

Experimental evidence of reduced sticking of nanoparticles on a metal grid

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Abstract

Filtering of NaCl, CaCl₂, (NH₄)₂SO₄ and NiSO₄ aerosol particles 7 – 20 nm in diameter by a stainless steel grid was studied in order to find out if there is perfect sticking or partial rebound. Our experiment used particles from a spray-drying process, the majority of which were electrically neutral. Penetration through the grid was measured by comparing the concentration downstream of the grid with the upstream concentration under otherwise identical conditions. Size selection was done with a scanning mobility particle sizer (SMPS). Filter penetration P as function of the particle diameter d_p was expressed by $-\ln(P(d_p)) = C d_p^{-x}$. The values of x determined were smaller than the theoretical value of 1.29, indicating

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enhanced penetration of small particles and deviation from the classical filtration model. Because of possible systematic errors in the size selection, we focus on the *differences* of x from material to material, which indicate different sticking probabilities. We apply a statistical test, which yields a 90% confidence level for the result: There is a sticking probability $< 100\%$ at least for NaCl particles and even more so for NiSO₄. This result is in contrast to former findings using metal and/or charged particles, and we speculate that the discrepancy is due to the smaller Hamaker constant of salts and that particle charge is important for the sticking probability.

Introduction and Background

Aerosol particles normally stick when they collide with surfaces. This phenomenon is uncontested and could be used for the definition of the term aerosol. The forces mainly involved are van der Waals forces, electrostatic forces and magnetic forces. For liquid droplets, capillary forces are dominant, and these may also play a role in adherence of solid particles, where a liquid bridge between particle and surface may form. This effect occurs in air, even if the relative humidity is below 100%, because of capillary condensation close to the contact area. Most of these forces may be absent, but van der Waals forces are always present. They give the “guarantee” for adherence of aerosol particles at their first collision. Considering that small molecules normally rebound when they hit a surface and that “normal” aerosol particles don't, it is clear that there must be a transition size range, where both possibilities exist. Since aerosol filtration fully relies on sticking, it is clear that this transition behavior is of great importance, especially in view of biological particles like viruses (e.g. Rhinovirus ± 30 nm; Hantavirus ± 60 nm), toxins (e.g. Botulin toxin ± 8 nm), components from combustion sources (diesel emissions) or large protein molecules but also regarding inorganic nanoparticles from a production process. HEPA filters are commonly used to avoid human exposure to particles, but if these would prove inefficient below a certain particle size or for particles with a rough surface providing a small contact area, other measures would have to be taken.

In 1991, Wang and Kasper modeled thermal rebound of nanosized particles under the assumption of pure van der Waals forces. Any model of this kind suffers from the fact that contact forces are hard to predict. They critically depend on the so-called contact distance, which depends on the surface structure on an atomic scale including

impurities and adsorbed gas molecules. There have been several efforts in obtaining experimental evidence for reduced nanoparticle sticking to surfaces. These include the studies by Alonso et al., 1999, Alonso et al., 1997, Ankilov et al. 2002, Balazy et al. 2004, Heim et al. 2005 and Ichitsubo et al., 1996. They all used electrostatic mobility classification to select a certain particle size and compared the concentration of this size class upstream and downstream of a filter, where diffusional particle deposition to a surface takes place. However, credible experimental evidence for rebound of solid particles from surfaces is not given by any of these references. Heim et al. (2005) point out the problems of these experiments that are mainly associated with imprecise size classification. If the particles are electrostatically classified from a size distribution that mainly consists of much larger particles, the test particles applied may, on an average, be much larger than indicated by the mobility interval they appear in. For example, any small turbulence in a mobility classifier introduces large particles into the selected mobility intervals at the small end of the size distribution. This leads to less diffusional deposition of the selected particles than expected for the nominal size, which is interpreted as reduced sticking. A similar effect is observed, if the mobility classifier is perfect, but particles are sampled from the steeply rising small particle end of the distribution. The average particle size in each interval selected is then larger than the nominal size of that interval (=mean between upper and lower cut-off).

The present study basically has the same problem, which means that we have to take the possibility into account that the real mean size of our test particles is larger than the nominal size. We eliminate this problem firstly by focusing our data analysis on *comparison* between different materials exhibiting the same size distributions. Any

difference in the results must then be an effect of the material, and material dependent effects must be related to sticking. This is so, because the transport of particles to a surface is controlled by diffusion in the size range of interest. The diffusion coefficient is defined equally well for any material by our mobility size classification due to the proportionality between the electrical mobility Z and diffusion coefficient D given by Einstein's relation $D = \frac{kT}{e} Z$. As a second measure to reduce the effect of any systematic error in the absolute mobility (or diffusion) equivalent size we measure, we focus on a quantity that contains size only as a *relative* measure.

In contrast to most former experiments examining particle sticking, our experiment is carried out with particles that are mostly uncharged. This is important, because we expect that charge has a critical influence on the sticking behavior. The experimental set-up to achieve this leads to rather large statistical errors, and our results are based on a regression line on over 40 data points. The present experimental concept is thus designed to identify the possible effect of incomplete sticking on a variety of materials and diameters below 20 nm without attempting any absolute quantitative analysis.

Theory

The filtration efficiency is defined by

$$E_f = \frac{N_{in} - N_{out}}{N_{in}}, \quad (1)$$

where N_{in} is the concentration of aerosol particles approaching the filter and N_{out} is the concentration leaving the filter. According to the classical aerosol filtration model for fiber filters and grids (Hinds, 1999; Cheng and Yeh, 1980) the penetration P , i.e. the

fraction of particles penetrating through the filter, and the filtration efficiency E_f are given by

$$P = 1 - E_f = \exp\left(\frac{-4\alpha E_s L}{\pi d_f}\right), \quad (2)$$

Where α is the packing density, E_s is the single fiber efficiency, L is the layer thickness of the filter and d_f is fiber diameter of the single fiber. The single fiber efficiency, E_s , is the product of several quantities that describe different filtration mechanisms, namely interception, impaction, diffusion, gravitation and electrostatic forces. Because we are dealing with extremely small particles and neutral fibres, the diffusion mechanism is strongly dominant, and the single fiber efficiency can be expressed as (Hinds, 1999):

$$E_s = E_D + E_{DR} = 2\left(\frac{d_f v_g}{D}\right)^{\frac{2}{3}} + 1.24 \frac{(d_p / d_f)^{\frac{2}{3}}}{\sqrt{Ku(d_f v_g / D)}}, \quad (3)$$

Where E_D is the single fiber efficiency for diffusion and E_{DR} accounts for the interaction between diffusion and interception. d_p is particle diameter, D is the particle diffusion coefficient, and v_g is the velocity of the carrier gas approaching the filter. Ku is the Kuwabara correction factor that compensates for the effect of neighboring fibers on the single fiber efficiency (Hinds, 1999),

$$Ku = -\frac{\ln \alpha}{2} - \frac{3}{4} + \alpha - \frac{\alpha^2}{4}. \quad (4)$$

The diffusion coefficient D depends on the particle diameter as (Hinds, 1999)

$$D = \frac{kTC_c}{3\pi\eta_g d_p}, \quad (5)$$

where k is Boltzmann's constant ($1.38 \cdot 10^{-23}$ J/K), T is the temperature in Kelvin, and η_g is the gas viscosity ($1.8 \cdot 10^{-5}$ Pa·s for air under standard conditions). C_c is the Cunningham slip correction factor (Hinds, 1999):

$$C_c = 1 + \frac{\lambda}{d_p} \left[2.34 + 1.05 \exp\left(-0.39 \frac{d_p}{\lambda}\right) \right], \quad (6)$$

where λ is the mean free path of gas molecules (66 nm for air under standard conditions).

We showed that for our particle size range equations 2 - 6 can be approximated very well by an expression of the form

$$-\ln(P(d_p)) = C d_p^{-x}, \quad (7)$$

where $x = 1.29$. This is close to the value for pure diffusional deposition in the free molecular range, $x = 4/3$. This follows from eqs. 3, 5 and 6 for $d_p \ll \lambda$, where

$E_s = E_d$. The value of $x = 4/3$ is independent of the filter geometry and the gas velocity. It holds equally well for a tube and a fibre filter and depends only on the filtering mechanism. Any effect that increases the penetration of small particles with respect to large ones results in a decrease of x . Thus measurement of a value of x smaller than the theoretical value indicates reduced sticking of small particles with respect to large ones. As the validity of eq. (7) with $x = 4/3$ is very well established, if diffusion is the only transport mechanism, any significant reduction of x with respect to this value must be due to reduced sticking.

Experiments

The experimental setup is shown in fig. 1. Gas flows are indicated with arrows and particle laden aerosol flows are indicated with fat arrows.

{Figure 1 about here}

Aerosol generation is followed by two identical filter holders and a Scanning Mobility Particle Sizer or SMPS (type 3936L25 by TSI.inc). The instrument was used in the normal scanning mode to measure concentrations and sizes simultaneously. The sheath flow was 10 liters per minute and the aerosol flow was 1 liter per minute. The scanning time (up) was 180 seconds. As a special care, the zero-offset of the CPC was checked but no offset was found. The testing aerosol is generated by nebulizing a 0.1 % salt solution with a collision nebulizer (type 6-jet van BGI.inc). The wet aerosol is mixed with dried, clean air in a mixing chamber with a dilution of 1:3. The dilution air is cleaned and dried with a gas cleaner (type 3074 by TSI.inc). The identical filter holders consist of brass and have a diameter of 10 cm. The gas flow through the filters was controlled with vacuum regulators attached to the local vacuum system and monitored with flow meters (type 4040D by TSI.inc). The air flow through both filter holders was the same, 15.0 liters per minute. The tubes connecting the filter holders to the SMPS system are identical conductive tubes and as short as possible (20 cm).

Filter holder 1 holds a 40 μm grounded stainless steel grid. It acts as a filter with a high penetration, which keeps the downstream particle concentration in a measurable range which was larger than $5 \cdot 10^2 \text{ cc}^{-1}$. Filter holder 2 is empty and the downstream concentration serves as a reference, representing the concentration upstream of the

filter. Thus the ratio of the concentrations measured behind the holders can be completely attributed to trapping in the filter material.

Blanco experiments showed that both filter holders had equal losses to the walls. Reliable concentration measurements with tolerable averaging times could be performed from particle sizes of 6 nm upwards. Above 20 nm, the variations with respect to theory were small, and we thus restricted our analysis to the range between 6 and 20 nm. The psd's from the generation of particles were reproducible within about 6%. To guarantee identical conditions for all the measurements, we left the set-up completely unchanged during the measuring period of about 3 weeks. Experiments were performed with four different salts. To have a high chance of observing differences in the sticking behavior, we chose materials that exhibit different crystal structures and therewith different shapes, namely

- Sodium Chloride (NaCl): cubic
- Calcium Chloride (CaCl₂): cubic
- Ammonium Sulfate ((NH₄)₂SO₄): orthorhombic
- Nickel Sulfate (NiSO₄): tetragonal

As the contact area is certainly important for sticking, it should be influenced by particle shape. Note that we incorporate possible effects of shape into “effects of material” in the context of this study. Different salts behave differently with respect to water vapor. The relevant macroscopic quantities are the point of deliquescence (water uptake under rising humidity) and the point of efflorescence (transfer of water to the vapor phase under falling humidity). Water adsorption may also play a role. The water content could influence sticking due to water bridges. The relative humidity in our experiment was 25%. The solutions dispersed had the same concentration of

0.1 % for each material. The particle size distributions were almost identical for all the experiments (fig.2). Separate measurements showed that more than 60% of the particles produced by the nebulizer were neutral below 20 nm.

{Figure 2 about here}

{figure 3 about here}

Results

Figure 3 shows the directly measured filtration efficiencies averaged over 3 consecutive measurements. The figure shows that the filtration efficiency of nickel sulfate is lower than the efficiency of sodium chloride, calcium chloride and ammonium sulfate. This result suggests that nickel sulfate has different filtration characteristics compared to the other materials. However, new mesh filters were used for each measurement to exclude any influence of deposited particles. That means that it is possible that the lower values for nickel sulfate are only due to the variations in the filter shape. So we cannot exclude that the filters are different in their filtration characteristics, and the changes from material to material may be due to such variations, at least in part. This is why we study the power x instead of direct measurements in the first place.

In order to corroborate the influence of the material on the filtration characteristics, we took a closer look at the size dependence, which should follow eq. (7) with $x=1.29$, if there is perfect sticking. Figure 4 shows an example of a double logarithmic plot of $-\ln P$ vs. d_p . In agreement with eq. (7) the data can be fit to straight lines, where the slopes indicate x . The fit for sodium chloride yields $x = 1.04$ and the one for Nickel sulfate yields $x = 0.91$. Lower values of x than 1.29 indicate that smaller

particles are filtered less efficiently with respect to larger ones. Thus a lower value of x indicates less efficient sticking of smaller particles within the same material.

{figure 4 about here }

Table 1 gives the values of x for the four particle materials. Each value is the average of 3 measurements and the error given is the standard deviation. Note that the values of the power x are always lower than the theoretical value of 1.29 and that the variance does not overlap with 1.29.

{Table 1 about here }

Discussion

As demanded by theory, none of the values for x shown in table 1 is larger than 1.29. The variances calculated from three measurements are below 10 % for each case. A statistical test (Devore, 2000) was performed on the values of x to decide whether the differences from material to material are significant. We used an upper-tailed two-sample t -test with the hypothesis $H_0: x_1 > x_2$ and the alternative hypothesis $H_a: x_1 = x_2$ with a confidence interval of 90% (Devore, 2000), where x_1 and x_2 are power x values for different materials and x_1 is the lower value of the two. The results are given in table 2. The value of x for nickel sulfate is lower than this value for all other three materials with a confidence level of 90%. The value for sodium chloride is lower than the one for ammonium sulfate with the same confidence level. The statistical test thus reveals that material dependent differences in x are statistically significant.

Table 2: upper tailed two-sample t -test; NiSO₄ has a lower value than the other materials.

{table 2 about here}

The results for x are significantly lower than the theoretical one for perfect or size independent sticking ($x=1.29$) in all cases. For a single material, this discrepancy could be due to a systematic error of the kind pointed out by Heim *et al.* (2005): In the range of the steep rise of the size distribution curve (fig. 2), the actual (mean) size selected by the DMA is larger than the nominal size, because some larger particles (the concentration of which is orders of magnitude higher) are mixed into the outlet aerosol. Thus the selected particles have a smaller diffusion coefficient than the nominal size indicates, leading to a penetration “too high” with respect to theory. This overestimation of the penetration rises with decreasing size, because the concentration decreases with size. However, such a systematic error would not explain the *differences* observed between the materials under conditions that were identical in every other respect. The fact that different values of x are found indicates an effect of the material with the confidence level of 90%. Thus any variation of x indicates a size-dependent sticking probability at least for those cases where x is smaller than the maximum value measured. In particular, $x((\text{NH}_4)_2\text{SO}_4) > x(\text{NaCl}) > x(\text{NiSO}_4)$ with a 90% confidence level. This means that there is no perfect sticking at least for NaCl and even less for NiSO₄. So even if (NH₄)₂SO₄ sticks perfectly, NaCl does not. This is in contradiction to Alonso et al. (1997). It is to be noted that Alonso et al. worked with 100% charged particles, though, while our particles are mainly neutral. In fact, this is a major difference of our experiment with respect to most publications examining sticking efficiency, where the charged aerosol coming directly from a

DMA is passed through the filter. The study of Heim et al., 2005 represents an exception in applying both charged and uncharged NaCl particles. Indeed, in the data presented in fig. 8 of that publication, neutral NaCl particles show a smaller penetration through a metallic mesh than charged ones. This result is consistent with incomplete sticking for the neutral particles, with rising tendency towards smaller sizes. Heim et al. name an artifact as the probable reason, but our present findings support the assumption that their deviations between charged and uncharged particles were indeed real.

Particle charge influence on the sticking probability is not straightforward, because the charge is transferred to a conducting surface at contact. Fig. 5 illustrates a possible mechanism explaining reduced thermal re-entrainment or rebound when the particle is charged. It is based on the recognition that the contact distance d plays a very critical role for van der Waals adherence to surfaces, mathematically becoming infinite at $d=0$. In step B, the van der Waals force is still weak, because adsorbed molecules hold the particle and the substrate at a distance. If the particle is charged, however, adherence is stronger due to the image force. This force is present until the charge has been conducted to the metal substrate. The adsorbed gas molecules, covering any surface, represent a barrier for this charge transfer. Only when they have been pushed aside by the particle, the charge can be transferred. The particle then adheres much more strongly to the substrate due to the reduced d in the van der Waals interaction. Thus particle charge enhances the sticking probability, because it makes thermal re-entrainment at stage B less probable. Charge transfer from the particle to the substrate is particularly slow for insulating particles (as NaCl particles). As long as the charge is there, the particle has time to decrease the mean contact distance. Besides pushing

aside adsorbate molecules, surface deformation and change of position to obtain a larger contact surface may also play a role.

{Figure 5 about here}

Conclusions

Our experiments show with a 90% confidence level that salt aerosol particles between 7 and 20 nm in diffusion equivalent diameter exhibit material dependent penetration through a wire mesh. Since filtration in this size range is governed by material independent diffusional transport to the filter surface, this implies differences in the sticking probability of the particles to the metal fibers under thermal impact. In particular, we conclude that a sticking probability smaller than 1 occurs for particles of NaCl and with still higher confidence for NiSO₄. Our findings are different from other studies, in which 100% sticking probabilities were demonstrated, part of them with even smaller particles. However, these studies mostly use metal particles that typically have Hamaker constants (determining the van der Waals forces) 5 – 10 times higher than those of salts. The apparent contradiction with Alonso et al. (1997) may be due to the fact that the majority of our particles are neutral in contrast to that study, and that charged particles have a higher sticking probability. The reduction of filter penetration of charged NaCl particles with respect to uncharged ones observed by Heim et al. (2005) points in the same direction, although interpreted differently in that publication. We hypothesize that charged particles have a higher sticking probability than uncharged ones, because the strong image force initially present induces a

smaller contact distance before the charge is neutralized, leading to a larger van der Waals force, which guarantees adherence.

The experiments performed do not allow any quantitative statements or solid conclusions on mechanisms involved. For example, the differences that we ascribe to “material” may be associated with particle shape, which influences the mean contact area. Further studies are needed to obtain the basis for adherence models valid for particles in the nanometer range. These should also include the phenomenon of deliquescence, i.e. uptake of water. In the present case, NaCl and $(\text{NH}_4)_2 \text{SO}_4$ were dry crystals, because they loose water below the humidity of 45% and 35%, respectively (point of efflorescence, see Martin (2000)), and our RH was 25%. While the point of deliquescence of NiSO_4 is not known, water uptake can certainly not serve as an explanation for the difference between NiSO_4 and the former two, because if NiSO_4 takes up water it would be expected to show perfect sticking.

As experiments with the technology presently available are difficult, our approach, which focuses on a quantity as the power x in the penetration law and comparison of identical experiments with the only difference being the particle material, should lead to quantitative results, if higher concentration sources for the nanometer range are applied. A comprehensive adherence model should contain particle shape, deformation (Young’s modulus and hardness), and the Hamaker constants of particles and surface. It should consider deliquescence and the presence of a surface liquid film.

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CAPTIONS OF FIGURES AND TABLES

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- Figure 5. Model of particle deposition: The particle diffuses to the surface (A) and contact van der Waals forces are initially weak (stage B), because adsorbed molecules act as spacers. Thermal re-entrainment or rebound is possible at this stage. If the particle is charged, this induces an image force, hindering re-entrainment and promoting decrease of the mean contact distance d (stage C). Charge neutralization is now possible, but van der Waals forces are drastically increased due to reduction of d .

Table 1: power x for different aerosol and filter materials.

Aerosol	power x
Theory	1.29
NaCl	$1.03 \pm 4.1\%$
CaCl ₂	$1.02 \pm 9.6\%$
(NH ₄) ₂ SO ₄	$1.13 \pm 2.7\%$
NiSO ₄	$0.87 \pm 8.1\%$

Table 2: statistical analysis of differences in the power x .

material x_1	material x_2	t -value	$t_{0.1}$	$t > t_{0.1}$
[values: table 1]	[values: table 1]	[-] calc.	[-] table	
(NH ₄) ₂ SO ₄	NiSO ₄	5.916	1.886	Yes
(NH ₄) ₂ SO ₄	NaCl	3.143	1.638	Yes
(NH ₄) ₂ SO ₄	CaCl ₂	1.816	1.886	No
NaCl	CaCl ₂	0.229	1.886	No
NaCl	NiSO ₄	3.564	1.638	Yes
CaCl ₂	NiSO ₄	3.621	1.638	Yes

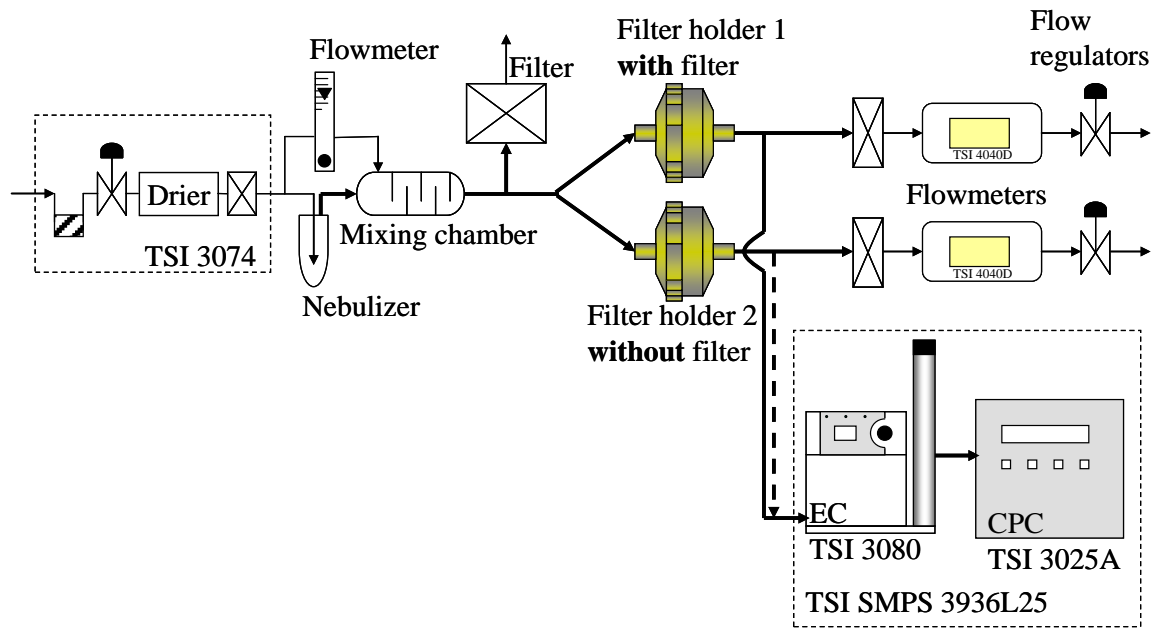


Figure 1: Schematic representation of the setup.

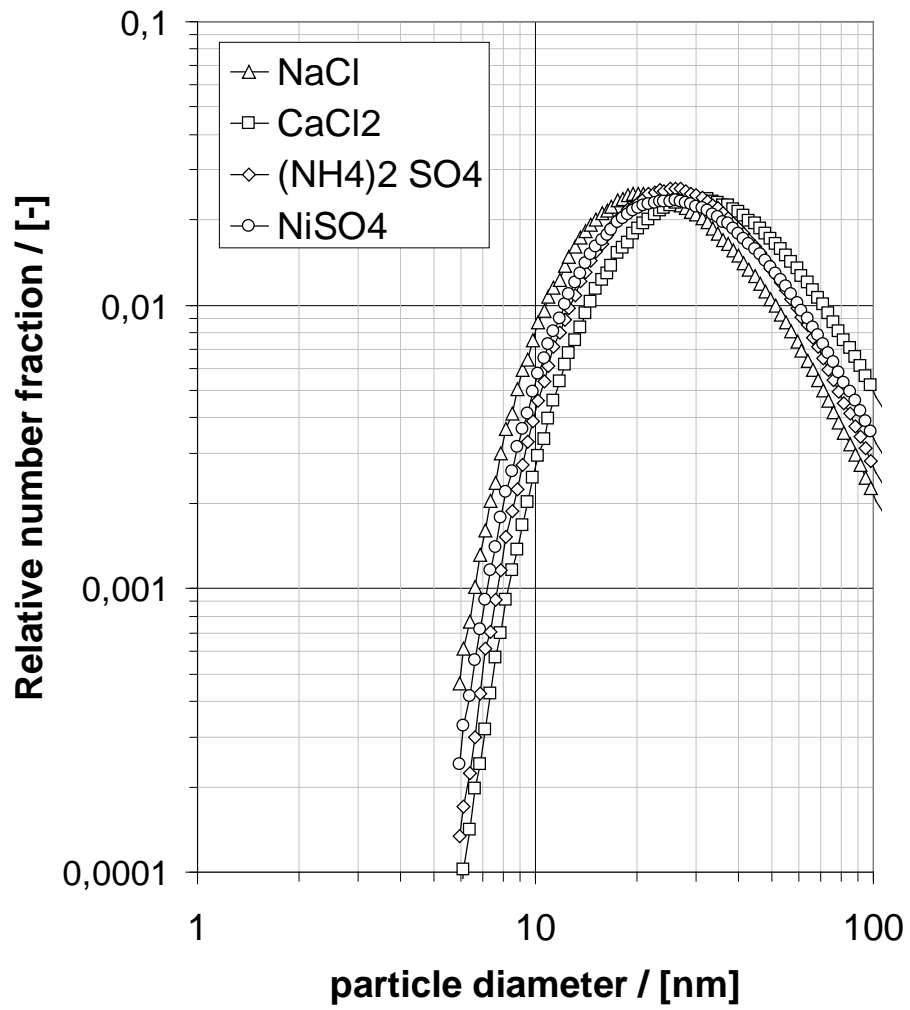


Figure 2: Measured particle size distributions of unfiltered aerosol (through filter holder 2).

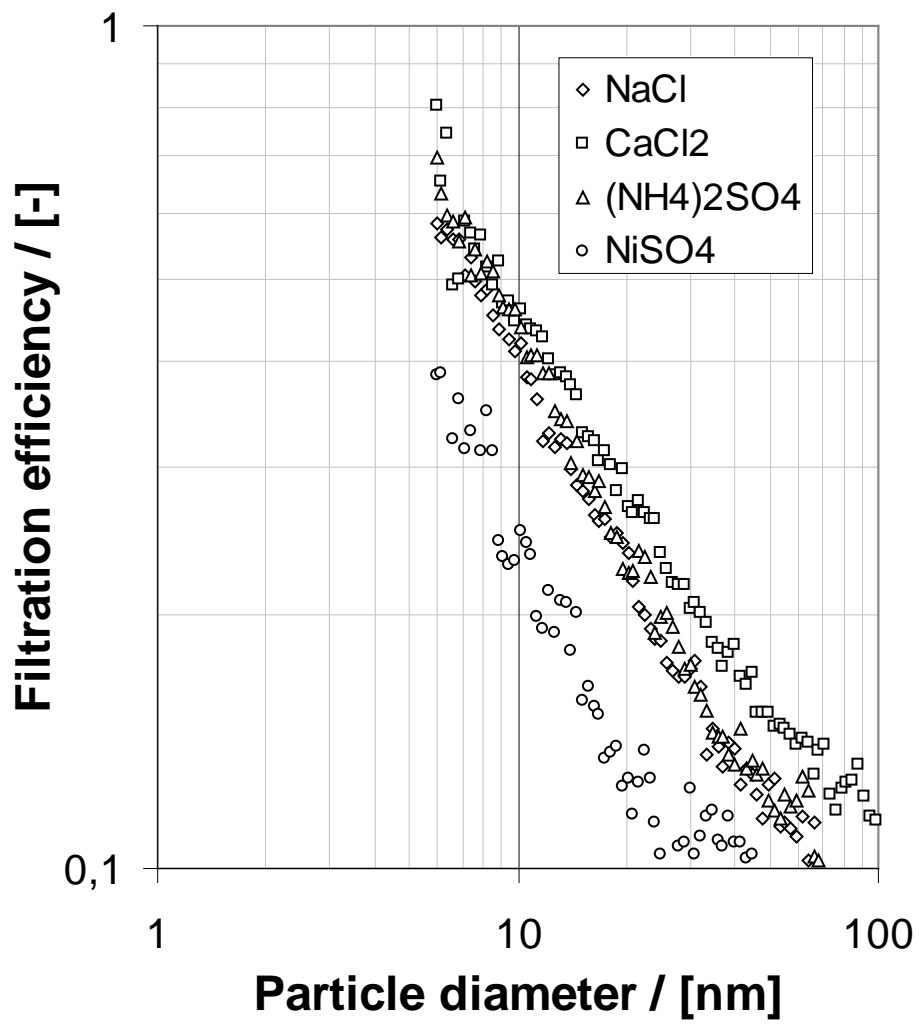


Figure 3: direct measurement of filtration efficiency.

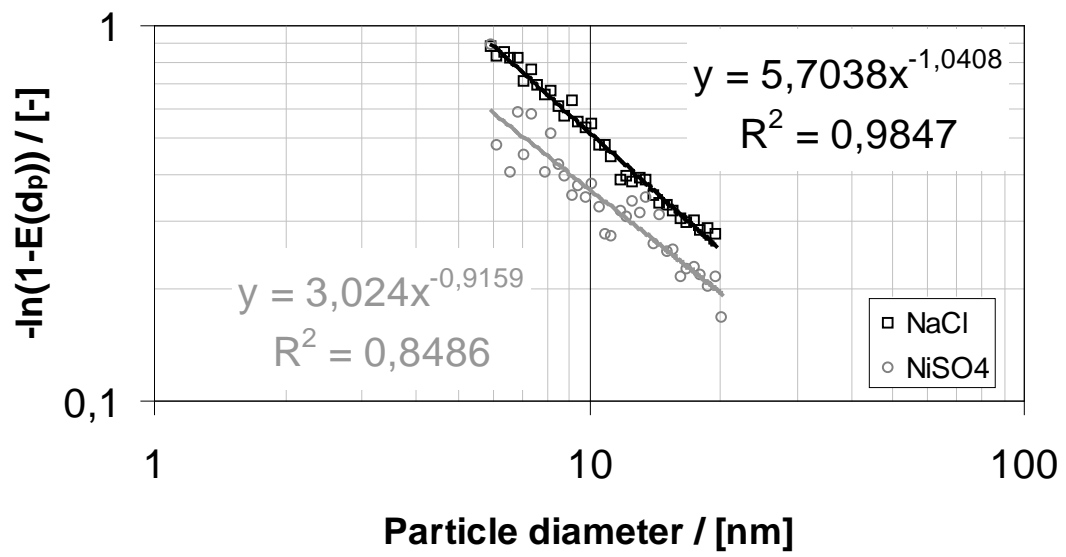


Figure 4: Filtration efficiency measurements (single runs): sodium chloride and nickel sulfate particles filtered by a metal grid. The power x is determined by a power-law fit.

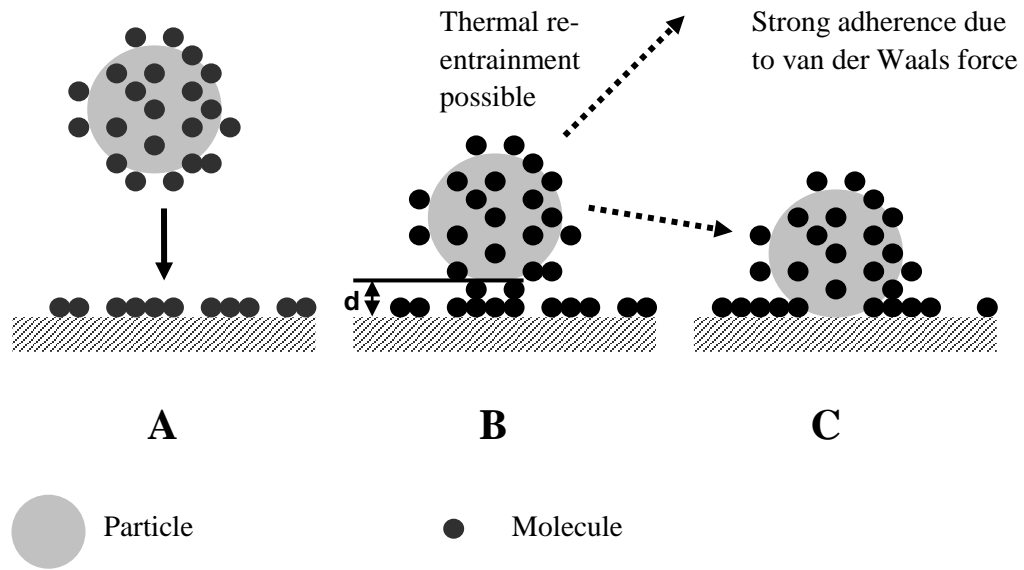


Figure 5. Model of particle deposition: The particle diffuses to the surface (A) and contact van der Waals forces are initially weak (stage B), because adsorbed molecules act as spacers. Thermal re-entrainment or rebound is possible at this stage. If the particle is charged, this induces an image force, hindering re-entrainment and promoting decrease of the mean contact distance d (stage C). Charge neutralization is now possible, but van der Waals forces are drastically increased due to reduction of d .

