GÉNÉRATION DE SPHÈRES D'ARGENT DE 2 À 100 NM POUR L'ÉTALONNAGE DES CPC ET DMA : CONFIGURATION ET VÉRIFICATION PAR TEM

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TITLE

Generating 2 to 100 nm Silver Spheres for CPC and DMA Calibration: Setup and TEM Verification

RESUME

Depuis des années, les particules ultrafines d'argent sont utilisées dans une grande variété d'applications (Ankilov, 2002; Giechaskiel, 2009; Wiedensohler, 2017). Cependant, le frittage des particules d'argent suscite un intérêt particulier chez les chercheurs (Ku, 2006; Zihlmann, 2014; Tuch, 2016; Silva, 2019). En particulier, l'étalonnage des CPCs pour mesurer les nanoparticules ultrafines dans l'atmosphère devient un sujet d'intérêt croissant, nécessitant des particules d'argent (EN 16976:2024), où le frittage est largement utilisé. De plus, les particules sphériques d'argent peuvent être utilisées pour l'étalonnage des DMA, où il est crucial de connaître la forme et la densité des particules de référence. Les travaux présentés ici visent à apporter plus de répétabilité et d'utilité dans divers domaines des sciences des aérosols utilisant des nanoparticules d'argent frittées.

Il a été démontré qu'il est possible de générer des particules d'argent de manière très stable et reproductible, atteignant une variation de ± 1 % pour le diamètre médian géométrique (GMD) et de ± 1,25 % pour la concentration totale, tout en offrant une gamme de tailles utilisables de 2 à 200 nm (Berger, 2023). Dans cette étape suivante, l'efficacité d'un dispositif de frittage est étudiée dans le but d'obtenir des particules d'argent sphériques pour l'étalonnage des CPC et des DMA. Le frittage des nanoparticules métalliques commence à des températures bien inférieures au point de fusion du matériau concerné (Ku, B. K., et al., 2006). Pour l'argent, les premiers effets de frittage peuvent être observés à des températures autour de 100 °C. Des travaux récents des auteurs ont confirmé ces observations en étudiant les changements de diamètre de mobilité électrique (Berger, 2024).

L'objectif de ce travail est de confirmer l'efficacité du four de frittage en analysant la morphologie des particules résultantes à l'aide d'images TEM. La taille des particules, le temps de résidence dans la zone de frittage et la température de frittage ont été variés pour caractériser les performances du système. Des images TEM ont été prises avant et après le frittage des particules d'argent. Les images TEM des particules avant frittage montrent la forme agglomérée des particules d'argent de 300 nm générées par la méthode d'évaporation-condensation. Les images TEM après frittage montrent qu'une température de frittage de 400 °C est suffisante pour obtenir des particules sphériques d'argent. Les résultats confirment la réduction de taille due au frittage, déjà observée (Berger, 2024). En outre, il est démontré que le dispositif présenté peut générer des sphères d'argent de 100 nm.

ABSTRACT

Apart from silver ultrafine particles being used in a broad variety of applications for years (Ankilov, 2002, Giechaskiel, 2009, Wiedensohler, 2017), sintering of silver particles has been of special interest to researchers (Ku, 2006; Zihlmann, 2014; Tuch, 2016). In particular calibrating CPCs for measuring ultrafine nanoparticles in the atmosphere is a topic of rising interest, where silver particles are required (EN 16976:2024) and sintering is widely used. Furthermore, spherical silver particles can be used for DMA calibration, where it is crucial to know shape and density of the reference particles. The work shown here is aimed at bringing more repeatability and usability to various fields of aerosol science which use sintered silver nanoparticles.

It has been shown that a very stable and reproducible silver particle generation is possible, achieving +- 1 % in GMD, and +- 1,25 % in total concentration while offering a usable size range of 2 – 200 nm (Berger, 2023). In this next step, the efficiency of a sintering setup is investigated, with the goal of achieving spherical silver particles for CPC and DMA calibration. Sintering of metallic nanoparticles starts at temperatures well below the melting temperature of the respective material (Ku, 2006). For silver, first sintering effects can be observed at temperatures around 100 °C. Recent work by the authors confirmed these findings by investigating changes in electrical mobility diameter (Berger, 2024).

The focus of this work is to confirm the sintering efficiency of the sintering oven by analysing the morphology of the resulting particles via TEM imaging. Particle size, residence time in the sintering stage and sintering temperature were varied to characterise the performance of the system. TEM images were taken before and after sintering of the silver particles. The TEM images of particles before sintering show the agglomerate shape of 300 nm silver particles generated by the evaporation-condensation method. The TEM images after sintering show that a sintering temperature of 400 °C is sufficient to achieve spherical silver particles. The results confirm the size reduction due to sintering shown before (Berger, 2024). Furthermore, it is shown that the setup presented can generate 100 nm silver spheres.

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INTRODUCTION & EXPERIMENTAL SETUP

In this work, the sintering efficiency of a Particle Sintering Device is investigated. Typically, metallic particles of agglomerate shape shrink during the sintering process. This is due to compaction, which leads to completely sintered particles exhibiting a spherical shape (Ku, 2006). Whether or not a particular sintering oven can achieve complete sintering of a given material at given temperature and flow rate settings, needs investigation. The authors present results for silver particles sintered in a Particle Sintering Device S8000, by Catalytic Instruments GmbH & Co. KG, Germany, running at temperatures between ambient and 700 °C. Results of two analytical methods are presented: One method uses a tandem DMA setup to analyse differences in electrical mobility diameter between unsintered and sintered silver particles. The other method uses Transmission Electron microscopy (TEM) images to visualise particles collected on a grid.

For both methods, a Silver Particle Generator (SPG) by Catalytic Instruments GmbH & Co. KG, Germany, was used to generate silver aerosol at a temperature of 1150 °C. This was made possible by using a high temperature insulation in the SPG, which is commercially available since late 2023 as an upgrade to the SPG base model. A residence chamber can optionally be installed at the SPG outlet. It comprises of two tubes with 35 mm ID and a total length of 480 mm. The goal of this component is to allow for more time for agglomeration to take place in the high concentration aerosol, yielding larger particles. The generated aerosol has been characterised before by recording particle size distributions (PSD) with an electrical mobility size spectrometer (Berger, 2024). After charge-conditioning the aerosol (TSI 3088 X-Ray Neutralizer by TSI Inc.), a single particle size is selected in an Electrostatic Classifier (EC, comprising of a TSI 3080 Electrostatic Classifier and a TSI 3081 LongDMA, both by TSI Inc.). The EC limited the aerosol flow rate to 1.55 L/min while maintaining a flow ratio of 1:10 (sheath flow rate 15.5 L/min). Therefore, the SPG main flow rate was set to 1.55 L/min. Carrier gas in all experiments is air. This monodisperse aerosol is either sent through the S8000 for sintering or through the bypass. The flow rate of the aerosol corresponds to a residence time in the hot zone of the S8000 of 2.6 to 9 s, depending on the sintering temperature. At 400 °C, the residence time is approx. 3.8 s.

For the tandem DMA method, the electrical mobility of the particles is analysed by recording a particle size distribution (PSD) with a Scanning Mobility Particle Size Spectrometer (SMPS) by TSI Inc., USA. It comprises a 3080 Electrical Classifier (EC), a 3081 Long Differential Mobility Analyzer (LDMA) and a 3776 Condensation Particle Counter (CPC) with a nominal d_{50} at 2.5 nm. Its sample flow of 1.5 L/min was combined with a sheath flow of 15 L/min in the EC, to achieve a 10:1 flow ratio. The resulting excess gas flow rate of 0.05 L/min is sent to a vent.

For the TEM method, the aerosol coming from the S8000 or bypass is directed through an Electrostatic Precipitator (EP, Grimm 5561 by GRIMM AEROSOL TECHNIK Ainring GmbH & Co. KG, Germany), where it is collected on a carbon film grid and send for TEM imaging.

Figure 1 shows a schematic of the experimental setup. Whether S8000 or the bypass (dashed line) is used, is specified in the respective subsection of the next chapter. The same applies to the route to DMA 2 or the EP.

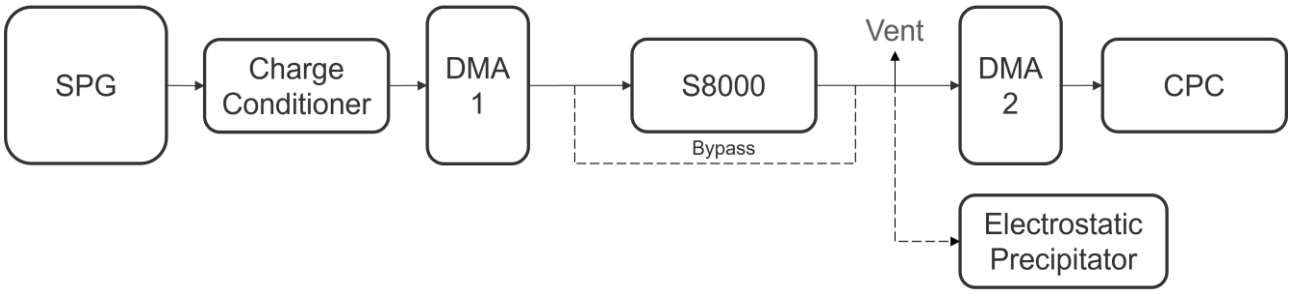

Figure 1 Experimental setup for the generation and characterisation of unsintered (using the bypass line) and sintered silver particles. A S8000 Particle Sintering Device was used as sintering furnace. Temperature in the Particle Sintering Device was varied between room temperature and 700 °C for electrical mobility analysis in the SMPS and was kept at 400 °C for TEM experiments.

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EXPERIMENTAL RESULTS & DISCUSSION

Figure 2 shows measured PSDs of silver aerosol generated in the SPG at 1150 °C, size-selected to an electrical mobility diameter of 200 nm, and sintered at different temperatures in the S8000. The different curves correspond to different setpoint temperatures of the S8000. The PSD at 20 °C shows the aerosol in its unsintered state. As expected, its GMD is close to 200 nm, as this is the size which has been selected upstream in DMA 1. The minor difference is due to instrument uncertainties of the two DMAs. The curve at 100 °C shows a reduction in GMD, indicating first sintering effects for silver particles at this temperature. This confirms results from the literature (Ku, 2006). The PSD for 200 °C is multimodal. This can be attributed to partial sintering, where some, but not all particles are exposed to enough thermal energy for compaction. When increasing the sintering temperature to 350 °C and above, the measured PSDs indicate that complete sintering is achieved, because there is no additional GMD change with further temperature increase. However, measured concentrations are reduced with higher sintering temperatures. This is due to thermophoretic losses, which increase with rising temperature.

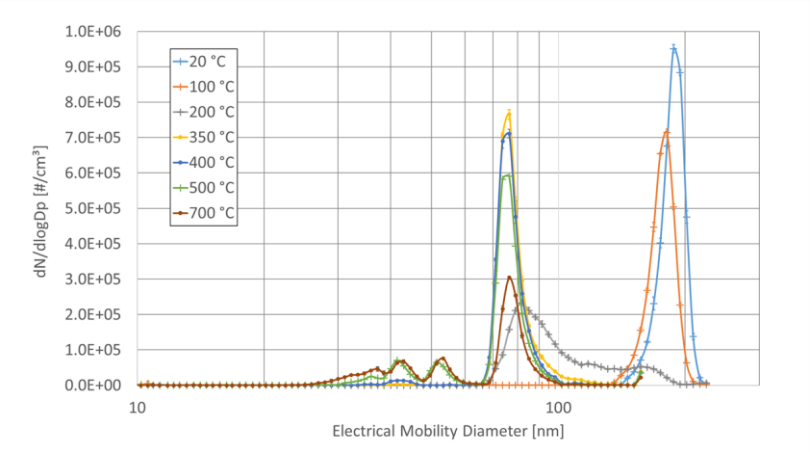

Figure 2 Measured particle size distributions of silver aerosol generated in the SPG at 1150 °C, size-selected to an electrical mobility diameter of 200 nm and sintered at different temperatures in a Particle Sintering Device S8000.

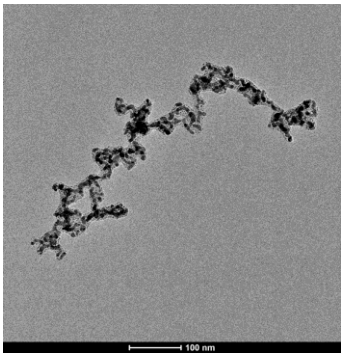

Figure 4 TEM image of a silver particle selected in DMA 1 with an electrical mobility diameter of 200 nm. It exhibits an agglomerate morphology.

Sintering in S8000 at 400 °C

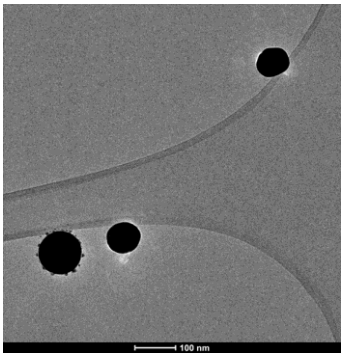

Figure 3 TEM image of silver particles selected in DMA 1 with an electrical mobility diameter of 200 nm, which have been sintered at 400 °C in the S8000. The resulting diameter is approx. 80 nm.

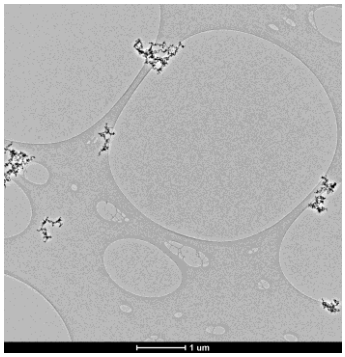

Figure 6 TEM image of silver particles selected in DMA 1 with an electrical mobility diameter of 300 nm. The particles show an agglomerate structure.

Sintering in S8000 at 400 °C

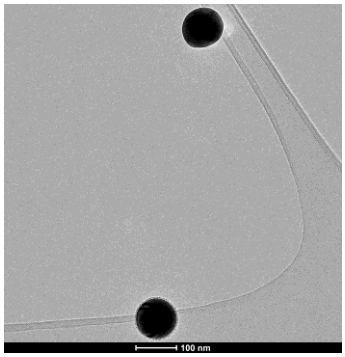

Figure 5 TEM image of silver particles selected in DMA 1 with an electrical mobility diameter of 300 nm, which have been sintered at 400 °C in the S8000. The resulting diameter is approx. 100 nm.

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The TEM images show the agglomerate shape of unsintered silver particles with electrical mobility diameters of 200 and 300 nm generated by the SPG (Figure 3, Figure 5). As the tandem DMA results shown above indicated complete sintering above a temperature of 350 °C, the authors chose 400 °C as sintering temperature for the TEM experiments. This temperature represents a compromise between thermophoretic losses and sufficient energy supply for particle compaction.

The resulting TEM images of the sintered silver particles show that 200 nm-sized agglomerates compact into 80 nm spheres (Figure 4), and 300 nm-sized agglomerates compact into 100 nm spheres (Figure 6). It can be concluded that the S8000 works well as a sintering device. Furthermore, these results confirm the authors' previous recommendation of using 400 °C as sintering temperature (Berger, 2023). The size reduction of 200 nm particles compacting to 80 nm spheres matches the results obtained by the tandem DMA method (200 nm to 75 nm GMD), and is in good agreement with the literature (Zihlmann, 2014).

An important outcome of this work is that the setup shown here is able to generate 100 nm silver spheres. As it is also possible to generate smaller particles and therefore smaller spheres by lowering the SPG temperature (Berger, 2023), it is possible to generate silver spheres in a wide range of sizes. This makes this setup useful for DMA calibration, as this is typically done with spherical particles of known composition and density. Furthermore, this setup can be used to generate calibration aerosol for calibration of CEN CPCs (CEN/TS 16976:2016), which demands spherical silver particles. As the generated silver spheres are thermally stable, this aerosol can also be used for Particle Count Reduction Factor (PCRF) calibrations of Particle Measurement Programme-compliant particle number counting systems (PNCS) used for Euro 6 and Euro 7 homologation measurements.

CONCLUSION

The results presented in this work show that it is possible to create silver spheres of 100 nm diameter with an SPG and a Particle Sintering Device S8000. With the experimental setup presented here a sintering temperature of 400 °C was sufficient to complete the sintering process, i. e. a higher temperature did not further change the GMD of the aerosol. TEM images showed, that silver particles where spherical after sintering at 400 °C in the S8000, confirming complete sintering. Future work should look into possibilities to increase available concentrations of 100 nm silver spheres. Furthermore, calibration use (CEN CPC-, PMP PNCS-, DMA calibration) of the setup shown here should be implemented in practice.

MOTS-CLÉS : aérosol, aérosol -générateur, nanoparticule, sintering / **KEYWORDS:** aerosol, generator, nanoparticle, sintering

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