Influence of semi-volatile species on particle hygroscopic growth

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HIGHLIGHTS

- Submicron aerosols were found as external mixtures in different environments (urban to remote).
- Hygroscopic properties are changed after thermo-desorption of the semi-volatile fraction.
- The change due to thermo-desorption can usually be explained using the Raoult effect.
- Additional kinetic or surface effects are needed on some occasions.

ARTICLE INFO

ABSTRACT

In this study, we use a Tandem Differential Mobility Analyser (TDMA) system combining particle volatilization and humidification conditioning (VH-TDMA) to test the effect of the gentle volatilization of a small fraction of the atmospheric particles on the particle hygroscopic growth in several environments (urban to remote). We first give an overview of the Hygroscopic Growth Factors (HGF) in these various environments, showing that in most of them, aerosol particles are externally mixed. We then show that the particle hygroscopicity can either be increased or decreased after thermal conditioning of the particle at moderate temperatures (50–110 °C). The hygroscopic growth factor changes induced by volatilization indicate that some volatile compounds, although present at low concentrations, can significantly influence the hygroscopic growth of particles in a way that can most of time be theoretically explained if simplified assumptions are used. However, simplified assumptions occasionally fail over several hours to explain hygroscopic changes, kinetic/surface effects observed at remote environments are suspected to be important.

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1. Introduction

Knowledge of the hygroscopic properties of atmospheric particles is important to better quantify their role in the climate. Uptake of water by atmospheric particles modifies the mass of aerosol particles, increases the particles size, and therefore their ability to diffuse solar radiation. An increase of the relative humidity from 40 to 80% for the global mean aerosol would, for example, result in an increase of the radiative forcing by a factor of 2.1 (Pilinis et al., 1995). Moreover, because hygroscopic growth is linked to the particle chemical composition, water uptake measurements have been used in the literature to infer the aerosol soluble fraction in various environments, which once parameterized, can be used in model calculations (Kandler and Schütz, 2008). Measurement of water

uptake also reveals the degree of mixing of an aerosol population. Whether the various constituents are externally or internally mixed in turn influences the optical properties of atmospheric aerosols (Lesins et al., 2002). At last, hygroscopic growth also gives key information linked to the cloud condensation nuclei (CCN) properties of aerosols, a major parameter in the so-called indirect effect (Twomey, 1977). A number of studies have therefore investigated water uptake by atmospheric aerosols in order to provide an unambiguous and reliable link between aerosol hygroscopic properties and the number of particles of an aerosol population activating to cloud droplets in a humid environment (Rissler et al., 2004; Kreidenweis et al., 2005).

The Köhler theory (1936) is classically used to describe the critical supersaturation at which a CCN of known size is activated, i.e. grows into a cloud droplet. The reliability of the model calculation depends on the input parameters, e.g. the surface tension, the molality of the solution formed on the aerosol particle, the fraction of soluble material, the protonation constants, Van't Hoff factor, etc... Most of these properties are often not measurable in

the field and input parameters are often simplified or reduced to a limited number of compounds, or compound families.

Approximated input parameters in the Köhler theory appear well suited to describe the activation of pure inorganic particulate matter (e.g., Ammonium Sulphate, Sodium Chloride etc.), but not always the behaviour of more complex mixture, that includes organic material (Wang et al., 2008). Organic compounds tend to have limited water solubility, which implies that they are less CCN active.

Water uptake/activity studies have been performed on many different organic species such as pure and internally mixed dicarboxylic acids (Prenni et al., 2003, 2001), saccharides (Chan et al., 2008; Rosenoern et al., 2005), humic and fulvic acids/HULIS, high molecular weight organics (Brooks et al., 2004; Dinar et al., 2007, 2006; Gysel et al., 2004; Petters et al., 2006; Wex et al., 2007; Ziese et al., 2008), polyols (Ekström et al., 2009; Marcolli and Peter, 2005), and secondary organic aerosols generated from various precursors (Baltensperger et al., 2005; Meyer et al., 2009; Prenni et al., 2007; Varutbangkul et al., 2006). While several studies have successfully predicted hygroscopic growth of some mixtures using the Zdanovskii–Stokes–Robinson (ZSR) mixing rule (Zdanovskii, 1936; Stokes and Robinson, 1966), deviation from this additive rule has also been encountered even for simple mixtures (Sjogren et al., 2007; Svenningsson et al., 2006; Zardini et al., 2008). Non-ideal mixing effects add to the difficulty of predicting the hygroscopic growth of complex aerosols.

Both volatility and hygroscopicity give indirect information on the aerosol chemical composition (Fletcher et al., 2007; Meyer et al., 2009). In particular, photooxidation of organic compounds in the gas phase may lead to semi-volatile secondary organic aerosols (SOA). These particles experience significant chemical changes while aging, which can be tracked with the study of their volatility properties. For instance, photooxidation of trimethylbenzenes in a smog chamber show that a substantial fraction of the organic aerosol mass is composed of oligomers, which, after aging for more than 20 h, result in a lower volatility SOA (Kalberer et al., 2004). An et al. (2007) also measured the volatility of SOA formed up to several hours of reaction between α-pinene and O_3. However, SOA formed during the first hours of oxidation has usually been found to be volatile at 100 °C for gas-phase photooxidation processes (An et al., 2007), and in-cloud oxidation processes (Michaud et al., 2009).

In this study, we investigate how natural semi-volatile compounds affect the particle ability to grow in a humid environment using the Volatility-Humidity tandem differential mobility analyzer (VH-TDMA) (Johnson et al., 2004; Villani et al., 2008). The VH-TDMA technique has been used to study the hygroscopic behaviour of partially volatilized marine aerosols (Johnson et al., 2005) but it can also be used to investigate the effect of aging on the hygroscopic properties of aerosols by using low volatilization temperatures (lower than 100 °C).

2. Instrument and methods

2.1. Description of the VH-TDMA unit

The need to gain some insight into the chemical nature of submicrometre aerosols has previously lead to the development of hygroscopic growth and volatility methods for aerosol research. Since hygroscopic growth depends on the chemical properties of the aerosol, sized particles of different composition can be distinguished through their differing growth response to humidification. Frequently, these properties are investigated using tandem differential mobility analyser (TDMA) systems (Rader and McMurry, 1986). Furthermore, volatile compounds can often be distinguished by the

differences in their volatilisation temperatures (i.e., with a V-TDMA system).

In this study, the method is based on a TDMA system combining volatilisation and humidification conditioning of the particles (Volatility Hygroscopicity Tandem Differential Mobility Analyser, VH-TDMA). The VH-TDMA is composed of two DMAs and CPCs (TSI 3010), separated by a thermo-desorbing unit, and a hydration device in series. A complete description of the instrument can be found in Villani et al. (2007 and 2008). The operation procedures alternate a DRY scan (bypassing thermo-desorption and humidity conditioning units) to control proper functioning of the two DMAs, one conventional H-TDMA scan to measure the hygroscopic growth factor (HGF) of monodispersed dry aerosol, one conventional V-TDMA scan to measure size reduction of monodispersed dry aerosol after thermal treatment at specified temperature, and one Volatility-Humidity scan to measure the HGF of thermally treated monodispersed aerosol.

The Hygroscopic growth factor (HGF) at 90% RH is measured as followed:

$$HGF = \frac{D_p^{90}}{D_p^{10}}$$

where D_p^{90} is the particle diameter at RH = 90% and D_p^{10} is the particle diameter at RH = 10%. The mean residence time of the aerosol in the pre-humidifier and in the subsequent line leading to DMA2 is about 6 s. In the DMA-CPC line, the particles stay for another 6 s before being finally counted, leading to an overall conditioning time of about 12 s.

The Volatility "growth" factor (VGF) can be derived from the Volatility scan (Villani et al., 2007). It is the relative size change of a particle due to thermal conditioning. For a given thermo-desorbing temperature $T°$, the relative size change is calculated as the ratio between the particle diameter at RH = 10% ($D_p^{10,T°}$) and the dry particle diameter at RH = 10% and ambient temperature ($D_p^{10,T_{amb}}$), thus:

$$VGF = \frac{D_p^{10,T°}}{D_p^{10,T_{amb}}}$$

For a thermo-desorbing temperature ranging from ambient temperature (20–25 °C) to 300 °C, the resulting residence time in the oven heating path (30 cm) is close to 1 s.

Logically, the Volatility-Hygroscopic growth factors (VHGF), that is the hygroscopic growth of a thermally processed particle is derived as:

$$VHGF = \frac{D_p^{90,T°}}{D_p^{10,T°}}$$

where $D_p^{90,T°}$ is the particle diameter at RH = 90% and $T° > T_{amb}$. The VHGF is therefore calculated considering the "new" diameter resulting from thermo-desorption. The modes are determined by fitting the distribution after an inversion procedure that accounts for the instrumental broadening of the modes caused by the finite width of the transfer functions of the DMAs and for the system transmission efficiency. For simplicity, it is assumed that the growth factors within each group of particles are normally distributed. The uncertainty on the VHGF measurements propagates from the uncertainty on the HGF measurements. It was pointed out in recent H-TDMA intercomparison workshops (Duplissy et al., 2009), that most variability in HGF measurements results from the RH control of DMA2. Because the VH-TDMA scans are performed under the same conditions of RH and because no RH