Measurements of the Hygrscopicity of Fresh and Aged Nanoparticles for Assessing their Toxicity

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INTRODUCTION

The ability of aerosol nanoparticles (NPs) to take up water and increase in size (i.e., their hygroscopicity) can severely change their deposition characteristics in the human respiratory tract (Löndahl et al., 2007). The hygrosocpicity of particles depends mainly on their size and chemical composition, which may differ between freshly emitted and aged nanoparticles. Hygroscopicity measurements conducted with the hygroscopic tandem differential mobility analyzer (HTDMA; Rader and McMurry,1986) are widely used for modeling the deposition characteristics of NPs in the human respiratory tract (e.g. Löndahl et al., 2008).

EXPERIMENTAL

In the frame of the CERASAFE project we measured the hygroscopic properties of fresh and aged antimony oxide (SbO_3/SbO_5) nanoparticles using an HTDMA system. In brief, an emulsion containing SbO_3/SbO_5 particles was aerosolized using an atomizer and their hygroscopicity was measured using the HTDMA system under two distinct conditions: i) without any additional treatment, and ii) when ozone was inserted in the system for simulating conditions of atmospheric aging. A thermal denuder (TD), able of reaching temperatures up to 380 °C was used upstream for evaporating any surfactants on the surface of the particles coming from the solution.

Initially, for corroborating that the anticoagulating agents in the emulsion of SbO_3/SbO_5 NPs were volatile, the size distribution of atomized and dried particles was measured at different temperature settings of the TD, using a Differential Mobility Analyzer (DMA; Knutson and Whitbey, 1975) and a Condensation Particle Counter (CPC; Agarwal & Sem, 1980; cf. fig 1). The hygroscopicity of SbO_3/SbO_5 nanoparticles was measured using the setup depicted in fig. 2 (i.e., the HTDMA) at three different temperature settings of the TD. The main operating principle of an HTDMA system is to size select particles with narrow size disutribution (i.e., monodisperse), using DMA-1. Particles are then exposed in well defined Relative Humidity (RH) conditions downstream DMA-1 by passing through a naffion membrange humidifier and their size distribution is then measured by the second DMA (i.e., DMA-2) and the CPC. In this way the Hygroscopic Growth Factor (HGF) of the sampled particles at variable RH conditions can be determined as: HGF(RH)= d_m(RH)/d_m(dry), where d_m(RH) and d_m(dry) are the mobility diameters of the humidified and dry particles, respectively. This experimental setup offers also the ability of exposing the monodisperse particles (i.e., downstream DMA-1) to ozone for simulating atmospheric aging conditions.

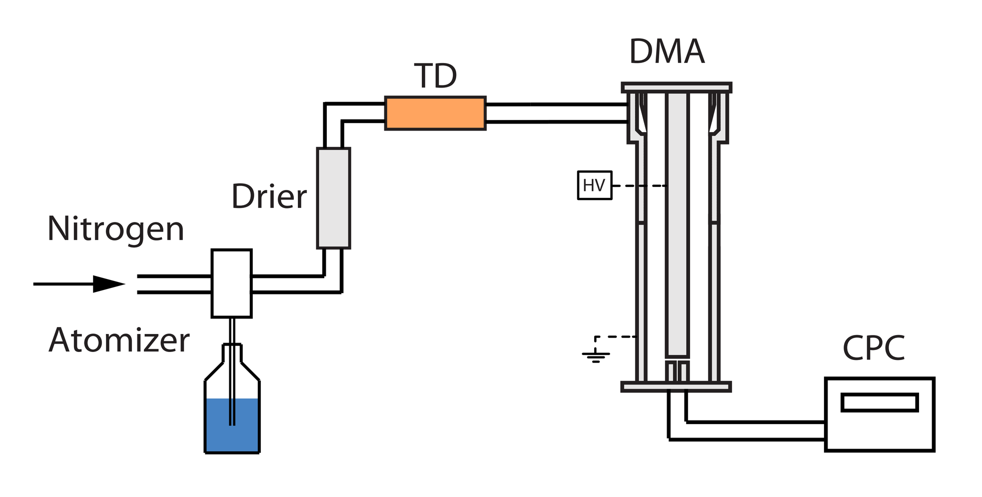

Fig.1: Experimental setup for corroborating the volatility of the anticoagulating agents contained in the emulsion of SbO3/SbO5 nanoparticles.

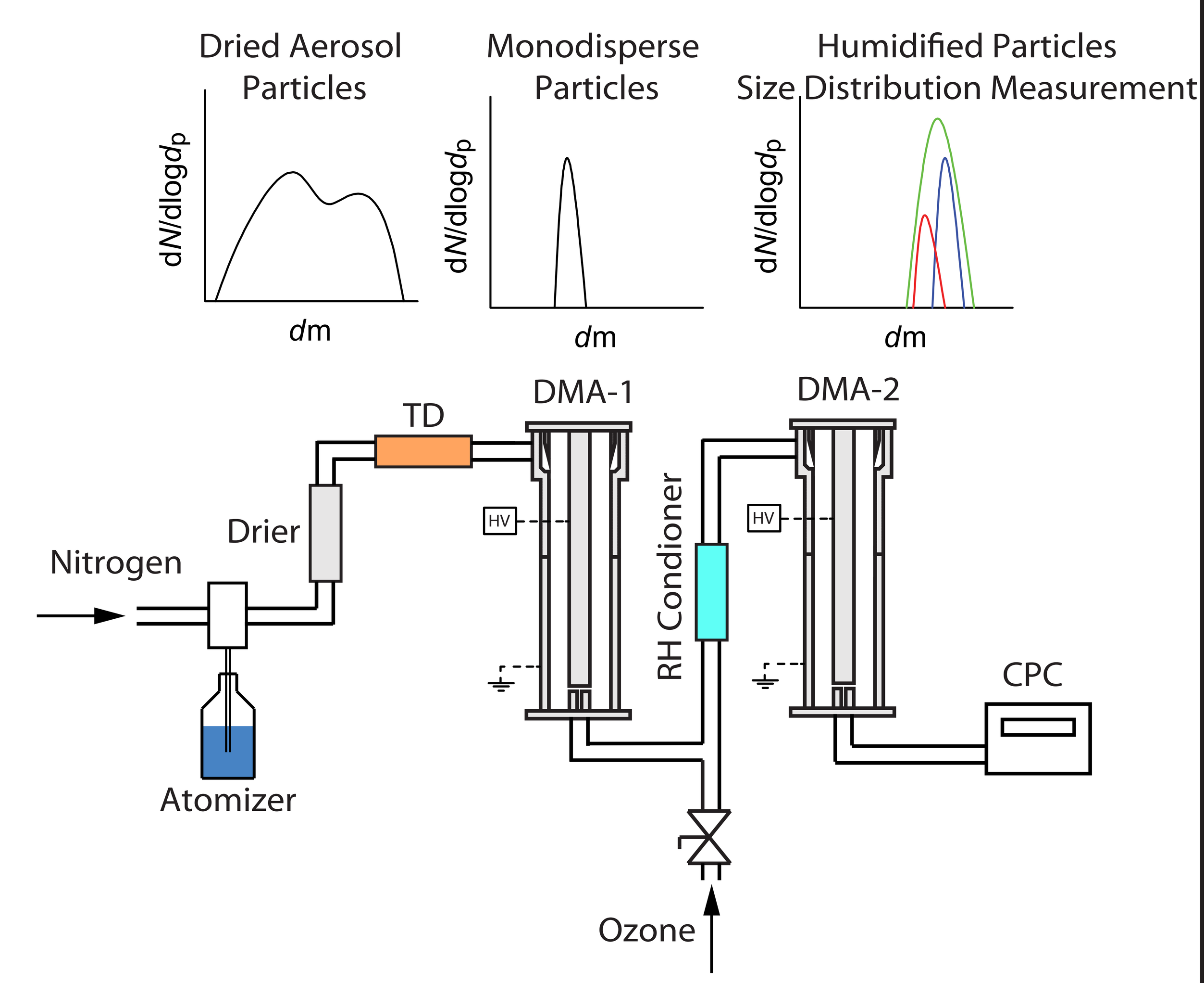

Fig.2: Experimental setup for measuring the hygroscopicity of fresh or aged (i.e., using ozone) SbO3/SbO5 nanoparticles.

RESULTS

- **Fig. 3:** Measured size distributions of polydisperse SbO_3/SbO_5 nanoparticles contained in an emulsion together with anticoagulating agents at various TD temperatures. As the temperature in the TD stages is increasing, the particle number concentration decreases together with the spread of the distribution, indicating the evaporation of volatile matter.
- **Fig. 4:** Measured hygroscopicity of 20-nm (i.e., dry mobility diameter) SbO_3/SbO_5 nanoparticles at various RH conditions and TD temperature settings without ozone. The lowest hygroscopicity is exhibited when the TD is operated at the highest temperaures, corroborating that, at least part of the measured particle hygroscopicity can be attributted to the anticoagulating agents, used in the emulsion. Interestingly the highest hygroscopicity is observed when the TD was operated at moderate temperatures, indicating that the hydrophobic part of the anticoagulating agents is more volatile.
- **Fig. 5:** Measured hygroscopicity of 20-nm (i.e., dry mobility diameter) SbO_3/SbO_5 nanoparticles at various RH conditions at the maximum TD temperature setting with ozone, together with the Geometric Standard Deviation (GSD; indication of mixing state) of the humidified particles size distrubutions. While the measured hygroscopicity of the aged SbO_3/SbO_5 nanoparticles is very high at elevated RHs (i.e., above 60%) the measured distributions of the humidified particles are clearly widened indicating the presence of other hygroscopic mode(s), similarly to when externally mixed particles are measured with the HTDMA. Since in these series of experiments all NPs were introduced into the gas phase via atomization, an internally mixing state would be expected and indeed was observed during the hygroscopicity experiments without using ozone. This clearly indicates a chemical reaction, most probably including ozone and left overs of the anticoagulating agents, resulting in changing the size distribution of the monodisperse particles or even in forming new particles having different sizes than those selected by DMA-1 (i.e., dry diameter of 20 nm).
- **Fig. 6:** Experiments exposing dry (i.e., RH< 30%) and denuded 20-nm monodisperse NPs at 380 ˚C, only to ozone further corroborated this finding, as their size distributions were significantly broadened, resulting in bigger particles which explain well the observed very high HGFs measured in the experiments conducted with ozone.

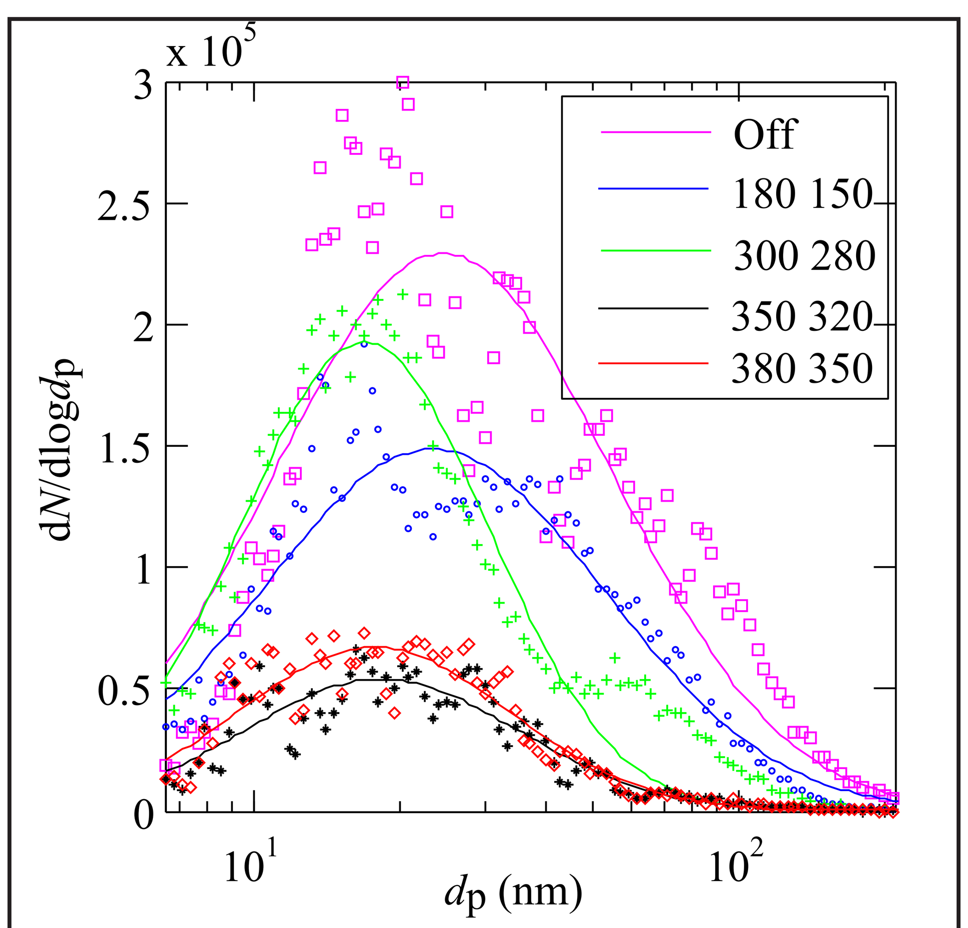

Fig.3: Size distributions of aerosolized SbO_3/SbO_5 obtained for different temperature settings of the TD (cf. Legend,for stage 1 and 2 in ˚C), using the setup of fig. 1.

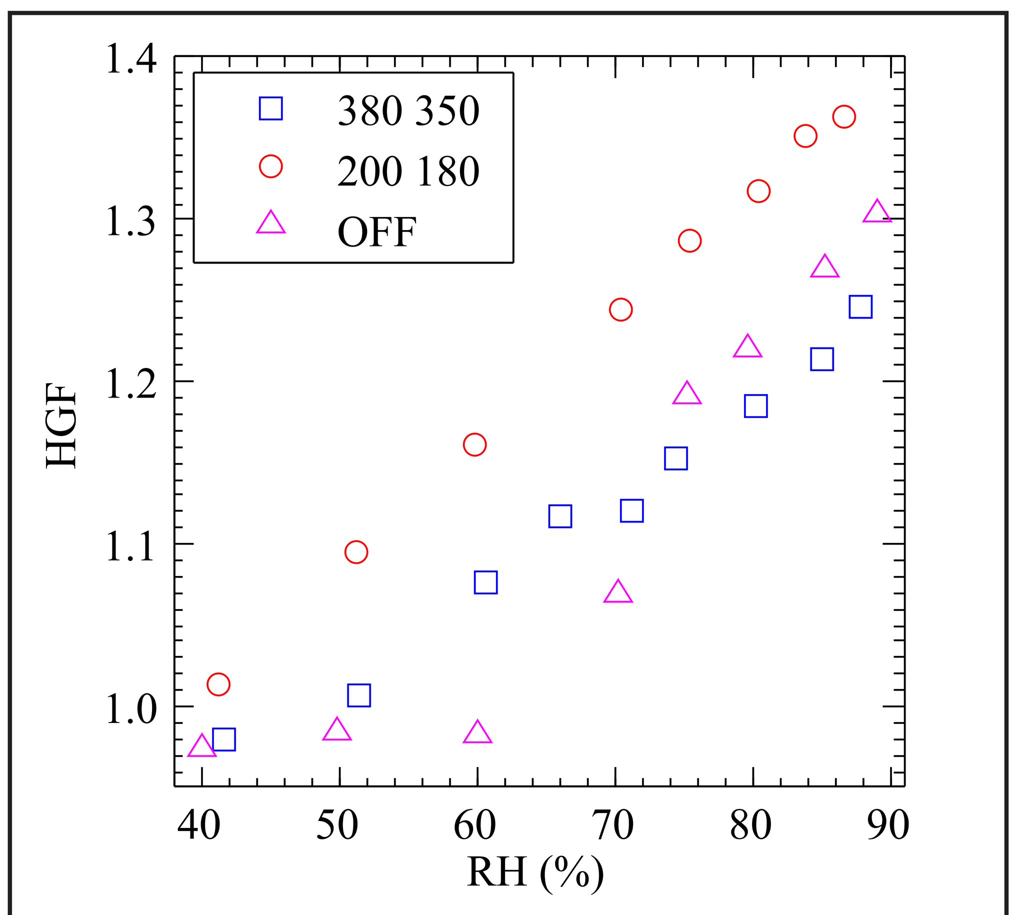

Fig. 4: Measured HGFs of 20-nm aerosolized SbO_3/SbO_5 particles at various RHs and different temperature TD settings, without using Ozone.

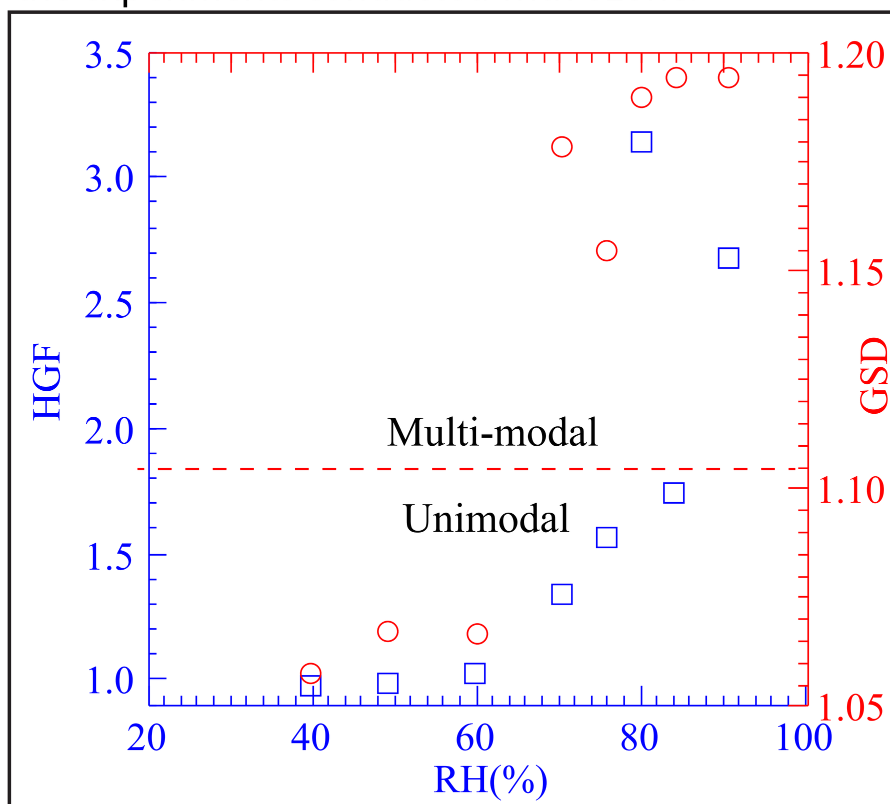

Fig. 5: Measured HGFs (blue squares) and GSDs (red circles) of 20-nm aerosolized SbO_3/SbO_5 particles at various RHs at the maximum temperature TD settings, using ozone for simulating atmosphering aging.

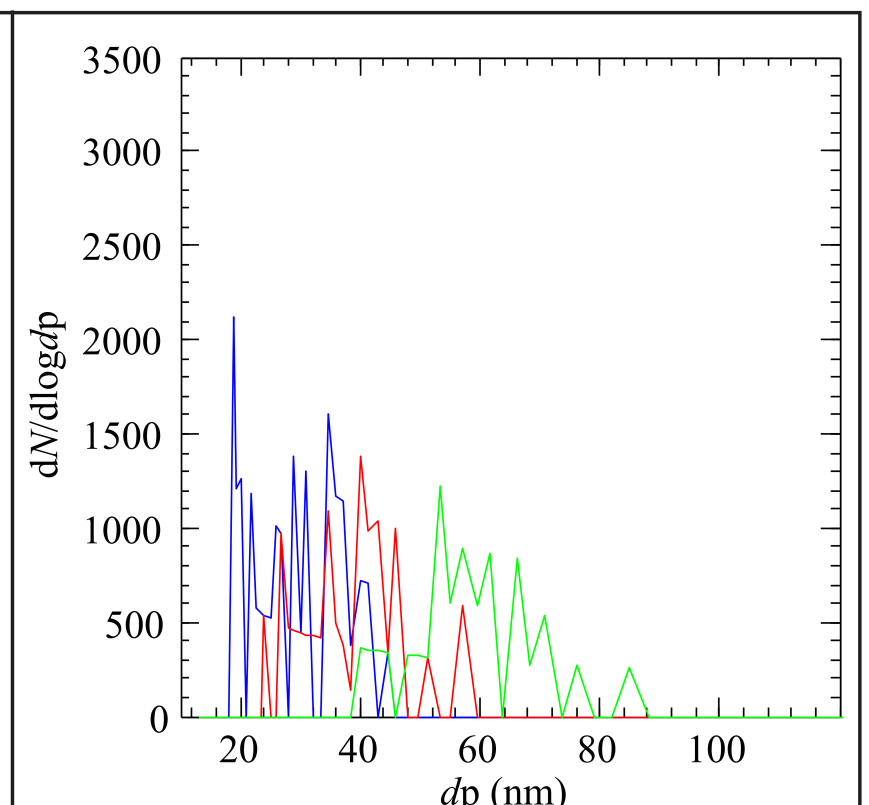

Fig. 6: Size distributions (i.e., measured by DMA-2 and the CPC) of dry (i.e., RH< 30%) and denuded **at 380 ˚C**, monodisperse 20-nm NPs (i.e., selected by DMA-1), when exposed only to ozone. Different colors indicate samples taken at different time periods of ozone exposure (i.e., blue at ca. 3, red at ca. 12 and green at ca. 20 min after inserting ozone).

CONCLUSIONS

+ Anticoagulating agents used in emulsions containing nanoparticles affect their hygroscopicity.
+ The specific anticoagulating agents are volatile and can be partially evaporated using a thermal denuder.
+ Leftovers of the anticoagulating agents (i.e., downstream a TD at 380 ˚C) react with ozone to change the size of the existing NPs .
+ It is essential therfore to avoid the use of any chemical additives, either used as preservatives or anticoagulating agents when testing the physicochemical properties of nanoparticles.
+ This may be achieved by introducing the nanomaterial in the gas phase using other aerosolizing techniques, such as the spark abbletion method (Tabrizi et al., 2009).
+ Future work will be conducted using the spark abbletion method for assesing the hygroscopic properties of ceramic/metal oxide nanoparticles.

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CERASAFE — SAFE PRODUCTION AND USE OF NANOMATERIALS IN THE CERAMIC INDUSTRY

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