Effect of silver particle shape on cut-off diameter of TSI 3790 CPCs

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Introduction: Concerns about adverse health effects of automotive exhaust aerosols have driven the regulatory authorities worldwide to limit the particulate emissions of diesel vehicles. With Euro 5b stage (2011 – [1] [2]) a particle number limit for automotive exhaust aerosols was added to the existing mass based limits. According to this regulation particles counters shall have a 50% counting efficiency for particles with a diameter of 23 nm and 90% counting efficiency for 41 nm particles.

The TSI CPC 3790 is based on the CPC 3772 with reduced temperature difference between saturator and condenser (3772: 17 K, 3790: 7.5 K). This shifts the cut-off diameter to the diameter required by the legislation. A possible downside of such an approach may be a dependency of the cut-off diameter on particle material or shape.

Silver particles generated by tube furnace generators are frequently used for the determination of CPC counting efficiency curves. Particles generated by this method are spherical if smaller than 20 nm in diameter and agglomerates if larger. Sintering of agglomerates after size selection by the generator DMA changes their morphology making them more spherical. Here we used this change of particle morphology to investigate the influence of particle shape on the cut-off diameter of the TSI 3790 CPC.

Methods: The TROPOS silver aerosol generator features a quench flow for faster cooling of the newly formed particles. Both oven flow and quench flow are controlled by mass flow controllers to ensure better stability of the size distribution of the silver particles and better repeatability of calibration settings. After dilution the particles are sintered at 450 deg. C. A cooling spiral is used to cool the aerosol down to room temperature.

The aerosol is then neutralized by a 370 MBq Kr85 bi-polar charger and fed into the DMA. We use a TROPOS made Hauke type short DMA at an aerosol flow of 1 l/min and a sheath air flow of 20 l/min for size selection. The high voltage of the DMA is continuously adjusted to the temperature and pressure in the DMA to ensure repeatable size selections under varying ambient conditions. After size selection, a turbulent diluter is used to add sufficient filtered air allowing parallel calibration of CPCs. The generated particles can then either be reheated to 350 deg. C (sintering) or bypass the sintering oven. A WCCAP reference SMPS system is used to measure size distributions fed to the candidate CPSs.

For this experiment we used to different setups of the system (Figure 1):

(a) CPC calibration: A CPC 3790 and a CPC 3772 were calibrated against a TSI 3068B electrometer with either sintered or not sintered silver particles. The size of the particles was determined using the reference SMPS.

(b) Particle morphology: Two custom made electrostatic precipitators were used to deposit both sintered and not sintered particles on grids for TSEM analysis. Two CPC 3772 have been used to determine deposition efficiency of the particles on the grids.

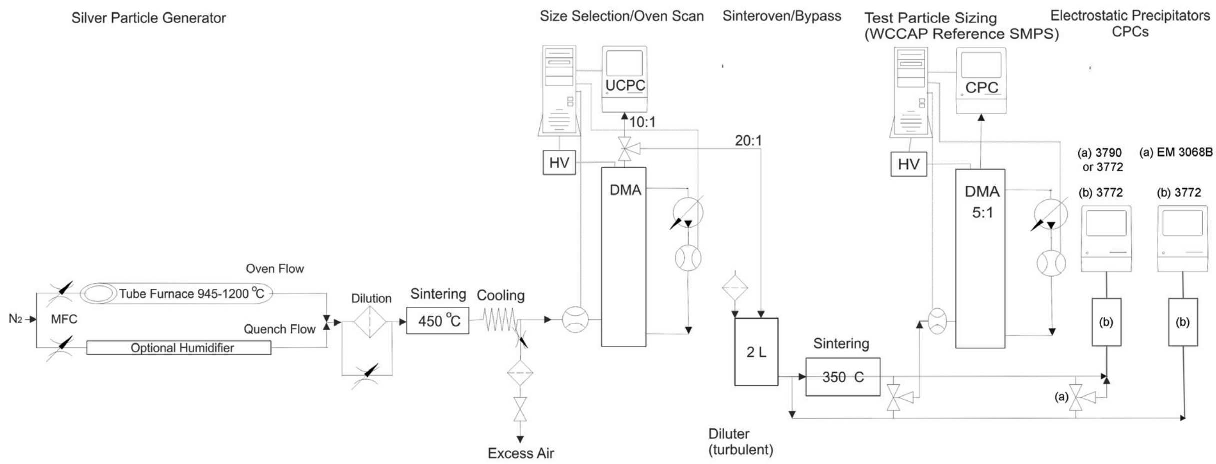

Fig. 1: Experimental Setup.

Measurements and Results: The effect of sintering on particle morphology of is visualized in figure. It shows electron micrographs of sintered (left) and un-sintered particles (right) with an initial diameters of 30 nm selected by the generator UDMA. Measurements with the SMPS show that sintered particles are smaller than originally selected by the generator UDMA. The shrinking of the particles is size dependent and becomes effective for particle sizes larger than 18 nm in diameter.

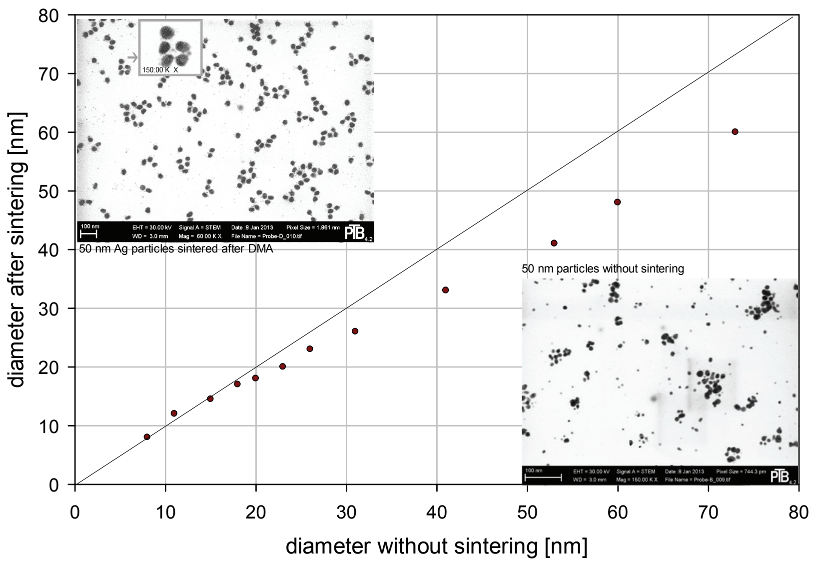

Figure 2: Effects of particle sintering on diameter and morphology of Ag aerosols.

To determine the effect of particle morphology on the detection efficiency curve of TSI 3790 CPCs we used both sintered and not sintered particles of identical sizes measured by the reference SMPS. The size dependent counting efficiency for not sintered particles (red triangles) and sintered particles (orange triangles) are shown in figure 3. This figure includes data for TSI 3772 CPCs (circles) as a reference.

Particle sintering after size selection shifts the cut-off curve of the 3790 type CPCs towards larger particles whereas the cut-off curve for 3772 CPCs (given as a reference) is not affected by sintering.

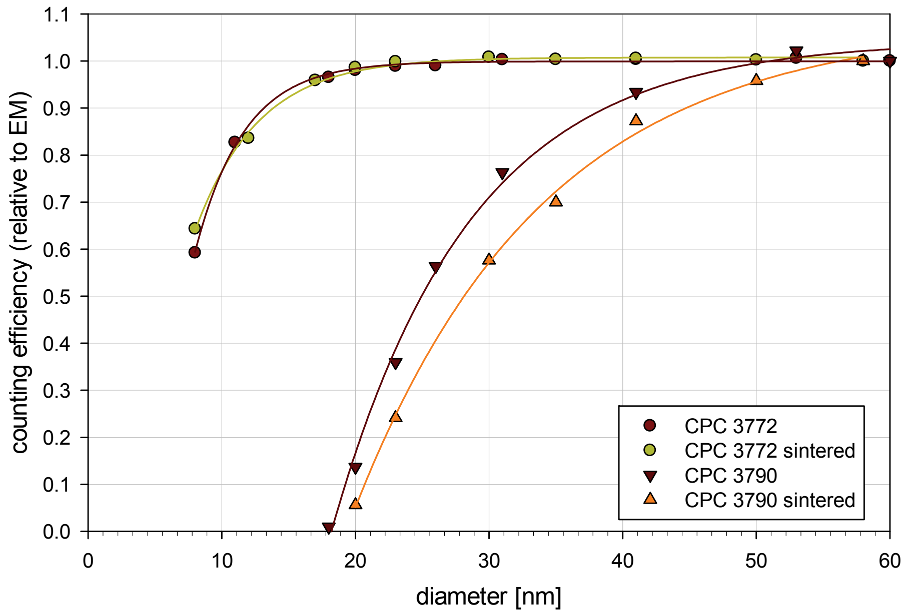

Fig. 3: Cut-off curves for TSI CPCs determined with sintered and un-sintered Ag particles

Conclusions: The cut-off curve of the TSI 3790 CPC for un-sintered Ag particles is similar to the published cut-off curve for emery oil determined by the manufacturer (Dp50=23 nm). With sintered Ag particles the counting efficiency curve (and the cut-off diameter) is shifted to larger particle sizes (Dp50=28 nm). Cut-off curves for TSI 3772 CPCs are not affected by particle sintering because sintering does not change particle morphology in the typical cut-off size range of these instruments. The observed shift of the cut-off diameter may be due to the different surface curvature or different surface area of sintered and not sintered particles.

For verification of the manufacturer provided counting efficiency curve of these CPCs silver particles should not be sintered after size selection. In engine test stands exhaust gases are typically thermally treated prior to measurements. This treatment makes the particles more spherical. The counting efficiency curve of TSI 3790 CPCs will be most likely affected by this change of particle morphology. A shift of the counting efficiency towards larger particles would artificially reduce particle number concentration measured in these setups.

References:

[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

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EMRP European Metrology Research Programme • Programme of EURAMET

PTB

TROPOS Leibniz Institute for Tropospheric Research

Member of the Leibniz Association

Introduction

Concerns about adverse health effects of automotive exhaust aerosols have driven the regulatory authorities worldwide to limit the particulate emissions of diesel vehicles. With Euro 5b stage (2011 – [1] [2]) a particle number limit for automotive exhaust aerosols was added to the existing mass based limits. According to this regulation particles counters shall have a 50% counting efficiency for particles with a diameter of 23 nm and 90% counting efficiency for 41 nm particles.

The TSI CPC 3790 is based on the CPC 3772 with reduced temperature difference between saturator and condenser (3772: 17 K, 3790: 7.5 K). With the reduced super-saturation the cut-off diameter is shifted to the diameter required by the legislation. The possible downside of such an approach may be a dependency of the cut-off diameter on particle material or shape.

Silver particles generated by tube furnace generators are frequently used for the determination of CPC cut-off curves. The original paper by Scheibel and Porstendörfer (1982 - [3]) on this method states that particles generated by this method are spherical if smaller than 20 nm in diameter and agglomerates if larger. Sintering of agglomerates after size selection by the generator DMA changes their morphology making them more spherical. Here we used this change of particle morphology to investigate the influence of particle shape on the cut-off diameter of the TSI 3790 CPC.

Methods

The TROPOS silver aerosol generator features a quench flow for faster cooling of the newly formed particles. In addition this flow dilutes the aerosol from the oven to minimize coagulation of primary particles after generation. Both oven flow and quench flow are controlled by mass flow controllers to ensure better stability of the size distribution of the silver particles and better repeatability of calibration settings. A dilution system consisting of a filter and a manual bypass valve allows for adjustment of the concentration. After dilution the particles are sintered at 450 deg. C. A cooling spiral is used to cool the aerosol down to room temperature.

The aerosol is then neutralized by a 370 MBq Kr85 bi-polar charger and fed into the DMA. We use a TROPOS made Hauke type short DMA at an aerosol flow of 1 l/min and a sheath air flow of 20 l/min for size selection. The high voltage of the DMA is continuously adjusted to the temperature and pressure in the DMA to ensure repeatable size selections under varying ambient conditions. The same DMA can be used to measure the oven size distribution using the TROPOS SMPS program.

After size selection, a turbulent diluter is used to add sufficient filtered air allowing parallel calibration of CPCs. The generated particles can then either be reheated to 350 deg. C (sintering) or bypass the sintering oven. A WCCAP reference SMPS system is used to measure size distributions fed to the candidate CPSs.

For this experiment we used to different setups of the system:

(a) CPC calibration: A CPC 3790 and a CPC 3772 were calibrated against a TSI 3068B electrometer with either sintered or not sintered silver particles. The size of the particles was determined using the reference SMPS.

(b) Particle morphology: Two custom made electrostatic precipitators were used to deposit both sintered and not sintered particles on grids for TSEM analysis. Two CPC 3772 have been used to determine deposition efficiency of the particles on the grids.

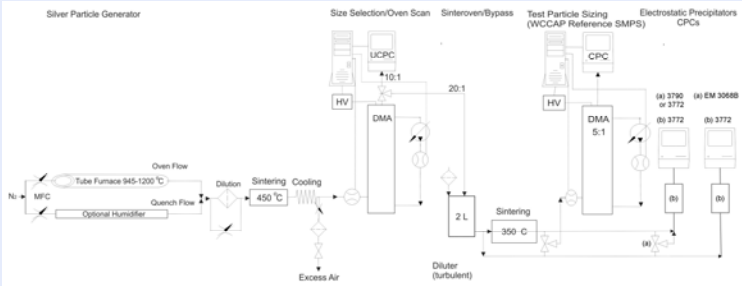

Fig. 1: Experimental Setup.

Measurements and Results

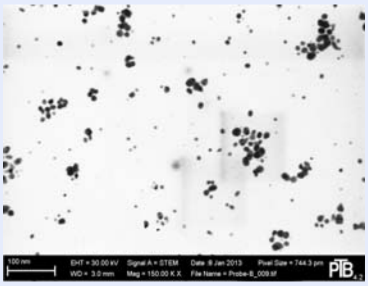

Fig. 2: TSEM picture of un-sintered Ag particles.

The effect of sintering on particle morphology of is visualized in figures 2 and 3. Both figures show particles with a initial diameters of 30 nm selected by the generator UDMA.

Figure 2 shows a electron micrograph of these particles without sintering. These particles are non-spherical and some of them of them form agglomerates.

Figure 3 shows particles of the same selected diameter after sintering. These particles are almost spherical without visible agglomerates.

Measurements with the SMPS show that sintered particles are smaller than originally selected by the generator UDMA. The shrinking of the particles is size dependent and becomes effective for particle sizes larger than 18 nm in diameter. Figure 4 shows the size of the particles after sintering compared to the size without sintering.

To determine the effect of particle morphology on the detection efficiency curve of TSI 3790 CPCs we used both sintered and not sintered particles of identical sizes measured by the reference SMPS.

The size dependent counting efficiency for not sintered particles (red triangles) and sintered particles (orange triangles) are shown in figure 5. This figure includes data for TSI 3772 CPCs (circles) as a reference.

Particle sintering after size selection shifts the cut-off curve of the 3790 type CPCs towards larger particles whereas the cut-off curve for 3772 CPCs (given as a reference) is not affected by sintering.

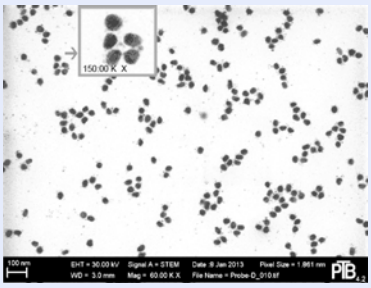

Fig. 3: TSEM picture of sintered Ag particles

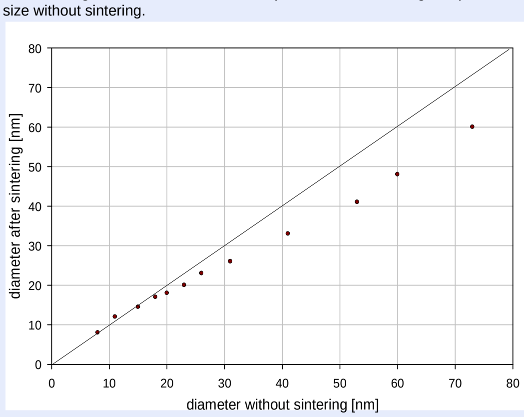

Fig. 4: Sintered Ag particles versus un-sintered.

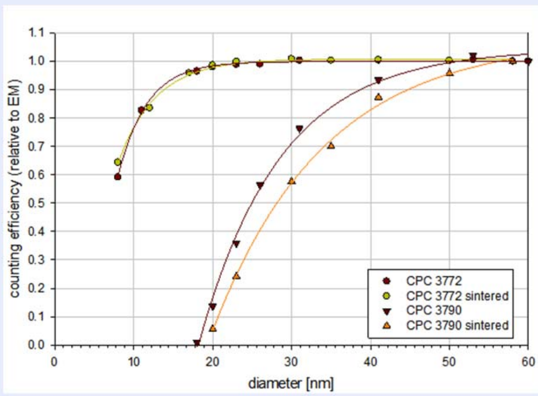

Fig. 5: Cut-off curves for TSI CPCs 3790 and 3772 determined with sintered and un-sintered Ag particles

Conclusions

The cut-off curve of the TSI 3790 CPC for un-sintered Ag particles is similar to the published cut-off curve for emery oil determined by the manufacturer (Dp50=23 nm). With sintered Ag particles the counting efficiency curve (and the cut-off diameter) is shifted to larger particle sizes (Dp50=28 nm). Cut-off curves for TSI 3772 CPCs are not affected by particle sintering because sintering does not change particle morphology in the typical cut-off size range of these instruments.

The observed shift of the cut-off diameter may be due to the different surface curvature or different surface area of sintered and not sintered particles.

Our findings show that the morphology silver particles affects the counting efficiency TSI 3790 CPCs. For verification of the manufacturer provided counting efficiency curve of these CPCs silver particles should not be sintered after size selection.

In engine test stands exhaust gases are typically thermally treated prior to measurements. This treatment makes the particles more spherical. The counting efficiency curve of TSI 3790 CPCs will be most likely affected by this change of particle morphology. A shift of the counting efficiency towards larger particles would artificially reduce particle number concentration measured in these setups.

References and Acknowledgement

[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

[3] Scheibel H.G. and Porstendörfer J. ‚Generation of monodisperse Ag- and NaCl aerosols with particle diameters between 2 and 300 nm, J. Aerosol Sci 2 113-126 (1983)

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