Generation and traceable electron-microscopic characterization of monodisperse silver aerosols for CPC calibration

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With the Euro 5 standard the European Union has introduced binding limits for the number of particles per kilometer that may be emitted from diesel vehicles, and with the Euro 6 standard these regulation will be expanded to petrol-driven cars. It is one aim of the Particle Measurement Program (PMP) to define the method to measure the number of emitted particles based on a condensation particle counter (CPC). Among other things, the sensitivity curve of the CPC is to be determined. PMP demands a detection efficiency of at least 50% for 23-nm particles and 90% for 41-nm particles. Usually the sensitivity curve is determined with the help of a reference DMA (differential mobility analyser) in a non-traceable way.

For legislative measurements or for type approval the calibration of CPCs has to be traceable to the international system of units (SI system), which may be accomplished using a reference aerosol with known number concentration and particle size [1]. Traceability of the particle size means presentation and dissemination of the SI unit ‘meter’ to nanometer-scale particles. In this contribution, we report on the generation of monodisperse silver aerosols and traceable size measurements of collected silver particles using a scanning electron microscope (SEM) in transmission mode (TSEM).

Following the approach of Scheibel [2], silver droplets were vaporized from silver granulate in a tube furnace. After dilution, sintering and cooling the size distribution of the produced silver nanoparticles was measured using a scanning mobility particle sizer (SMPS), see Fig. 1a. From these distribution monodisperse size fractions may be classified by means of a DMA, see Fig. 1b. In order to facilitate size measurements by TSEM the silver particles were deposited on TEM grids (copper grids holding a thin film of amorphous carbon) using an electrostatic precipitator (ESP) [3].

The use of a transmission detector in an SEM has numerous advantages over both SEM and transmission electron microscopy (TEM) [4]. Besides measurements traceable to the SI unit ‘metre’, it offers high resolution and the possibility of accurate simulations based on fundamental scattering theory. Thus, TSEM is ideally suited for highly accurate, traceable size measurements of nanoparticles, as has been demonstrated for water-based samples [5]. Initial TSEM examinations of silver aerosol samples revealed good homogeneity and allocation across the TEM grid as well as regular size distributions, see Fig. 2a and 2b, respectively.

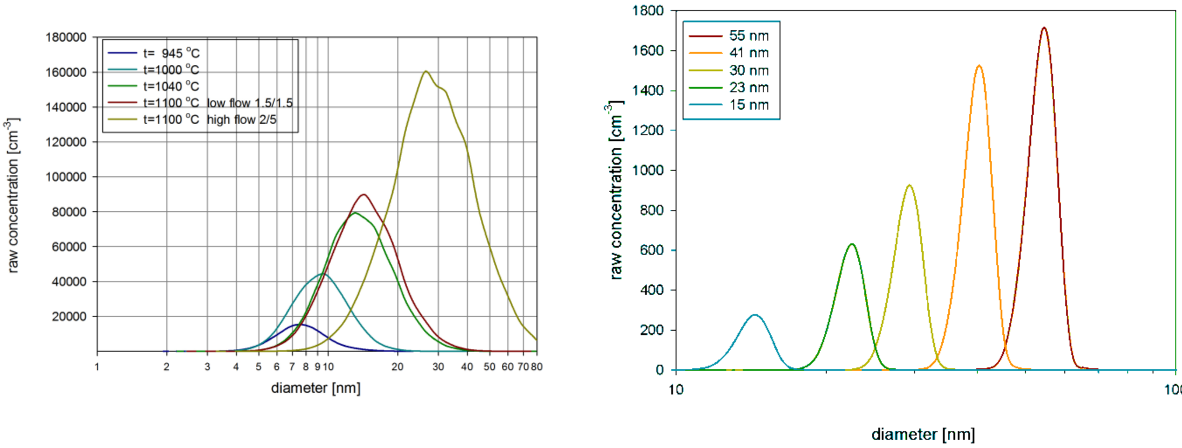

Figure 1: Size distribution of silver nanoparticles (a) as generated for various oven temperatures and (b) after classifying by DMA.

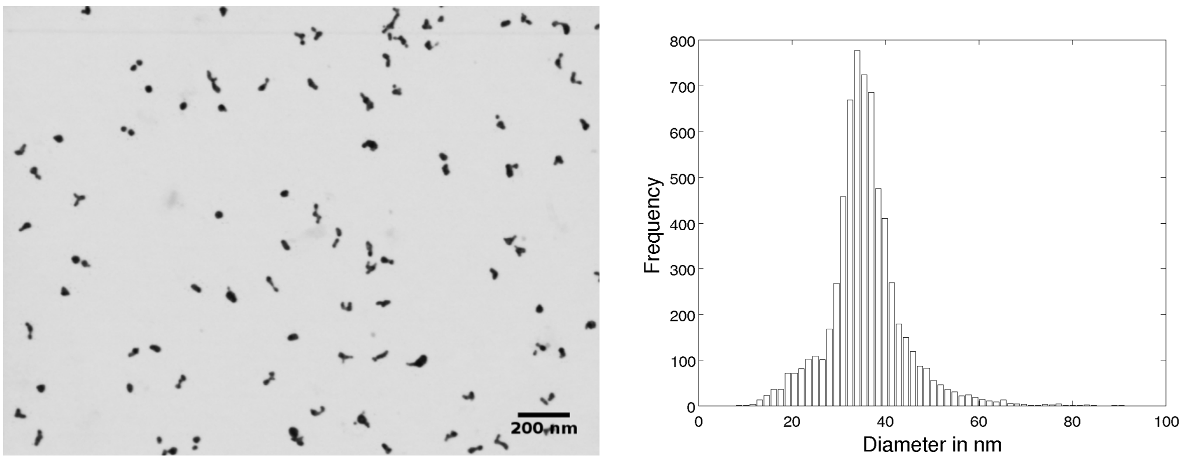

Figure 2: (a) TSEM micrograph of silver particles deposited on a TEM grid, (b) equivalent-area size distribution as measured by TSEM.

Literature:

[1] European Joint Research Project ENV02 PartEmission: Emerging requirements for measuring pollutants from automotive exhaust emissions, summary report available at http://www.ptb.de/emrp/partemission-publications.html

[2] Scheibel H, Porstendörfer J. Generation of monodisperse Ag- and NaCl-aerosols with particle diameters between 2 and 300 nm. Journal of Aerosol Science. 1983;14(2):113-26

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[5] Klein T, Buhr E, Johnsen KP, Frase CG. Traceable measurement of nanoparticle size using a scanning electron microscope in transmission mode (TSEM). Measurement Science and Technology. 2011;22(9):094002.

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1. Particle Measurement Program (PMP)

· Limits for the number of particles that may be emitted from cars (Euro 5+6)

· Aim: To define the method to measure the number of emitted particles based on a CPC

· Prerequisite: Determination of the sensitivity curve of the CPC

· Requirement: Detection efficiency of at least 50% for 23-nm particles and 90% for 41-nm particles

2. Traceable calibration of CPC detection efficiency

· Requirement for legislative measurements and for type approval

· Non-traceable calibration using a reference DMA not sufficient

· May be accomplished using a reference aerosol with known number concentration and particle size [1]

3. Aerosol generation

· Silver droplets are vaporized from silver granulate in a tube furnace [2]

· Subsequent dilution, sintering and cooling steps

· Monodisperse size fractions may be classified by means of a DMA

· Deposition on TEM grids using an ESP [3] for TSEM measurements

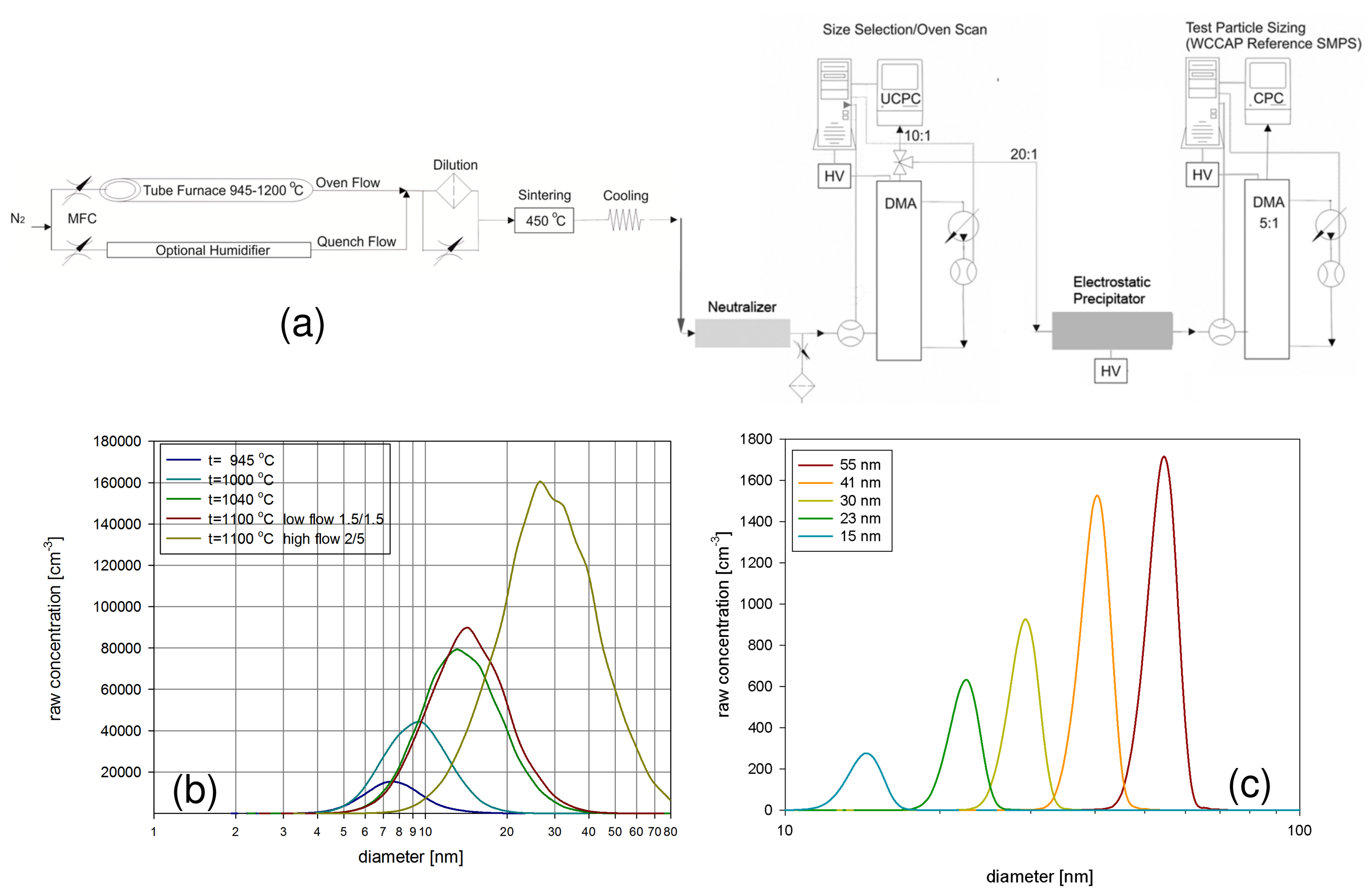

Figure 1: *Scheme of the aerosol generation and measurement (a) together with size distributions of the aerosol as generated for various oven temperatures (b) and after classifying by DMA (c).*

Literature:

EMRP European Metrology Research Programme ▸ Programme of EURAMET

[1] EMRP ENV02 PartEmission: Emerging requirements for measuring pollutants from automotive exhaust emissions, www.ptb.de/emrp/partemission.html
[2] Scheibel H. and Porstendörfer J. J. Aerosol Sci. **14**, p. 113 (1983)
[3] Dixkens J. and Fissan H. Aerosol Sci. Technol. **30**, p. 438 (1999)
[4] Klein T. et al. Adv. Imag. Electr. Phys. **171**, p. 297 (2012)
[5] Klein T. et al. Meas. Sci. Technol. **22**, p. 094002 (2011)

4. SEM in transmission mode (TSEM)

· Resolution superior to other SEM imaging modes [4]

· Accurate simulations based on fundamental scattering theory [4]

· Possibility of traceable size measurements of nanoparticles [5]

· Automated image acquisition by batch processing

· Commercially available transmission detector in a Zeiss Supra 35 VP

Calibration of SEM pixel size:

· 2D-grating with 144 nm pitch (150-2D from ASM Inc.)

· Grating pitch traced back to the SI unit "meter" by laser diffraction

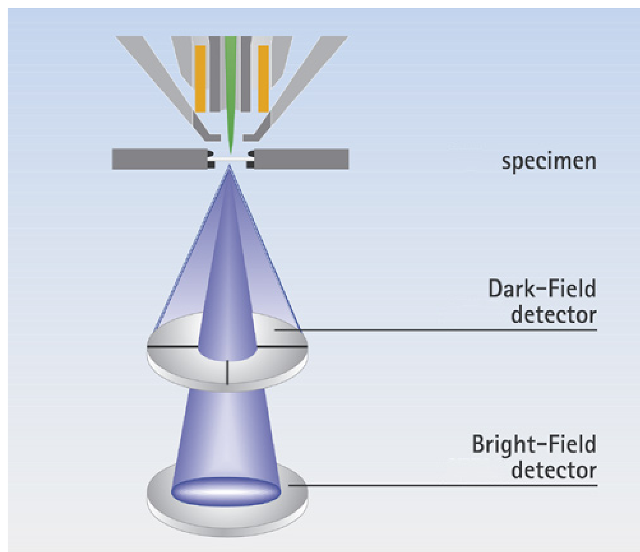

Figure 2: *Schematic drawing of transmission detector consisting of seperate dark-field and bright-field semiconductor detector elements, image courtesy of Carl Zeiss NTS GmbH.*

5. Preliminary results

· TSEM - Traceable mean diameter of a sphere exhibiting the same projected area: 37.4 nm with an expanded uncertainty of 1.8 nm

· SMPS - Mean mobility diameter: 42.1 nm

· Good homogeneity and allocation across the TEM grid

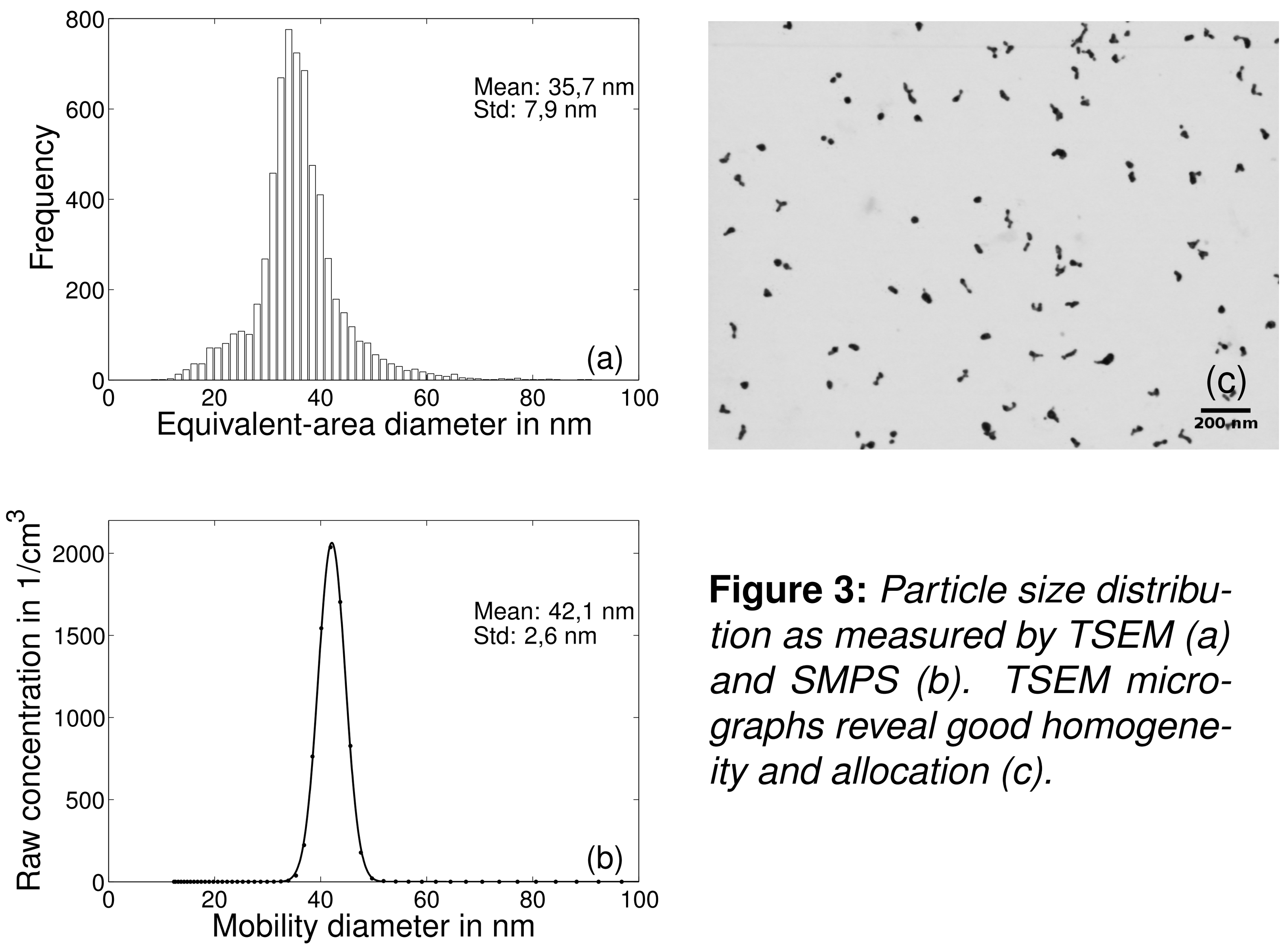

Figure 3: *Particle size distribution as measured by TSEM (a) and SMPS (b). TSEM micrographs reveal good homogeneity and allocation (c).*

6. Conclusion

· Legislative demand for traceable calibration of detection efficiency of SMPS

· Usage of monodisperse silver aerosol

· Traceable size measurements by means of TSEM

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