Calibration service for mobility measurements based on reference material for monodisperse spherical particles in aerosols

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Abstract

Reference nanoparticles are commonly delivered and stored as suspensions. One reason is that agglomeration of the nanoparticles can be avoided or strongly reduced using appropriate additives. To use nanoparticle suspensions for the calibration of mobility analysers, the suspensions must be aerosolized, dried and diluted. And, of course, the size of the nanoparticles needs to be known with sufficiently low uncertainty. For the determination of the particle size distribution, two methods have been applied in this study. One method uses a Scanning Electron Microscope in transmission mode (TSEM) and the other makes use of Atomic Force Microscopy (AFM). Both methods analyse particles which are deposited on surfaces. In addition, the aerosolized particles are measured with a Scanning Mobility Particle Sizer (SMPS).

Instrumentation

Commercially available particles made of gold and polysterene latex (PSL) were used in this study, see table 1 . Aiming for reliable size measurements of nanoparticles, a special SEM technique using a transmission electron detector ("Transmission Scanning Electron Microscopy", TSEM) has been proven to be valuable [1]. The measurement setup consists of a standard SEM (Zeiss Supra 35 VP) equipped with a transmission detector placed underneath the sample. The AFM used in this analysis is a Dimension 3100m Metrology AFM, equipped with 3 capacitive sensors for full closed-loop control. Its capabilities have been investigated thoroughly [2]. For the evaluation of the uncertainty associated with the measured particle size we applied the internationally accepted rules described in the 'Guide to the expression of uncertainty in measurement' (GUM) [3].

For aerosolisation of suspensions containing certified particles two generators are commonly used: Atomizer or electrospray. Atomizing suspensions with atomizers (e.g. TSI 3076, Topas ATM 220, Palas UGF) is applicable for particles with diameters above 100 nm. Below that diameter the size distribution of the certified particles is covered by a huge amount of residual particles originating from pure solution droplets. This effect can be minimized by using very pure water only to a certain degree. As an alternative, the electrospray TSI 3048 was evaluated for the aerosolisation of particles below 100 nm. With the electrospray, the residues are well separated from particles with diameters > 20 nm. For 200 nm PSL particles, a Topas ATM 220 atomizer was used with a solution consisting of 18 drops of the original PSL solution diluted by 100 ml of ultrapure water.

Particle material	Size	Manufacturer	Product Number
Gold	20 nm	TedPella	15705-1
Gold	30 nm	TedPella	15706-1
Gold	40 nm	TedPella	15707-1
Silver	40 nm	TedPella	15707-1SC
Gold	100 nm	TedPella	15708-9
PSL	200 nm	Thermo-Scientific	3200A

Table 1: Summary of suspensions with spherical particles.

Parameter	Gold 20 nm	Gold 30 nm	Gold 40 nm	Gold 100 nm	PSL 200 nm	Silver 30 nm	Gold 20 nm	Gold 30 nm	Gold 40 nm
Measurement instrument	TSEM	TSEM	TSEM	TSEM	TSEM	AFM	AFM	AFM	AFM
Mean particle size in nm	21.0	29.8	44.5	103.8	208.9	31.8	17.2	26.7	38.0
Expanded uncertainty (k=2) in nm	1.9	2.0	2.2	3.9	7.2	1.6	1.4	1.5	1.9
Standard deviation in nm	1.4	2.7	4.4	9.3	9.1	8.2	2.0	3.0	5.9
Mode size in nm	20.7	29.6	43.4	103.2	210.3	31.0	19.0	28.0	*n.a.*
Number of analyzed particles	9397	2038	2202	2382	4431	364	410	151	83

Table 2: Results of the size measurements with TSEM and AFM on various particle suspensions

Since the stability of the aerosol generation with the original electrospray TSI 3048 did not satisfy the needs, it was modified as follows: a) The ^{210}Po neutralizer (initially 185 MBq, t_{50} = 138 days) was replaced by a ^{241}Am neutralizer (37 MBq, t_{50} = 432 years) in order to increase the half-life of the neutralizer. b) The pressure gauge was changed in order to expand the range from 0…345 mbar (5 psig) to 0…>700 mbar. c) The pressure chamber was tightened by gluing the capillary with epoxy resin adhesive to the enclosing tube that ends in a Swagelok fitting. d) Tests have shown that the electrospray runs in a more stable manner with the buffer solution at a concentration of 2 mM of ammonium acetate instead of 20 mM as indicated in the user manual.

Results

The comparison shows fair agreement between the ‘stepwise mode’ and the ‘SMPS mode’ at the evaluated settings, see table 3. The relative deviation increases for decreasing particle diameter. Comparison of the mean diameter from the ‘SMPS mode’ with TSEM measurements (see table 2) shows good agreement for the nominal 40 nm gold particles. For 20, 30 and 100 nm gold particles, SMPS measurements systematically lead to a larger diameter than TSEM measurements. The tendency towards larger deviations between SMPS and TSEM for decreasing particle diameter supports the conjecture that deviations might be due to the slip correction which has to be applied in the size analysis of airborne particles.

Parameter	Gold 20 nm	Gold 30 nm	Gold 40 nm	Gold 100 nm	PSL 200 nm
DMA voltage at peak concentration	469 ± 3 V	904 ± 9 V	1536 ± 25 V	4685 ± 45 V[1]	2564 ±10 V[2]
Mode particle size calculated according to ISO 15900	24.0 ± 0.4 nm	33.8 ± 0.6 nm	44.6 ± 1.0 nm	107.4 ± 1.5 nm	201 ± 3 nm
Expanded uncertainty (k=2) of the mode size from DMA	0.8 nm	1.2 nm	2.0 nm	3.0 nm	6 nm
Number concentration at peak	~ 200 cm^{-3}	~ 200 cm^{-3}	~ 100 cm^{-3}	~ 60 cm^{-3}	~ 300 cm^{-3}
Mean particle size SMPS	23.5 ± 0.1 nm	33.0 ± 0.4 nm	44.2 ± 0.4 nm	107.3 ± 0.4 nm	197 ± 1 nm
Mode particle size SMPS	23.4 ± 0.1 nm	32.9 ± 0.4 nm	44.1 ± 0.4 nm	106.7 ± 1.2 nm	196 ± 1 nm
Number concentration (integral)	~ 9000 cm^{-3}	~ 4000 cm^{-3}	~ 6000 cm^{-3}	~ 2000 cm^{-3}	~ 5000 cm^{-3}

Table 3: Measurements of the nanoparticle samples under test in the ‘DMA-mode’ and ‘SMPS-mode’

Due to the relatively small amount of particles measured with the AFM, the methods are compared separately for the relevant sizes. As can be seen in figure 1, there is a systematic bias between the AFM and the other techniques. As the particle size is determined by the AFM by the height of the particle above the reference surface, effects such as vertical particle deformation upon adhesion have a greater impact on the one-dimensional AFM measurement in comparison to the lateral measurement of the TSEM.

Conclusions

In combination with the size calibration using TSEM or AFM and the evaluated procedure to aerosolize the particles, the suspended gold particles with sizes between 20 nm and 100 nm appear to be promising as reference particles for DMA calibration with regard to automotive applications. This is based on the assessment of the associated uncertainty in sizing (< 5%), the roundness of the particles, and the width of the size distribution. Nevertheless, the deviations between different sizing methods for particles below 100 nm have to be better understood before particles in this size range can be established as reference materials for DMA calibration.

[1] Sheath flow 3 L/min
[2] Long DMA TSI 3081

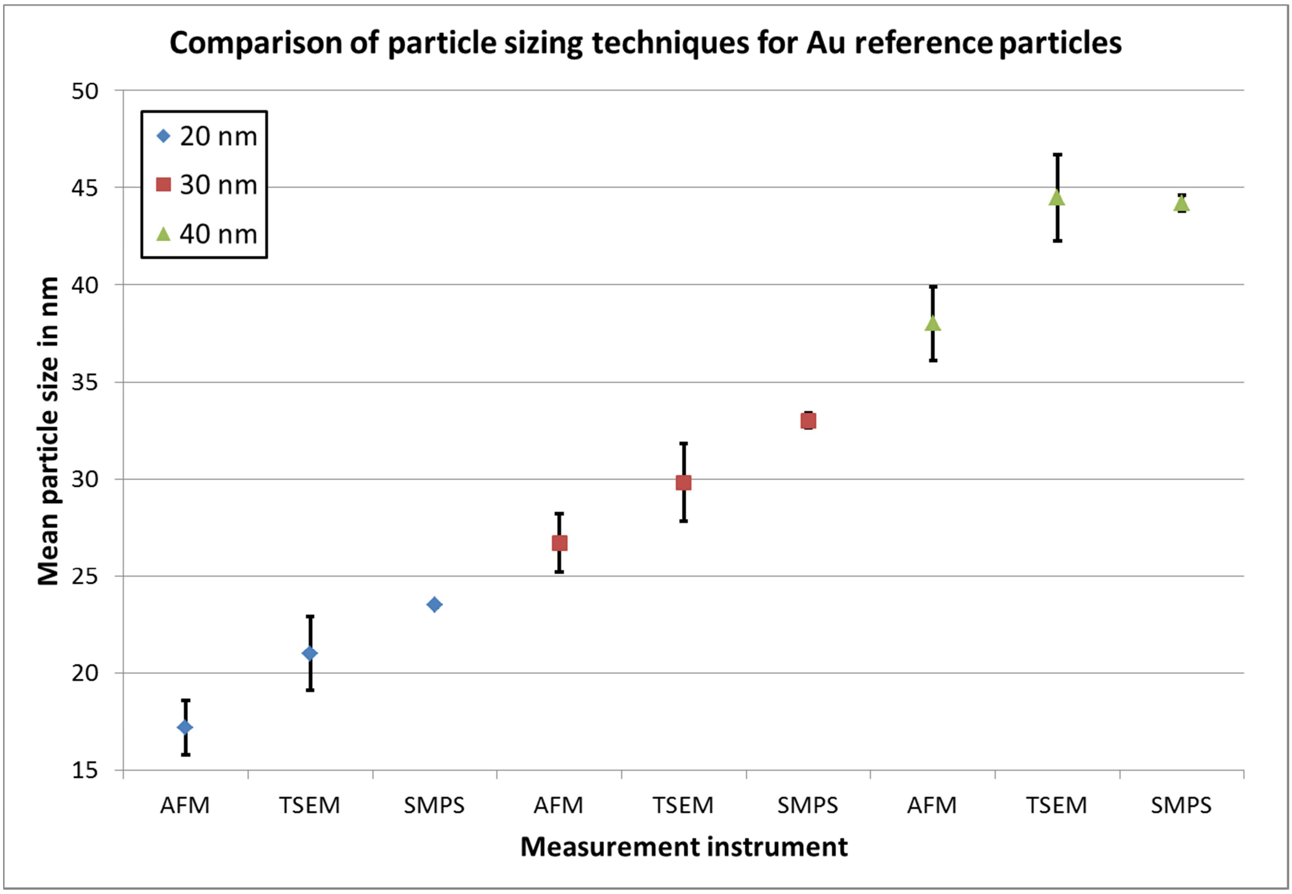

Figure 1: Where suspensions have been measured with all three techniques (20 nm, 30 nm and 40 nm Au particles), this figure graphically shows the results. The error bars correspond to the methods' expanded uncertainties (k=2). Note the systematic size bias of the methods.

References

[1] *Buhr E, Senftleben N, Klein T, Bergmann D, Gnieser D, Frase C G, Characterisation of nanoparticles by scanning electron microscope in transmission mode, Meas. Sci. Technol. 20, 084025 (2009)*

[2] *Garnæs J, Kofod N, Kühle A, Nielsen C, Dirscherl K, Blunt L, Calibration of step heights and roughness measurements with atomic force microscopes, Precision Engineering 27 (1) (2003), pp. 91-98*

[3] *Guide to the expression of uncertainty in measurement (GUM). Joint Committee for Guides in Metrology. JCGM 100 (2008).*

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EMRP European Metrology Research Programme ▸ Programme of EURAMET
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EURAMET European Association of National Metrology Institutes

Introduction

Concerns related to the adverse health effects of automotive exhaust aerosols have driven the regulatory authorities worldwide to limit the particulate emissions of diesel vehicles. The particulate emission performance at a certification stage is traditionally monitored gravimetrically, by means of collecting samples from a Constant Volume Sampler (CVS). Recognizing that the gravimetric procedure would not be sensitive enough to discriminate between the very efficient wall flow Diesel Particulate Filters (DPFs) and flow through particulate filters, a particle number limit was also introduced which became effective at a Euro 5b stage (9/2011 – [1], [2]).

Reference nanoparticles are commonly delivered and stored as suspensions. One reason is that agglomeration of the nanoparticles can be avoided or strongly reduced using appropriate additives. To use nanoparticle suspensions for the calibration of mobility analysers, the suspensions must be aerosolized, dried and diluted. And, of course, the size of the nanoparticles needs to be known with sufficiently low uncertainty.

For the determination of the particle size distribution, two methods have been applied in this study. One method uses a Scanning Electron Microscope in transmission mode (TSEM) and the other makes use of Atomic Force Microscopy (AFM). Both methods analyse particles which are deposited on surfaces.

The advantage of this procedure is that the calibration of the particle sizer can be repeated with the same standard several times, as long as the suspension is not soiled or the particles are not agglomerated. The risk or disadvantage of this method is that the measured diameter of deposited particles may differ from the diameter after aerosolization.

Commercially available particles made of gold and polysterene latex (PSL) were used in this study, see table 1 . Finally, the reference particles were also measured by a Scanning Mobility Particle sizer (SMPS).

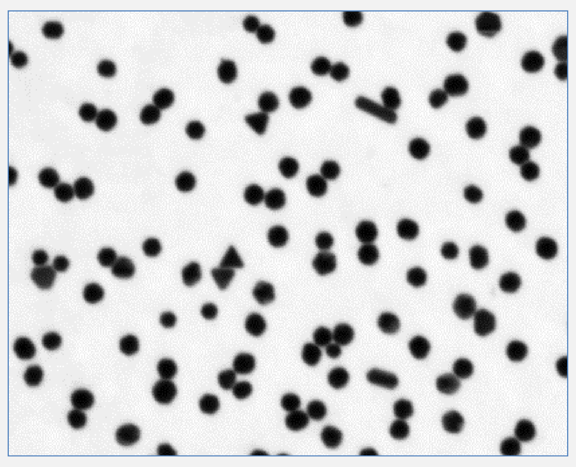

Figure 1: Example of a TSEM image of the 30 nm Au particles

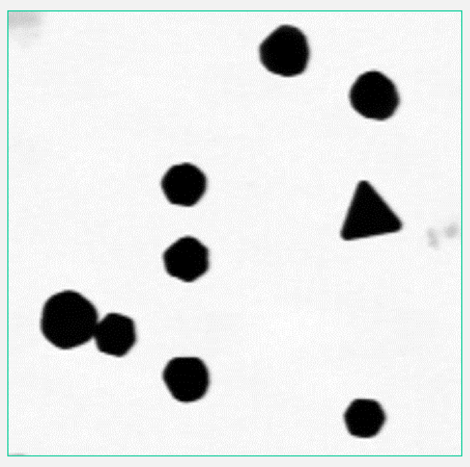

Figure 2: Example of a TSEM image of the 100 nm Au particles

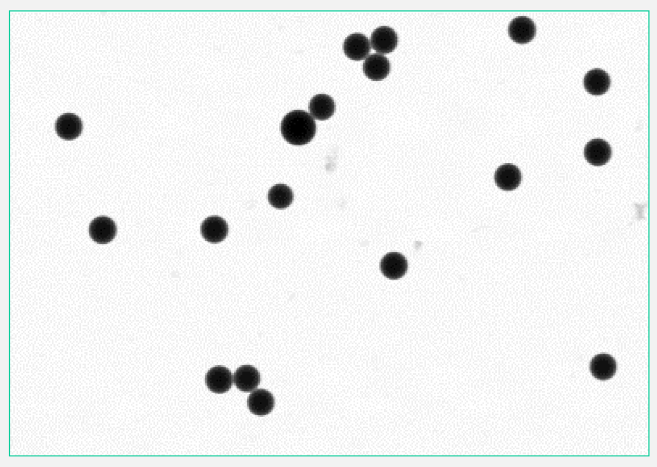

Figure 3: Example of a TSEM image of the 200 nm PSL particles

[1] Regulation No. 83: Uniform provisions concerning the approval of vehicles with regard to the emission of pollutants according to engine fuel requirements http://www.unece.org/fileadmin/DAM/trans/main/wp29/wp29regs/r083r4e.pdf

[2] Commission Regulation (EC) No 692/2008 of 18 July 2008 implementing and amending Regulation (EC) No 715/2007 of the European Parliament and of the Council on type-approval of motor vehicles with respect to emissions from light passenger and commercial vehicles (Euro 5 and Euro 6) and on access to vehicle repair and maintenance information. http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2008:199:0001:0136:EN:PDF

Calibration set-up

Aiming for reliable size measurements of nanoparticles, a special SEM technique using a transmission electron detector ("Transmission Scanning Electron Microscopy", TSEM) has been proven to be valuable [3]. The measurement setup consists of a standard SEM (Zeiss Supra 35 VP) equipped with a transmission detector placed underneath the sample. For image examples, see figures 1-3.

The AFM used in this analysis is a Dimension 3100m Metrology AFM, equipped with 3 capacitive sensors for full closed-loop control. Its capabilities have been investigated thoroughly [4]. See figure 4 for an example image.

For the evaluation of the uncertainty associated with the measured particle size we applied the internationally accepted rules described in the 'Guide to the expression of uncertainty in measurement' (GUM) [5].

Table 2 sums up all results from the measurements.

Particle material	Size	Manufacturer	Product Number
Gold	20 nm	TedPella	15705-1
Gold	30 nm	TedPella	15706-1
Gold	40 nm	TedPella	15707-1
Silver	40 nm	TedPella	15707-1SC
Gold	100 nm	TedPella	15708-9
PSL	200 nm	Thermo-Scientific	3200A

Table 1: Summary of suspensions with spherical particles.

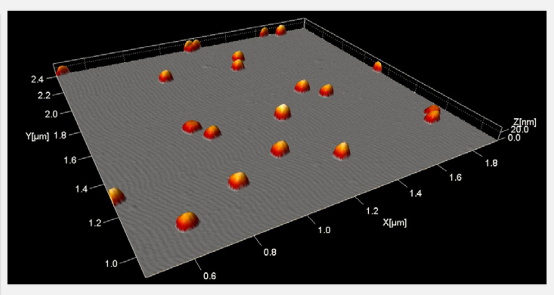

Figure 4: Example of an AFM image of the 20 nm Au particles

Parameter	Gold 20 nm	Gold 30 nm	Gold 40 nm	Gold 100 nm	PSL 200 nm	Silver 30 nm	Gold 20 nm	Gold 30 nm	Gold 40 nm
Measurement instrument	TSEM	TSEM	TSEM	TSEM	TSEM	AFM	AFM	AFM	AFM
Mean particle size	21.0 nm	29.8 nm	44.5 nm	103.8 nm	208.9 nm	31.8 nm	17.2 nm	26.7 nm	38.0
Expanded uncertainty (k=2) of the mean size	1.9 nm	2.0 nm	2.2 nm	3.9 nm	7.2 nm	1.6 nm	1.4 nm	1.5 nm	1.9 nm
Spread of size distribution (standard deviation of particle size)	1.4 nm	2.7 nm	4.4 nm	9.3 nm	9.1 nm	8.2 nm	2.0 nm	3.0 nm	5.9 nm
Spread of size distribution (standard deviation of particle size) in % of mean particle size	6.6 %	9.1 %	9.8 %	9.0 %	4.4 %	26 %	11.8 %	11.3 %	15.5 %
Mode size	20.7 nm	29.6 nm	43.4 nm	103.2 nm	210.3 nm	31.0 nm	19.0 nm	28.0 nm	*too few particles*
Median size	20.9 nm	29.7 nm	43.9 nm	103.3 nm	209.9 nm	27.9 nm	17.7 nm	27.3 nm	38.9 nm
Number of analyzed particles	9397	2038	2202	2382	4431	364	410	151	83

Table 2: Results of the size measurements with TSEM and AFM on various particle suspensions

[3] Buhr E, Senftleben N, Klein T, Bergmann D, Gnieser D, Frase C G, Characterisation of nanoparticles by scanning electron microscope in transmission mode, Meas. Sci. Technol. 20, 084025 (2009)

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Aerosolisation results and conclusions

For aerosolisation of suspensions containing certified particles two generators are commonly used: Atomizer or electrospray.

Atomizing suspensions with atomizers (e.g. TSI 3076, Topas ATM 220, Palas UGF) is applicable for particles with diameters above 100 nm. Below that diameter the size distribution of the certified particles is covered by a huge amount of residual particles originating from pure solution droplets. This effect can be minimized by using very pure water only to a certain degree. As an alternative, the electrospray TSI 3048 was evaluated for the aerosolization of particles below 100 nm. With the electrospray, the residues are well separated from particles with diameters > 20 nm. For 200 nm PSL particles, a Topas ATM 220 atomizer was used with a solution consisting of 18 drops of the original PSL solution diluted by 100 ml of ultrapure water.

Since the stability of the aerosol generation with the original electrospray TSI 3048 did not satisfy the needs, it was modified as follows ,see figure 5: a) The ^{210}Po neutralizer (initially 185 MBq, t_{50} = 138 days) was replaced by a ^{241}Am neutralizer (37 MBq, t_{50} = 432 years) in order to increase the half-life of the neutralizer. b) The pressure gauge was changed in order to expand the range from 0…345 mbar (5 psig) to 0…>700 mbar. c) The pressure chamber was tightened by gluing the capillary with epoxy resin adhesive to the enclosing tube that ends in a Swagelok fitting. d) Tests have shown that the electrospray runs in a more stable manner with the buffer solution at a concentration of 2 mM of ammonium acetate instead of 20 mM as indicated in the user manual.

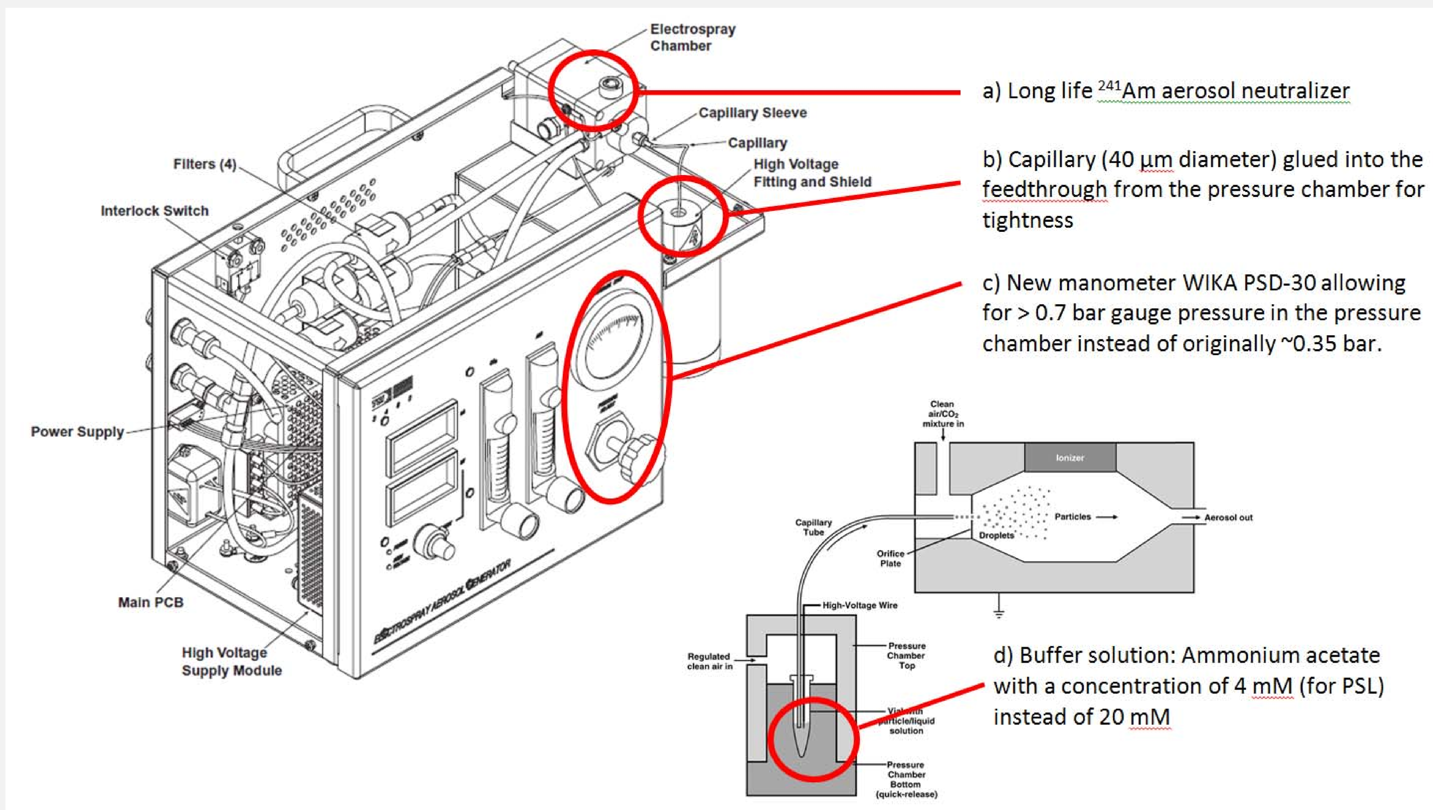

Figure 5: Modifications on TSI 3048 Electrospray

Parameter	Gold 20 nm	Gold 30 nm	Gold 40 nm	Gold 100 nm	PSL 200 nm
DMA voltage at peak concentration	469 ± 3 V	904 ± 9 V	1536 ± 25 V	4685 ± 45 V²	2564 ±10 V¹
Mode particle size calculated according to ISO 15900	24.0 ± 0.4 nm	33.8 ± 0.6 nm	44.6 ± 1.0 nm	107.4 ± 1.5 nm	201 ± 3 nm
Expanded uncertainty (k=2) of the mode size from DMA	0.8 nm	1.2 nm	2.0 nm	3.0 nm	6 nm
Number concentration at peak	~ 200 cm^{-3}	~ 200 cm^{-3}	~ 100 cm^{-3}	~ 60 cm^{-3}	~ 300 cm^{-3}
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Table 3: Measurements of the nanoparticle samples under test in the 'DMA-mode' and 'SMPS-mode'

¹ Long DMA TSI 3081
² Sheath flow 3 L/min

The comparison shows fair agreement between the 'stepwise mode' and the 'SMPS mode' at the evaluated settings, see table 3. The relative deviation increases for decreasing particle diameter. Comparison of the mean diameter from the 'SMPS mode' with TSEM measurements (see table 2) shows good agreement for the nominal 40 nm gold particles. For 20, 30 and 100 nm gold particles, SMPS measurements systematically lead to a larger diameter than TSEM measurements. The tendency towards larger deviations between SMPS and TSEM for decreasing particle diameter supports the conjecture that deviations might be due to the slip correction which has to be applied in the size analysis of airborne particles.

Due to the relatively small amount of particles measured with the AFM, the methods are compared separately for the relevant sizes. As can be seen in figure 6, there is a systematic bias between the AFM and the other techniques. As the particle size is determined by the AFM by the height of the particle above the reference surface, effects such as vertical particle deformation upon adhesion have a greater impact on the one-dimensional AFM measurement in comparison to the lateral measurement of the TSEM:

In combination with the size calibration using TSEM or AFM and the evaluated procedure to aerosolize the particles, the suspended gold particles with sizes between 20 nm and 100 nm appear to be promising as reference particles for DMA calibration with regard to automotive applications. This is based on the assessment of the associated uncertainty in sizing (< 5%), the roundness of the particles, and the width of the size distribution. Nevertheless, the deviations between different sizing methods for particles below 100 nm (see figure 6) have to be better understood before particles in this size range can be established as reference materials for DMA calibration.

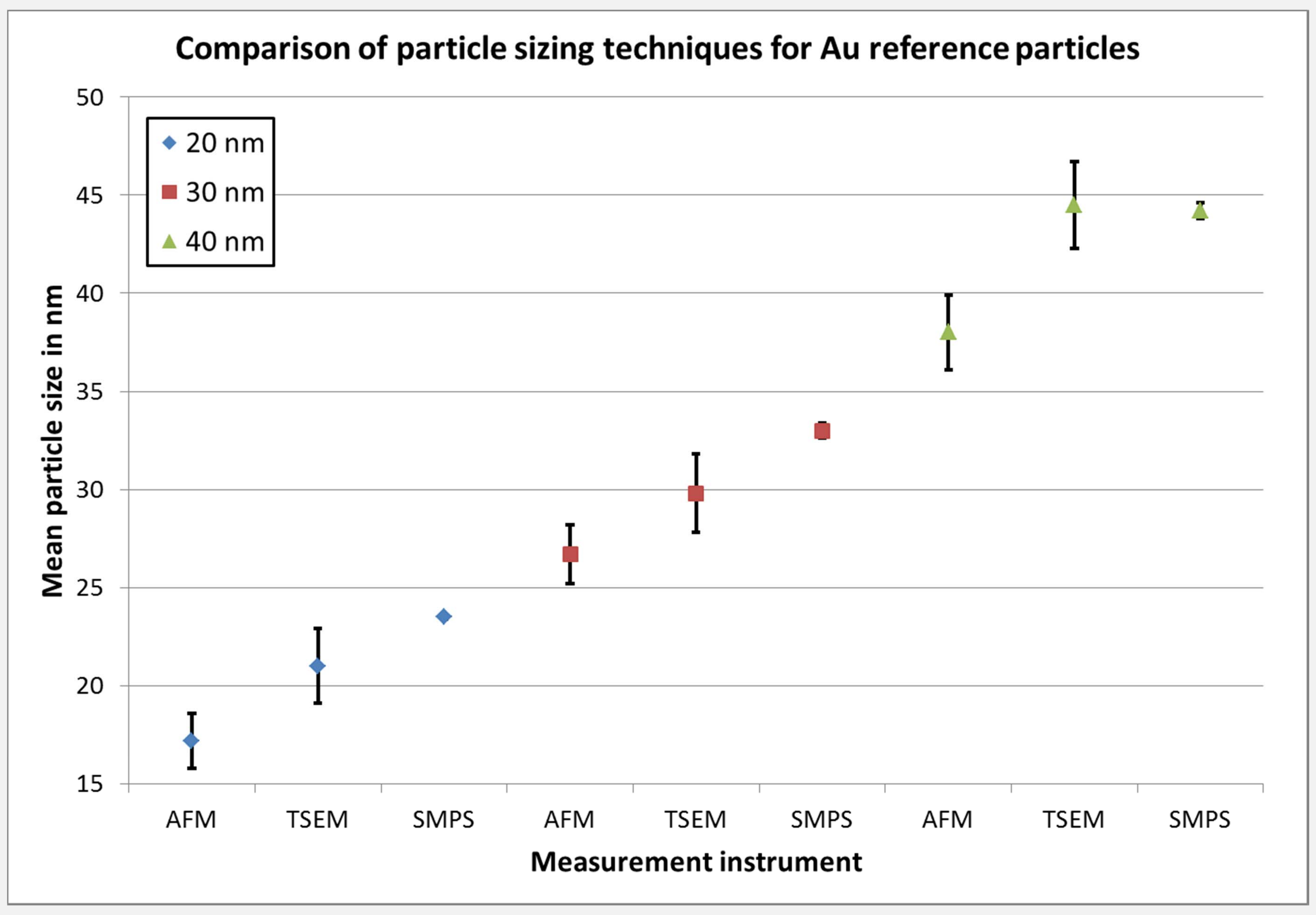

Figure 6: Where suspensions have been measured with all three techniques (20 nm, 30 nm and 40 nm Au particles), this figure graphically shows the results.The error bars correspond to the methods' expanded uncertainties (k=2). Note the systematic size bias of the methods.

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