Behavior of Aerosol Nanoparticles Released into Simulated Workplace Environment

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ABSTRACT

Aerosol nanoparticles (NPs) released to workplace air will form larger agglomerates and bind to ambient aerosol particulates. The changing nature of NPs makes it difficult to standardize test methods, both for inhalation toxicological studies and for measurement of exposure levels at workplaces. Within the framework of the EU funded research project, NANOTRANSPORT (FP6), we have proposed model exposure scenarios based on analysis of real workplace situations. Experimental work has been carried out to simulate the scenarios in an exposure chamber. The agglomeration dynamic of primary Pt nanoparticles, as well as interactions between the primary NPs and background aerosols were investigated.

Keywords: aerosol nanoparticles, agglomeration, aerosol dynamic, exposure scenarios.

1 INTRODUCTION

The production and use of engineered nanoparticles (NP) in industry provides new opportunities for making advanced materials with unique physical, chemical and biological properties. On the other hand, there are increasing concerns over possible human health and environmental risks associated with the use of engineered NPs. Human exposure to NPs is most likely to occur at wok places where NPs are produced or used. To ensure workplace safety, it is essential to have a clear understanding of possible exposure scenarios, including knowledge of the nature of NPs and their concentration at the receptor (workers).

The NANOTRANSPORT project addresses the behavior of aerosols released to ambient air from NP manufacturing. The objective of this work is to investigate physical changes which NP aerosols undergo after release into the workplace environment under realistic scenarios. This information is essential to understand the characteristics of NPs when they reach a human receptor after transport over a distance from a NP source.

Based on analysis of real workplace situations, model exposure scenarios were developed and illustrated in Fig. 1.

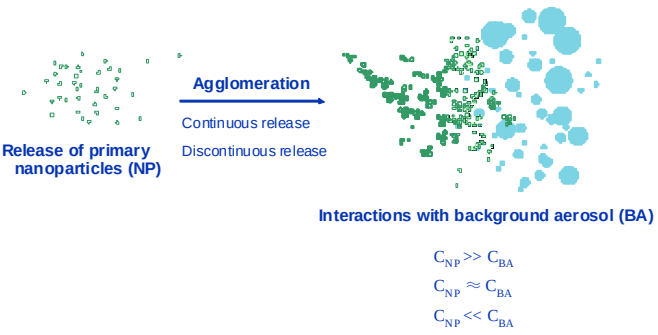


Figure 1: Model exposure scenarios used for the study (C_{NP}: nanoparticle concentration, C_{BA}: background concentration).

The model exposure scenarios in Figure 1 include the release of primary NPs into an environment with background aerosols (BA) in different concentration levels. Three concentration levels of BAs are chosen to represent the situations where $C_{NP}>>C_{BA}$, $C_{NP} \sim C_{BA}$ or $C_{NP}<<C_{BA}$. For example, in case of a clean room environment the concentration of BAs is much lower than NPs released in the air. In workplaces where BAs from ambient air are present, the concentration of BA can be in a similar range to or even higher than NPs. Both a continuous release and a pulse-wise discontinuous release of NPs are considered in the study. A continuous release may occur when there is a leak in the NP manufacturing system, and a pulse wise release may happen in case of an accident. Re-dispersion of powder formed NP agglomerates is not considered for this study.

2 EXPERIMENT

An experimental program was designed to investigate aerosol dynamic behavior of freshly generated Pt nanoaerosols in an exposure chamber, under different conditions defined in the model exposure scenarios in Figure 1. Details of the experimental work can be found in the publication by Seipenbusch et al. [1]. A brief description of the methods is given in this section.

2.1 Experimental set-up

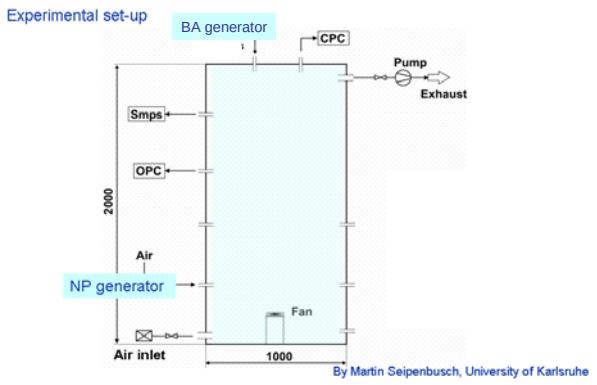


Figure 2: Experimental set-up showing the aerosol chamber used for studying behavior of nanoparticles (NP) after release in simulated workplace environments with or without background aerosols (BA).

The aerosol chamber has a dimension of 1x1x2 m and a volume of 2 m³. A hot wire generator was used to generate Pt aerosol particles. Freshly generated NPs were directly released into the chamber through the inlets on the wall at the bottom, while reference BA particles were released through the inlet on the ceiling.

Particle-size distribution of aerosol was monitored on-line at different places in the chamber along the wall and on the ceiling of the chamber. Scanning mobility particle sizer (SMPS, Grimm Series 5.400 and DMA, Grimm Vienna/Reischl) was used to measure the size distribution for fine particles, while an optical particle counter (OPC, Grimm portable aerosol spectrometer model 1.109) was used for coarse particles. Parameters, such as, convective flow rate, concentrations of NPs and background aerosols were varied to simulate different exposure scenarios.

A speed-adjustable fan was placed on the bottom of the chamber. For the experiments presented in this paper, a fan speed of 4.5 m/s was selected to ensure a rapid mixing of aerosols in the chamber. No significant differences were observed in particle concentrations measured at different sampling point along the wall.

The platinum aerosols generated were spherical NPs with a median diameter of 7-8 nm. The NP concentration at the source was adjustable in a range from $7x10^4$ to $8x10^6$ cm^{-3}.

The reference BA particles were generated from sprays of a oily substance, di(2-ethylhexyl) sebacate (DEHS), using a collision atomizer. The oil droplets had a media size between 200 and 250 nm and the concentration was set to $3x10^4$ and $2x10^5$ cm^{-3} to simulate workplace environment with lower and higher BA concentrations, respectively. A typical indoor background particle concentration lies in the range between10^3 to 10^5 cm^{-3}.

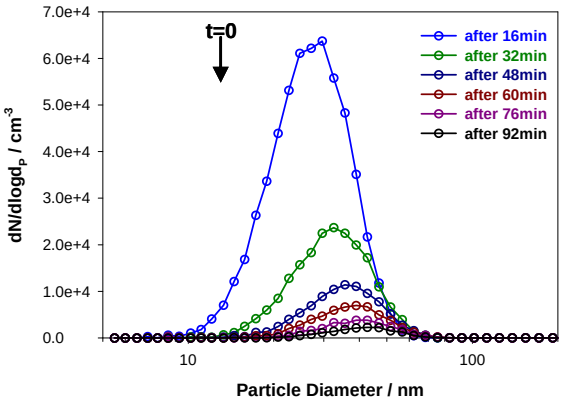
3 RESULTS AND DISCUSSIONS

3.1 Nanoparticles released in a clean room

For the case of a clean room environment, where the BA concentration is much lower than NPs released (C_{NP}>>C_{BA}), the temporal evolution of particle size distributions measured inside the chamber are depicted in Figure 3a and b for two different types of release scenarios:

- Scenario 1: a pulse of Pt NPs is released into a clean chamber (<1 particle cm^{-3})
- Scenario 2: a flow of NPs are continuously released into the clean chamber.

a.



b.

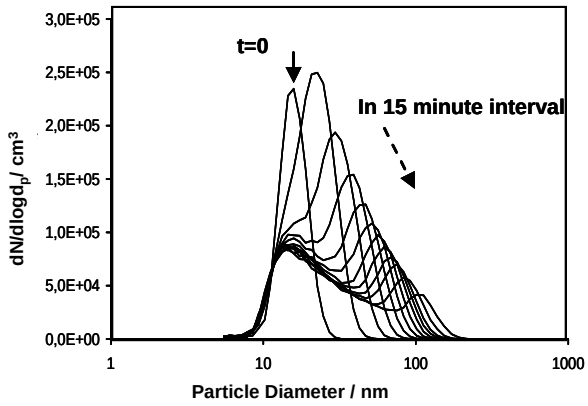


Figure 3: Particle number size distribution measured after Pt nanoparticles (NP) are released into a particle-free chamber. a: release of a pulse of NPs, b: continuous release of a flow of NPs.

When a pulse of NPs is released (Figure 3a), the particle size distribution measured in the chamber shifts gradually to larger size range (ca. 100 nm), while the particle number reduces, implying agglomeration among NPs. The agglomerate sizes are still in nanoscale, in the range between 20 to 100 nm. With increasing time, turbulent deposition plays a more important role, which also contributes to the decrease of particle number concentration in the chamber.

When NPs are continuously released, the particle size distribution changes first considerably with the time; but after certain initial time, a relative stable particle size distribution with two characteristic peaks in the range of 20 and 100 nm appear. The peak at ca. 20 nm is due to continuous input of freshly generated NPs and the second peak around 100 nm is assigned to agglomerates. The auto-agglomeration process stabilizes typically in the size range between 100 and 200 nm, where particle collision processes slow down.

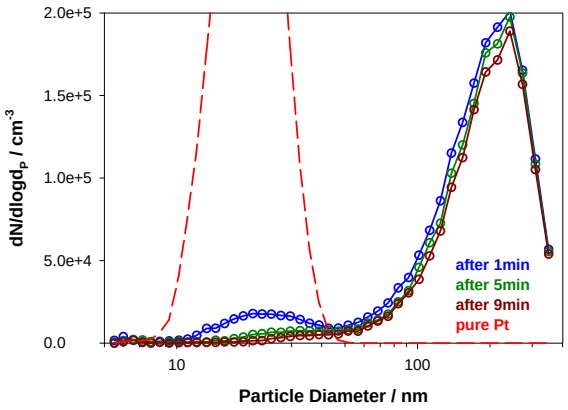
Results of the experiment in Figure 3 also demonstrate the time scale of particle size evolution under the concentration range between $1x10^5$ and $5x10^5$ cm^{-3}. For a lower concentration range of < 10^4 cm^{-3}, the agglomeration process is expected to be slower, in the order of an hour; workers in the environment may be exposed to primary NPs. On the other hand, when NP concentration is higher then > 10^7 cm^{-3}, agglomeration may occur within seconds; even workers standing close to the source are very likely exposed to agglomerates rather then primary NPs.

3.2 Nanoparticles released in a chamber with background aerosols

Figure 4 and 5 show the size distributions of NPs released into an environment with a higher ($2x10^5$ cm^{-3}) or a lower ($3x10^4$ cm^{-3}) concentration of BAs, respectively. For each BA concentration, results of a pulse wise release and a continuous release of NPs are discussed below. For both types of NPs release, the concentration of BAs in the chamber is pre-defined and BA particles are not replenished during the experiment.

When BA concentration is relatively high (Figure 4a and b), the concentration of NPs drops drastically as soon as NPs are introduced into the chamber and come into contact with BA particles. The larger sized BA particles act here as scavengers for NPs. For pulse wise NP release (Figure 4a), within few minutes, the peak of primary NPs at around 10 nm disappear as all NPs are attached to the large sized BAs between 200 and 250 nm. Even when NPs are continuously added to the chamber (Figure 4b), the concentration of primary NPs is still too low to be visible in the size distribution. The slow decrease in the BA concentration over a time period of four hours is due to deposition of the heavy agglomerates, as BAs (oil droplets) are increasingly loaded with platinum NPs. In contrast, for the results in Figure 4a only a limited amount (a pulse) of NPs are introduced into the chamber and the peak of BAs remains nearly unchanged. It should also be noticed that the monitoring time for the experiment in Figure 4a is much shorter (ca. 10 minutes) than that in Figure 4b (over four hours).

a.



b.

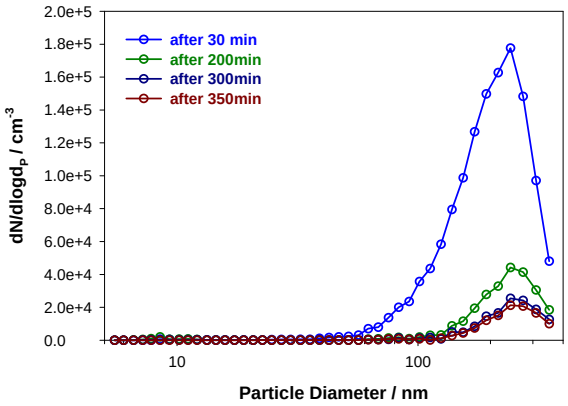
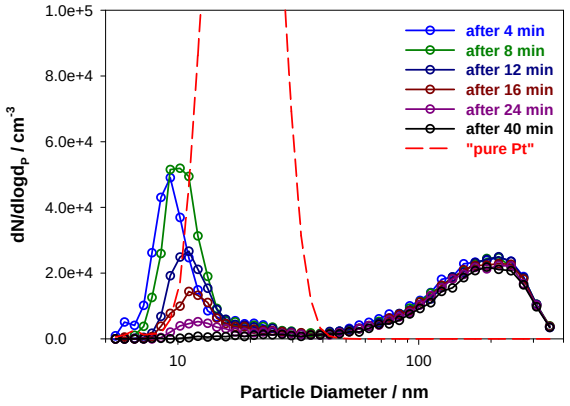


Figure 4: Particle number size distribution measured after NPs released into a chamber with a high concentration of background aerosol (DEHS) ($2x10^5$ cm^{-3}). a: release of a pulse of NPs, b: continuous release of a flow of NPs.

For the scenarios presented in Figure 5, where the concentration of BAs is relatively low, both the peak of primary NPs at around 10 nm and that of BAs at 200- 250 nm are visible in the size distribution. In case of pulse wise release (Figure 5a), the peak at 10 nm reduces rapidly with increasing time; after 40 minutes most NPs are bound to BAs and disappear from the size distribution. When NPs are continually fed to the system (Figure 5b), after 30

minutes the concentration of BAs is not sufficiently high to scavenger all the incoming NPs, and consequently, a portion of primary NPs remains in the system over a long period of time. Under this situation NPs may simultaneously undergo auto-agglomeration and heterogeneous agglomeration. The small NP agglomerates formed in the size range between 20 and 100 nm can again attach to the larger BA particles and hidden in the size distribution of BAs between 200 and 250 nm. As comparison, for the scenarios presented in Figure 3 auto-agglomerations occur among NPs, whereas in Figure 4 heterogeneous agglomeration between NPs and BAs predominant.

a.



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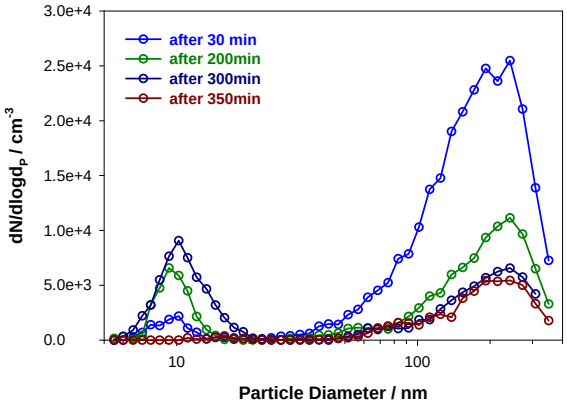

Figure 5: Particle number size distribution measured after NPs released into a chamber with a low concentration of background aerosol (DEHS) ($3x10^4$ cm^{-3}). a: release of a pulse of NPs, b: continuous release of a flow of NPs.

4 CONCLUSIONS

We have shown with our experiments that primary NPs undergo rapid changes in their particle size distribution when released to workplace air. The time scale of the particle size evolution is mainly dependent on the concentration of NPs at the source and that of BAs.

The agglomerates formed under different scenarios of NP release (e.g. continuous or discontinuous release, source concentration of NP, ratio of NP and background particles, particle size) are different in terms of particle size distribution and attachment to ambient particles. Consequently, NPs when reach the human receptor can have a different particle size and chemical composition compared to the original NPs at the source. To assess occupational health risks, information on toxicity of agglomerates and stability of agglomerates are needed, in addition to the toxicity of NP in primary form.

When monitoring NPs in workplace air, NP may not be detected in the size range where they were originally emitted; as NPs form agglomerates and attach to background aerosols. Therefore, the size range of agglomerate should also be monitored. Moreover, measurement equipments able to identify particle chemical composition need to be applied in order to detect NPs attached to background aerosols.

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[1] Seipenbusch, M., A. Binder, and G. Kasper, Temporal Evolution of Nanoparticle Aerosols in Workplace Exposure. Ann. Occup. Hyg., 2008. 52(8): p. 707-716.