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Aerosolization of monodisperse spherical gold particles as reference for calibration of mobility analyzers

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Within work package 1 “automotive combustion particle metrics” of the EMRP project ENV02 PartEmission, reference materials have been established to calibrate mobility particle sizers with monodisperse, spherical reference particles. Calibration of mobility analyzers on one hand requires traceable measurement of the geometric diameter of the reference particles, and on the other hand, the reference particles have to be available in an aerosol. In the present work, we have studied the aerosolization of spherical gold particles between 20 nm and 40 nm nominal diameter from commercially available colloid solutions (TedPella, Inc.) as one possibility to generate the reference aerosol. The advantage of aerosolization of particle size standards from colloid solutions is the reusability of the solution. Once the particles are characterized (by a traceable measurement of the geometrical diameter), the colloid solution can be stored and transferred to different laboratories, and thus serve as a size standard for several mobility analyzers. However, aerosolizing colloid solutions is challenging due to both the existence of residual particles originating from the liquid phase and the possibility that the diameter of the reference particles is biased by deposits from the solution. We present an optimized procedure for the aerosolization together with a discussion of the reliability of this method.

Aerosolization of a colloid solution with a nebulizer is only possible for particle sizes larger than about 100 nm. For smaller particle sizes, the reference particles are usually not clearly distinguished from the residual particles in a mobility size spectrum. Even if the peak of the rediduals seems clearly distinguishable from the one of the suspended particles, overlap of the peaks may shift the apparent mode diameter of the reference particles towards a smaller size. The use of an electrospray generator substantially reduces the droplet size as compared to a nebulizer, and hence shifts the size range of the residual particles well below the size of the reference particles. However, stable operation of the TSI 3480 electrospray generator used in the present work required the following modifications:

- The original manometer has been replaced by a WIKA PSD-30 manometer allowing for > 0.7 bar gauge pressure in the pressure chamber instead of originally around 0.35 bar.
- The capillary was glued into the feedthrough from the pressure chamber for tightness.
- A 2 mM ammonium acetate buffer solution was used instead of a 20 mM solution.
- The original ^{210}Po neutralizer has been replaced by a ^{241}Am neutralizer to increase the half-life of the neutralizer.

Colloid solutions contain additives to stabilize the solution, i.e. prevent the suspended particles from agglomerating. In order to investigate the influence of these additives on the resulting aerosol, we subjected the original solution to a cleaning procedure consisting of centrifugation (around 6000 rpm during 20 min) and subsequent replacement of the virtually particle-free head space of the solution by water or an ammonium acetate buffer solution. The cleaning step was repeated, and we investigated the resulting size distributions as a function of the number of performed cleaning cycles with a scanning mobility particle sizer (SMPS, TSI 3085, 3.0 lpm sheath flow, 0.3 lpm aerosol flow). We found that the original solution had to be removed in at least three consecutive cleaning cycles to prevent deposits from biasing the particle size and, in the case of nominal 20 nm reference particles, from overlapping the size distribution of the reference particles.

Figure 1 displays the size spectra of a solution containing nominal 30 nm gold particles without cleaning, after three cleaning cycles, and after five cleaning cycles. It is obvious that after three cleaning cycles, both amount and size of the residual particles are substantially reduced. However, applying more than three cleaning cycles seems to reverse the cleaning effect, such that amount and size of the residual particles increase again. This is most likely due to compounds from the sample vials dissolving progressively with increasing

number of centrifugation cycles. In our procedure where standard vials were used, a number of three centrifugation steps appears to be an optimum.

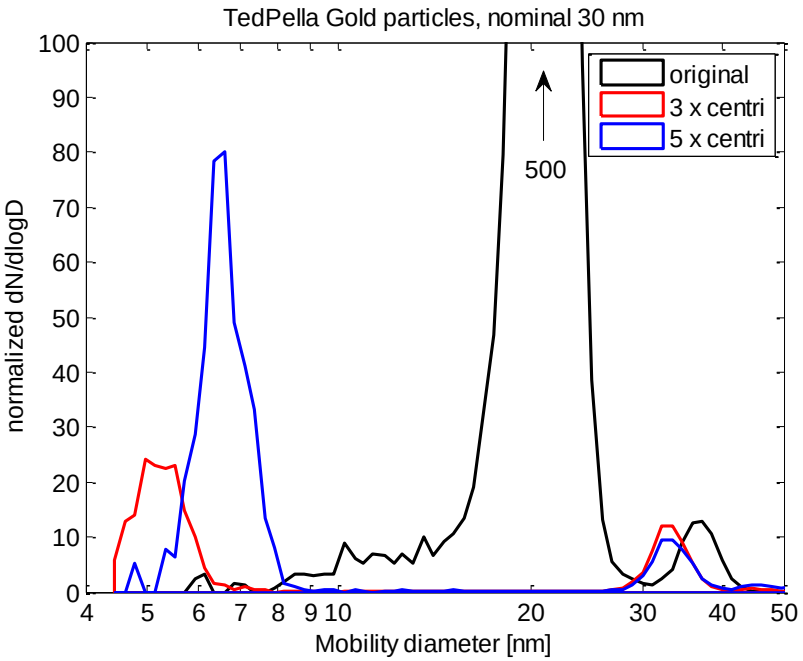

Figure 1: Size distributions of electrosprayed solutions containing nominal 30 nm gold particles after zero, three, and five cleaning cycles

An effect of the amount of original solution remaining in the sample on the measured mobility diameter of the reference particles is also visible in Fig. 1. Figure 2 displays the measured mode mobility diameter of nominal 20 nm and 30 nm particles as a function of the number of performed cleaning cycles.

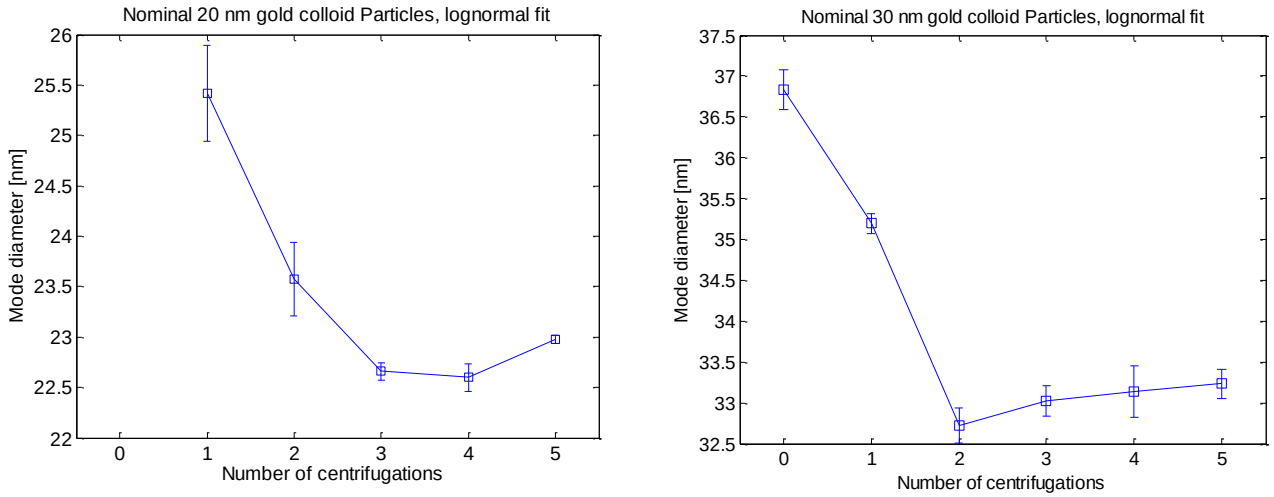

Abbildung 2: Measured mode mobility diameter as a function of the number of cleaning cycles (centrifugations). For nominal 20 nm particles, the mode diameter cannot be determined in the original solution (zero centrifugations), because the size distribution of the residual particles from the original solution covers the size range of the suspended gold particles.

One can conclude from these measurements that after three centrifugation cycles, the original solution is sufficiently diluted that its effect on particle size is negligible. In the aerosol resulting from the original solution,

the measured mobility diameter of the reference particles is around 10% larger than after three cleaning cycles. This effect of impurities increasing the measured diameter of particles in aerosolized suspensions has been reported e.g. by Park et al. (2012). It is not clear whether the slight increase of the particle diameter in Fig. 2 for more than three cleaning cycles is significant (note that the “kink” in the curve at two centrifugations for nominal 30 nm particles is due to a larger sample flow used in that measurement. We have observed a decreasing measured particle diameter for increasing sample flow in the DMA). However, an increase of the particle diameter for increasing number of cleaning cycles is plausible for more than three cycles, in view of the fact that the size of the residual particles increases (cf. Fig. 1). Assuming that all droplets leaving the cone jet of the electrospray have equal size, it is reasonable to estimate an upper limit for the mass of deposits distributed over the surface of a reference particle from the maximum size of residual particles present in the size distribution. Accordingly, the diameter of a 20 nm particle should not be increased by deposits by more than 0.9% after three centrifugation cycles. Although this is not negligible, it has to be seen in relation with the precision at which the particle mobility diameter can be determined. We found the uncertainty in the measurement of the mobility diameter with a DMA (TSI 3085 with equal settings as in the present work) according to ISO 15900 to be 1.7 % for 20 nm particles, which is larger than the 0.9% potential increase of the particle diameter due to impurities. For a particle diameter of 30 nm or above, the effect of the observed residuals on the diameter of the reference particles is negligible.

Comparison of the mobility diameter measured by an SMPS in the present work with TSEM measurements of the geometric diameter performed by E. Buhr and T. Klein at PTB (Germany) reveals a systematically larger size resulting from the SMPS measurements. The factor between SMPS (after three cleaning cycles) and TSEM diameter decreases from 1.18 for nominal 20 nm particles to 1.04 for nominal 40 nm particles. This discrepancy is too large to be explained by residual material in the SMPS measurement. Possible reasons are imperfect sphericity of the reference particles (with the associated effect on the ratio between geometric and mobility diameter) or a deficiency of the slip correction factor used in the evaluation of SMPS data. Sampling the particles after the SMPS and analysis by TSEM might provide more insight into eventual inaccuracy of the slip correction factor.

Reference

- J.Y. Park, P.H. McMurry, and K. Park (2012). Production of Residue-Free Nanoparticles by Atomization of Aqueous Solutions. Aerosol Science and Technology, 46: 354 – 360.

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25 June 2012

Outline

1 Framework

2 Electrospray – Principle and Modifications

3 Procedure of Sample Preparation

4 Results

5 Conclusions

EMRP
European Metrology Research Programme
Programme of EURAMET
The EMRP is jointly funded by the EMRP participating countries within EURAMET and the European Union

1 Motivation

- EMRP: European Metrology Research Programme
- JRP ENV02 PartEmission: Emerging requirements for measuring pollutants from automotive exhaust emission
- WP1: Automotive combustion particle metrics
- Task 1.1: Generation of automotive combustion calibration aerosols
- Deliverable 1.1.1: Generation of a monodisperse aerosol as size standard for calibration of mobility analyzers between 23 nm and 100 nm ⟶ calibration service

- Details about JRP ENV02: ⟶ Poster 29, J. Schlatter

Requirements for the calibration of mobility analyzers:

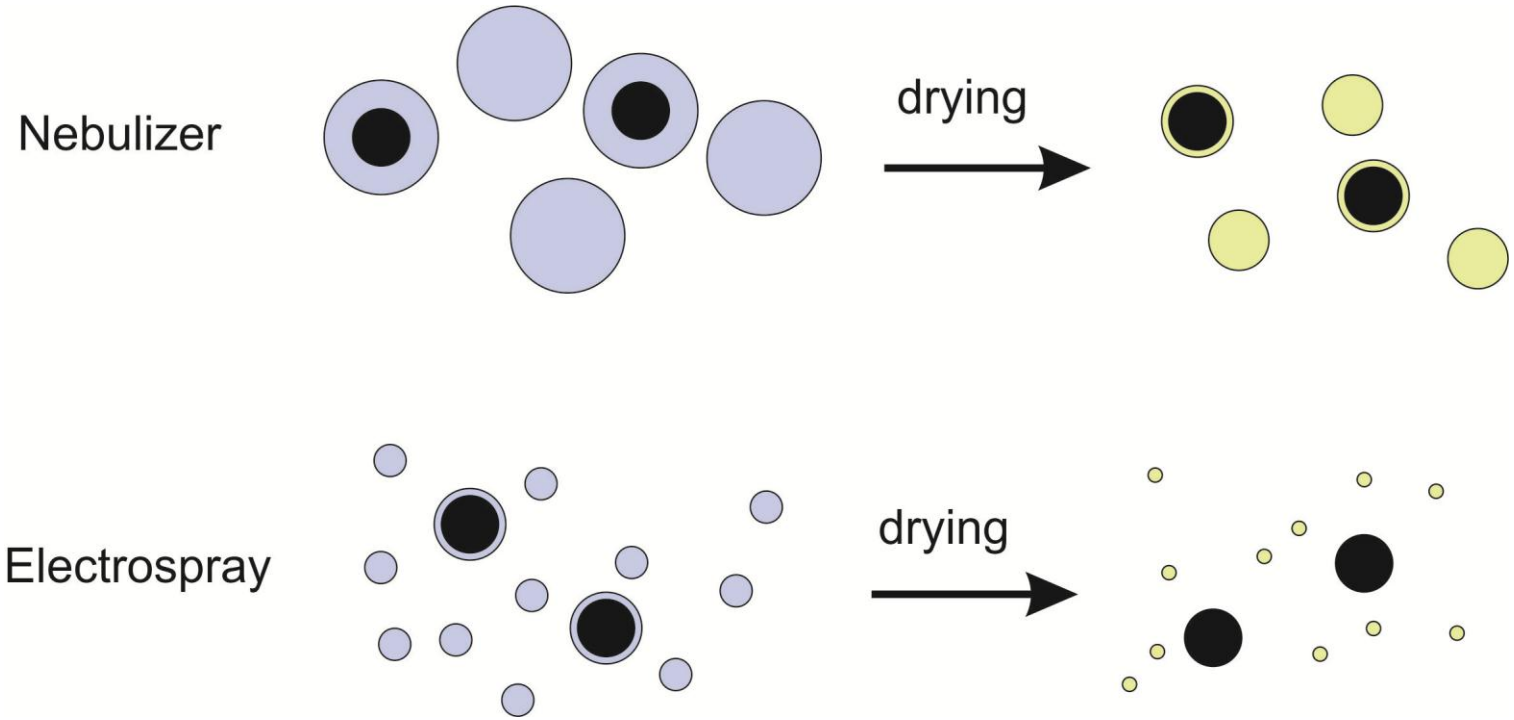
- Generation of a reference aerosol
    - By condensing Ag vapor (IfT)
    - By atomizing colloid solutions (METAS)
- Traceable size measurement of the reference particles
    - Geometrical diameter obtained from AFM and TSEM measurements (DFM, PTB)

Atomizing colloid solutions:

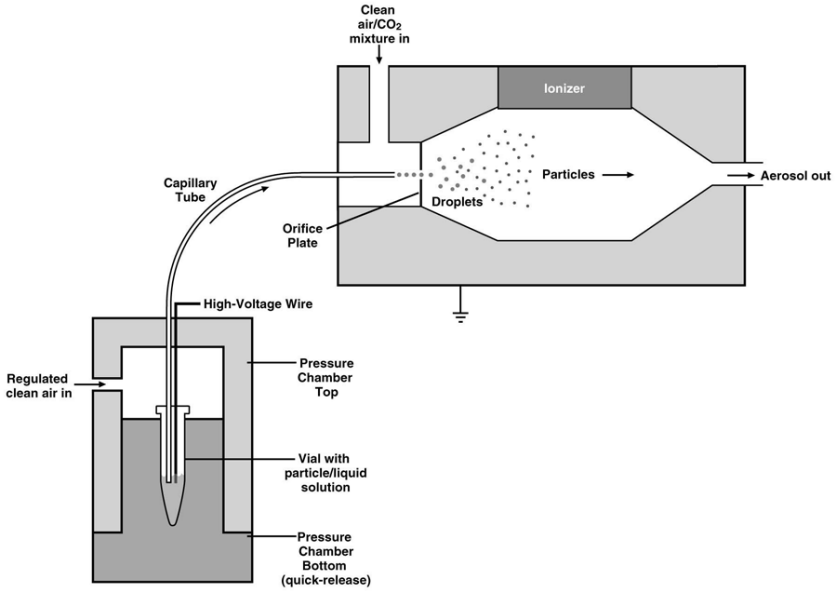
- Advantage: Characterized reference particles can be transported and used in different laboratories
- Drawback: Difficulty to avoid bias by possible influence of the solution on the particle mobility diameter

2 Electrospray – Principle and Modifications

Why use an electrospray…?



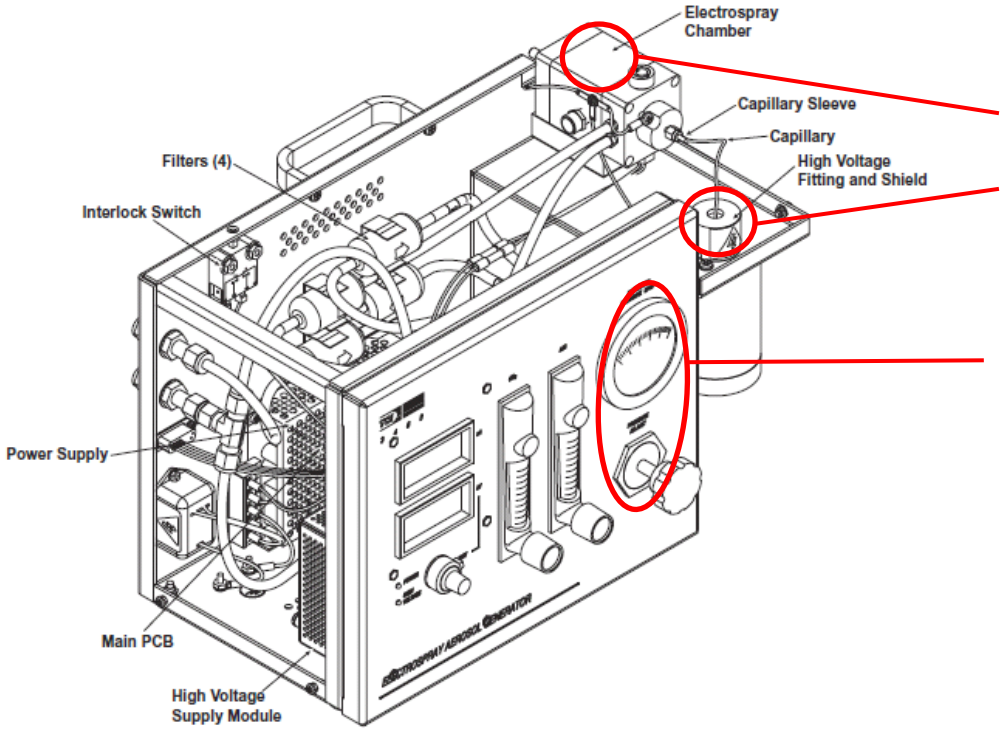
⟹ Nebulizing particle suspensions only works for particles > 100 nm.



Electrospray TSI 3480 – Principle

- Liquid pressed through capillary (d = 40 µm) set to HV
- Electrical field forms a cone jet at the end of the capillary

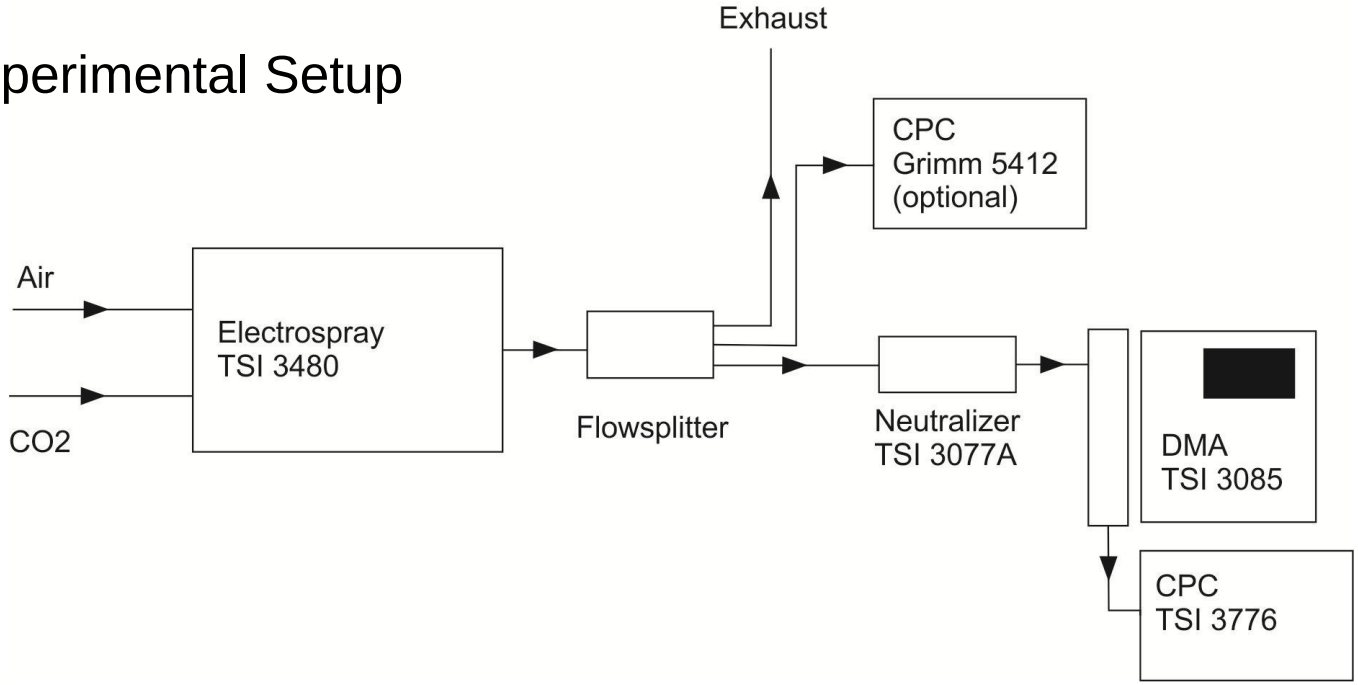
- Tiny droplets leave the cone and are dried and neutralized



Modifications at METAS

- Long life ^{241}Am aerosol neutralizer
- Capillary glued into the feedthrough from the pressure chamber for tightness
- New manometer WIKA PSD-30 allowing for > 0.7 bar gauge pressure in the pressure chamber instead of originally ~0.35 bar.
- 2 mM instead of 20 mM ammonium acetate buffer solution

Experimental Setup

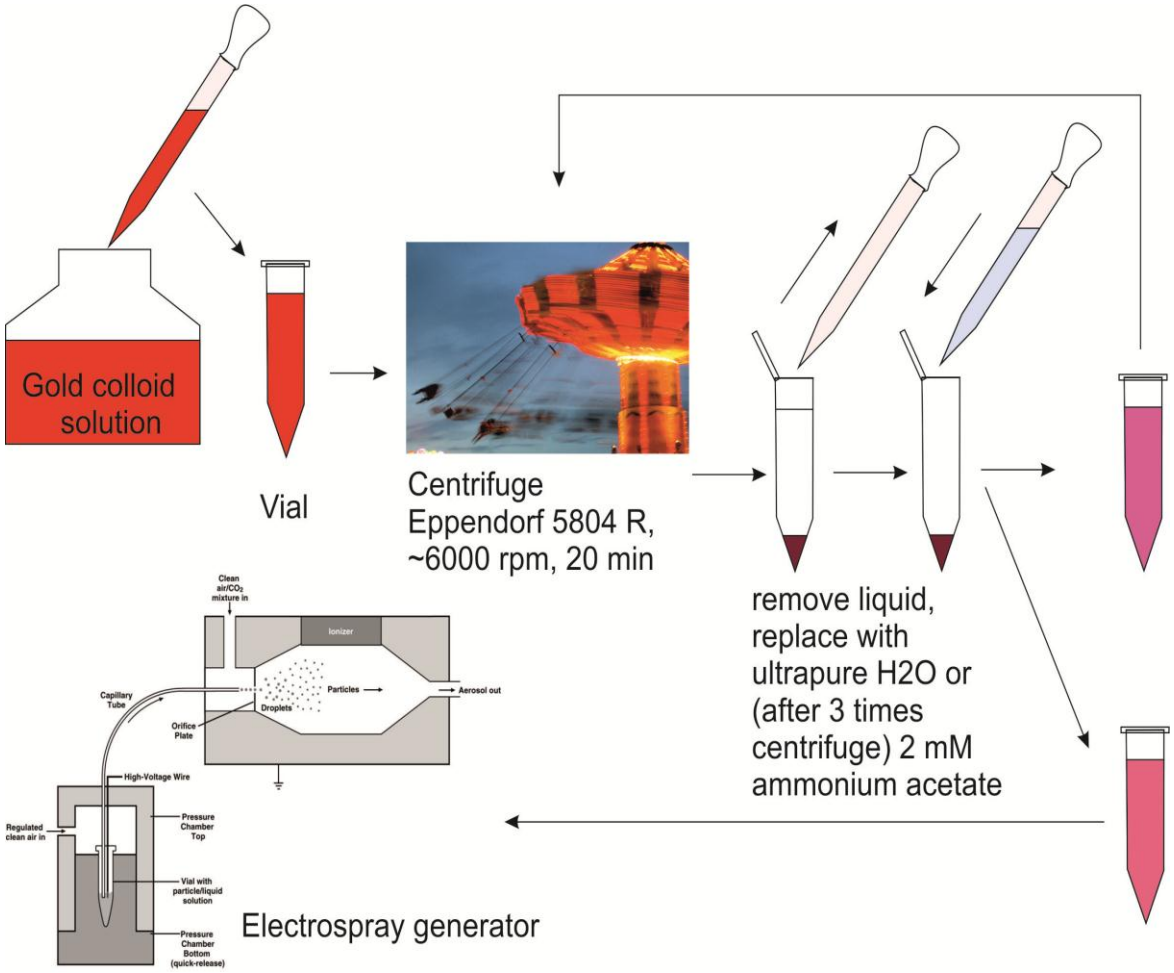


Scope of the experiments

- Calibration of the TSI 3085 mobility analyzer by SMPS scan and/or DMA method (according to ISO 15900)

  ⟶ Calibration is only valid for the settings at which the calibration is done!
- Separation of gold particles from residual particles
- Influence of the particle solution on the mobility diameter of the Au particles
- Comparison of the measured mobility diameter with TSEM and AFM measurements

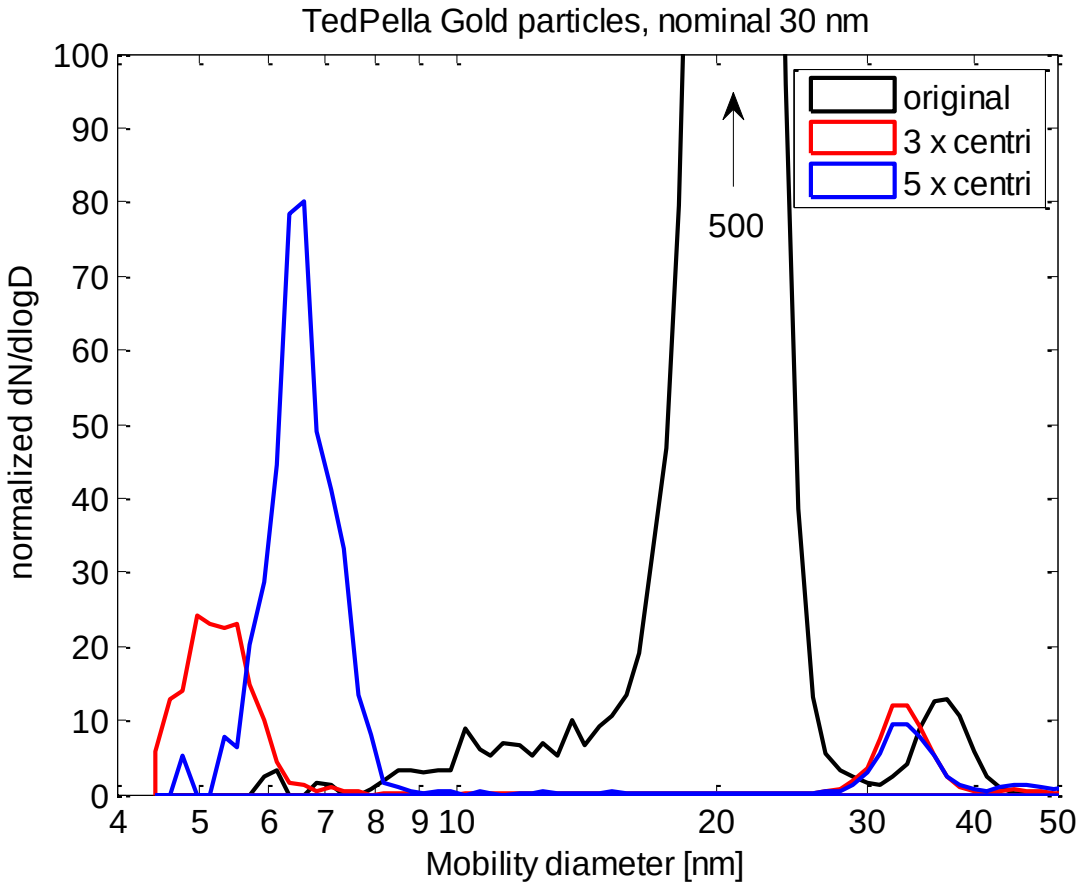
3 Procedure of Sample Preparation



- Colloid solutions from TedPella, Inc. with spherical gold particles of 20, 30, and 40 nm nominal diameter
- Remove original solution by multiple centrifugation
- 40 nm particles: Increase particle number density by factor 5 for sufficient concentration in the aerosol
- Only centrifuge with water to avoid degradation of the sample!

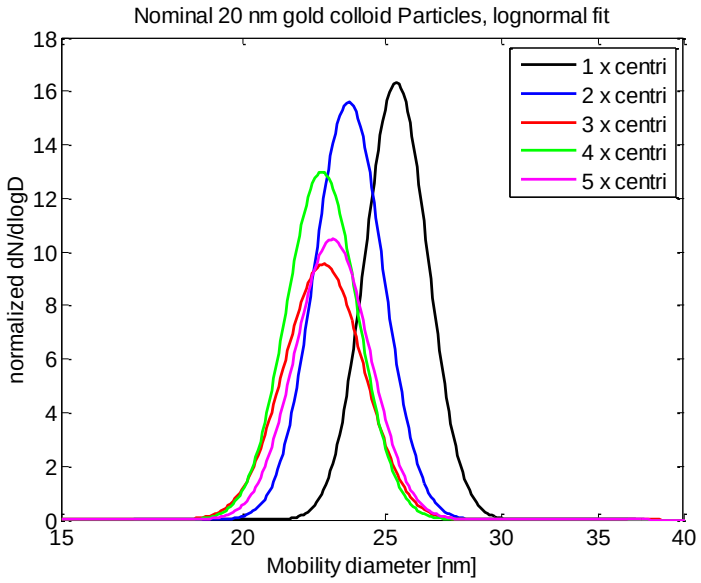
4 Results

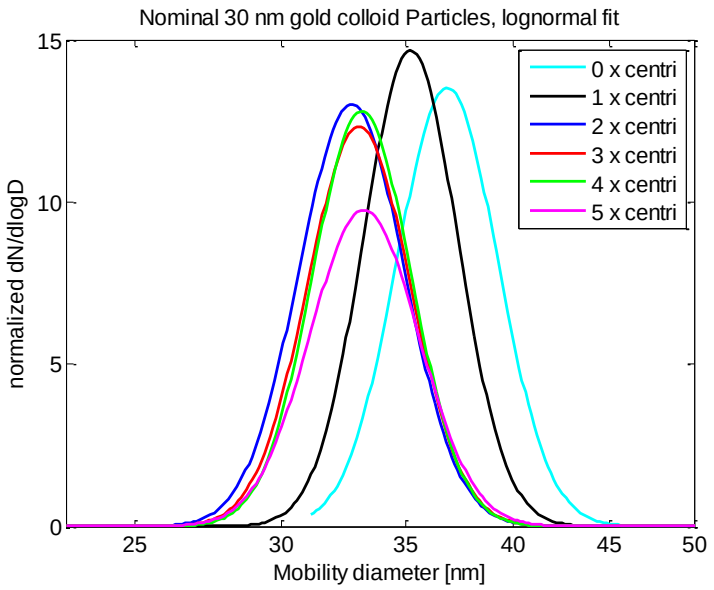
Residual particles from the solution

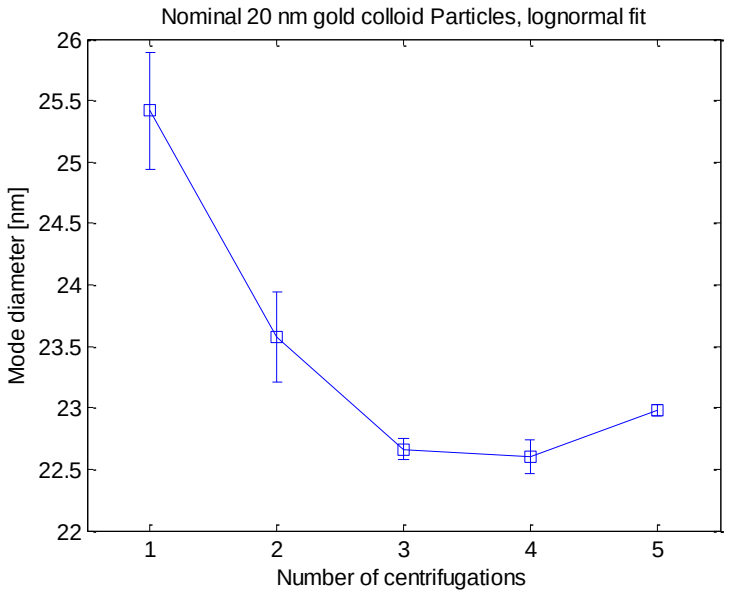


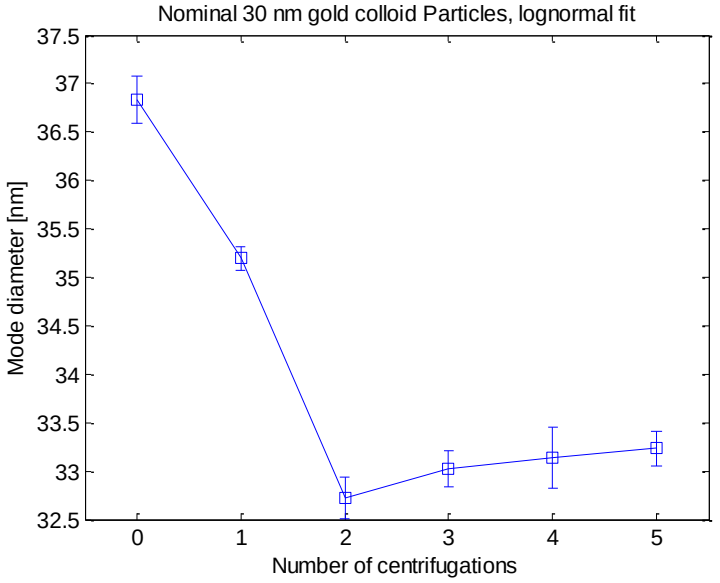
- Additives in the original solution produce a large amount of residual particles
- Reference particles < 30 nm are well separated from the residuals only after centrifugation
- 3 consecutive centrifugations substantially reduce size and number concentration of residuals
- After more than 3 centrifugation cycles, contamination arises

Influence of the solution on the measured mobility diameter



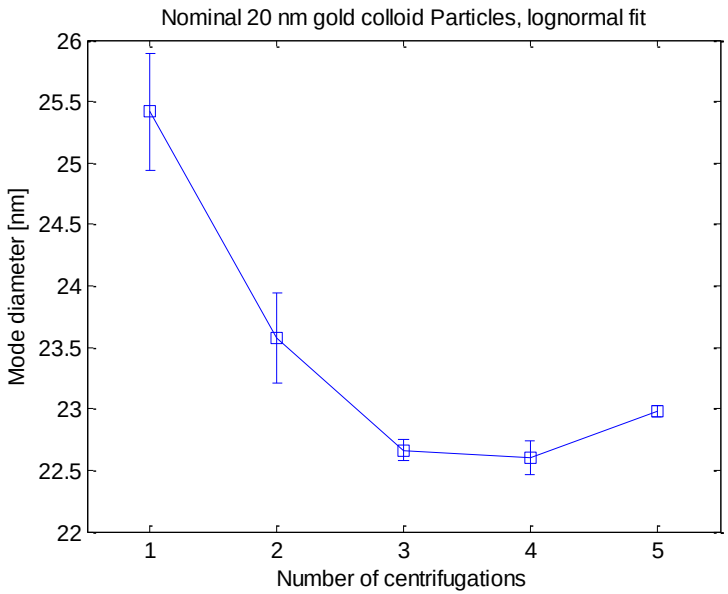


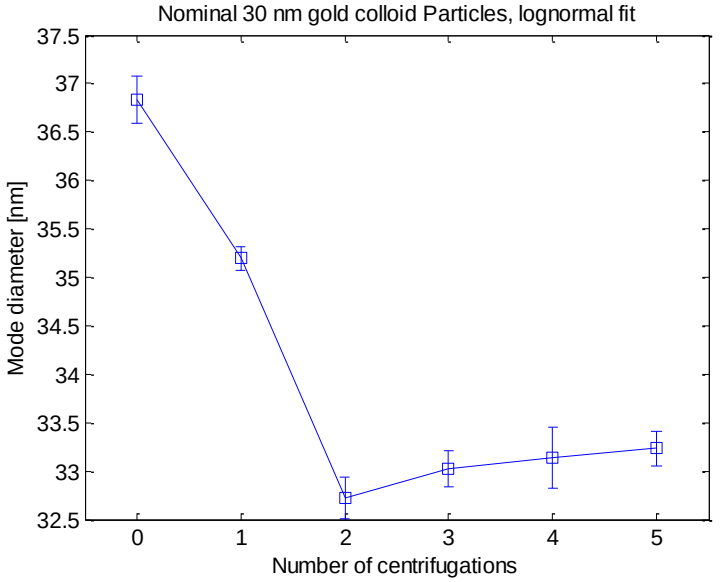




Influence of the solution on the measured mobility diameter

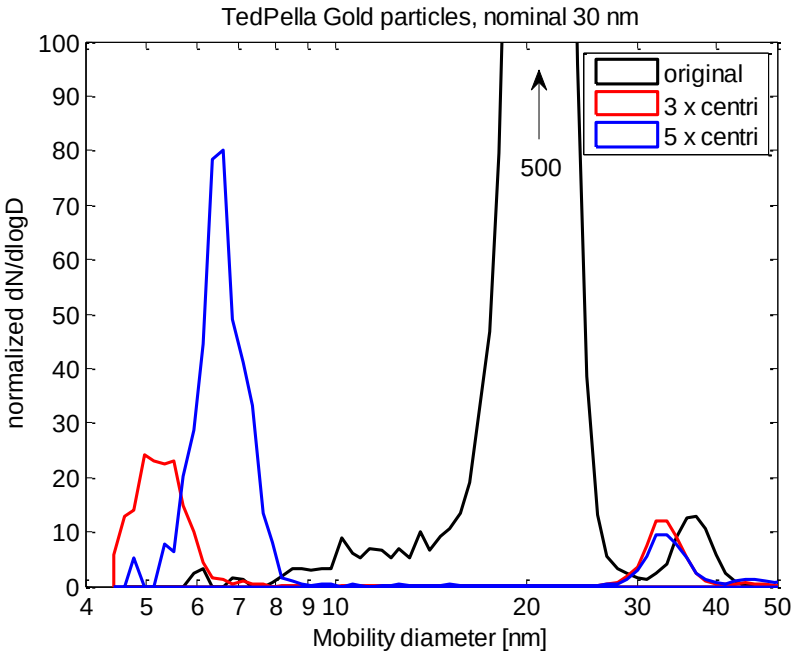
- The original solution leaves deposits on the particles which increase the particle mobility diameter by around 10%
- After three centrifugations, the original solution is diluted beyond a significant effect on the particle diameter
- Nominal 30 nm: Increase in mode diameter after 5 centrifugations probably due to contamination
- Nominal 20 nm: Minimum at 2 centrifugations is due to a higher sample flow (0.7 instead of 0.3 lpm) in the DMA!





Are there deposits from the buffer solution on the gold particles?

- After 3 centrifugation cycles, the particle solution contains residuals at max. ~ 6 nm.
- Increase in diameter for a 20 nm particle: 0.9 %.
- The uncertainty of the mobility diameter determined with a DMA according to ISO 15900 is 1.7% for 20 nm particles.



⇒ The electrosprayed solution is unlikely to significantly increase the particle diameter.

⇒ PFA vials might help avoiding contamination

Comparison SMPS / DMA mobility diameter vs. geometric diameter from TSEM

(TSEM measurements by E. Buhr and T. Klein (PTB, Germany)

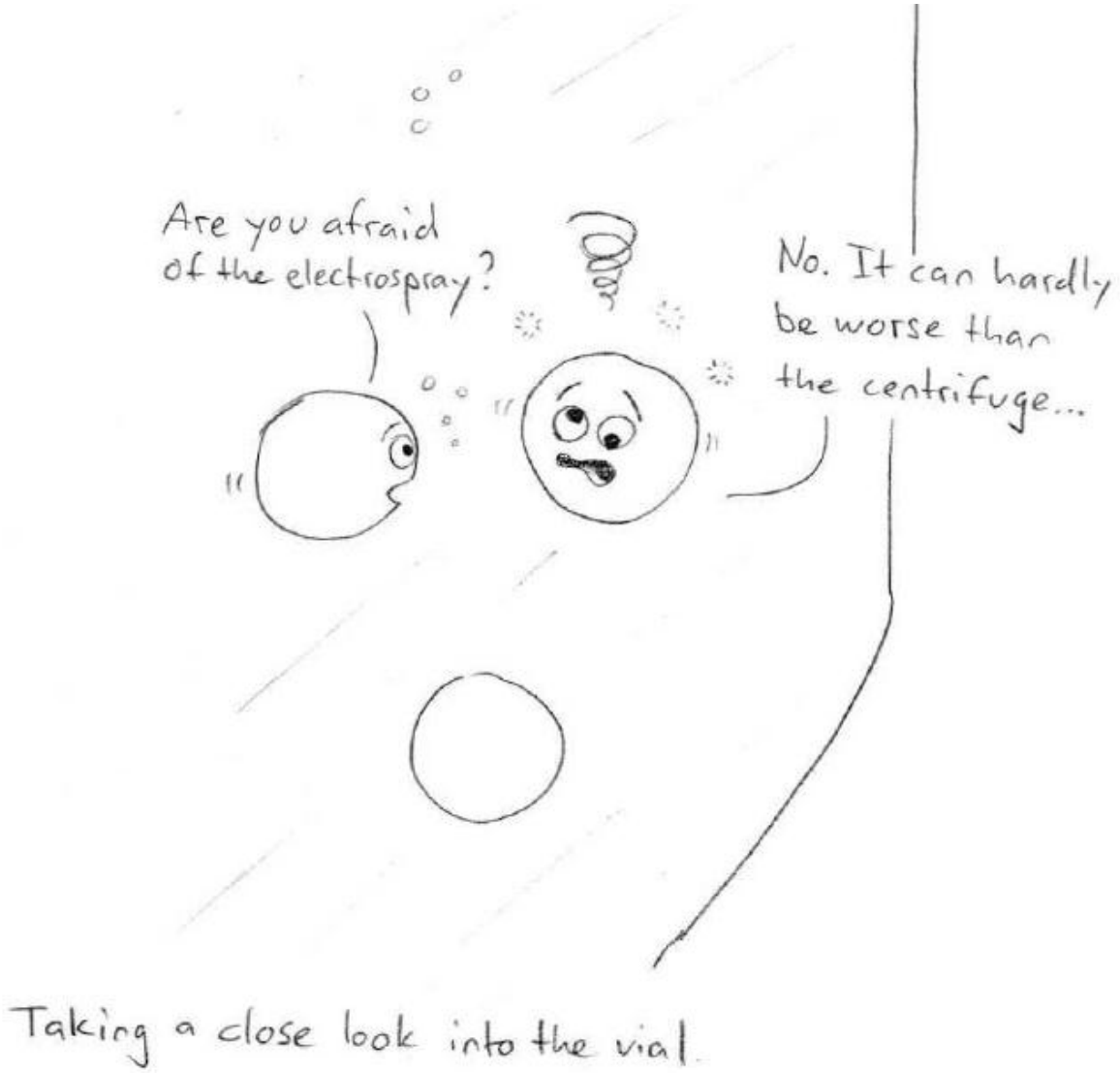
Nominal diameter	20 nm	30 nm	40 nm
TSEM mode diam	20.4 nm	29.3 nm	42.9 nm
SMPS mode diam	$23.4^{+0.3}_{-0.1}$ nm	32.9 ± 0.4 nm	44.1 ± 0.4 nm
Factor SMPS/TSEM	1.15	1.12	1.03

- SMPS measures systematically larger than TSEM
- Relative difference increases with decreasing particle size
- Residuals from the buffer solution cannot explain the discrepancy
- Imperfect sphericity or slip correction factor might be responsible for the discrepancy

5 Conclusions

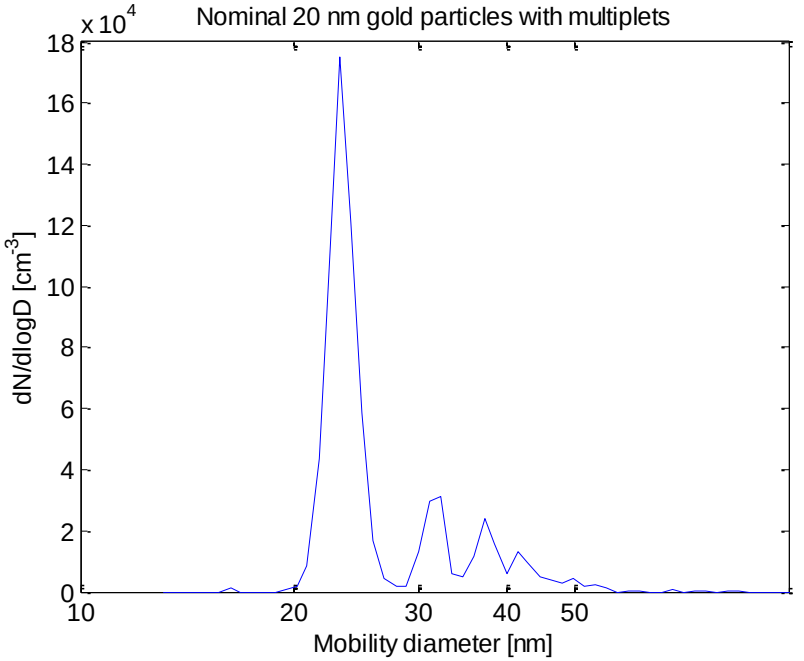
- Modified TSI 3480 electrospray generator allows to aerosolize gold particles between 20 and 40 nm
- 3 centrifugation cycles are necessary to avoid influence from original solution on particle diameter
- Residuals from buffer solution are present, but are unlikely to significantly influence the measured particle diameter
- SMPS mobility diameter systematically higher than TSEM geometric diameter – due to asphericity or slip correction or…?

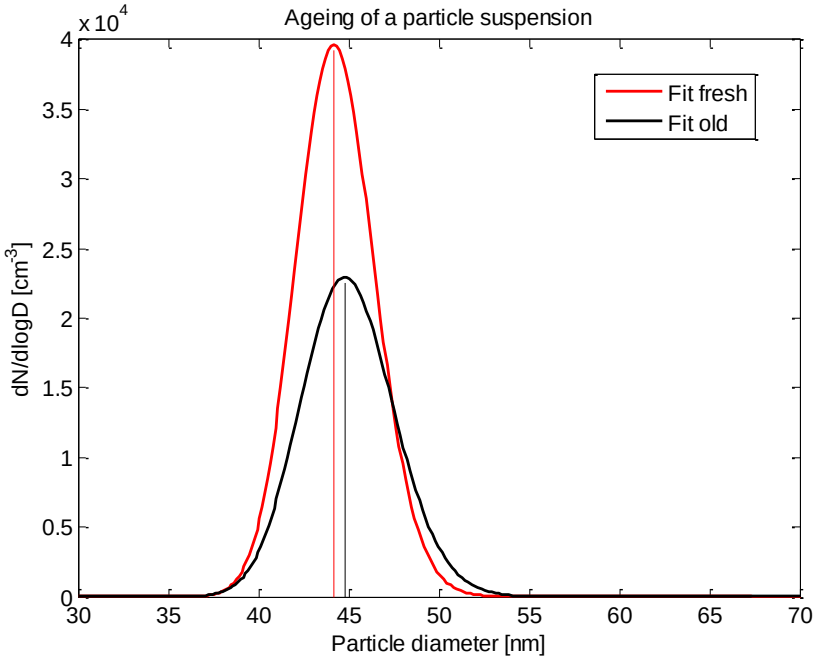
Thank you!


Are you afraid of the electrospray?
No. It can hardly be worse than the centrifuge...
Taking a close look into the vial

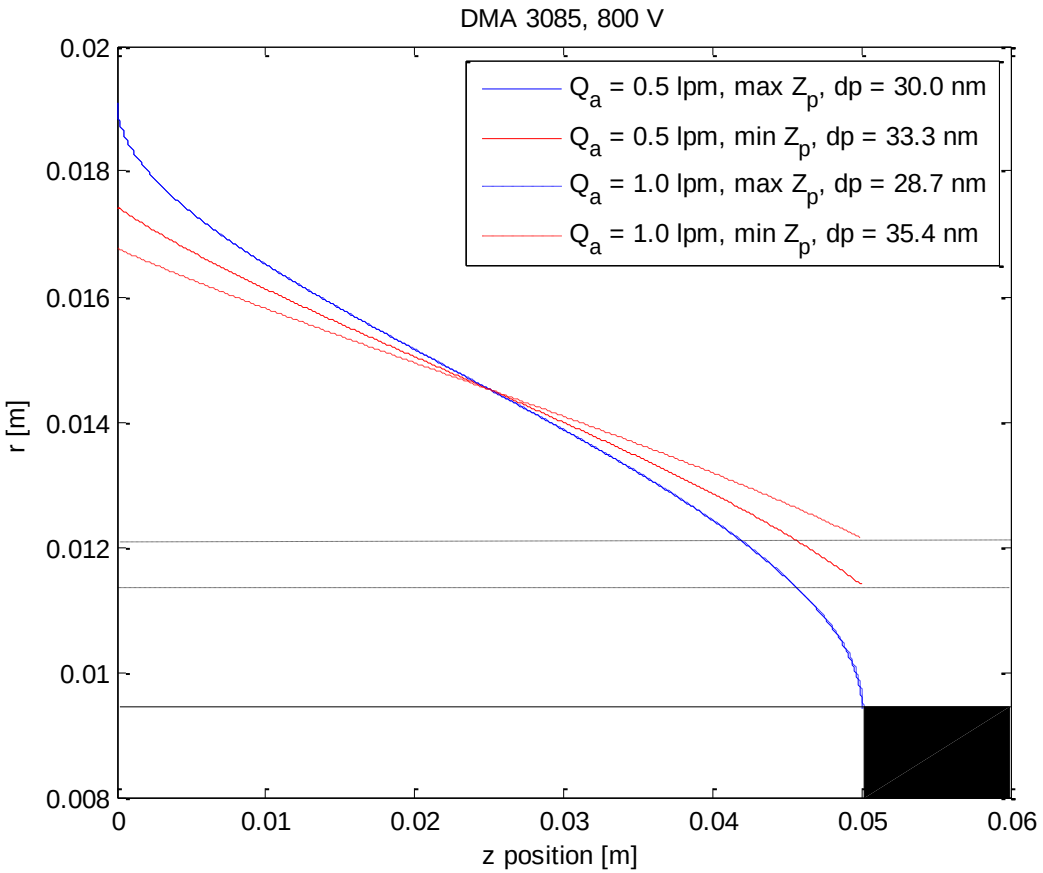
Appendix A: Stability of the buffer solution

- Multiplets have been observed for individual samples
- Without the original solution, particles are not stabilized and can agglomerate
- Agglomerates are easily distinguished from reference particles
- Ageing of the buffer solution increases particle diameter
- After 1 day: 44.2 nm → 44.8 nm (+1.4 %)
- Use prepared samples on the same day!
- PFA vials might prevent ageing





Appendix B: DMA Trajectories



- Selected electrical mobility:

$$Z_p^* = \frac{q_{sh}}{2\pi r_{in} E_{in} L}$$

(e.g. Wang and Flagan, 1990)

- Independence from aerosol flow also holds for laminar profile:
- The particle diameter at peak of the transfer function is the same for 0.5 lpm and for 1.0 lpm sample flow
- Smaller diameter measured at higher aerosol flow might be due to imperfections of the laminar profile in transition zones, or due to size dependent diffusion losses

Ref: S. C. Wang and R. C. Flagan (1990). Scanning Electrical Mobility Spectrometer. Aerosol Science and Technology 13:230–240

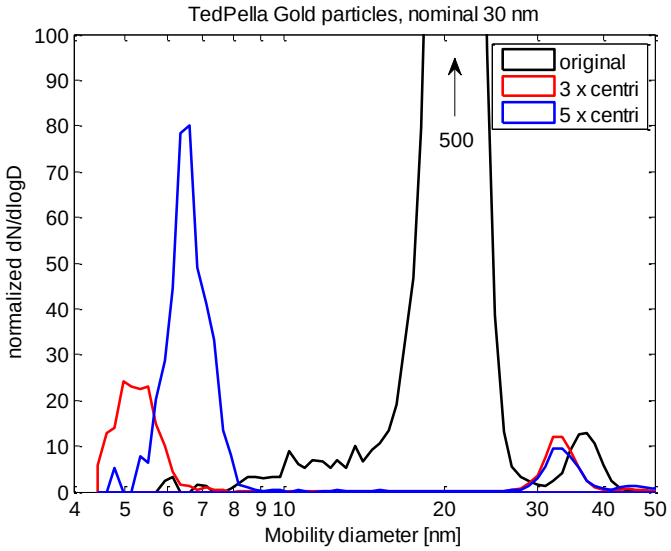
Appendix C: Multiplets

- Observed multiplets are most likely due to agglomeration of particles in the buffer solution prior to electrospraying.
- The occurrence of electrospray-droplets containing several independent particles is highly unlikely:
- The lack of observable particles down to 3 nm from a 20 mM buffer solution coarsely limits the droplet diameter to 28 nm.
- For nominal 20 nm particles, the particle density in the solution is 7E11 cm-3 (TedPella).
- On average, 7.7E-6 particles per electrospray-droplet.
- Probability for 2 particles in the same droplet of 28 nm diameter is 3E-11 (according to Poisson distribution).

Are there deposits from the buffer solution on the gold particles?

- 20 mM ammonium acetate buffer solution ⟶ no significant particle counts down to 3 nm (TSI 3776).
- Assume all electrospray droplets contain the same amount of liquid.
- For particles ≥ 20 nm, a 3 nm particle distributed over the surface increases the diameter by < 0.1%.

- After 3 centrifugation cycles, the particle solution contains residuals at max. ~ 6 nm.
- Increase in diameter for a 20 nm particle: 0.9 %.
- The uncertainty of the mobility diameter determined with a DMA according to ISO 15900 is 1.7% for 20 nm particles.



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⟹ PFA vials might help avoiding contamination