STABILITE, REPRODUCTIBILITE ET COMMANDABILITE D'UN NOUVEAU GENERATEUR DE PARTICULES D'ARGENT COMPRENANT UN TRAITEMENT THERMIQUE AVEC UNE ETAPE DE FRITTAGE

STABILITY, REPRODUCIBILITY AND CONTROLLABILITY OF A NOVEL SILVER PARTICLE GENERATOR INCLUDING THERMAL TREATMENT WITH A SINTERING STAGE

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TITRE/TITLE

Stabilité, reproductibilité et contrôlabilité d'un nouveau générateur de particules d'argent comprenant un traitement thermique avec une étape de frittage / Stability, Reproducibility and Controllability of a Novel Silver Particle Generator including thermal treatment with a sintering stage

RESUME

Les particules d'argent ultrafines sont utilisées dans une grande variété d'applications depuis des années (Ankilov et al., 2002, Giechaskiel, et al., 2009, Wiedensohler, et al., 2017, etc.) et la demande dans l'industrie et le monde universitaire est en augmentation, en particulier pour des sources de particules d'argent mieux contrôlables et plus reproductibles (Hammer et al., 2022).

En partant d'un four tubulaire typique pour la génération d'aérosol d'argent par évaporation-condensation, un nouveau dispositif a été développé en visant les meilleurs niveaux possibles de stabilité, de reproductibilité et de contrôlabilité de sa génération d'aérosol et en offrant simultanément au client une liberté maximale en termes de réglage.

Nous montrons que le générateur de particules d'argent disponible dans le commerce est très stable pendant plusieurs heures (+- 1 % en GMD, +- 1,25 % en concentration totale), a une excellente reproductibilité (variation journalière : +- 10 % en GMD, +- 20 % en concentration totale) et est capable de générer des particules dans la gamme de taille de 2-200 nm avec des concentrations de particules supérieures à 1000 / cm³. En outre, nous montrons la contrôlabilité de la distribution de la taille des particules par la variation de la température et du débit.

Les images TEM montrent que les particules sont sphériques dans la gamme de taille inférieure à 20 nm et présentent une forme agglomérée avec des tailles plus grandes. Nos résultats montrent que les particules agglomérées peuvent être rendues sphériques par frittage. Nous étudions l'effet de différentes températures de frittage et de différents temps de séjour sur la distribution de la taille des particules.

ABSTRACT

Silver ultrafine particles have been used in a broad variety of applications for years (Ankilov et al., 2002, Giechaskiel, et al., 2009, Wiedensohler, et al., 2017, etc.) and demand in industry and academia is increasing; particularly for better control and more reproducible silver particle sources (Hammer et al., 2022).

Typical tube furnaces for the evaporation-condensation generation of silver aerosol have challenges in reproducibility. A novel device has been developed targeting best possible levels of stability, reproducibility, and control of aerosol generation, while simultaneously offering the customer maximum freedom in terms of adjustability.

We show that the commercially available Silver Particle Generator is stable for multiple hours (± 1 % in GMD, ± 1,25 % in total concentration), has an excellent reproducibility (day to day variation: ± 20 % in GMD, ± 20 % in total concentration) and is capable of generating particles in the size range of 2-200 nm with particle concentrations higher than 1000 #/cm³. Furthermore, we show the controllability of the particle size distribution via variation of temperature and flow.

TEM images show that particles are spherical in the size range below 20 nm and exhibit an agglomerate shape with larger sizes. Our results show that agglomerated particles can be made spherical by sintering. We investigate the effect of different sintering temperatures and residence times on the particle size distribution.

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

1. INTRODUCTION

The need for a stable and easily available source of particles for calibration purposes of condensation particle counters (CPC) in multiple applications has been expressed (Yli-Ojanperä, Jaakko, et al.). The challenge to find materials for calibration purposes, that show a similar detection and counting probability as the material being investigated, maintains a major challenge in industry and research. Environmental aerosols, consisting of a wide range of organic, non-organic, soot-like, metal, ion, and semi-volatile materials, are best to be detected when a CPC is calibrated with a source of silver particles (ISO 27891:2015). Similarly silver particles have been accepted for calibration of CPCs for brake wear emission measurements (ECE/TRANS/WP.29/GRPE/2023/4). Currently the calibration of CPCs for soot measurements of ultrafine particles from combustion processes, such as combustion engines, turbine engines, but as well stoves and open fireplaces is still not uniquely regulated. Many CPCs are calibrated with emery oil (Liu et al., 2005), which demonstrated very specific difference in the detection probability, or soot, generated in a soot generator with optional post treatment to remove organic compounds. Silver seems to be highly suitable due to its inert property as well as the shape of a non-spherical agglomerates at larger sizes, similar to soot particles (Hammer et al., 2022). Hence correction factors are applied to correct for the detection efficiencies of different materials. We present a silver particle generator, that serves as a highly stable particle source of silver nano particles, generated at a touch of a button, that allow a size range between 2 to 200 nm to cover all needs for calibration of CPCs, allows calibration at larger sizes (> 20 nm) with spherical silver nano particles via a sintering process, and can guarantee a distinct calibration with only one element - silver - when using nitrogen as a carrier gas. The remarkable ease of use to define your desired size range as well as the reproducibility of larger particles including spherical shapes, is shown in this work. We provide data collected in different setups, that show the variability as well as the simplicity of the device from a user perspective.

2. EXPERIMENTAL SETUP

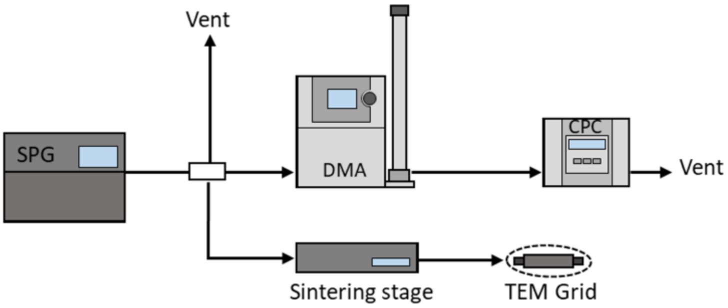

Figure 1. Experimental setup for the evaluation of the aerosol produced by the Silver Particle Generator (SPG). Particle size distributions are recorded with a DMA 3080 (column 3081) and a CPC 3776 (d_{50} = 2.5 nm). TEM imaging is done with untreated particles aswell as with particles sintered at 600, 700 and 800 °C.

Figure 1 shows a schematic of the experimental setup used in this work. Silver particles are generated in a Silver Particle Generator (SPG) by Catalytic Instruments GmbH & Co. KG, Germany, using air or nitrogen as a carrier gas. The device offers several temperature and gas flow rate settings in order to tune the resulting particle size distribution, which is measured with an electrostatic classifier (EC, DMA 3080 and a column 3081) by TSI Inc., USA, in combination with a CPC 3776 by TSI Inc., USA (d_{50} = 2.5 nm, sample flow rate setting 0.3 Lpm). To investigate the influence of SPG temperature on the generated aerosol, a temperature sweep from 900 °C to 1100 °C was carried out. Furthermore, the gas flow rate through the generator was varied from 1 to 5 Lpm.

For TEM imaging, a TEM grid was installed after the SPG outlet to collect the generated polydisperse silver particles. An additional sintering oven, operated at 600, 700 and 800 °C with an subsequent cooling stage, was inserted in between the SPG and the TEM grid with the goal of re-shaping agglomerate-shaped particles into spheres. The sintered particles were collected on the TEM grid for analysis.

3. RESULTS AND DISCUSSION

With manual selection of the electrical mobility diameter at the EC, the SPG produces the size-dependent particle concentrations shown in Figure 2 a). From 2 to 200 nm, a concentration of more than 1000 #/cm³ is achieved. Its particle generation is very stable (1σ: ± 1 % in GMD, ± 1,25 % in total concentration) over many hours, as exemplarily depicted in Figure 2 b) for SPG Mode 2 (1100 °C, 2 Lpm of air flow, no dilution flow). The day-to-day variation is shown in Figure 2 c), GMD and total concentration vary by ± 20 % at most.

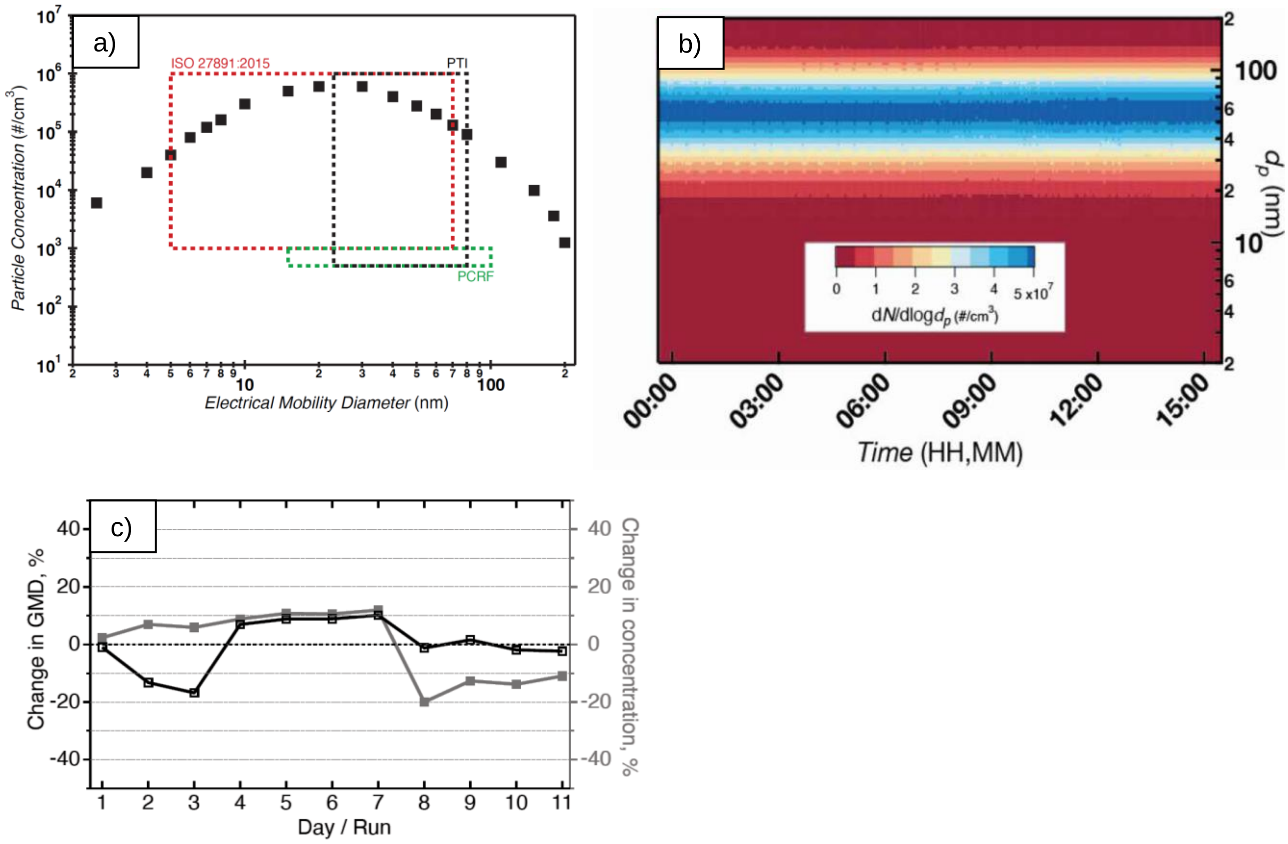

Figure 2. Particle size distribution (a), stability (b) and reproducibility (c) of the aerosol generated by the Silver Particle Generator (SPG). Graph a) shows concentrations after the electrostatic classifier manually set to depicted sizes. The plotted data is a combination of SPG Mode 1 (1000 °C, 2 Lpm generator air flow rate, no dilution) and Mode 2 (1100 °C, 2 Lpm generator air flow rate, no dilution). Graph b) shows the particle size distribution resulting from SPG Mode 2, recorded every three minutes for 15 hours, highlighting the excellent stability of the aerosol generation. Graph c) shows the day-to-day variability of GMD and total concentration of SPG Mode 2 aerosol.

The generated particle size distributions of the temperature sweep are shown in Figure 3 a). Error bars indicate one standard deviation of the mean value of multiple size scans. It can be observed that in the temperature range investigated, higher temperatures lead to larger particle sizes. Error bars are large at lower temperatures and get very small at higher temperatures. This shows that the stability of the aerosol generation is better at high temperatures. Peak height increases from 900 °C to 1000 °C, where it reaches a plateau reaching up to 1100 °C. Particle generation starts at an indicated temperature of 900 °C, which is below the melting point of silver (961 °C). This can be explained with a fraction of silver molecules with high energy being able to leave the solid phase (sublimation). These molecules then nucleate to particles.

Geometric mean diameter (GMD), geometric standard deviation (GSD) and total concentration of the particle size distributions in Figure 3 a) are plotted as a function of generator temperature in Figure 3 b). Error bars indicate one standard deviation of the mean value of multiple size scans. GMD rises with rising temperature. The higher the temperature, the more silver evaporates and is available for nucleation, generating higher particle concentrations (see increase in total concentration from 900 to 1050 °C). The higher the concentration, the more agglomeration takes place, increasing the particle size. GSD increases with rising temperatures. The particle size distribution becomes wider due to agglomeration, which is a statistically driven process of particles of various sizes colliding. Agglomeration reduces the total concentration, as it results in fewer, larger particles. This effect counteracts the increase in concentration over temperature, so that above 1000 °C, the total concentration reaches a plateau. Development effort is being invested to be able to investigate higher temperatures, to find out whether the observed trends prevail and larger particles can be produced.

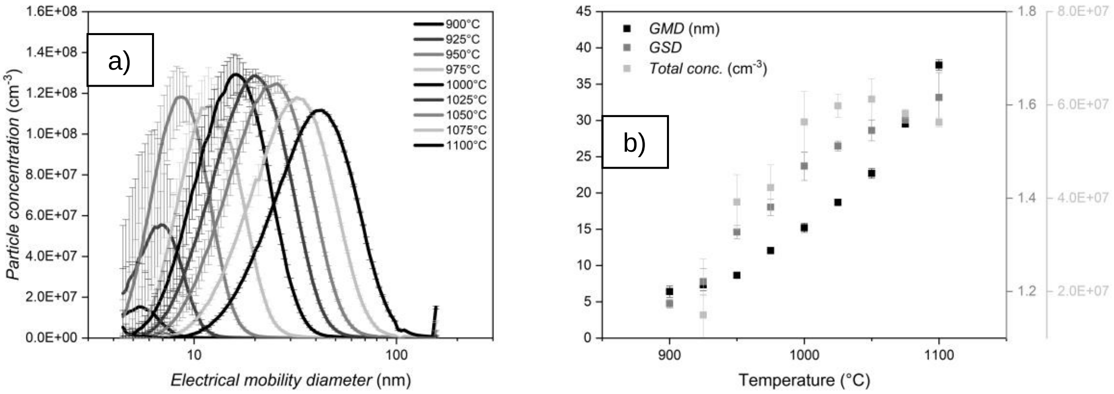

Figure 3. Resulting particle size distributions of a sweep of SPG generator temperature from 900 to 1100 °C (a). Mean particle size increases with generator temperature. GMD, GSD and total concentration of the PSDs shown in a) are plotted over temperature in graph b).

Figure 4 shows the resulting GMD, GSD and total concentration when varying the generator main flow rate from 1 to 5 Lpm (stepsize 1 Lpm) while maintaining a generator temperature of 1100 °C. When focussing on 2 Lpm and more, SPG main flow has only a minor effect on GMD, GSD and total concentration. This is well suited for the adaption to experiment setup needs (e. g. adding or removing a CPC from the setup), as it would not change the aerosol properties much. For a main flow of 1 Lpm, GMD, GSD and concentration are substantially lower. It should be investigated, whether an even lower main flow could yield a smaller GSD that could be considered a monodisperse aerosol.

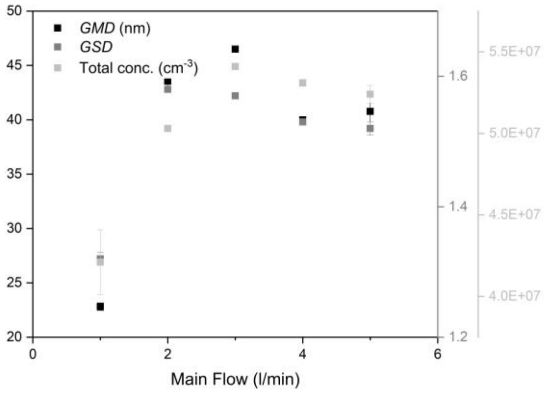

Figure 4. GMD, GSD and total concentration of PSDs generated with various SPG main flows while maintaining a generator temperature of 1100 °C.

Figure 5 shows TEM images of four different particle collections on TEM grids. Particles were generated in the SPG at 1100 °C with a main flow rate of 2 Lpm of N_2 and no dilution flow rate. 0.874 Lpm of this aerosol was directly collected on the TEM grid without sintering (a), or sintered in a Particle Sintering Unit by Catalytic Instruments GmbH & Co. KG at 600 °C (b), 700 °C (c), or 800 °C (d) and subsequently collected on the TEM grid. Residence times in the sintering oven were estimated to be 1.9 s (b), 1.7 s (c), and 1.6 s (d). Image a) shows that larger particles from the SPG have a agglomerate shape similar to soot, consisting of multiple agglomerated silver spheres. Smaller particles (< 20 nm) are spherical. Sintering at 600 °C does not have much effect on the shape of the agglomerates, see image b). Image c) shows, that sintering at 700 °C leads to more compact particle shapes. The best result is obtained when sintering at 800 °C, image d). Most particles are spherical, and even the largest agglomerates have a compact shape. Longer residence time in the sintering oven should be investigated, as it could further enhance the sintering process and potentially lead to spherical particles even at very large sizes.

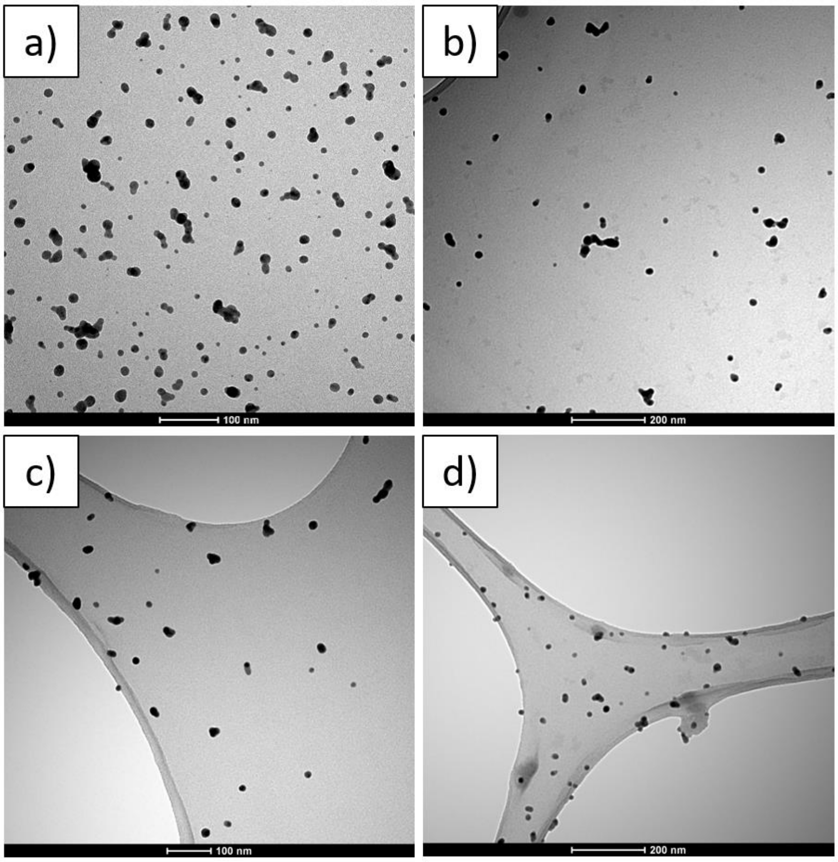

Figure 5. SPG Mode 2 (1100 °C, 2 Lpm of N_2 flow rate, no dilution) particles are analysed via TEM imaging. a) unsintered particles, b) particles after sintering at 600 °C, c) particles after sintering at 700 °C, d) particles after sintering at 800 °C

4. SUMMARY

We demonstrate that the SPG meets all criteria for a reliable particle source. Excellent stability and good repeatability as well as great adjustability make it a well-suited device for instrument calibrations. Moreover, it is easy to use so that no previous knowledge is necessary to achieve reliable and reproducible results. TEM images show that SPG silver particles are spherical if small (< 20 nm) and exhibit an soot-like agglomerate shape if larger. Furthermore, we show that sintering is effective at transforming agglomerates into spherical particles. More exciting results are yet to come with the patented SPG technology, as higher temperatures, larger particles and other materials are currently being investigated.

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