10^{-2}$</td>
</tr>
<tr>
<td>$A_3$</td>
<td>$1.024 \cdot 10^{-5}$</td>
<td>$2.252 \cdot 10^{-3}$</td>
<td>$1.437 \cdot 10^{-4}$</td>
</tr>
<tr>
<td>$A_4$</td>
<td></td>
<td>$-2.06 \cdot 10^{-5}$</td>
<td></td>
</tr>
</tbody>
</table>

3.6.2 Solution Surface Tension

The surface tension of pure water $\sigma_w$ [J/m$^2$] as a function of temperature $T$ [$^\circ$C] is given in Seinfeld and Pandis (1998):

$$\sigma_w(T) = 0.0761 - 1.55 \cdot 10^{-4} \cdot T$$  \hspace{1cm} (A3.2)

The surface tension of a solution $\sigma_{\text{sol}}$ shows in good approximation a linear dependence on the salt molality $m_{\text{salt}}$ (Seinfeld and Pandis, 1998)

$$\sigma_{\text{sol}}(m_{\text{salt}} \cdot T) = \sigma_w(T) + \beta \cdot m_{\text{salt}}$$  \hspace{1cm} (A3.3)
3. Hygroscopicity of Aerosol Particles at Low Temperatures

where $\beta_s$ is a salt specific coefficient and values are listed in Table 3.3 (Chen, 1994).

### Table 3.3: Coefficients for the Calculation of the Solution Surface Tension (Chen, 1994)

<table>
<thead>
<tr>
<th>Salt</th>
<th>(NH$_4$)$_2$SO$_4$</th>
<th>NaCl</th>
<th>NaNO$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta_s$</td>
<td>2.17</td>
<td>1.64</td>
<td>1.12</td>
</tr>
</tbody>
</table>

#### 3.6.3 Water Activity of (NH$_4$)$_2$SO$_4$ Solution

The concentration and temperature dependence of the water activity $a_w$ of electrolyte solutions can be described by Pitzer’s mole fraction based model (Pitzer, 1991). Model parameters for (NH$_4$)$_2$SO$_4$ are published in Clegg et al. (1995), and the water activity is calculated by the following equation

$$\ln(a_w) = \ln(x_w) + \frac{2A I_x^{3/2}}{1 + \rho I_x^{1/2}} - x_M x_Y B_{MX} \exp(-\alpha_{MX} I_x^{1/2}) -$$

$$x_M x_Y B_{MX} \exp(-\alpha_{MX} I_x^{1/2}) + x_I^2 (W_{w, MX} + (x_I - x_w) U_{w, MX} ) +$$

$$4x_w x_M x_Y (2 - 3x_w) V_{w, MX}$$

(A3.4)

The subscripts $w$, $M$, $X$, and $I$ stand for the solvent water, the cation NH$_4^+$, the anion SO$_4^{2-}$, and the sum of these ions, respectively, and $x$ is the molar ratio. The model constants $\rho$, $\alpha_{MX}$, and $\alpha'_I$ are temperature independent. The Debye-Hückel parameter $A_i$ is given for several temperatures in Clegg and Brimblecombe (1995). The coefficients $B_{MX}$, $B_{MX}$, $W_{w, MX}$, $U_{w, MX}$, and $V_{w, MX}$ and their derivatives with respect to temperature are given for 25 °C, and they were integrated to other temperatures. All coefficients for the temperatures 20 °C and −10 °C are listed in Table 3.4.

### Table 3.4: Coefficients To Calculate the Water Activity of (NH$_4$)$_2$SO$_4$ Solution

<table>
<thead>
<tr>
<th>Temp</th>
<th>20 °C</th>
<th>−10 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\rho$</td>
<td>13.0</td>
<td>13.0</td>
</tr>
<tr>
<td>$\alpha_{MX}$</td>
<td>13.0</td>
<td>13.0</td>
</tr>
<tr>
<td>$\alpha'_I$</td>
<td>1.50</td>
<td>1.50</td>
</tr>
<tr>
<td>$A_x$</td>
<td>2.8923</td>
<td>2.7634</td>
</tr>
<tr>
<td>$B_{MX}$</td>
<td>13.7298984</td>
<td>1.1043888</td>
</tr>
<tr>
<td>$B_{MX}'$</td>
<td>−21.3757307</td>
<td>−47.3542891</td>
</tr>
<tr>
<td>$W_{w, MX}$</td>
<td>−2.29903871</td>
<td>−4.6021552</td>
</tr>
<tr>
<td>$U_{w, MX}$</td>
<td>2.165604209</td>
<td>2.564384665</td>
</tr>
<tr>
<td>$V_{w, MX}$</td>
<td>−2.1048037</td>
<td>−1.08506335</td>
</tr>
</tbody>
</table>

#### 3.6.4 Water Activity of NaCl Solution

The water activity $a_w$ is related to the osmotic coefficient $\phi$ by the following equation

$$\ln(a_w) = \phi \ln(x_w)$$

(A3.5)

where $x_w$ is the molar ratio of water.

The concentration and temperature dependence of the osmotic coefficient $\phi$ of electrolyte solutions can be described by Pitzer’s molality based model (Pitzer, 1991)
\[ \phi = 1 + \left| z_M z_X \right| f^\phi + m \frac{2 u_M u_X}{u} B_{MX}^\phi + m^2 \frac{2 (u_M u_X)^{3/2}}{u} C_{MX}^\phi \] (A3.6)

where

\[ u = u_M + u_X \] (A3.7)

\[ f^\phi = -\frac{A_p I_m^{1/2}}{1 + b I_m^{1/2}} \] (A3.8)

\[ A_p = \frac{1}{3} \left( \frac{2 \pi N_0 \rho_w}{1000} \right)^{1/2} \left( \frac{e^2}{D k T} \right)^{3/2} \] (A3.9)

\[ B_{MX}^\phi = \beta_{MX}^{(0)} + \beta_{MX}^{(1)} \exp(-\alpha d_m^{1/2}) \] (A3.10)

\[ \beta_{MX}^{(0)}(T) = w_6 + \frac{w_7}{T} + w_8 \ln(T) + w_9 T + w_{10} T^2 + \frac{w_{11}}{T - 227} + \frac{w_{12}}{680 - T} \] (A3.11)

\[ \beta_{MX}^{(1)}(T) = w_{13} + \frac{w_{14}}{T} + w_{15} T + \frac{w_{16}}{T - 227} \] (A3.12)

\[ C_{MX}^\phi = w_{17} + \frac{w_{18}}{T} + w_{19} \ln(T) + w_{20} T + \frac{w_{21}}{T - 227} \] (A3.13)

**Table 3.5:** Coefficients for the Calculation of the Osmotic Coefficient of NaCl Solution (Mokbel et al., 1997)

<table>
<thead>
<tr>
<th>( w_i )</th>
<th>Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>( w_6 )</td>
<td>25.000115</td>
</tr>
<tr>
<td>( w_7 )</td>
<td>-653.05872</td>
</tr>
<tr>
<td>( w_8 )</td>
<td>-4.4871462</td>
</tr>
<tr>
<td>( w_9 )</td>
<td>0.010995543</td>
</tr>
<tr>
<td>( w_{10} )</td>
<td>-0.0000047</td>
</tr>
<tr>
<td>( w_{11} )</td>
<td>-1.1938067</td>
</tr>
<tr>
<td>( w_{12} )</td>
<td>5.4518092</td>
</tr>
<tr>
<td>( w_{13} )</td>
<td>-0.483091</td>
</tr>
<tr>
<td>( w_{14} )</td>
<td>119.32133</td>
</tr>
<tr>
<td>( w_{15} )</td>
<td>0.0014068</td>
</tr>
<tr>
<td>( w_{16} )</td>
<td>-4.234548</td>
</tr>
<tr>
<td>( w_{17} )</td>
<td>0.40642361</td>
</tr>
<tr>
<td>( w_{18} )</td>
<td>-6.106870</td>
</tr>
<tr>
<td>( w_{19} )</td>
<td>-0.07538358</td>
</tr>
<tr>
<td>( w_{20} )</td>
<td>0.000137088</td>
</tr>
<tr>
<td>( w_{21} )</td>
<td>0.27649564</td>
</tr>
</tbody>
</table>

The model parameters for NaCl salt are published in Mokbel et al. (1997). The constants are as follows: molality \( m \) of the solution, charge \( z_M \) and \( z_X \) and stoichiometric factors \( u_M \) and \( u_X \) of the ions \( M \) and \( X \), Avogadro’s number \( N_0 \), Boltzman constant \( k \), density \( \rho_w \) and dielectric constant \( D \) of water, temperature \( T \) [K], and elementary charge \( e \). The model constants \( b \) and \( a \) have the values 1.2 kg\(^{1/2}\) mol\(^{-1/2}\) and 2.0 kg\(^{1/2}\) mol\(^{-1/2}\), respectively. Values for the Debye-Hückel parameter \( A_p \) are listed in Pitzer (1991). The coefficients \( w_6 \) to \( w_{21} \) for the temperature-dependent ion-interaction parameters \( \beta_{MX}^{(0)}, \beta_{MX}^{(1)} \), and \( C_{MX}^\phi \) are listed in Table 3.5. The molal ionic strength \( I_m \) is defined as \( I_m = 0.5 \sum m_i z_i^2 \), where the summation goes over all ions with molalities \( m_i \) and charges \( z_i \).
3.6.5 Water Activity of NaNO₃ Solution

To our knowledge, there is no literature data available for the calculation of the water activity $a_w$ of NaNO₃ solution at temperatures below 0 °C. As discussed above (cf. Results, section 3.4) it is a good approximation to neglect the temperature dependence of the water activity at temperatures below 25 °C. Therefore, water activity values of NaNO₃ solution at the temperature 25 °C (Tang and Munkelwitz, 1994) are used for the calculation of the theoretical growth curves at 20 °C as well as at −10 °C

$$ a_w = 1.0 - 5.52 \cdot 10^{-3} x + 1.286 \cdot 10^{-4} x^2 - 3.496 \cdot 10^{-6} x^3 + 1.843 \cdot 10^{-8} x^4 $$  \hspace{1cm} (A3.14)

where $x$ is the solute mass percentage.

3.7 Literature Cited


4. Jet Engine Combustion Particle Hygroscopicity

Properties of jet engine combustion particles during the PartEmis experiment: Hygroscopicity at subsaturated conditions


M. Gysel¹, S. Nyeki¹, E. Weingartner¹, U. Baltensperger¹, H. Giebl², R. Hitzenberger², A. Petzold³, and C.W. Wilson⁴

Abstract. Hygroscopic properties of combustion particles were measured online with a Hygroscopicity Tandem Differential Mobility Analyzer (H-TDMA) during PartEmis jet engine combustor experiments. The combustor was operated at old and modern cruise conditions with fuel sulfur contents (FSC) of 50, 410 and 1270 µg g⁻¹, and hygroscopic growth factors (HGF) of particles with different dry diameters were investigated at relative humidities RH ≤ 95%. HGFs increased strongly with increasing FSC (HGF[95% RH, 50 nm, modern cruise] = 1.01 and 1.16 for low and high FSC, respectively), and decreased with increasing particle size at fixed FSC, whereas no significant difference was detected between old and modern cruise. HGFs agreed well with a two-parameter theoretical model which provided an estimate of the sulfuric acid content of dry particles, indicating a nearly linear dependence on FSC.

4.1 Introduction

Possible effects of aviation induced particle emissions in the upper troposphere and the lowermost stratosphere are alteration of natural cirrus clouds (Ström and Ohlsson, 1998) and initiation of formation of additional cirrus clouds (Boucher, 1999). Hygroscopic properties of jet engine combustion particles have been previously investigated in airborne studies (Pitchford et al., 1991; Hagen et al., 1992). These studies have shown that combustion particles originating from standard jet fuel are hygroscopic. Such hygroscopic behavior has been commonly attributed to sulfuric acid adsorbed on black carbon particles, which is known to increase water uptake below saturation (Wyslouzil et al., 1994).

An extensive set of aerosol measurements were conducted on a jet engine combustor test-rig in order to measure the microphysical and chemical properties of combustion particles during the EU PartEmis project (measurement and prediction of emissions of aerosols and gaseous precursors from gas turbine engines) (Wilson et al., 2003). A main focus was the influence of combustor operating conditions and fuel sulfur content (FSC) on particle properties. Microphysical properties and emission indices of combustion particles during the PartEmis test campaign in January to February 2001 are presented by

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Petzold et al. (2003). The hygroscopic properties of the particles at subsaturated conditions are presented in this paper and linked to their behavior at supersaturated conditions in a companion paper (Hitzenberger et al., 2003).

4.2 Methods

The jet engine combustor was operated on a test-rig at QinetiQ, Farnborough, UK. Two different engine operation conditions (old and modern cruise conditions; inlet temperature $T = 566$ and $766 \text{ K}$, respectively) and three different FSC levels ($50$, $410$ and $1270 \text{ µg g}^{-1}$) were investigated. After exit from the combustor, the sample was immediately cooled down to $\sim150 \text{ °C}$, and then diluted by a factor of $\sim65$ with filtered air at about $25 \text{ °C}$. More details of the experimental setup are given by Wilson et al. (2003).

The particle hygroscopic properties were measured at ambient conditions using a Hygroscopicity Tandem Differential Mobility Analyzer (H-TDMA) system, similar to the instrument described by Weingartner et al. (2002). Briefly, a monodisperse fraction of dry combustion aerosol was selected with a first DMA. This monodisperse aerosol was then humidified, and the resulting particle size distribution was measured by scanning the whole size range with a second DMA and Condensation Particle Counter. The H-TDMA was kept at constant temperature ($T \sim 25 \text{ °C}$), and the RH was determined by measurement of the system temperature and sheath air dew point using dew point mirrors. At constant conditions the RH accuracy is $\pm1.2\%$ at $95\%$ RH, but it may be reduced due to RH-changes during the growth factor measurement. The DMAs were operated with a closed-loop sheath air setup, which allows a growth factor accuracy of $\pm0.01$. Hygroscopic growth factors (HGF) $g_{\text{exp}}(RH) = D(RH)/D_0$ were measured in the range $\sim70$ to $95\%$ RH for particles with dry (RH $\leq 7\%$) diameters of $D_0 = 30$, $50$ and $100 \text{ nm}$.

4.3 Theoretical Model

Two different models for the hygroscopic growth of combustion particles, Model A for spherical particles and Model B for agglomerates, are shown in Figs. 4.1a–b, respectively. Both models assume an insoluble soot core surrounded by a sulfuric acid coating under dry conditions. The water content of the sulfuric acid coating depends on RH. At equilibrium the particle diameter of the mixed particle can be described by a theoretical HGF $g_{\text{th}}$ as follows (Pitchford and McMurry, 1994):

$$g_{\text{th}}(RH) = \frac{D(RH)}{D_\varepsilon} = \left[1 + \varepsilon \left(g_{\text{sol}}(RH) - 1\right)^3\right]^{1/3},$$

where $D$ and $D_\varepsilon$ are the humid and dry volume equivalent diameters, respectively, $\varepsilon$ is the soluble volume fraction, and $g_{\text{sol}} = D_{\text{sol}}/D_{\varepsilon,\text{sol}}$ is the theoretical HGF of a pure soluble particle. HGFs $g_{\text{sol}}$ for sulfuric acid are calculated with Köhler theory as described by Gysel et al. (2002). The Kelvin correction is included in the size dependence of $g_{\text{sol}}$, according to Pitchford and McMurry (1994). Empirical values for the water activity and the surface tension of sulfuric acid at room temperature are reported by Tang (1996) and Chen (1994), respectively. Equation 4.1 describes $g_{\text{sol}}(RH)$ in terms of volume equivalent diameters for both Model A and Model B. Experimental results achieved with the H-TDMA are measured and presented in terms of mobility diameters. To compare theoretical ($g_{\text{th}}$) with experimental HGFs ($g_{\text{exp}}$), a mobility correction factor $f$ is introduced: $g_{\text{exp}} = f \cdot g_{\text{th}}$. As mobility and volume equivalent diameters are equal for spherical particles, the mobility correction factor is $f = 1$ for Model A. The sulfuric acid volume fraction $\varepsilon_{\text{A}}$ was adjusted to
fit the experimental HGF at 95% RH. Model B assumes that non-spherical dry particles are transformed into spheres at sufficiently high RH, as a result of water uptake by the soluble coating (reversible) and by restructuring of the insoluble core (irreversible). Therefore the ratio of mobility to volume equivalent diameter decreases with increasing RH until the particle is spherical and hence experimental (mobility) HGFs are smaller than the corresponding volume equivalent values. In order to model mobility growth factors in the high RH range the mobility correction factor \( f \) is used as a RH independent parameter \( f \leq 1 \) in Model B. The two free parameters, \( f \) and \( \varepsilon_B \), were varied to fit experimental HGFs in the range RH = 70–95%.

Figure 4.1: Theoretical models for hygroscopic growth.

Figure 4.2 shows a comparison between measured and theoretical HGFs for \( D_0 = 50 \) nm particles at high FSC and modern conditions. Model A, which does not consider restructuring and shape effects, is not able to satisfactorily describe hygroscopic growth, while Model B agrees well with experimental results at high RH (see Fig. 4.2). Comprehensive investigations of gas and particulate phase exhaust properties as well as modeling approaches indicated that sulfuric acid is mainly responsible for the observed hygroscopic growth, but the minor influences of water-soluble organics, coating-core interactions or mobility correction deficiencies cannot be fully excluded. Model B and experiment differ at low RH, since \( f \) is a constant fitted to high RH HGFs. The absolute difference at RH = 10% (\( 1 - f = 5\% \) in this case) is equal to the sum of reversible shape and irreversible restructuring effects. Despite this small shortcoming, Model B is at present considered to be optimal, and hence only results using this model are presented below.

Figure 4.2: Experimental HGFs compared with two different models. Models A and B were fitted to experimental results at RH = 95% and RH = 70–95%, respectively.
4.4 Results

HGFs of $D_0 = 50$ nm particles for different FSC levels are shown in Fig. 4.3 for modern conditions. Results for old conditions were comparable and are hence not shown here. The combustion particles are not hygroscopic at low FSC with a HGF of only $g_{exp}(95\%) = 1.01$. This is less than the equivalent of one monolayer of water, which can be explained with water adsorption only. Accordingly, the estimated sulfuric acid volume fraction $\varepsilon = 0.6\%$ is negligible. At medium and high FSC, particles are distinctly more hygroscopic with HGFs of 1.10 and 1.16 at RH = 95%, respectively. Due to an identical experimental setup (except for FSC level) this increased water uptake can most likely be attributed to sulfuric acid, which forms during combustion, and adsorbs onto particles during cooling and dilution.

![Figure 4.3: Experimental and theoretical HGFs at FSC = 50, 410, and 1270 $\mu$g g$^{-1}$.](image)

The effect of varying dry diameter $D_0$ at a constant FSC is next considered in Fig. 4.4, which illustrates hygroscopic properties of particles with different $D_0$ at medium FSC and modern conditions. The HGFs of particles with dry diameters $D_0 = 30$, 50, and 100 nm measured at RH = 95% are 1.14, 1.10 and 1.03, respectively. Distinctly increasing HGFs with decreasing dry particle size were observed for all conditions, despite the Kelvin effect which counteracts this tendency. This size dependent hygroscopic behavior is attributed to a higher sulfuric acid volume fraction on smaller particles (see $\varepsilon_B$ in Table 4.1). The observed size dependence of the sulfuric acid fraction at a fixed FSC originates from the relatively larger mass accommodation of smaller particles by condensation of gaseous sulfuric acid. Again, results were similar for old conditions, i.e. differences between old and modern condition were distinctly smaller than the influences of FSC and of particle dry diameter $D_0$.

The width of the monodisperse aerosol size distribution at high RH compared to the original width at low RH provides information about the aerosol mixing state. The standard deviation $\sigma$ increased from 1.048 without humidification to 1.063 at 95% RH ($D_0 = 50$ nm, high FSC), which corresponds to a small range in growth factors from 1.141 to 1.173 (median 1.157). Hence particles were internally mixed with nearly identical hygroscopic properties. The internal mixture was also confirmed by volatility measurements (Petzold et al., 2003) for particles larger than $D_0 = 30$ nm.
4.5  Discussion

The results of all different combustor operating conditions, FSC levels, and particle dry sizes are summarized in Table 4.1. HGFs are given as interpolated (by Model B) experimental values at RH = 95%. The parameters $\varepsilon_B$ and $f$ are the corresponding model parameters for Model B.

Experimental HGFs and estimated sulfuric acid volume fractions $\varepsilon_B$ show that hygroscopic particle properties are comparable at old and modern conditions, whereas the FSC level and particle dry size have a strong influence on the particle hygroscopicity. $\varepsilon_B$ depends nearly linearly on the FSC for a fixed particle size. The trend of increasing $\varepsilon_B$ with decreasing particle size is supported by volatility measurements at 120 °C. In earlier studies, water-soluble volume fractions of combustion particles investigated during airborne experiments were estimated to be ~10% ($D_0 = 34–49$ nm; Hagen et al., 1992), and ~16% ($D_0 = 90–110$ nm; Pitchford et al., 1991). This does not necessarily indicate an opposite trend with particle size compared to our data, since FSC levels were not reported.

Estimated shape and restructuring effects ($1 - f$) increase with increasing HGFs for a fixed particle size, indicating that restructuring occurs only at sufficiently high water uptake. This behavior was corroborated by additional experiments where particles were re-dried, as well as in studies of diesel engine particles (Weingartner et al., 1997). Mobility corrections were larger for smaller particles, which is atypical for combustion particles. This can partially be attributed to the larger growth of smaller particles at a fixed FSC, but model deficiencies could somewhat compromise mobility correction estimates.

Estimates of critical supersaturation $S_{crit} [%] \equiv RH[%] - 100\%$ for droplet activation were obtained from theoretical growth curves (Model B) according to the classical definition of Köhler theory. Increasing hygroscopicity with increasing FSC measured under subsaturated conditions results in lower values predicted for $S_{crit}$. Due to the Kelvin effect $S_{crit}$ is larger for smaller particles, despite the higher water-soluble fraction of small particles.

Hygroscopic properties under subsaturated conditions were also used to estimate cloud condensation nuclei (CCN) concentrations by combining extrapolated $S_{crit}$ values with particle number size distributions measured by a SMPS system (see Petzold et al., 2003), as illustrated in Fig. 4.5. Estimated $S_{crit}$ values at a constant FSC are interpolated with so called critical lines. The critical lines for insoluble but wettable (Kelvin activation) and for pure sulfuric acid particles are also given. The number size distribution (right axis) is given as an example for one high FSC test point. CCN concentrations were also directly
Table 4.1: Summary of Experimental Results and Model Parameters of the Hygroscopic Properties of Combustion Particles

<table>
<thead>
<tr>
<th>Condition</th>
<th>FSC</th>
<th>$D_0$</th>
<th>HGF at 95% RH</th>
<th>$\varepsilon_B$</th>
<th>$f$</th>
<th>$S_{crit}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Old</td>
<td>50</td>
<td>30</td>
<td>1.01</td>
<td>1.2</td>
<td>0.98</td>
<td>4.5</td>
</tr>
<tr>
<td>Old</td>
<td>50</td>
<td>50</td>
<td>1.01</td>
<td>0.7</td>
<td>0.99</td>
<td>2.8</td>
</tr>
<tr>
<td>Old</td>
<td>50</td>
<td>100</td>
<td>1.00</td>
<td>0.1</td>
<td>1.00</td>
<td>1.7</td>
</tr>
<tr>
<td>Modern</td>
<td>50</td>
<td>30</td>
<td>1.02</td>
<td>1.6</td>
<td>0.99</td>
<td>4.2</td>
</tr>
<tr>
<td>Modern</td>
<td>50</td>
<td>50</td>
<td>1.01</td>
<td>0.6</td>
<td>0.99</td>
<td>2.9</td>
</tr>
<tr>
<td>Modern</td>
<td>50</td>
<td>100</td>
<td>1.00</td>
<td>0.2</td>
<td>1.00</td>
<td>1.6</td>
</tr>
<tr>
<td>Old</td>
<td>410</td>
<td>30</td>
<td>1.11</td>
<td>10.0</td>
<td>0.94</td>
<td>2.5</td>
</tr>
<tr>
<td>Old</td>
<td>410</td>
<td>50</td>
<td>1.06</td>
<td>3.4</td>
<td>0.97</td>
<td>1.8</td>
</tr>
<tr>
<td>Old</td>
<td>410</td>
<td>100</td>
<td>1.02</td>
<td>0.7</td>
<td>0.99</td>
<td>1.2</td>
</tr>
<tr>
<td>Modern</td>
<td>410</td>
<td>30</td>
<td>1.14</td>
<td>8.8</td>
<td>0.97</td>
<td>2.5</td>
</tr>
<tr>
<td>Modern</td>
<td>410</td>
<td>50</td>
<td>1.10</td>
<td>5.0</td>
<td>0.98</td>
<td>1.5</td>
</tr>
<tr>
<td>Modern</td>
<td>410</td>
<td>100</td>
<td>1.03</td>
<td>1.2</td>
<td>0.99</td>
<td>1.0</td>
</tr>
<tr>
<td>Old</td>
<td>1270</td>
<td>30</td>
<td>1.28</td>
<td>25.0</td>
<td>0.93</td>
<td>1.7</td>
</tr>
<tr>
<td>Old</td>
<td>1270</td>
<td>50</td>
<td>1.19</td>
<td>13.0</td>
<td>0.93</td>
<td>1.1</td>
</tr>
<tr>
<td>Old</td>
<td>1270</td>
<td>100</td>
<td>1.06</td>
<td>2.7</td>
<td>0.98</td>
<td>0.7</td>
</tr>
<tr>
<td>Modern</td>
<td>1270</td>
<td>30</td>
<td>1.23</td>
<td>21.0</td>
<td>0.93</td>
<td>1.9</td>
</tr>
<tr>
<td>Modern</td>
<td>1270</td>
<td>50</td>
<td>1.16</td>
<td>9.5</td>
<td>0.95</td>
<td>1.2</td>
</tr>
<tr>
<td>Modern</td>
<td>1270</td>
<td>100</td>
<td>1.07</td>
<td>3.0</td>
<td>0.97</td>
<td>0.7</td>
</tr>
</tbody>
</table>

The accuracy of experimental growth factors is limited by counting statistics, and it is better than ±0.01. The sample variability is of the order of ±0.02 and ±0.03 at medium and high FSC, respectively.

Figure 4.5: Critical supersaturation for droplet activation as a function of dry particle size.
measured (Hitzenberger et al., 2003) at a supersaturation of $S_{CCNC} = 0.755\%$ at this test point, indicated by the horizontal dash-dotted line. The intersections (O) of this line with the critical lines for Kelvin activation ($D_{crit} = 280$ nm), sulfuric acid ($D_{crit} = 30$ nm), and partially soluble high FSC level combustion particles ($D_{crit} = 92$ nm) mark the corresponding critical activation diameters $D_{crit}$. Integration of the number size distribution above these critical diameters then provides the estimated CCN concentrations for this specific high FSC test point under the assumption of Kelvin activation, sulfuric acid, and partially soluble combustion particles, respectively. Square symbols in Fig. 4.5 mark the critical diameters at $S_{CCNC} = 0.755\%$ for low ($D_{crit} = 246$ nm) and medium FSC ($D_{crit} = 138$ nm) combustion particles. Estimated activation diameters agree with activation diameters obtained from measured CCN concentrations and number size distributions within ±16% at low and medium FSC and within ±36% at high FSC for both cruise conditions (see Hitzenberger et al. (2003) for detailed comparison), which is fair agreement when considering the above assumptions.

4.6 Conclusions

This study showed that water uptake by combustion particles under subsaturated conditions is generally independent of combustor operating conditions evaluated, but increases significantly with increasing FSC level, which is attributed to an increasing amount of sulfuric acid adsorbed on the particles. This results in a reduction of the critical diameter for droplet activation at supersaturated conditions, confirmed by a comparison with measured CCN concentrations. Particulate aircraft emissions acting as CCN or ice nuclei might modify natural cirrus clouds or induce additional cirrus cloud formation. This potential impact is expected to increase with increasing FSC level. On the other hand, the influence of FSC level on contrail formation has been shown to be small (Schumann et al., 2002), although the observed trends of slightly increased threshold temperature and increased ice particle number concentration agree with a reduction of critical supersaturation for CCN activation as deduced from the results in this study.

4.7 Acknowledgments

The PartEmis project is funded by the European Commission and by the Swiss Bundesamt für Bildung und Wissenschaft under contract no. G4RD-CT-2000-00207 and 99.0632, respectively. The support of the QinetiQ test-rig operation crew during the experiments is highly appreciated.

4.8 References

4. Jet Engine Combustion Particle Hygroscopicity


5. CCN Activation of Jet Engine Combustion Particles

Properties of jet engine combustion particles during the PartEmis experiment. Hygroscopic growth at supersaturated conditions


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Abstract. During the EU Project PartEmis, the microphysical properties of aircraft combustion aerosol were investigated. This study is focused on the ability of exhaust aerosols to act as cloud condensation nuclei (CCN). The combustor was operated at two different conditions representing old and modern aircraft engine technology. CCN concentrations were measured with the University of Vienna CCN counter (Giebl et al., 2002) at supersaturations around 0.7%. The activation ratio (fraction of CCN in total aerosol) depended on the fuel sulphur content (FSC) and also on the operation conditions. CCN/CN ratios increased from 0.93 through 1.43 to 5.15 \( \cdot 10^{-3} \) (old cruise conditions) and 0.67 through 3.04 to 7.94 \( \cdot 10^{-3} \) (modern cruise conditions) when FSC increased from 50 through 410 to 1270 µg/g. The activation behaviour was modelled using classical theories and with a semi-empirical model (Gysel et al., 2003) based on measured hygroscopicity of the aerosol under subsaturated conditions, which gave the best agreement.

5.1 Introduction

Emissions of particles by aircraft contribute to the aerosol in the upper troposphere and lowermost stratosphere (UTLS) and are currently under intense investigation (IPCC, 2001). Insoluble carbonaceous particles emitted from aircraft engines play an important role in contrail formation (Kärcher, 1999) and have a high potential to initiate cirrus cloud formation via heterogeneous freezing processes. They require saturation ratios close to unity with respect to liquid water at typical UTLS temperatures for ice nuclei (IN) activation. A coating with H₂SO₄ reduces the critical saturation ratio considerably (DeMott et al., 1997).

Previous laboratory studies investigated the activation ratio \( R_{act} \) (defined as the number fraction of CCN) in combustion aerosols at liquid water supersaturations \( \leq 1\% \). Reported values of the \( R_{act} \) vary from 0.008 (Hudson et al., 1991) to 0.3 (Whitefield et al., 1993). In situ measurements in aircraft plumes yielded \( R_{act} \) from \( \leq 0.01 \) (Pitchford et al., 1991) to 0.5 (Hudson and Xie, 1998) at a supersaturation of 0.8–1.0%. Comparable measurements for

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5. CCN Activation of Jet Engine Combustion Particles

IN activation are not available. A maximum IN-$R_{act}$ of about 0.2 was estimated from near field measurements in an aircraft plume (Petzold et al., 1997).

In the framework of the PartEmis project (Wilson et al., 2003) the effect of operation conditions and fuel sulphur content (FSC) on the microphysical and chemical properties of the emitted particles was investigated. This paper will focus on the CCN activation of combustion aerosol particles. Microphysical and chemical properties (Petzold et al., 2003) and the hydration properties at water subsaturated conditions (Gysel et al., 2003) are investigated elsewhere.

5.2 Experimental Methods

The combustor of the QinetiQ TRACE engine (Wilson et al., 2003) was operated at two conditions with different inlet temperatures representing the gas path temperatures of older ($T = 566$ K, “old operating conditions”) and more modern ($T = 766$ K, “modern operating conditions”) jet engines. Fuels with three different sulphur contents (FSC; 50, 410 and 1270 $\mu$g g$^{-1}$) were used. A sampling probe was moved stepwise with 11 different positions through the combustor exit plane. Each sampling condition (probe position, FSC and operation condition) was assigned a test point number. The exhaust gas was cooled immediately to 150 °C. Part of this cooled exhaust was diluted ca. 70 ms after entering the sampling probe by a factor of about 65 using pre-filtered ambient air which resulted in a sample temperature between 20 and 25 °C, relative humidity $\leq$10% and pressure of 1020–1050 hPa). All instruments providing data for this study were sampling from the diluted line. The travel time of the aerosol between the sampling ports of the CN and humidity and volatility DMAs and the CCN counter was ca. 0.2 sec. Because of the high dilution and large line diameter (21.2 mm), no appreciable losses of particles are expected between the sampling ports, so the data should be comparable.

The CCN concentration was measured at supersaturations $S$ between 0.53 and 0.75% in the diluted sample stream with the University of Vienna cloud condensation nuclei counter (CCNC-Univ; Giebl et al., 2002), which is based on a static thermal diffusion chamber. CCN that can be activated at the selected $S$ grow to large (>10 µm) droplets which are illuminated by a laser beam, photographed with a CCD camera (sampling frequency of 15/sec) and counted on-line. The counting efficiency was 1.0 ± 0.09.

5.3 Theoretical Models

5.3.1 Classical Models (Köhler, Kelvin, Coated Sphere)

CCN are a subset of the atmospheric aerosol and are defined as particles that undergo (theoretically) unlimited growth when exposed to a water vapour supersaturation equal to or larger than a specified $S$ in a CCN counter. The equilibrium size of soluble particles is described by Köhler theory, while Kelvin theory describes the equilibrium diameter for insoluble but wettable particles (e.g., Pruppacher and Klett, 1997). In this paper, we used the equations given by Giebl et al. (2002) to calculate the activation diameters of soluble and insoluble particles for the $S$ set in the CCNC. As the predominantly insoluble combustion particles are known to contain also some volatile, semivolatile, and water soluble material, we used also a modified Köhler equation for a particle with an insoluble core and a coating of a soluble substance (coated sphere model) (Pruppacher and Klett, 1997). Volatility measurements (Petzold et al., 2003) gave volatile mass fractions of 1, 3 and 5% for low, mid and high FSC in the size range of CCN.
All the models described in this section assume spherical particles or aqueous solution droplets containing only a single solute with well defined physico-chemical properties. In the case of our measurements, neither the full chemical composition of the material nor the variation in chemical composition of particles in a narrow size class are known, so we assumed the volatile and/or soluble material to be H₂SO₄.

5.3.2 HTDMA Model

The humidity growth of the combustion aerosol was investigated under subsaturated conditions (Gysel et al., 2003) with a hygroscopicity tandem differential mobility analyser (H-TDMA) for size fractions 30, 50 and 100 nm. Experimental growth factors were fitted by a semi-empirical model (HTDMA model), assuming an insoluble core with a H₂SO₄ shell of variable thickness. Potential restructuring of the core was also included. Estimates of the volume fraction ε of H₂SO₄ showed a marked decrease of ε for increasing particle size. The ε were similar to or smaller than the volatile fractions (e.g. for particles of \(D = 100\) nm, \(ε = 0.2, 1.2,\) and \(3\%\) for modern cruise conditions and low, medium, and high FSC) in the size range of measured activation diameters. Extrapolation of modelled growth curves to supersaturated conditions yielded size dependent critical \(S\) values, which were used to estimate CCN concentrations (details in Gysel et al., 2003). Error bars in Fig. 5.3 indicate the sensitivity of CCN estimates to lower and upper limits of HTDMA model parameters.

5.4 Results

5.4.1 Measured and Modelled CCN Activation

CCN concentrations were measured at each test point. At the beginning of the measurement period, \(S\) was unstable because of technical reasons. The first five data points for old cruise conditions and low FSC are therefore not considered in the discussion of CCN properties. As expected, the CCN concentration increased with increasing FSC (see Fig. 5.3 below, concentrations multiplied by the dilution ratio for comparability with other studies). The most interesting parameters for activation studies, however, are the activation ratio \(R_{act}\) and the apparent activation diameter, which is the minimum diameter of a dry combustion particle that may be activated as a CCN at a certain supersaturation.

During PartEmis, the total CN concentration \((D ≥ 10\) nm) was measured with CN counters (Petzold et al., 2003) and the number size distribution was measured with an SMPS system (Scanning Mobility Particle Spectrometer) (Wilson et al., 2003) for all test points and fitted with lognormal functions. In general, the shape of all measured distributions was found to be rather similar. Both the average value over all probe positions and the standard deviation of the count median diameter (CMD, see Table 5.1) of these fitted distributions depended only very weakly on operation conditions or FSC. At the large particle end, however, where concentrations are very low, the measured data points scattered widely. As potential CCN have sizes in this range, the measured distributions were used rather than the fitted lognormal ones to calculate \(R_{act}\) and the apparent activation diameter.

As a first step, an apparent activation diameter (CCN-D) was obtained from the measured size distributions as the lower cut size leading to number concentrations equal to the measured CCN concentrations. CCN-D decrease from 237 and 301 nm at low FSC to 147 and 146 nm at high FSC for old and modern cruise conditions, respectively. Activation diameters were also calculated for all models. Table 5.1 shows these diameters as averages...
over all probe positions for each operation condition and all models, while Fig. 5.1 gives the values for all the test points.

The Köhler model (H₂SO₄ particles) predicts critical diameters that are distinctly (80% to 90%) smaller than measured CCN-D which is expected because large combustion particles are not completely water soluble. The assumption of completely insoluble particles (Kelvin model) provides the largest critical diameters. Kelvin-D are 26 and 8% at low FSC and 98 and 98% at high FSC larger than CCN-D under old and modern conditions. This indicates that the soluble fraction of the particles increases from low FSC to high FSC level. The coated sphere model (Coated-D) underestimates critical diameters by 45 to 55% under all conditions. The HTDMA model (HTDMA-D) provides the best predictions of CCN-D. HTDMA-D agree within ±16% with CCN-D at low and medium FSC. At high FSC HTDMA-D are 36% smaller than CCN-D.

### Table 5.1: Average Values (Top Lines) and Standard Deviations (Next Lines) Over All Test Points Within One Set of Measurements of Apparent Activation Diameters (CCN-D). Predicted Activation Diameters for all models (Kelvin-D, Köhler-D, Coated-D, and HTDMA-D)

<table>
<thead>
<tr>
<th>Test Condition</th>
<th>OL</th>
<th>OM</th>
<th>OH</th>
<th>ML</th>
<th>MM</th>
<th>MH</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCN D, nm</td>
<td>244.3</td>
<td>200.3</td>
<td>146.9</td>
<td>301.1</td>
<td>179.6</td>
<td>145.6</td>
</tr>
<tr>
<td></td>
<td>13.4</td>
<td>18.4</td>
<td>16.7</td>
<td>43.5</td>
<td>13.4</td>
<td>11.2</td>
</tr>
<tr>
<td>Kelvin D, nm</td>
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<td>290.3</td>
<td>324.3</td>
<td>315.7</td>
<td>288.5</td>
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<td></td>
<td>10.5</td>
<td>2.4</td>
<td>3.5</td>
<td>11.7</td>
<td>7.2</td>
<td>6.0</td>
</tr>
<tr>
<td>Koehler D, nm</td>
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<td>30.1</td>
<td>29.7</td>
<td>32.0</td>
<td>31.4</td>
<td>29.6</td>
</tr>
<tr>
<td></td>
<td>0.7</td>
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<td>0.2</td>
<td>0.8</td>
<td>0.5</td>
<td>0.3</td>
</tr>
<tr>
<td>Coated D², nm</td>
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<td>94</td>
<td>79</td>
<td>137</td>
<td>99</td>
<td>79</td>
</tr>
<tr>
<td></td>
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<td>0</td>
<td>0</td>
<td>4</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>HTDMA D, nm</td>
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<td>208</td>
<td>94</td>
<td>292</td>
<td>157</td>
<td>93</td>
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<tr>
<td>CMD, nm</td>
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<td>4.8</td>
<td>4.8</td>
<td>1.9</td>
<td>3.3</td>
<td>2.8</td>
</tr>
<tr>
<td>CCN activation ratio · 10⁻³</td>
<td>1.00</td>
<td>1.43</td>
<td>5.15</td>
<td>0.67</td>
<td>3.04</td>
<td>7.94</td>
</tr>
<tr>
<td></td>
<td>0.34</td>
<td>0.51</td>
<td>0.72</td>
<td>0.19</td>
<td>0.80</td>
<td>3.83</td>
</tr>
</tbody>
</table>

The count median diameters (CMD) of the number size distributions and the activation ratios (fractions of CCN-activated particles relative to the total particle concentration) are also given.

*Volatile fractions 1, 3, and 5% for low, medium, and high FSC.

The effect of cruise conditions on the CCN-D is unclear (see Table 5.1 and Fig. 5.1). Differences between old and modern cruise conditions are +26, −10, and −1% at low, medium and high FSC. Similar trends were observed for hygroscopic properties under subsaturated conditions (Gysel et al., 2003), which is reflected by differences of predicted HTDMA-D between old and modern cruise conditions of +5.4, −25, and −1% for low, medium and high FSC.

The ratio ($R_{act}$) of measured CCN concentrations to the total number concentrations of particles $\geq 10$ nm was calculated for all conditions. For modelling $R_{act}$, estimated CCN concentrations obtained by summing the size distributions using the activation diameters as lower cut size were used. Figure 5.2 shows measured as well as the modelled $R_{act}$ for all test points. The measured $R_{act}$ at low FSC are near the Kelvin $R_{act}$ and increase with increasing FSC without reaching $R_{act}$ calculated with the coated sphere model.

Compared to typical ambient atmospheric aerosols, where CCN/CN ratios are of the order of 0.2 to 0.6 for maritime air and 0.004 to 0.02 for continental air (Pruppacher and
5.4 Results

Klett, 1997), measured $R_{act}$ in the combustor exhaust is low with values around 0.001 at low and mid FSC and 0.01 at high FSC (see Table 5.1). The values are within the range given in the literature (see Introduction, section 5.1) for combustion and aircraft aerosol, but significantly lower than 0.3 as found by Whitefield et al. (1993) for ca. 1000 ppm FSC and 0.5 (Hudson and Xie, 1998). Part of this difference could be due to different $S$ (the high literature values were obtained for $S = 0.8–1\%$) or FSC (not always reported).

Figure 5.1: Apparent activation diameter for old and modern conditions (open triangles and solid diamonds, resp.); theoretical values for the Kelvin (insoluble), Köhler ($H_2SO_4$), coated sphere (coated insoluble) and HTDMA model are added as lines. X values are test point numbers.

Figure 5.2: Fraction of CCN-activated combustion aerosol particles (≥10 nm) at a supersaturation of 0.7%; values are given for old (open triangles) and modern (solid diamonds) conditions, lines refer to predictions of the Köhler (solid) and Kelvin (dashed), coated sphere (dotted) and HTDMA model (dashed-dotted). X values are test point numbers.
5.4.2 Estimated CCN Concentrations

As an example, estimated CCN concentrations are shown in Fig. 5.3 for modern cruise conditions (all FSC). For low FSC the activation of the particles seems to follow Kelvin theory, while the increased $\text{H}_2\text{SO}_4$ content under mid and high FSC results in an enhanced activation. For low FSC, both Kelvin activation and the HTDMA model reproduce the measured CCN concentrations best. For mid and high FSC the measured concentrations are best reproduced by the HTDMA model, which overestimates the CCN concentrations under modern cruise conditions only by factors of about 2 and 7. For old cruise conditions, the modelled CCN concentrations are 0.5 and 0.7 (low and mid FSC) and 8 (high FSC) times the measured concentrations.

![Figure 5.3: Measured CCN concentrations (diamonds) compared to CCN concentrations estimated from the models for modern cruise conditions and low (left), medium (centre) and high FSC (right). The error bars correspond to the maximum and minimum CCN concentrations estimated from the HTDMA model. Full lines: Kelvin, squares: HTDMA, dotted: coated sphere. Topmost line: Köhler model.](image)

5.5 Discussion

The measured $R_{\text{act}}$ and activation diameters depend on the FSC. CCN-D decreases with increasing fuel sulphur content. These findings agree well with the hygroscopic behaviour at subsaturated conditions (Gysel et al., 2003). All calculated activation diameters are in the size range (ca. 30–300 nm) where the aerosol was found to be completely internally mixed with respect to volatile and semivolatile material (Petzold et al., 2003) as well as to their hygroscopic behaviour (Gysel et al., 2003).

Regarding all FSC, the coated sphere model reproduces CCN-D best among the classical models, but predicted values are 45 to 55% smaller. In the case of $R_{\text{act}}$, the Kelvin model gives the best fit among the classical models under low FSC and also at medium FSC and old cruise conditions. On the other hand, the HTDMA model, which uses parameters measured under subsaturated conditions, gives the best fit to the measured data under all conditions.
Several interpretations of these findings are possible. Calculations of the activation diameter of spherical particles coated with 1% H$_2$SO$_4$ showed that the thickness of the shell would be only 0.43 and 0.46 nm (for old and modern conditions), which is insufficient for coating the insoluble core with a monolayer of H$_2$SO$_4$ molecules. At medium and high FSC, the layer thickness is 1 nm and 1.3 nm. In both these cases, contiguous H$_2$SO$_4$ layers are theoretically possible. If the soluble material is not distributed evenly among all particles in the size range of possible CCN, only the particles with the largest fractions of this material will be activated. The combustion particles collected at 150 °C contain about 30% OC by mass (Petzold et al., 2003). Some of this OC could be water soluble and/or surface active or could form a surface film that might inhibit water uptake to some extent. The presence of soluble material other than H$_2$SO$_4$ will influence the activation behaviour of combustion particles, but the available information is insufficient to predict this influence.

5.6 Summary and Conclusions

In the combustion aerosol, measured CCN (at $\approx$0.7% supersaturation) activation ratios $R_{act}$ depended on FSC. An increase of FSC by a factor of 25 resulted in an increase of the $R_{act}$ by a factor of 12. The $R_{act}$ determined in this experiment are 0.001 and 0.008 at low and high FSC, which is low compared to literature values. Except for the low FSC case, the more modern operation conditions produced $R_{act}$ that were nearly twice as high as those for the old conditions. Apparent activation diameters were found to decrease from 236.6 and 301.1 nm at low FSC to 146.9 and 145.6 nm at high FSC for old and modern conditions. The Köhler model (soluble particles) cannot reproduce measured activation properties. The Kelvin model (insoluble but wettable particles) provides good predictions for low FSC, but activation diameters (ratios) are increasingly overestimated (underestimated) at medium and high FSC. This indicates that the soluble fraction of the combustion particles increases from low values at low FSC level to relatively large values at high FSC. The coated sphere model, which equates the measured volatile fraction with soluble H$_2$SO$_4$, underestimates the activation diameter by 45 to 55% under all conditions. A small amount of semivolatile organics with low or absent water-solubility adsorbed on the combustion particles might be one reason for this discrepancy. The HTDMA model, which also assumes that the hygroscopic material is H$_2$SO$_4$, but estimates CCN concentrations using parameters obtained from the hygroscopicity measurements, gives the best fit to the measured data for all FSC levels.

5.7 Acknowledgments

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5.8 References

5. CCN Activation of Jet Engine Combustion Particles


6. Hygroscopicity of Humic-Like Organic Matter

Hygroscopic properties of water-soluble matter and humic-like organics in atmospheric fine aerosol

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Abstract. Ambient continental-rural fine aerosol (K-puszta, Hungary, PM₁.₅) was sampled on quartz fibre filters in winter and summer 2001. Water-soluble matter (WSM) was extracted in MilliQ-water, and, in a second step, solid phase extraction was used to isolate the less hydrophilic fraction (ISOM) of the water-soluble organic matter (WSOM) from inorganic salts and remaining most hydrophilic organic matter (MHOM). This approach allowed to investigate a major fraction of WSOM isolated in pure form from ambient aerosols. Hygroscopic properties of both WSM and ISOM extracts as well as of aquatic reference fulvic and humic acids were investigated using a Hygroscopicity Tandem Differential Mobility Analyser (H-TDMA). ISOM deliquesced between 40–60% and 30–55% relative humidity (RH), in winter and summer, respectively, and hygroscopic growth factors at 90% RH were 1.08–1.11 and 1.16–1.17. The hygroscopicity of ISOM is comparable to secondary organic aerosols obtained in smog chamber experiments, but lower than the hygroscopicity of highly soluble organic acids. Hygroscopic behaviour of investigated fulvic and humic acids had similarities to ISOM, but hygroscopic growth factors were slightly smaller and deliquescence was observed at higher RH (75–85% and 85–95% RH for fulvic acid and humic acid, respectively). These differences probably originate from larger average molecular weight and lower solubility of fulvic and humic acids.

Inorganic composition data, measured ISOM hygroscopicity, and a presumable value for the hygroscopicity of the small remaining MHOM fraction were used to predict hygroscopic growth of WSM extracts. Good agreement between model prediction and measured water uptake was observed with differences (by volume) of +1% and −5% in winter, and −18% and −12% in summer. While deliquescence properties of WSM extracts were mainly determined by the inorganic salts (42–53 wt % of WSM), the WSOM accounted for a significant fraction of particulate water. At 90% RH, according to model predictions and measurements, about 80% (62%) of particulate water in winter (summer) samples are associated with inorganic salts and about 20% (38%) with WSOM. The relative contributions of both distinguished WSOM fractions, ISOM and MHOM, remain uncertain since

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MHOM was not available in isolated form, but the results suggest that the less abundant MHOM is also important due to its presumably larger hygroscopicity.

6.1 Introduction

Hygroscopic growth of atmospheric aerosol particles plays an important role in numerous atmospheric processes such as climate forcing, visibility degradation, cloud formation and heterogeneous chemistry. In recent years the influence of inorganic salts on these effects has been mainly investigated. Only several inorganic salts constitute the major part of the inorganic aerosol fraction (Heintzenberg, 1989), which is relatively well-characterised regarding its hygroscopic properties (Clegg et al., 1998; Ansari and Pandis, 1999). However, recent experimental and modelling studies strongly indicate that water-soluble organic matter (WSOM) contained in atmospheric aerosol particles is also important. It was also suggested, based on the partitioning of WSOM and water-insoluble organic matter (WINSOM) between fog droplets and interstitial aerosol particles, that WSOM plays an important role in the droplet nucleation process (Facchini et al., 1999). Furthermore organic species are potential candidates to delay or inhibit efflorescence (Choi and Chan, 2002a) of atmospheric aerosols.

WSOM, in contrast to the inorganic aerosol fraction, is composed of hundreds (or even thousands) of individual species (Saxena and Hildemann, 1996), where each contributes only a small mass fraction towards WSOM. Different approaches are generally used to determine the influence of WSOM on the hygroscopic behaviour under subsaturated RH conditions of ambient aerosols. Previous laboratory studies, investigating the hygroscopic properties of organic model substances, have mostly focused on pure and mixed low molecular weight organic acids such as carboxylic acids, dicarboxylic acids, and multifunctional organic acids or their salts (Na et al., 1995; Peng et al., 2001; Peng and Chan, 2001; Prenni et al., 2001; Choi and Chan, 2002b), and on their mixtures with inorganic salts (Cruz and Pandis, 2000; Lightstone et al., 2000; Choi and Chan, 2002a,b; Hämeri et al., 2002). First theoretical models for the prediction of the hygroscopic growth of mixed inorganic/organic aerosols were recently introduced by several investigators (Clegg et al., 2001; Ming and Russell, 2001; Ming and Russell, 2002). The hygroscopic properties of artificial secondary organic aerosol obtained by oxidation of typical volatile organic precursors in smog chambers have also been investigated (Virkkula et al., 1999; Cocker III et al., 2001a,b; Saathoff et al., 2003). Apart from the hygroscopic properties of organics under subsaturated conditions, their cloud condensation nuclei activity under supersaturated conditions has also been investigated in recent studies (Cruz and Pandis, 1997; Cruz and Pandis, 1998; Corrigan and Novakov, 1999; Prenni et al., 2001; Giebl et al., 2002).

It is more difficult to determine the influence of WSOM in real ambient particles. Towards this aim, hygroscopicity measurements are generally combined with chemical analysis of the inorganic and organic aerosol fractions. Excess water, which cannot be explained by the water uptake of the inorganic aerosol fraction, is then attributed to the organic aerosol fraction. Depending on the sampling location, considerable amounts of excess water have been reported in field studies by (Saxena et al., 1995; Swietlicki et al., 1999; Dick et al., 2000; Speer et al., 2003) when using this method.

The solid phase extraction method, recently developed and characterised by Varga et al. (2001), allows a major fraction of WSOM (so-called isolated organic matter, ISOM, mainly less hydrophilic compounds) to be isolated from total water-soluble matter (WSM). Several studies on ISOM from atmospheric aerosols at the high-alpine site Jungfraujoch, Switzerland (Krivácsy et al., 2001) and at the continental-rural site K-puszta, Hungary (Varga et al., 2001; Kiss et al., 2002; Galambos et al., 2003) showed that ISOM mainly
6.1 Introduction

consists of humic-like substances and that it contributes up to 70 wt % to WSOM. The remaining smaller fraction of WSOM, which cannot be isolated from inorganic salts so far, consists of the most hydrophilic organic matter (MHOM). Figure 6.1 illustrates the classification scheme defined according to the chemical characterisation applied in this study. A complete list of acronyms and symbols is provided in the glossary (section 6.6).

In order to further characterise the water-soluble organic aerosol fraction, WSM and ISOM were extracted from fine aerosol filter samples obtained during summer and winter field campaigns at the Hungarian Global Atmosphere Watch (GAW) site K-puszta. These WSM and ISOM extracts were characterised by Galambos et al. (2003) and Nyeki et al. (2003) regarding their chemical properties and volatility, respectively, and their hygroscopic properties were investigated in this study using a Hygroscopicity Tandem Differential Mobility Analyser (H-TDMA) (Rader and McMurry, 1986). Hygroscopic properties of aquatic reference fulvic and humic acids were also investigated for comparison with ISOM, since ISOM has been shown to have many chemical similarities with humic substances. Furthermore, comprehensive chemical information about the WSM samples and measured ISOM properties were used to model the hygroscopic growth of WSM in order to assess the contribution of WSOM to the total particulate water. Apart from these main topics, these experiments revealed unusual hysteresis behaviour of the humic substances and ISOM samples, which was further investigated in specific hydration/dehydration experiments.

6.2 Experimental Methods

6.2.1 Aerosol Sampling, Sample Preparation and Chemical Characterisation

Details about aerosol sampling and sample preparation may be found elsewhere (Galambos et al., 2003). Briefly, two winter and two summer fine aerosol Hi-Vol samples (PM$_{1.5}$, particulate matter with diameter $D \leq 1.5 \, \mu m$) were collected in 2001 at the continental-rural
site K-puszta, Hungary. Samples are defined here as “KPYYMMDD”, indicating the sampling site and the start date of sampling. Aqueous WSM was obtained by soaking portions of the aerosol filters in MilliQ-water. Solid phase extraction (Varga et al., 2001) was used in a second step in order to separate water-soluble atmospheric humic matter (ISOM, less hydrophilic under acidic conditions) from inorganic salts. However, organic compounds that were very hydrophilic under acidic conditions (MHOM) could not be isolated from inorganic salts. Detailed chemical characterisation of PM$_{1.5}$, WSM, and ISOM was performed by Galambos et al. (2003).

Figure 6.1 illustrates the mean composition of the investigated aerosol samples as obtained by Galambos et al. (2003). A large fraction of PM$_{1.5}$ is composed of WSM (~76 wt %), including inorganic salts (~36 wt %) as well as WSOM (~40 wt %). The water-insoluble fraction (~24 wt %) consists of WINSOM and black carbon (BC). The sum of all carbon containing species is defined as total carbonaceous matter (TCM).

Investigated reference materials were aquatic Nordic reference fulvic and humic acids (NRFA and NRHA, respectively, International Humic Substances Society IHSS, product No. 1R105F and 1R105H, isolated from Hellrudmyra tarn, Norway) and Aldrich humic acid sodium salt (NaHA, product No. H16752, isolated from crude lignite).

6.2.2 Aerosol Generation
ISOM and WSM extracts had to be transformed into aerosol particles again in order to perform hygroscopicity measurements using the H-TDMA technique. WSM solutions were directly obtained in the form of aqueous extracts (see above) with concentrations of about 140–290 mg/l. Dry ISOM extracts were dissolved in MilliQ-water, by using an ultrasonic bath for about 20 minutes. Resulting concentrations were about 160–350 mg/l for the ISOM extracts. Dry NRFA, NRHA and NaHA samples were dissolved in MilliQ-water without using an ultrasonic bath. However, NRFA and NRHA could not be completely dissolved with this method. In order to remove suspended undissolved particles, all WSM, ISOM and reference solutions were filtered through a syringe membrane with a 0.22 µm pore size (Millex GV 13 mm, Millipore, USA). Artificial aerosol particles were then generated by nebulization of the solutions, and subsequently dried (RH < 5%) in a silica gel diffusion dryer with a residence time of about 300 s. The nebulizer (TSI 3076 type) was operated with artificial air (80% N$_2$ >99.999%, 20% O$_2$ >99.995%). Dried aerosol particles were neutralised and fed into the H-TDMA for the hygroscopicity measurement. Aerosols generated with this procedure are internally mixed, and the chemical composition of the individual particles is representative of the PM$_{1.5}$ average WSM or ISOM composition. Scanning Electron Microscopy (SEM) micrographs of ISOM (KP010126) and NRFA particles with dry diameters of $D_0 \approx 100$ nm (selected using a Differential Mobility Analyser (DMA) and sampled on nucleopore filters) are shown in Fig. 6.2. Dry particles from all samples were found to be nearly spherical.

6.2.3 Hygroscopicity Measurement
The hygroscopic growth factor $g$ of a particle is defined as

$$g(RH) = \frac{D(RH)}{D_0} ,$$  \hspace{1cm} (6.1)

where $D_0$ is the particle dry diameter, and $D(RH)$ is its diameter at a specific RH. The hygroscopic growth factor $g$ indicates the relative size increase of particles due to water uptake. The H-TDMA system (Fig. 6.3) is described in detail by Weingartner et al. (2002) and Gysel et al. (2002). An additional prehumidifier was used in this study, and is described.
later. Briefly, a monodisperse fraction \( D_0 \approx 100 \text{ nm} \) of dried neutralised \(^{85}\text{Kr} \) bipolar charger aerosol particles was selected with a first DMA (DMA1; TSI 3071). This monodisperse aerosol was then humidified, and the resulting particle size after humidification was measured by scanning the whole size range with a second DMA (DMA2) and a Condensation Particle Counter (CPC, TSI model 3022).

Figure 6.2: SEM micrographs of \( D_0 \approx 100 \text{ nm} \) particles, which were produced by atomising ISOM (on the left) and NRFA solution (on the right). Dark holes are the filter pores.

Figure 6.3: Hygroscopicity Tandem Differential Mobility Analyser with optional prehumidifier.

Mean diameter \( D_m \) and standard deviation \( \sigma \) (normal distribution) were obtained using an inversion algorithm based on the original TDMAFIT QBASIC program by Stolzenburg and McMurry (1988). The H-TDMA was kept at a constant temperature \( T \approx 25 \text{ °C} \) (DMA2 was submersed in a well-mixed water bath), and the relevant RH (\( RH_{DMA2} \)) was determined by measurement of the system temperature and DMA2 sheath air dew point using a dew point mirror (Edge Tech, Model DewPrime II). At constant conditions the RH accuracy is \( \Delta RH_{DMA2} = \pm 1.2\% \) at 95% RH. Both DMAs were operated with a closed loop sheath air setup, which allowed the growth factor to be determined with an accuracy of \( \Delta g \approx \pm 0.003 \). The humidification section consisted of an optional prehumidifier and a follow-on RH-conditioner. RH values after the prehumidifier \( (RH_P) \) and after the RH-conditioner \( (RH_C) \) were also monitored using capacitive RH sensors. Due to the closed loop setup, \( RH_{DMA2} \) equilibrates with \( RH_C \) after a time delay of a few minutes for small \( RH_C \) changes (cf. Fig. 6.4). Four measurement modes can be selected depending on the settings of \( RH_P \) and \( RH_C \). Fig. 6.4 shows a time series of \( RH_P, RH_C, \) and \( RH_{DMA2} \) during a complete measurement cycle (NRFA). The four different H-TDMA modes are:

- **Dry reference diameter \( D_0 \)** (Fig. 6.4a):
  
  This mode is used to measure the dry reference diameter \( D_0 \) of the particles selected with the first DMA. Both humidifiers are switched off. The RH throughout the whole H-TDMA equilibrates with the incoming dry aerosol air, i.e. \( RH_P, RH_C, \) and \( RH_{DMA2} \) are lower than 5%. In this case the particles don’t undergo any change, and the diameter \( D_0 \) measured in DMA2 represents precisely the (electrical mobility) diameter of the dry
particles selected with DMA1. $D_0$ is used as the reference diameter for all experimental growth factors $g$ (cf. eq 6.1).

- **Growth factors under decreasing RH conditions $g_{\text{decr}}(RH)$ (Fig. 6.4b):**
  This mode is used to measure hygroscopic growth factors during dehydration. The prehumidifier is set to a high RH ($RH_P \geq 95\%$), and $RH_C$ is successively increased. In this case $RH_P \geq RH_C \geq RH_{\text{DMA2}}$, i.e. the particles undergo strictly decreasing RH conditions, while passing through the instrument. Hence growth factors are labelled as $g_{\text{decr}}(RH_{\text{DMA2}})$). $RH_{\text{DMA2}}$ increases slowly during the measurement of growth factors under decreasing RH conditions since the aerosol air introduces additional humidity in the closed-loop sheath air flow ($RH_C \geq RH_{\text{DMA2}}$).

- **Growth factors under increasing RH conditions $g_{\text{incr}}(RH)$ (Fig. 6.4c):**
  This mode is used to measure hygroscopic growth factors during hydration. The prehumidifier is bypassed ($RH_P \leq 5\%$), and $RH_C$ is successively decreased. In this case is $RH_P \leq RH_C \leq RH_{\text{DMA2}}$, i.e. the particles undergo strictly increasing RH conditions, while passing through the instrument. Hence growth factors are labelled as $g_{\text{incr}}(RH_{\text{DMA2}})$. $RH_{\text{DMA2}}$ decreases slowly during the measurement of growth factors under increasing RH conditions since the aerosol air reduces the humidity of the closed-loop sheath air flow ($RH_C \leq RH_{\text{DMA2}}$).

- **RH-dependent restructuring of the particles $g_{\text{restr}}(RH)$ (Fig. 6.4d):**
  This measurement provides the so-called restructuring factor $g_{\text{restr}}(RH_P)$, i.e. the size change of initially dry particles if they are exposed to a certain $RH_P$ and dried up again. The RH in the prehumidifier is varied, while the RH-conditioner is used as a dryer ($RH_C$ and $RH_{\text{DMA2}} \leq 5\%$).

![Figure 6.4: Typical measurement cycle with the H-TDMA (NRFA sample). Abbreviations are RH after prehumidifier ($RH_P$), RH after RH-conditioner ($RH_C$), and RH in DMA2 ($RH_{\text{DMA2}}$). Dry, monodisperse particles initially selected in DMA1 are then successively exposed to $RH_P$, $RH_C$, and $RH_{\text{DMA2}}$. a) Measurement of dry diameter $D_0$, b) growth factor $g_{\text{decr}}(RH_{\text{DMA2}})$ under decreasing (!) RH conditions, c) growth factor $g_{\text{incr}}(RH_{\text{DMA2}})$ under increasing (!) RH conditions, and d) restructuring $g_{\text{restr}}(RH_P)$.

### 6.3 Theory

Three fundamentally different models are used in this study. The suitability of the theoretical ideal solution model and the empirical $\gamma$-model to provide parameterisations of the experimentally observed hygroscopic growth characteristics is compared and evaluated.
In addition, the ideal solution model provides a rough estimate of the average molecular weight of the ISOM. The aim of the more sophisticated mixed particle model is to make a “hygroscopicity closure”, i.e. to investigate the individual contributions of the inorganic, ISOM, and MHOM fractions to the hygroscopic growth of the WSM samples.

6.3.1 Ideal Solution Model

The hygroscopic growth of soluble particles as a function of RH is described by the Köhler theory (Pruppacher and Klett, 1997; Seinfeld and Pandis, 1998). For an ideal solution the equilibrium RH above a flat surface is equal to the mole fraction \( x_w \) of water in the solution (Raoult’s law). Generally Raoult’s law is valid for diluted solutions, i.e. large growth factors close to or above water vapour saturation, while care has to be taken at lower RH. In this study the ideal solution model is used as the best possible approach to describe the hygroscopic growth of ISOM samples, since no information about real water activity values is available. For the case of a spherical droplet of diameter \( D \), the Kelvin correction factor \( S_{Kelvin} \) accounts for the water vapour pressure increase over a curved surface. The resulting relation between the equilibrium RH and the droplet diameter \( D \) for an ideal solution is (Köhler equation):

\[
RH = x_w(D) \cdot S_{Kelvin}(D) = x_w(D) \cdot \exp \left( \frac{4 M_w \zeta}{R T \rho_w D} \right),
\]

(6.2)

where \( M_w \) and \( \rho_w \) are the molar weight and the density of water, \( \zeta \) is the surface tension of the solution, \( R \) is the ideal gas constant, and \( T [K] \) is the temperature. Due to lack of information the solution surface tension \( \zeta \) is approximated by the surface tension of pure water. This has less effect on theoretical growth factors \( g_{th} \) under subsaturated RH conditions, but the use of eq 6.2 under supersaturated conditions to estimate critical supersaturation and diameter values would profit from more precise \( \zeta \) values. Generally the mole fraction \( x_w \) is defined as:

\[
x_w = \frac{n_w}{n_w + n_s},
\]

(6.3)

where \( n_w \) is the molar number of water molecules and \( n_s \) is the number of solute molecules (or ions if the molecules dissociate in aqueous solution). The mole fraction \( x_w \) of a droplet depends on \( g_{th} \) and the average molar volume per solute molecule (or ion) \( v_s \):

\[
x_w(g_{th}, v_s) = \frac{\frac{g_{th}^3 - 1}{g_{th}^3 - 1 + \frac{M_w}{\rho_w v_s}}}{M_w},
\]

(6.4)

Equation 6.4 includes the approximation, that the volume change due to mixing is zero, independent of solution concentration, i.e. the solute and solvent volumes are additive.

Equation 6.2 determines the equilibrium mole fraction \( x_w \) of an ideal solution at a given RH, and eq 6.4 relates this concentration to the corresponding theoretical hygroscopic growth factor \( g_{th} \). \( v_s \), the only parameter determining the hygroscopicity of an ideal solution, is used to fit theoretical growth curves to experimental results obtained for ISOM. \( v_s \) depends on the solute average molar weight \( M_w \), density \( \rho_s \), and van’t Hoff factor \( i_s \) of the solute:
6. Hygroscopicity of Humic-Like Organic Matter

\[ v_s = \frac{M_s}{\rho_s \cdot i_s} \]  \hspace{1cm} (6.5)

The van’t Hoff factor \( i_s \) is equal to the number of dissociated ions per molecule. Equation 6.5 was used to obtain an estimate of \( M_s \) from fitted \( v_s \) values, whereas values assumed for ISOM density (\( \rho_{\text{ISOM}} = 1500 \text{ kg/m}^3 \)) and van’t Hoff factor (\( i_{\text{ISOM}} = 1 \)) are discussed below.

6.3.2 Empirical \( \gamma \)-Model

The empirical \( \gamma \)-model is frequently used in literature (Swietlicki \textit{et al.}, 2000; Peng \textit{et al.}, 2001; Weingartner \textit{et al.}, 2002; Massling \textit{et al.}, 2003) to describe the hygroscopic growth of ambient as well as that of organic particles. It is a simple one-parameter relation:

\[ g_{\text{ab}} = (1 - RH / 100\%)^\gamma \]  \hspace{1cm} (6.6)

where \( \gamma \) is the model parameter. Even though this model is restricted to \( RH < 100\% \), it is quite useful to quantify the hygroscopic growth of aerosol particles. \( \gamma \) was determined for all samples by fitting the model to experimental growth factors at 90% RH. The overall RH dependence of experimental growth factors measured in this study is generally better reproduced by the ideal solution model compared to the \( \gamma \)-model (see below), but nevertheless the latter is included here, since it allows a comparison with results from other studies.

6.3.3 Mixed Particle Model

The hygroscopic growth factor \( g_{\text{WSM}} \) of a mixed WSM particle can be estimated from the growth factors \( g_{\text{Inorg}}, g_{\text{ISOM}}, \text{and } g_{\text{MHOM}} \) of “pure” inorganic, ISOM, and MHOM particles, and from their respective volume fractions \( \varepsilon_{\text{Inorg}}, \varepsilon_{\text{ISOM}}, \text{and } \varepsilon_{\text{MHOM}} \) in the mixed particle:

\[ g_{\text{WSM}} = \left( \varepsilon_{\text{Inorg}} g_{\text{Inorg}}^3 + \varepsilon_{\text{ISOM}} g_{\text{ISOM}}^3 + \varepsilon_{\text{MHOM}} g_{\text{MHOM}}^3 \right)^{1/3} \hspace{1cm} (6.7) \]

Equation 6.7 is equivalent to the Zdanovskii-Stokes-Robinson relation (ZSR relation, Chen \textit{et al.}, 1973), it includes the approximation of independent hygroscopic behaviour of the inorganic, ISOM, and MHOM fractions. Hygroscopic properties of mixtures of carboxylic, dicarboxylic, or multifunctional organic acids with single inorganic salts under subsaturated RH conditions have been previously investigated in laboratory experiments by Hansson \textit{et al.} (1998), Cruz and Pandis (2000), Lightstone \textit{et al.} (2000), Choi and Chan, (2002b), Härmeri \textit{et al.} (2002), and Chan and Chan (2003). Experimental results often indicate fair agreement with ZSR predictions, but according to a more detailed analysis of literature data (Chan and Chan, 2003) positive or negative interactions between organic and inorganic compounds are likely, depending on mixed species and concentrations.

In this study, \( g_{\text{ISOM}}(RH) \) is experimentally determined. The growth factor of the MHOM fraction is not known, but a value of \( \gamma = 0.163 \) (empirical \( \gamma \)-model) is representative of highly soluble organic acids (Peng \textit{et al.}, 2001) such as malonic acid (dicarboxylic acid), citric acid, malic acid and tartaric acid (hydroxy-carboxylic acids). Hence growth factors calculated with \( \gamma_{\text{MHOM}} = 0.163 \) are used as a best guess for \( g_{\text{MHOM}}(RH) \). The composition of the inorganic fraction is known from the chemical analysis of the WSM samples (Galambos \textit{et al.}, 2003). Excess anions were compensated by H\(^+\) to adjust the charge balance. The thermodynamic aerosol inorganics model (AIM) by Clegg \textit{et al.} (1998; http://www.hpc1.uea.ac.uk/~e770/aim/aim.htm) for the H\(^+\)-NH\(_4^+\)-Na\(^+\)-SO\(_4^{2-}\)-NO\(_3^-\)-Cl\(^-\)-
6.3 Theory

H$_2$O system (AIM2-III) was used to determine corresponding growth factors $g_{\text{Inorg}}$. The minor cations Ca$^{2+}$ and K$^+$ were replaced by a proper amount of Na$^+$ since they are not supported by AIM2-III.

The overall hygroscopic growth of the WSM samples was modelled (eq 6.7) with the growth factors $g_{\text{Inorg}}$, $g_{\text{ISOM}}$, and $g_{\text{MHOM}}$ of the three WSM fractions (curves “Inorganic+ISOM+MHOM” in Figs. 6.6 and 6.7). The contribution of the inorganic fraction (curve “Inorganic”) was determined by treating the ISOM and MHOM fractions as inert with respect to water uptake (i.e. $g_{\text{ISOM}} \equiv 1$ and $g_{\text{MHOM}} \equiv 1$). Analogously, the curves “ISOM”, “MHOM”, and “Inorganic+ISOM” were calculated. A discussion of assumptions and approximations which affect all these model curves follows.

The conversion of measured carbon mass fractions into organic volume fractions ($\varepsilon_{\text{ISOM}}$ and $\varepsilon_{\text{MHOM}}$) depends on the organic matter to carbon mass conversion factors, determined by Galambos et al. (2003, see section 6.4.1) and on the densities $\rho_{\text{Inorg}}$, $\rho_{\text{ISOM}}$, and $\rho_{\text{MHOM}}$. Due to a lack of information a value of 1500 kg/m$^3$, which is appropriate for carboxylic and multifunctional organic acids (Saxena et al., 1995; Peng et al., 2001) was assumed for $\rho_{\text{ISOM}}$ and $\rho_{\text{MHOM}}$. The density $\rho_{\text{Inorg}}$ was determined from the volume weighted average of the individual salts, which are present in the dry particle according to the AIM output. However, salts effectively present in the solid particle may differ from the thermodynamic AIM prediction, which is a Gibbs free energy minimization, but fortunately $\rho_{\text{Inorg}}$ depends only slightly on the various salt combinations that are theoretically possible for a given ion composition. The solution density $\rho_{\text{sol}}$ is approximated by the ratio of total mass to total volume of added inorganic, ISOM, MHOM and water fractions, assuming that the volume of mixing is zero. The replacement of Ca$^{2+}$ and K$^+$ cations by Na$^+$ has little effect on $g_{\text{Inorg}}$ due to their small abundance compared to the major ions. Apart from the unknown accuracy of the ZSR relation for these organic/inorganic WSM mixtures, modelled growth curves are most sensitive to the value of $\rho_{\text{ISOM}}$, since it directly changes the volume fraction of less hygroscopic ISOM ($\varepsilon_{\text{ISOM}}$) and that of distinctly more hygroscopic inorganic salts ($\varepsilon_{\text{Inorg}}$) in opposite direction.

6.3.4 Mobility Correction Factor $f$

Equations 6.2 and 6.4 (ideal solution model), eq 6.6 ($\gamma$-model), and eq 6.7 (mixed particle models) describe theoretical growth factors $g_{\text{th}}$ in terms of volume equivalent diameters. Experimental results achieved with the H-TDMA are measured and presented in terms of electrical mobility diameters. To compare modelled growth factors $g_{\text{mod}}$ with experimental results, a mobility correction factor $f$ is introduced for $g_{\text{th}}$:

$$g_{\text{mod}} = f \cdot g_{\text{th}} \quad .$$

Possible effects included in $f$ are:

- Liquid particles at sufficiently high RH are spherical and compact, and hence volume equivalent and measured electrical mobility diameters are equal. Dry particles are also nearly spherical but cracks or cavities in the particle structure cannot be excluded (despite of the spherical shape seen in Fig. 6.2) and are possible, since large droplets leaving the nebulizer are suddenly exposed to very low RH in the diffusion dryer, leading to very fast water evaporation and crystallisation of the particles. Such particles have dynamic shape factors larger than 1, resulting in dry mobility diameters, $D_0$, larger than the corresponding volume equivalent diameters. Theoretical growth factors have to be adjusted with a correction factor $f \leq 1$ to account for such an overestimation of experimental dry diameters $D_0$. 

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The correction factor $f$ also accounts for possible deficiencies of the assumption that the volume of mixing of deliquescent particles is zero, i.e. that the individual species volumes are additive in solution.

For the ISOM and the reference humic substances the correction factor $f$ is chosen as the experimental value

$$f = g_{\text{dec}} (RH_{\text{DMA2}} \leq 5\%) \equiv g_{\text{recr}} (RH_{P} \geq 95\%)$$

since it is assumed that restructured particles at $RH_{\text{DMA2}} \leq 5\%$ are spherical and compact after the previous cycle of deliquescence ($RH_{P} \geq 95\%$) in the prehumidifier and subsequent drying in the RH-conditioner ($RH_{C} \leq 5\%$). Since no growth factors under decreasing RH conditions are available for the WSM samples, the correction factor $f$ is chosen as the smallest measured growth factor under increasing conditions in this case. The mobility correction factor is always applied to the ideal solution model, the empirical $\gamma$-model, and the mixed particle model. However, modelled growth factors $g_{\text{mod}}$ corrected with a RH independent mobility correction factor $f$ are comparable only with experimental results of deliquescent particles at sufficiently high RH or under decreasing RH conditions, since the dynamic shape factor does not change substantially before deliquescence.

### 6.4 Results and Discussion

#### 6.4.1 Chemistry of Atmospheric Samples

A summary of PM$_{1.5}$ chemical composition as determined for the investigated samples by Galambos et al. (2003) is given in Table 6.1. It is assumed that PM$_{1.5}$ at K-puszta is dominated by inorganic salts and carbonaceous matter (i.e. PM$_{1.5} = \text{inorganic salts} + \text{TCM}$), as it has been found in earlier mass closure experiments by Zappoli et al. (1999). Total mass concentrations of inorganic salts were directly measured using ion-chromatography while mass concentrations of carbonaceous species were determined by multiplication of the measured carbon mass concentration with mass conversion factors suitable for each class of compounds. ISOM mass conversion factors were between 1.81 and 1.91 as determined for each sample by elemental analysis (Galambos et al., 2003). General conversion factors of 2.3, 1.6 and 1.1 were applied for MHOM, WINSOM, and BC, respectively (Kiss et al., 2002). The apportionment of total water-insoluble carbonaceous matter into WINSOM and BC was not determined for all samples (Galambos et al., 2003), but this does not affect mass fractions of WSOM which are important for growth modelling (see below). Thus, only TCM (= WSOM + WINSOM + BC) mass concentrations are somewhat uncertain for KP010126 and KP010726. About 70% and 85% of PM$_{1.5}$ winter and summer samples, respectively, are water-soluble. The water-soluble mass itself is on average composed of 47% inorganic salts, 36% ISOM, and 17% MHOM with small seasonal differences except for a small trend towards a larger organic fraction in summer.

#### 6.4.2 Hygroscopicity of Atmospheric WSM and ISOM Samples

Growth factors $g$, mobility correction factors $f$ and model parameters $\gamma$ of all investigated WSM and ISOM extracts are listed in Table 6.2. In the following, results will be discussed with respect to humidograms obtained for each summer and winter sample. The hygroscopic behaviour of the KP010816-ISOM and -WSM extracts under increasing RH conditions is illustrated in Fig. 6.5. WSM is seen to be distinctly more hygroscopic compared to ISOM. Starting at dry conditions, there is first a small size decrease at around
20% RH to a growth factor of \( g_{\text{WSM}} = 0.96 \). This small restructuring is attributed to a mobility effect, i.e. a reduction of the dynamic shape factor when a first fraction (supposably organic) of the WSM particle is dissolved and a spherical particle is formed, and possibly also to a negative volume of mixing with water (cf. discussion of Fig. 6.10). Hence the smallest detected growth factor at low RH is chosen as the mobility correction factor \( f \) for the WSM samples (see above). At RH > 25% there is continuous water uptake onto WSM particles, resulting in a growth factor of \( g_{\text{WSM}} = 1.49 \) at 90% RH. While the initial size decrease at low RH is common for all four WSM extracts, the two winter samples exhibited a more gradual growth characteristic between 40 and 80% RH in contrast to the continuous growth of both summer samples (cf. also Figs. 6.6 and 6.7). This different deliquescence behaviour between summer and winter samples probably arises from seasonal differences of the inorganic composition. For example ammonium nitrate is practically absent in summer due to its volatility (Galambos et al., 2003). At RH > 70% values, hygroscopic growth factors are comparable for summer and winter WSM extracts.

Table 6.1: Aerosol Chemical Composition of Hi-Vol Atmospheric Filter Samples

<table>
<thead>
<tr>
<th>sample</th>
<th>PM(_{1.5})</th>
<th>TCM</th>
<th>inorg. salts</th>
<th>WSM of PM(_{1.5})</th>
<th>inorg. salts of WSM</th>
<th>ISOM of WSM</th>
<th>MHOM of WSM</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>µg/m(^3)</td>
<td>µg/m(^3)</td>
<td>µg/m(^3)</td>
<td>wt %</td>
<td>wt %</td>
<td>wt %</td>
<td>wt %</td>
</tr>
<tr>
<td>KP010112</td>
<td>33.5</td>
<td>23.4</td>
<td>10.1</td>
<td>65</td>
<td>47</td>
<td>36</td>
<td>17</td>
</tr>
<tr>
<td>KP010126</td>
<td>13.7</td>
<td>8.5</td>
<td>5.2</td>
<td>72</td>
<td>53</td>
<td>33</td>
<td>14</td>
</tr>
<tr>
<td>KP010726</td>
<td>11.7</td>
<td>7.4</td>
<td>4.3</td>
<td>89</td>
<td>42</td>
<td>40</td>
<td>18</td>
</tr>
<tr>
<td>KP010816</td>
<td>21.4</td>
<td>13.4</td>
<td>8.0</td>
<td>80</td>
<td>47</td>
<td>36</td>
<td>17</td>
</tr>
</tbody>
</table>

*PM\(_{1.5}\) was calculated under the assumption that the aerosol is composed of exclusively carbonaceous matter and water-soluble inorganic salts.

Figure 6.5: Hygroscopic growth factors of KP010816-ISOM and -WSM samples.

ISOM exhibits no distinct growth below 50%, but the particle size increases continuously at RH > 50%, resulting in growth factors of \( g_{\text{ISOM}} = 1.11 \) and 1.17 at 85 and 90% RH, respectively. However, \( g_{\text{ISOM}} \) was slightly larger in summer than in winter (see Table 6.1). Possible reasons for this difference are varying precursor substances, i.e. more anthropogenic influence in winter, and faster (photo-)chemical oxidation in summer. Small differences were also observed in the chemical composition, as total mass to carbon mass
Hygroscopic growth factors of ISOM are comparable to the hygroscopicity of secondary organic aerosol mass, which was obtained in recent smog chamber studies by oxidation of α-pinen, β-pinen, limonene, m-xylene, or 1,3,5-trimethylbenzene (Virkkula et al., 1999; Cocker III et al., 2001a,b; Saathoff et al., 2003), but it is distinctly lower than the hygroscopic growth of highly soluble organic acids such as malonic acid, citric acid, malic acid and tartaric acid (Peng et al., 2001).

### Table 6.2: Deliquescence Relative Humidity and Model Parameters

<table>
<thead>
<tr>
<th>Sample</th>
<th>Growth factor</th>
<th>Deliquescence</th>
<th>Mobility correction</th>
<th>γ-model</th>
<th>Ideal solution model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>g(90%)</td>
<td>DRH°</td>
<td>f</td>
<td>γ*</td>
<td>M†</td>
</tr>
<tr>
<td>KP010112-ISOM</td>
<td>1.08</td>
<td>50–60</td>
<td>0.96</td>
<td>0.050</td>
<td>495</td>
</tr>
<tr>
<td>KP01026-ISOM</td>
<td>1.11</td>
<td>40–55</td>
<td>0.97</td>
<td>0.059</td>
<td>405</td>
</tr>
<tr>
<td>KP010726-ISOM</td>
<td>1.16</td>
<td>30–45</td>
<td>0.98</td>
<td>0.073</td>
<td>315</td>
</tr>
<tr>
<td>KP010816-ISOM</td>
<td>1.17</td>
<td>45–55</td>
<td>0.98</td>
<td>0.075</td>
<td>300</td>
</tr>
<tr>
<td>KP010112-WSM</td>
<td>1.48</td>
<td>n.a.‡</td>
<td>0.96</td>
<td>0.189</td>
<td>n.a.</td>
</tr>
<tr>
<td>KP01026-WSM</td>
<td>1.52</td>
<td>n.a.</td>
<td>0.95</td>
<td>0.203</td>
<td>n.a.</td>
</tr>
<tr>
<td>KP010726-WSM</td>
<td>1.52</td>
<td>n.a.</td>
<td>0.96</td>
<td>0.199</td>
<td>n.a.</td>
</tr>
<tr>
<td>KP010816-WSM</td>
<td>1.49</td>
<td>n.a.</td>
<td>0.96</td>
<td>0.193</td>
<td>n.a.</td>
</tr>
<tr>
<td>NaHA</td>
<td>1.18</td>
<td>60–75</td>
<td>0.94</td>
<td>0.097</td>
<td>n.a.</td>
</tr>
<tr>
<td>NRFA</td>
<td>1.13</td>
<td>75–85</td>
<td>1.01</td>
<td>0.049</td>
<td>510</td>
</tr>
<tr>
<td>NRHA</td>
<td>1.06</td>
<td>85–95</td>
<td>0.98</td>
<td>0.034</td>
<td>765</td>
</tr>
</tbody>
</table>

°The given RH values indicate the range between deliquescence onset and completion.
*The model parameter γ was fitted to the experimental growth factor at 90% RH.
†M is obtained by fitting the ideal solution model to experimental results. The given M estimates are only valid under the following assumptions: The density of the organic solute is ρ = 1500 kg/m³, and the van’t Hoff factor of the organic molecules is i = 1 (see text for the discussion of these assumptions).
‡not applicable.

An attempt to quantify the individual contributions of the inorganic, ISOM, and MHOM fractions to the overall hygroscopic growth of the WSM particles was done with the mixed particle model. Modelled and measured growth factors agreed well and comparison results are shown in Table 6.3, along with the percentages w of water associated with the individual WSM fractions at 90% RH for all four samples. Figs. 6.6 and 6.7 illustrate the various mixed particle model results compared to experimental results for the KP010112-WSM and KP010726-WSM extracts, which are representative of investigated winter and summer samples, respectively. The inorganic fraction dominates the water uptake of WSM extracts in the RH range above deliquescence with a contribution of about w_{inorg} ≈ 59–80% of total measured particulate water at 90% RH. Correspondingly, the contribution of the WSOM is about w_{WSOM} ≈ 41–20% at 90% RH. Within the WSOM, the contribution of the ISOM is about w_{ISOM} ≈ 6–9% and the contribution of the MHOM, determined as the difference w_{MHOM} = w_{WSOM} − w_{ISOM}, is about w_{MHOM} ≈ 14–32%. The partitioning of particulate water between different WSM fractions is quite constant in the range 75% < RH < 95%.
Figure 6.6: Contributions of the inorganic, ISOM, and MHOM (according to $\gamma_{\text{MHOM}} = 0.163$) fractions to the hygroscopic growth of the KP010112-WSM sample.

Figure 6.7: Contributions of the inorganic, ISOM, and MHOM (according to $\gamma_{\text{MHOM}} = 0.163$) fractions to the hygroscopic growth of the KP010726-WSM sample.
Table 6.3: Model Accuracy at 90% RH (Mixed Particle Model) and Attribution of Particulate Water $w$ to the Different Fractions of WSM

<table>
<thead>
<tr>
<th>sample</th>
<th>model accuracy*</th>
<th>inorganic salts</th>
<th>WSOM</th>
<th>ISOM</th>
<th>MHOM&lt;sup&gt;†&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>KP010112-WSM</td>
<td>1%</td>
<td>80%</td>
<td>20%</td>
<td>6%</td>
<td>14%</td>
</tr>
<tr>
<td>KP010126-WSM</td>
<td>-5%</td>
<td>79%</td>
<td>21%</td>
<td>6%</td>
<td>15%</td>
</tr>
<tr>
<td>KP010726-WSM</td>
<td>-18%</td>
<td>59%</td>
<td>41%</td>
<td>9%</td>
<td>32%</td>
</tr>
<tr>
<td>KP010816-WSM</td>
<td>-12%</td>
<td>65%</td>
<td>35%</td>
<td>9%</td>
<td>26%</td>
</tr>
</tbody>
</table>

*Difference between prediction of the complete inorganic+ISOM+MHOM model and measured water uptake.
†Estimate from difference between measured value and model prediction for the inorganic+ISOM fraction.

Excess water $w_{WSOM}$ concentrations obtained in this study for the continental-rural K-puszta aerosol are within the range of results of earlier studies on ambient particles using an H-TDMA (Saxena et al., 1995; Swietlicki et al., 1999; Dick et al., 2000) or a humidity controlled beta gauge (Speer et al., 2003) combined with chemical analysis. Saxena et al. (1995) attributed about $w_{WSOM} \approx 25$–$40\%$ of excess water at 80–88\% RH to the organic fraction of non-urban aerosol in the Grand Canyon. At an urban site in Los Angeles, particulate water was in contrast reduced by the presence of organic substances, i.e. the effective water content was about 25–35\% smaller at 83–93\% RH than predicted from the inorganic fraction. Excess water amounts of about $w_{WSOM} \approx 0$, 20, 44, 69\% were observed by Dick et al. (2000) for rural aerosol in the Smoky Mountains with organic mass fractions of about 32, 40, 58, 73\%, respectively. In another study, Speer et al. (2003) estimated on average about $w_{WSOM} \approx 20\%$ of excess water associated with the organic fraction of a semi-rural aerosol. The hygroscopic growth of aged continental aerosol investigated at Great Dun Fell in northern England by Swietlicki et al. (1999) was explained by the water uptake of the inorganic fraction only, as long as there was only little or no photochemical activity. But they also detected excess water, probably associated with organic compounds, during a period with intense photochemical activity.

Among the three mixed particle model versions used in this study, good agreement between measured and reconstructed hygroscopic growth of WSM extracts is obtained with the complete mixed particle model (“Inorganic+ISOM+MHOM”, see Figs. 6.6 and 6.7), which accounts for the water uptake by inorganic salts, ISOM, and uses an estimate ($\gamma_{MHOM} = 0.163$) for the hygroscopicity of MHOM, which is the only remaining undetermined WSM fraction (see above). Total modelled water uptake (by volume) is 1\% larger to 5\% smaller in winter and 12\% to 18\% smaller in summer compared to experimental results. The reason for this slightly lower model accuracy in summer is unclear, since the inorganic to organic mass ratio of WSM samples is quite independent of season. However, possible reasons could be greater effective MHOM hygroscopicity in summer analogous to greater ISOM hygroscopicity, higher average WSOM density, or stronger positive interactions between inorganic and organic solutes. As discussed above, modelled growth curves are most sensitive to the assumption of ISOM density $\rho_{ISOM}$ apart from uncertainties of the estimated MHOM hygroscopicity, the ZSR relation accuracy, and real solution densities. Hence $\rho_{ISOM}$ was varied from 1000 to 1800 kg/m$^3$ to indicate the model uncertainty at selected RHs (error bars of curve “Inorganic+ISOM+MHOM”).

Despite a comprehensive characterisation of the K-puszta aerosol, the estimated contribution of the MHOM fraction to the water uptake (i.e. the difference between “WSM experiment” and “Inorganic+ISOM”, Table 6.3) is still quite uncertain regarding all the model assumptions. Nevertheless the modelling results show that the hygroscopic growth characteristic of WSM is dominated by the inorganic fraction, but that a considerable
6.4 Results and Discussion

Amount of water is associated with WSOM, whereas contributions from the ISOM and MHOM fractions are probably of comparable relevance. At this point it has to be emphasized that the results of this study are representative of the average WSM composition of the fine aerosol mode PM$_{1.5}$, and that hygroscopic growth factors of WSM extracts are presumably slightly larger than growth factors of the original ambient aerosol particles since the ambient particles additionally contain a small fraction of WINSOM and BC. However, additional water-insoluble compounds in the particles do not affect percentages of water uptake associated with different WSM fractions, and growth factors of ambient particles could be deduced analogously to the mixed particle model (eq 6.7) by using $g_{\text{WINSOM+BC}} \equiv 1$.

Besides particulate water associated with WSOM, another important topic of current research is the possible effect of WSOM on the deliquescence and efflorescence behaviour of inorganic salts (Cruz and Pandis, 2000; Choi and Chan, 2002a,b; Hämeri et al., 2002). The AIM2-III model is not generally intended to be applied to calculating the properties of metastable (supersaturated) solutions, though this option is available. Nevertheless, approximate growth curves for decreasing RH conditions were calculated to obtain more information about the deliquescence behaviour of WSM extracts. The comparison of experimental results with modelled growth curves under increasing and decreasing RH conditions indicates that WSM extracts are fully deliquescent at around RH > 75–80%. The gradual deliquescence under increasing RH conditions is fairly well reproduced by the model, but the formation of hydrates (and also of letovicite in case of the KP010726-WSM extract) had to be suppressed in AIM2-III. However, it is not possible to decide which salt species were really present, but it can still be concluded that the large organic fraction contained in the WSM extract did not completely suppress the crystallisation of some inorganic salts under the very dry conditions (RH < 5% for ~300 s) in the diffusion dryer, nor was the deliquescence behaviour of the solid inorganic salts dramatically changed. This is in agreement with results obtained by Chan and Chan (2003) for mixtures of NaCl and (NH$_4$)$_2$SO$_4$ with humic substances.

6.4.3 Hygroscopicity of Humic Reference Substances

Since ISOM has been characterised by different analytical techniques as primarily being composed of humic-like substances, hygroscopic properties of humic reference substances were also investigated. Growth factors (left ordinate) as a function of RH (upper abscissa) are shown in Fig. 6.8a–d for KP010112-ISOM, NaHA, NRFA, and NRHA, respectively. All four samples showed hysteresis behaviour basically similar to KP010726-ISOM (Fig. 6.9, detailed discussion below). Growth factors at 90% RH of NaHA, NRFA, and NRHA are 1.18, 1.13, and 1.06, respectively, which is in the same range as atmospheric ISOM samples. These results show that there are qualitative similarities between the hygroscopic behaviour of ISOM and humic reference substances, but the deliquescence transition of the reference substances is at higher RH, indicating a lower solubility. The growth factors and deliquescence RHs of NRHA and NRFA could even be somewhat biased towards larger growth factors and lower RH, respectively, if residuals filtered after initial sample dissolution (see above) consisted mainly of the least soluble and possibly least hygroscopic molecules.

6.4.4 Deliquescence and Hysteresis of Organic Samples

A closer analysis of ISOM growth characteristics highlights some uncommon hysteresis features. Figure 6.9 shows hygroscopic growth factors (left ordinate) of the KP010726-ISOM extract on an enlarged growth scale. Under increasing RH conditions (cf. curve $"g_{\text{ incr}}"$) the particle size increases continuously from RH < 5% to RH = 30%, followed by a decrease of the particle diameter during deliquescence between 30 and 45% RH. Above
Figure 6.8: Hygroscopic properties of particles generated from ISOM, NaHA, NRFA and NRHA solutions: a-d) Hygroscopic growth factors (left ordinate) and broadening (right ordinate) of the monodisperse aerosol as a function of RH (upper abscissa). e-h) Restructuring (left ordinate) and standard deviation (right ordinate) after restructuring as a function of prehumidifier RH (lower abscissa).
45% there is again distinct particle growth up to 95% RH. Experimental growth factors under decreasing RH conditions (cf. curve “\(g_{\text{decr}}\)”) are equal to \(g_{\text{incr}}\) between 95 and 45% RH. Below 45% evaporation with decreasing RH continues, ending with a particle size that is smaller than initially selected. However, at the very lower end of the \(g_{\text{decr}}\) measurement (RH < 5%) the particle size increases again towards the initially selected diameter. This indicates that crystallisation occurs under these very low RH conditions. The uncommon hysteresis behaviour, i.e. the size reduction during deliquescence, was detected for all ISOM extracts and it was highly reproducible.

Each growth factor measured with a H-TDMA is an average value of all particles of the monodisperse aerosol fraction, since it is determined from modal diameters under dry and humid conditions. In parallel, the trend of the modal standard deviation, \(\sigma\) (normal distribution), during hygroscopic growth indicates the mixing state of the aerosol. \(\sigma\) remains constant (increases) during hygroscopic growth, if growth factors of individual particles are equal (different). Figure 6.10 illustrates the changes of the monodisperse size distribution at different RH for NaHA (cf. corresponding \(g\) and \(\sigma\) in Fig. 6.8b). The line “RH = 2%” corresponds to the initially selected monodisperse aerosol fraction \((D_0 = 104 \text{ nm})\). Under increasing RH conditions the particles grow homogeneously to a mean diameter of \(D = 110 \text{ nm}\) at 51% RH, i.e. there is no change of the standard deviation \(\sigma\). From 51 to 79% RH the mean particle size increases only slightly to \(D = 112 \text{ nm}\), but there is a distinct broadening of the monodisperse size distribution. Between 79 and 89% RH there is again homogeneous growth up to a diameter of \(D = 121 \text{ nm}\). Under decreasing RH conditions the modal diameter decreases continuously without any further change of the size distribution shape, ending with a diameter of \(D = 99 \text{ nm}\) at 5% RH (line “RH = 5% (decreasing RH)”)

Thus the hygroscopic growth of NaHA particles is always homogeneous, except for the deliquescence transition between 60 and 75% RH, where there is a broadening of the monodisperse aerosol. ISOM (cf. Figs. 6.8a and 6.9) as well as NRFA (Fig. 6.8c) and NRHA (Fig. 6.8d) exhibit this characteristic decrease of the electrical mobility diameter accompanied by a parallel increase of \(\sigma\) during deliquescence too.

Figure 6.9: Hygroscopic growth factors (left ordinate) and corresponding standard deviations (right ordinate) of the KP010726-ISOM sample under increasing and decreasing RH conditions.
A priori one would expect no broadening of the monodisperse aerosol fraction during growth for these internally mixed aerosols composed of particles with identical composition (see above). But how can the broadening during deliquescence be explained? Concluding from the continuous evaporation under decreasing RH conditions, particles are most probably liquid solution droplets once they were exposed to high RH, which may also exist at low RH as metastable supersaturated solutions. Accordingly, the transition under increasing RH conditions identified by the size reduction and the broadening of $\sigma$, corresponds to deliquescence, i.e. the dissolution of the solid particles. There are mainly two possible reasons (cf. also section “mobility correction factor”) explaining a mobility diameter decrease during deliquescence despite the parallel water uptake: a) the dynamic shape factor of the solid particles is larger than 1, i.e. they are not perfectly spherical and they have cracks or cavities, leading to a decrease of the electrical mobility diameter only when the particles are transformed into compact spheres during dissolution b) the volume of mixing of humic-like substances with water is negative causing a real size decrease in terms of electrical mobility and volume equivalent diameters. Variations of the solid particle density and of the initial dynamic shape factor between individual particles then lead to the observed broadening of the monodisperse aerosol fraction during deliquescence despite identical chemical composition. However, at this point it has to be mentioned, that the hysteresis of all humic-like substances is small compared to the hysteresis of inorganic salts (e.g. (NH$_4$)$_2$SO$_4$), and could only be detected due to the high instrument resolution (cf. KP010726 in Fig. 6.9). This uncommon decrease in mobility diameter at deliquescence is most probably not of atmospheric importance, but it should be kept in mind as a potential source of discrepancies between results obtained with different techniques, e.g. if mobility diameter growth factors are compared with mass gains.

![Figure 6.10](image)

**Figure 6.10:** Size changes and broadening of the monodisperse NaHA-aerosol at different RH. Initial dry size ($D_0 = 103$ nm) marked with a vertical line.

The relatively small growth below deliquescence is attributed to a surface effect, where the most soluble compounds might form a liquid solution shell. Water adsorption alone is not sufficient to explain this growth, since a growth factor of 1.05 (e.g. NRFA at 52% RH, Fig. 6.8c) corresponds to an equivalent of ~6 monolayers of water.

For all WSM samples a small size decrease in parallel with a broadening of the monodisperse aerosol was observed under increasing RH conditions somewhere between
6.4 Results and Discussion

10 and 40% RH (cf. Fig. 6.5–6.7). This indicates that WSOM and possibly also some inorganic salts of the WSM particles already dissolve at this low RH.

6.4.5 Restructuring

The restructuring $g_{\text{rest}}(R_{H_p})$ of ISOM, NaHA, and NRFA particles as a function of prehumidifier RH ($R_{H_p}$) was also measured (Figs. 6.8e–g). In this instrument mode (cf. Fig. 6.4d) particles are selected under dry conditions in DMA1, exposed to a certain $R_{H_p}$, dried again in the RH-conditioner and the restructured dry size is measured in DMA2. No restructuring or broadening below deliquescence RH was detected for ISOM and NaHA, i.e. the hygroscopic growth under increasing RH conditions in the range $RH < DRH$ is reversible. Through the deliquescence transition there is continuous restructuring (decrease of $g_{\text{rest}}$) accompanied by a broadening of the standard deviation. This indicates that the reduction of the electrical mobility diameter during dissolution is irreversible on this timescale (~5 seconds residence time after the RH-conditioner), which is in agreement with the observation of supersaturated solutions and growth factors $g_{\text{decr}} < 1$ at low RH under decreasing RH conditions. There is no further restructuring or broadening above the deliquescence transition, confirming that in this RH range, size changes under increasing or decreasing RH conditions are only a result of water condensation or evaporation. While the restructuring behaviour of NRFA is similar to ISOM and NaHA during deliquescence and at higher RH, it is different below deliquescence. Restructuring factors $g_{\text{rest}}$ larger than 1 in the RH range below deliquescence indicate that the hygroscopic growth of NRFA is to some extent irreversible on this timescale.

6.4.6 Empirical $\gamma$-Model and Ideal Solution Model

Empirical growth curves ($\gamma$-model) were fitted to experimental growth factors at 90% RH of WSM, ISOM and humic reference substances (see Figs. 6.5, 6.8, and 6.9). The empirical $\gamma$-model is not able of reproducing the observed hygroscopic growth factors very precisely. Nevertheless, the relative agreement between fitted and measured growth factors under decreasing RH conditions is better than $\pm 6\%$ in the range from 60 to 90% RH for all WSM samples, and better than $\pm 4\%$ and $\pm 3\%$ in the entire RH range for all ISOM samples and humic reference substances, respectively. The $\gamma$-model is hence a simple but useful tool to describe the hygroscopic growth of WSM, ISOM, and humic reference substances.

The ideal solution model was applied to describe the hygroscopic growth of ISOM and humic reference substances, where $v_s$ was used to fit theoretical growth curves to experimental results (cf. eq 6.4). It reproduces the experimental growth characteristic of ISOM and humic reference substances much better compared to the empirical $\gamma$-model (see Figs. 6.5, 6.8, and 6.9). The relative agreement between measured and modelled growth factors in the entire RH range is better than $\pm 1\%$ and $\pm 2\%$ for all ISOM samples and humic reference substances, respectively. The $\gamma$-model is hence a simple but useful tool to describe the hygroscopic growth of WSM, ISOM, and humic reference substances.

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samples on the surface tension of water and (NH₄)₂SO₄-solution (Kiss et al., 2003b) samples showed that ISOM reduces the surface tension typically by about 40% at a moderate concentration of 1 g/l. On the other hand, $M_{\text{ISOM}}$ estimates increase only about 10% if one assumes a 50% reduction of surface tension by ISOM. Kiss et al. (2003a) determined the average molar weight of ISOM extracted from filters sampled at K-puszta between March 1999 and June 2000. They reported values of 200–300 and 215–345 kg/kmol using liquid chromatography mass spectrometry and vapour pressure osmometry, respectively. This is good agreement between these three approaches regarding the fact that molecular weight estimates of humic substances often vary more than an order of magnitude depending on the applied experimental technique.

Molar weight estimates, also assuming a density of $\rho_{\text{ISOM}} = 1500$ kg/m³ and a van’t Hoff factor of $i_{\text{ISOM}} = 1$, for NaHA, NRFA, and NRHA are 216, 510, and 765 kg/kmol, respectively. $M_w$ estimates for the NRFA and NRHA samples are thus larger than estimates for ISOM. This is in agreement with the stronger refractory character of NRFA and NRHA during volatilisation compared to ISOM (Nyeki et al., 2003). Distinctly larger molar weights (number averaged) of 2180 kg/kmol and 4410 kg/kmol for NRFA and NRHA, respectively, have previously been reported by Pettersson et al. (1994). However, they used size exclusion chromatography which has been reported to give higher average molecular weight estimates for humic substances than other techniques (Leenheer et al., 2001). A value of $M_{\text{NaHA}} \approx 3300$ kg/kmol (average by weight) was reported by Wolf et al. (2001) for NaHA. The molar weight estimate of 216 kg/kmol, obtained in this study for NaHA, is most probably too low, since the sodium ions are expected to dissociate, and the van’t Hoff factor is hence $>1$. If one considers a sodium mass fraction of $\sim$9 wt % (Aldrich product analysis) and assumes that all sodium ions dissociate, one would end up with a van’t Hoff factor of $i_{\text{NaHA}} \approx 6.5$ and an average molar weight (before dissociation) of $M_{\text{NaHA}} \approx 1400$ kg/kmol, but also these corrected values are not reliable since the deduction is highly sensitive to small uncertainties of the initial value.

6.5 Conclusions

Ambient continental-rural fine aerosol was sampled on quartz filters and WSM was extracted in MilliQ-water. Solid phase extraction was subsequently used to isolate ISOM, constituting the major (less hydrophilic) fraction of WSOM, from inorganic salts and the remaining MHOM. Extensive chemical characterisation of these extracts was carried out by Galambos et al. (2003), while hygroscopic properties were investigated here using a H-TDMA instrument.

ISOM hygroscopicity was comparable to secondary organic aerosols, which were obtained in smog chamber studies by oxidation of typical gaseous precursors, but lower than the hygroscopicity of highly soluble organic acids. Deliquescence was already observed at moderate RH between 30 and 60% for different ISOM samples. Differences between summer and winter samples were small, but there is a trend towards larger hygroscopicity and lower deliquescence RH in summer. Köhler theory for ideal solutions was used to estimate the average molar weight of ISOM. Resulting $M_w$ estimates of 300–495 kg/kmol assuming a van’t Hoff factor of $i_{\text{ISOM}} = 1$ and a density of $\rho_{\text{ISOM}} = 1500$ kg/m³ are in good agreement with earlier investigations of K-puszta ISOM using liquid chromatography mass spectrometry and vapour pressure osmometry. Aquatic fulvic and humic acids were also investigated for comparison with ISOM. Although some similarities in hygroscopic behaviour were observed, fulvic and humic acids were slightly less hygroscopic and deliquescence occurred at higher RH compared to ISOM. This indicates a lower average molecular weight and higher solubility of ISOM. Deliquescence of ISOM, fulvic acid, and humic acid was characterised by a small but nevertheless uncommon
decrease in mobility diameter. This behaviour is probably not of atmospheric importance, but it is a potential source of discrepancy between different techniques to measure hygroscopic growth of particles. Comprehensive chemical information and measured hygroscopic properties of ISOM were used to model the hygroscopic growth of the WSM. Good agreement between model predictions and measurements was obtained. The analysis of modelled and measured WSM growth factors showed furthermore that between 20 and 40% of total particulate water is associated with WSOM. This finding confirms results from earlier studies that, apart from inorganic salts, organic compounds are also actively involved in atmospheric processes in which particle hygroscopic properties are crucial. The relative contributions of the distinct WSOM fractions, ISOM (67–71 wt %) and MHOM (29–33 wt %), remains uncertain since MHOM was not available in isolated form, but the results suggest that the less abundant MHOM was also important due to its presumably larger hygroscopicity.

6.6 Glossary

Abbreviations were generally adopted from literature. However, an “M” (matter) instead of a “C” (carbon) as the last letter (e.g. WSOM instead of WSOC) is used to clearly distinguish between the mass of carbonaceous compounds and their carbon mass content.

6.6.1 Acronyms

AIM aerosol inorganic model
BC black carbon
CPC condensation particle counter
DMA differential mobility analyser
DRH deliquescence relative humidity
H-TDMA hygroscopicity tandem differential mobility analyser
ISOM isolated organic matter
KPYYMMDD sample labels indicating the site K-puszta and the sampling date
MHOM most hydrophilic organic matter
NaHA Aldrich humic acid sodium salt
NRFA nordic reference fulvic acid
NRHA nordic reference humic acid
PM$_{1.5}$ particulate matter with diameter $D \leq 1.5 \mu m$
SEM scanning electron microscopy
TCM total carbonaceous matter
WINSOM water-insoluble organic matter
WSM water-soluble matter
WSOM water-soluble organic matter
ZSR relation Zdanovskii-Stokes-Robinson relation
6. **Hygroscopicity of Humic-Like Organic Matter**

6.6.2 **Symbols**

- $D$: particle diameter
- $D_0$: dry reference diameter
- $f$: mobility correction factor
- $g$: hygroscopic growth factor ($D/D_0$)
- $g_{decr}$: hygroscopic growth factor under decreasing RH conditions (dehydration)
- $g_{incr}$: hygroscopic growth factor under increasing RH conditions (hydration)
- $g_{restr}$: restructuring factor
- $g_{th}$: theoretical hygroscopic growth factor
- $i_s$: van’t Hoff factor of the solute
- $M_w$: molar weight of water
- $M_s$: molar weight of the solute
- $n_w$: molar number of water molecules
- $n_s$: molar number of solute molecules (or ions)
- $R$: ideal gas constant
- $RH_C$: relative humidity in the RH-conditioner
- $RH_{DMA2}$: relative humidity in the second DMA
- $RH_P$: relative humidity in the prehumidifier
- $S_{Kelvin}$: Kelvin correction factor
- $T$: temperature
- $x_w$: mole fraction of water
- $\gamma$: model parameter of the $\gamma$-model
- $\varepsilon$: volume fraction
- $\nu_s$: molar volume per solute molecule (or ion)
- $\rho$: mass density
- $\rho_w$: density of water
- $\varsigma$: surface tension
- $\sigma$: standard deviation (normal distribution) of the monodisperse aerosol

6.7 **Acknowledgements**

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6.8 References


6. Hygroscopicity of Humic-Like Organic Matter


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6. Hygroscopicity of Humic-Like Organic Matter


7. Summary and Discussion

Atmospheric aerosols are involved in many atmospheric processes like visibility degradation, radiative forcing and cloud formation. An anthropogenic increase of atmospheric aerosol burdens may hence affect the earth climate. Hygroscopic properties of the particles play a crucial role for these effects, since e.g. scattering cross section and cloud condensation nuclei (CCN) activity of the particles depend on their hygroscopic water uptake as a function of relative humidity (RH).

The studies presented in this thesis focussed on the characterisation of hygroscopic properties of different aerosol types. This includes the investigation of inorganic test aerosols and free tropospheric aerosol at the Swiss high-alpine research station Jungfraujoch by means of a new low-temperature hygroscopicity tandem differential mobility analyser (H-TDMA) (chapters 2 and 3), the characterisation of fresh combustion particles emitted by a jet engine combustor (chapters 4 and 5), and the evaluation of the influence of water-soluble organic matter on the hygroscopic properties of a continental-rural background aerosol (chapter 6).

7.1 Low-Temperature H-TDMA

Atmospheric aerosols react sensitively to temperature changes due to its effect on the partitioning of volatile organic and inorganic species between gas and particulate phase. It is hence crucial to determine properties of aerosols at ambient temperatures in order to prevent artefacts due to evaporation or condensation of volatile compounds.

Hygroscopic growth factors, defined as the particle diameter at high RH divided by its initial dry diameter $D_0$ at $RH < 10\%$, of ambient aerosol particles are commonly measured with a H-TDMA. In order to investigate hygroscopic properties of atmospheric particles at ambient temperatures prevailing at the high-alpine research station Jungfraujoch (Switzerland, 3580 m asl), a new low-temperature H-TDMA was developed which enables measurements in the temperature range between $T = -20$ and $+30 \degree C$ for the first time (chapter 2).

The instrument was extensively tested in laboratory experiments (chapter 3), where hygroscopic growth factors of typical inorganic aerosol constituents ((NH$_4$)$_2$SO$_4$, NaCl, and NaNO$_3$) were measured as a function of RH at $T = 20 \degree C$ and $-10 \degree C$. Experimental results were compared with theoretical growth curves calculated with semiempirical thermodynamic models. The instrument proved to detect hygroscopic growth factors with high accuracy and high time resolution. Deliquescence RH (DRH) of (NH$_4$)$_2$SO$_4$ and NaCl particles increased slightly with decreasing temperature, and experimental growth factors of all investigated salt particles showed only a weak temperature dependence, both in agreement with literature. Therefore, to a first approximation, it is possible to neglect the temperature dependence of the water activity for theoretical calculations in the temperature range $-10 < T < 25 \degree C$ for the investigated inorganic salts. Besides it was observed that NaCl particles, generated with a nebulizer and a subsequent diffusion dryer, experience a significant restructuring at $RH < DRH$. This effect has most probably no atmospheric impact, but care has to be taken when using NaCl as a reference for the calibration of H-TDMA instruments.

Field measurements within the first Cloud and Aerosol Characterization Experiment (CLACE) at the Jungfraujoch were conducted in winter, when the station is mainly located in the free troposphere (FT) (chapter 2). The humidograms of FT particles were measured at around ambient temperature ($T = -10 \degree C$) in order to prevent artefacts due to evaporation of volatile compounds. Observed growth factors of particles with $D_0 = 50$, 100, and 250 nm
were almost as high as for pure (NH$_4$)$_2$SO$_4$ particles and nearly independent of initial dry size, except for the influence of the Kelvin effect. This indicates that the particles consisted mainly of water-soluble and distinctly hygroscopic substances.

Continuous hygroscopic growth over the whole RH range was observed instead of a gradual deliquescence, indicating that the particles remained at least partially liquid even at low RH (10%). It is important to know whether FT particles undergo a hysteresis or not, since e.g. optical properties of aqueous solutions and dry solid particles differ distinctly. A possible reason for the absence of efflorescence as observed during the CLACE campaign could be the complex mixture of inorganic salts and probably many organic species. Strong effects on deliquescence and efflorescence RH of mixtures containing one inorganic salt and one organic acid have been reported for some organic acids (Choi and Chan, 2002). Marcoll et al. (2003) have shown that the DRH of aqueous solutions of mixtures of dicarboxylic acids decreases with increasing number of species, and a further decrease of DRH has been observed with addition of an inorganic salt to the organic mixture. An option to further study this phenomenon would be to isolate water-soluble organic matter from the JFJ aerosol with the solid phase extraction technique (Varga et al., 2001) and to investigate its effects on the deliquescence behaviour of inorganic salts.

The hygroscopic growth of particles investigated during the CLACE winter campaign at the Jungfraujoch was furthermore characterised by nearly monomodal growth distributions, which means that in the investigated size range the free tropospheric aerosol was to a large extent internally mixed. This is an important result since the direct radiative forcing of an aerosol depends strongly on the mixing state of light absorbing and light scattering material (Jacobson, 2000; Chung and Seinfeld, 2002).

![Figure 7.1](image_url)

**Figure 7.1**: Typical examples of measured hygroscopic growth distribution at RH = 85% in Milan and at the Jungfraujoch. The dashed line is the distribution of the originally dry, monodisperse aerosol particles with a modal diameter of $D_0 = 100$ nm. Data from chapter 2, Baltensperger et al. (2002) and Weingartner et al. (2003).

Growth factor distributions at $RH = 85\%$ of originally dry, monodisperse aerosol particles with a modal diameter of $D_0 = 100$ nm are shown in Fig. 7.1 for the urban aerosol at Milan (Baltensperger et al., 2002) and the Jungfraujoch winter (chapter 2) and summer (Weingartner et al., 2003) aerosol. The Milan aerosol is an external mixture of less and
more hygroscopic particles. The Jungfraujoch aerosol is by contrast characterised by a narrow distribution of hygroscopic growth factors indicating an internally mixed aerosol. Hygroscopic growth factors are highest for the Jungfraujoch winter aerosol, when the station is mainly located in the free troposphere, and they are smaller in summer, when the station is partially influenced by the planetary boundary layer. Smallest growth factors were observed at Milan, which is close to aerosol sources. This indicates that atmospheric aging processes lead to a substantial increase in particle hygroscopicity and to a conversion of externally mixed aerosols towards internally mixed aerosols.

Hygroscopic growth factors measured in this study for the JFJ aerosol have successfully been used by Nessler et al. (2003) to explain differences between particle number size distributions simultaneously measured outdoors at ambient conditions (low temperature, high RH) and indoors at room temperature (low RH). However, differences could be explained with hygroscopic growth only in those cases where no small volatile particles were present. It is planned to use such corrections to convert existing time series of aerosol light scattering properties measured at dry indoor conditions to corresponding values at ambient RH.

7.2 Jet Engine Combustion Particles

Hygroscopic properties and CCN activity of jet engine combustion particles were investigated during the EU PartEmis project (measurement and prediction of emissions of aerosols and gaseous precursors from gas turbine engines) (Wilson et al., 2003; Petzold et al., 2003). A special focus of this study was the influence of combustor operating conditions and fuel sulphur content (FSC) on the particle properties. For that, a jet engine combustor was operated on a test-rig with two different power settings representative of older and more modern jet engines at cruise conditions (old and modern cruise conditions, respectively), and three different fuels with FSCs of 50, 410, and 1270 µg g\(^{-1}\) (low, medium, and high FSC, respectively), where the medium FSC fuel is representative of the current fleet average. Exhaust was sampled directly at the combustor exit. Black carbon mass and particle number emission indices (Petzold et al., 2003) obtained during PartEmis show that old and modern cruise conditions simulated represent a range of jet engines which are currently in use (see Fig. 7.2).

7.2.1 Hygroscopic Properties at Subsaturated RH Conditions

Hygroscopic growth factors of soot mode particles with dry diameters \(D_0 = 30, 50, \) and 100 nm were measured as a function of RH using an H-TDMA (chapter 4). These measurements revealed that the FSC has a strong effect on particle hygroscopic activity. Particles were not hygroscopic at low FSC with an observed growth factor at 95% RH of 1.01 for \(D_0 = 50\) nm particles at modern cruise conditions. This growth factor is equivalent to less than a monolayer of adsorbed water. Corresponding growth factors at medium and high FSC were 1.10 and 1.16, respectively. This distinct enhancement of particle hygroscopicity with increasing FSC is attributed to an increasing amount of hygroscopic sulphuric acid adsorbed on the insoluble soot particles. No clear trend was observed for the influence of old and modern cruise conditions evaluated. Hygroscopic growth factors depended also on the dry particle diameter. Distinctly increasing growth factors with decreasing dry particle size were observed for all conditions, despite the Kelvin effect which counteracts this tendency. This size dependent hygroscopic behaviour is attributed to a higher sulphuric acid volume fraction on smaller particles, as a result of the relatively larger uptake of sulphuric acid by smaller particles. The measurements showed also that the combustion particles in the investigated size range were internally mixed regarding their hygroscopic
properties, which is in agreement with investigations on particle volatility (Petzold et al., 2003).

![Figure 7.2: Comparison of black carbon mass (EI_{BC}) and particle number (EI_{N_{10} D \geq 10 \text{ nm}}} emission indices (per kg fuel burnt) for aircraft at cruise conditions (Petzold et al., 1999, Schumann et al., 2002) and PartEmis results for old and modern cruise conditions (medium FSC). Numbers in brackets represent the year of engine certification. Adapted from Petzold et al. (2003).](image)

A theoretical model based on Köhler theory was used to describe measured hygroscopic growth curves. The combustion particles were assumed to consist of an insoluble soot core with a soluble sulphuric acid coating. The sulphuric acid volume fraction and a mobility correction factor, accounting for deviations from spherical shape and potential core restructuring, were used as free parameters to fit theoretical growth curves to experimental results. Growth curves modelled with this simple two-parameter theoretical model (H-TDMA model) agreed well with experimental results in the investigated range from about 75–95% RH. Estimates of sulphuric acid volume fractions obtained from these model results depended nearly linear on the FSC, indicating that a constant fraction of the fuel sulphur is recovered on the particles as sulphuric acid.

The presence of sulphuric acid on the soot particles was not proved by direct measurements. However, there were complementary measurements and also modelling studies which confirmed that most probably sulphuric acid is mainly responsible for the observed hygroscopic growth. Gaseous S(VI) (SO$_3$ and H$_2$SO$_4$) was detected in the hot exhaust. Katragkou et al. (2003) measured a fuel sulphur conversion efficiency, defined as the fraction of total sulphur converted to S(VI), of 0.35–1.4% at the combustor exit, independent of investigated combustor operating conditions and FSC levels. This amount of sulphuric acid is potentially sufficient to form a coating on the soot particles of the thickness needed to explain the observed hygroscopic growth. While the semivolatile sulphuric acid partitions to the gas phase at high temperatures, it may condense on existing soot particles or form new particles by homogeneous nucleation after sufficient cooling of the exhaust through dilution. A kinetic model was used by Vancassel et al. (2003) to simulate homogeneous nucleation of the binary system H$_2$O-H$_2$SO$_4$ and formation of a sulphuric acid coating on the soot particles after dilution. Depending on model assumptions, they needed a sulphur conversion efficiency between 2.5 and 6% as a model input value to explain experimentally observed nucleation mode particle concentrations.
(Petzold et al., 2003), whereas the latter value is an absolute upper limit. The sulphuric acid coating thickness of soot particles and corresponding theoretical growth factors, obtained with a sulphur conversion efficiency of 2.5%, agreed well with experimental results of this study, and particularly also the size dependence of hygroscopic properties was confirmed.

Theoretical growth curves fitted to the experimental results were also used to estimate the critical supersaturation for CCN activation for each investigated FSC and particle size. Larger hygroscopic growth factors at higher FSC result in lower values predicted for the critical supersaturation. Due to the Kelvin effect, critical supersaturation is larger for smaller particles, despite the higher water-soluble fraction of small particles. These estimates of FSC and size dependent critical supersaturation values obtained with the H-TDMA model were used to estimate CCN concentrations at supersaturated conditions. The comparison with direct CCN measurements is summarised in the next section.

### 7.2.2 CCN Activation at Supersaturated RH Conditions

CCN concentrations of the jet engine combustor exhaust were measured at a supersaturation of $S \approx 0.7\%$ ($S = RH - 1$) using a static thermal gradient CCN counter (CCNC) (chapter 5). Measured values were used to derive activation ratios and apparent activation diameters, since variations of CCN concentration may be a result of either changing particle properties or particle concentration. The activation ratio is defined as the CCN concentration divided by the total particle concentration ($D \geq 10$ nm), and the apparent activation diameter was obtained from the measured size distributions as the lower cut size leading to number concentrations equal to the measured CCN concentrations.

Measured activation ratios and activation diameters depended strongly on FSC. An increase of FSC from 50 to 1270 µg g$^{-1}$ resulted in an increase of the activation ratio by a factor of 5 and 12, and a decrease of the activation diameter from 237 and 300 nm to 147 and 146 nm, for old and modern cruise, respectively. Activation ratios and activation diameters at the same FSC differed sometimes between investigated operation conditions, but there was no general trend from old to modern cruise conditions. The activation ratios determined in this experiment were 0.01 and 0.8% at low and high FSC, respectively, which is at the lower end of literature values. However, the applied supersaturation was sometimes slightly larger than here and FSC levels were not always reported.

Different theoretical models were used to predict activation ratios and activation diameters for the jet engine combustion aerosol. In a first model, all particles were assumed to be insoluble but wettable, i.e. all particles with a diameter equal or larger than the Kelvin diameter will be activated (Kelvin model). The opposite extreme was the Köhler model, assuming all combustion particles to be completely water-soluble (sulphuric acid). Two further models basically assumed an insoluble soot core with a soluble sulphuric acid coating, whereas the soluble volume fraction was assumed to be equal to the volatile material (Coated sphere model) obtained from volatility measurements (Petzold et al., 2003), or it was deduced from particle hygroscopicity at subsaturated RH conditions using the H-TDMA model.

The Kelvin model delivers good estimates for activation ratios and activation diameters at low FSC, but it underestimates activation ratios and overestimates activation diameters increasingly at medium and high FSC. This indicates that the soluble volume fraction of the combustion particles increases from low values at low FSC to relatively large values at high FSC. The Köhler model clearly overestimates CCN activation at all FSC levels, which is in agreement with the fact that soot particles are not at all completely water-soluble. The best agreement with measurements for all FSC was obtained with the H-TDMA model, which predicts activation diameters well ($\pm 16\%$) at low and medium FSC, and underestimates activation diameters to some extent ($\sim 36\%$) at high FSC. The coated sphere model gives the correct trend of decreasing activation diameters with increasing FSC, but predicted
values are always 45–55% too small. A small amount of volatile organics with low or absent water-solubility adsorbed on the combustion particles might be the reason for this systematic deviation.

The studies conducted during the PartEmis experiment provided a consistent picture of the microphysical properties of the combustion particles. Particles with diameters $D \geq 30$ nm are internally mixed soot particles. These particles are not hygroscopic at low FSC, but sufficiently hydrophilic to be activated as CCN if the supersaturation exceeds the critical value for Kelvin activation. A higher FSC leads to a higher sulphuric acid concentration in the hot exhaust gas which condenses on the existing soot particles and forms, if the sulphuric acid concentration is high enough, new volatile particles by homogeneous nucleation after cooling of the exhaust by cold dilution air. The increasing thickness of the water-soluble coating with increasing FSC results in increasing hygroscopic growth factors at subsaturated RH conditions. This hygroscopic growth enables the particles to overcome the Kelvin barrier at lower supersaturation, which was confirmed by decreasing CCN activation diameters and increasing CCN activation ratios with increasing FSC measured at a fixed supersaturation. Investigated engine operation conditions had, unlike the FSC, no clear effects on the microphysical properties of the combustion particles, except for smaller particle number concentrations and slightly larger median diameters at modern cruise conditions (Petzold et al., 2003).

Particulate emissions acting as CCN or ice nuclei might modify natural cirrus clouds or induce additional cirrus cloud formation. This potential impact is expected to increase with increasing FSC, due to the reduction of critical supersaturation for CCN activation. The ability of these combustion particles to act as ice nuclei was not investigated in this study. However, it has previously been shown that a sulphuric acid coating on soot particles may also lead to a reduction of the critical RH needed for ice formation onset at low temperatures (DeMott et al., 1999).

Results obtained here for combustion particle hygroscopicity and CCN activity are only conditionally applicable for contrail formation processes, since supersaturation achieved there is distinctly larger and timescales are shorter. However, trends of slightly increased contrail formation threshold temperature and increased ice particle number concentration at high FSC (Schumann et al., 2002) agree with a reduction of critical supersaturation for CCN activation.

### 7.3 Water-Soluble Organic Matter in Atmospheric Aerosol

Water uptake by atmospheric aerosol at high RH was formerly mainly attributed to the hygroscopic inorganic aerosol constituents. However, recent studies on ambient particles have shown that in many cases a considerable amount of particulate water is associated with water-soluble organic matter (WSOM). The aim of this study (chapter 6) was to investigate hygroscopic properties of water-soluble humic-like organic matter isolated from atmospheric aerosol and to assess its contribution to the overall particulate water uptake.

Water-soluble matter (WSM) was extracted from atmospheric fine aerosol ($\text{PM}_{1.5}$, $D \leq 1.5$ $\mu$m) sampled in winter and summer 2001 at the continental-rural background station K-puszta, Hungary, on two filter samples for each season. In a second step, solid phase extraction was used to isolate a major fraction (less hydrophilic) of WSOM from inorganic salts and the remaining most hydrophilic organic matter (MHOM). The resulting isolated organic matter (ISOM) has many chemical similarities with humic substances and is hence called humic-like matter. Extensive chemical characterisation of these extracts was carried out by Galambos et al. (2003), while hygroscopic properties of ISOM and WSM were investigated using a H-TDMA instrument. This approach allowed the direct
7.3 Water-Soluble Organic Matter in Atmospheric Aerosol

Investigation of hygroscopic properties of a major fraction of atmospheric WSOM and a nearly complete hygroscopicity closure for the WSM to be conducted for the first time.

The average fine aerosol composition in terms of the classes defined here is shown in Fig. 7.3a for the investigated samples. About 76% of PM$_{1.5}$ was water-soluble matter, of which about 47, 36, and 17% were inorganic salts, ISOM, and MHOM, respectively. WSOM is hence an important constituent of PM$_{1.5}$ at K-puszta, and the solid phase extraction enables isolating about two thirds of it in pure form.

Figure 7.3: Contributions of different compound classes to a) dry particulate matter with diameter $D \leq 1.5$ µm (PM$_{1.5}$) and to b) particulate water at 90% RH. Box widths are proportional to the average contributions in all investigated samples. Abbreviations are: water-insoluble organic matter (WINSOM), black carbon (BC), most hydrophilic organic matter (MHOM), isolated organic matter (ISOM), water-soluble matter (WSM), water-soluble organic matter (WSOM), and total carbonaceous matter (TCM). See text for hatched area.

Deliquescence of initially dried ISOM particles was observed between 40–60% and 30–55% RH and hygroscopic growth factors at 90% RH were 1.08–1.11 and 1.16–1.17 for winter and summer samples, respectively. Köhler theory for ideal solutions was used to estimate the average molar weight of ISOM. This results in $M_w$ estimates of 300–495 kg/kmol when assuming a van’t Hoff factor of $i = 1$ and a density of $\rho = 1500$ kg/m$^3$, which is in good agreement with earlier investigations of K-puszta ISOM using liquid chromatography mass spectrometry and vapour pressure osmometry (Kiss et al., 2003b).
The hygroscopicity of ISOM is comparable to the hygroscopicity of secondary organic aerosols obtained in smog chamber experiments, but lower than that of highly soluble organic acids and inorganic salts. Hygroscopic behaviour of aquatic reference fulvic and humic acids, which were investigated for comparison, had similarities to ISOM, but hygroscopic growth factors were slightly smaller, and deliquescence was observed at higher RH (75–85% and 85–95% RH for fulvic acid and humic acid, respectively). These differences probably originate from the larger average molecular weight and lower solubility of fulvic and humic acids.

Inorganic composition data, measured ISOM hygroscopicity, and a presumed value for the hygroscopicity of the small remaining MHOM fraction were used to predict hygroscopic growth of WSM extracts. The contributions of different compound classes were assumed to be additive (Zdanovskii-Stokes-Robinson relation). Good agreement was obtained with an average difference of -8% between model prediction and measured water uptake. While deliquescence properties of WSM extracts were mainly dominated by the inorganic salts, the WSOM accounted for a significant fraction of particulate water. At 90% RH, according to model predictions and measurements, about 80% (62%) of particulate water in winter (summer) samples are associated with inorganic salts and accordingly about 20% (38%) with WSOM. The distribution of particulate water between different classes is quite constant in the range 75–95% RH. Figure 7.3b shows the estimates of relative contributions of different compound classes to particulate water at 90% RH averaged over all four samples. The contributions to water uptake are seen to be larger for inorganic salts and smaller for WSOM compared to their contributions to dry PM$_{1.5}$, but still WSOM remains important regarding particle hygroscopic properties. The hatched area indicates the amount of particulate water, which was not predicted by the model. Possible reasons for this small remaining difference are model uncertainties like e.g. density of dry ISOM, underestimation of MHOM hygroscopicity, or positive interactions between inorganic salts and organic species leading to enhanced water uptake. The relative importance of ISOM and MHOM remains hence uncertain, but the results suggest that the less abundant MHOM is also important due to its presumably larger hygroscopicity. One should hence aim for a supplementary method enabling the isolation of MHOM towards an improved understanding of the whole WSM.

This study showed that ISOM is moderately hygroscopic, and that the WSOM contributes to the hygroscopic growth of the investigated continental-rural background aerosol. WSOM is hence also expected to play an important role for CCN activation at supersaturated conditions. However, ISOM has most probably also strong effects on the surface tension of solution droplets (Kiss et al., 2003a). The influence of ISOM (and if available also of MHOM) on CCN activation should hence be investigated with specific measurements using a CCN counter along with supplementary surface tension measurements.

### 7.4 References


Glossary

Acronyms and symbols are always defined with their first use in each chapter. The lists below explain those acronyms and symbols which are repeatedly used in this work.

**Acronyms**

AIM aerosol inorganic model  
BC black carbon  
CCN cloud condensation nuclei  
CCNC cloud condensation nuclei counter  
CLACE cloud and aerosol characterization experiment  
CMD count median diameter  
CN condensation nuclei  
CPC condensation particle counter  
DMA differential mobility analyser  
DMPS differential mobility particle sizer  
DRH deliquescence relative humidity  
EC elemental carbon  
ERH efflorescence relative humidity  
FSC fuel sulphur content  
FT free troposphere  
GAW global atmosphere watch  
HGF hygroscopic growth factor  
H-TDMA hygroscopicity tandem differential mobility analyser  
HULIS humic-like substances  
IN ice nuclei  
ISOM isolated organic matter  
JFJ Jungfraujoch  
MHOM most hydrophilic organic matter  
OC organic carbon  
PartEmis EU project “measurement and prediction of emissions of aerosols and gaseous precursors from gas turbine engines”  
PBL planetary boundary layer  
PM$_{1.5}$ particulate matter with diameter $D \leq 1.5$ µm  
RH relative humidity  
SEM scanning electron microscopy  
SMPS scanning mobility particle sizer  
SPE solid phase extraction  
TCM total carbonaceous matter
UNIFAC: UNIQUAC functional group activity coefficients model
UNIQUAC: universal quasi-chemical
UTLS: upper troposphere lowermost stratosphere
WINSON: water-insoluble organic matter
WSM: water-soluble matter
WSOM: water-soluble organic matter
ZSR relation: Zdanovskii-Stokes-Robinson relation

**Symbols**

- $a_w$: water activity
- $C_c$: Cunningham slip correction
- $D$: diameter
- $D_0$: dry diameter
- $e$: partial pressure of water
- $e_d$: equilibrium water vapour pressure over a solution droplet
- $e_{sol}$: equilibrium water vapour pressure over a flat solution
- $e_w$: saturation vapour pressure of water
- $f$: mobility correction factor
- $g$: hygroscopic diameter growth factor
- $M$: molar weight
- $n$: mol number
- $R$: ideal gas constant
- $R_{act}$: activation ratio
- $RH$: relative humidity
- $S$: supersaturation
- $S_{Kelvin}$: Kelvin correction factor
- $t$: time
- $T$: temperature
- $x_w$: mole fraction of water
- $\gamma_w$: activity coefficient of water
- $\varepsilon$: volume fraction
- $\rho$: mass density
- $\chi$: dynamic shape factor
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Publications


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