Analytical strategies for a systematic characterization of nanoparticle release from commercial spray products for exposure quantification and risk assessment

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ABSTRACT

Nanoparticle containing sprays are categorized as critical consumer products due to their direct exposure path via lungs. Recent studies proposed first analytical concepts for simulated exposure experiments and proper risk assessment. Nevertheless these studies lack from systematic evaluation. This work aims on providing necessary knowledge for identification of the most critical nanoparticle types and consumer spray application. The goal is to provide optimization and validation of analytical concepts for proper quantification and a proportion of guidelines for appropriate analytical simulation experiments.

Keywords: Consumer sprays, exposure assessment, analytical approach

1 NANOPARTICLES IN CONSUMER PRODUCTS

The number of nanoparticle containing consumer and worker products increased over the last 10 years from a few to several hundreds and their number is expected to increase in the future. Market survey studies identified silver, zinc oxide, titanium dioxide, carbon and silica as most often used nanomaterials, in the different consumer product categories (e.g. textiles, food and food storage, cosmetics or household chemicals or sports equipment), but little data is available on market share of nanoproducts. More information about nanoparticle types and materials in general, their applications, and the toxic potential is nicely reviewed in Krystek et. al. [1]. Recent knowledge on toxicity of nanomaterials was summarized by Krug and Wick [2] while exposure assessment was reviewed e.g. by Kuhlbusch et al. [3] for occupational health and by D. Brouwer [4] for precaution banding tools. There is no review on consumer exposure due to nanoparticle containing spray products so far.

Sprays that contain nanoparticles were identified as most critical class of worker and consumer products due to the direct exposure pathway via lungs which implies an enhanced health risk [5-8]. Currently no consistent terminology for spray labeling exists. So either "nanoparticle containing", "nanotechnology" or just "nano" labeled spray products can be found. However, also sprays without nano label exist even if they contain nanoparticles.

2 ANALYTICAL APPROACH FOR RELIABLE EXPOSURE EXPERIMENTS

In a first step market available nanoparticle containing spray products must be categorized with respect to critical spray application, predominant nanoparticle types and concentration levels. Than in a next concepts for appropriate analytical setups should be proposed, to check the performance of methods known by the literature and to optimize and validate it. In the end a validated and exactly specified "ready to go" setup will be received. Therefore analytical concepts for nanoparticle characterization in original spray suspensions and in the generated aerosol are needed. Hereby a literature survey should help to evaluate previously proposed analytical setups in terms of given information, general performance, prospects and limitations. Therefore an optimization by identifying the knowledge gaps and providing concepts how to fill them and the validation of these concepts with lab experiments are of major importance.

The understanding of NP behavior during the spray application is of major importance. It is known from the work of Hagendorfer [9] that droplet size and with it the final size of the nanoparticles and its agglomerates are strongly dependent on the type of spray vessel. Other factors like the solvent type and the nozzle size are proposed to have a strong effect on type and behavior of nanoparticles in the aerosol. To study these factors systematically by taking measurements under different conditions with well-defined systematic spray products should help to generate a basis for a more reliable prediction model.The data generated should feed a model. With this model an already existing model [9-11] will be amplified by factors like coagulation, diffusion or aggregation. The aim is to model spray scenarios, so that time consuming measurements are no longer necessary for each new spray device.

Having alll these informations real consumer spray products can be analyzed in this way that real spray processes are simulated. So a realistic risk assessment can be done. The diverse application time of different products as well as the variable spray vessels will be taken into account.

3 ANALYTICAL SETUP

3.1 Standardized nanoparticle solution

For characterization of the spray chamber a nanoparticle containing aerosol was generated by sprayin a Ag nanoparticle suspension. Before each experiment an aqueous suspension of 50 mg/L silver@citrate nanoparticles was freshly preparedby the way that an stock solution was put into the ultrasonic bath for 1 hour and than diluted with DI water. A Milipore, Mili-Q A-10 water unit (Milipore AG) was used for the production of 18 MΩ cm deionised water (DI-water).

Silver nanoparticles with citrate coating were provided by NanoSys GmbH - Fluids and Consulting, Switzerland.

3.2 Spray dispensers

Two different types of spray dispensers were used for the experiments. On the one hand a propellent gas spray dispenser produced by Preval (Preval, Mörlenbach, Germany) and on the other hand a pump dispenser purchased by VWR (VWR, Switzerland).

3.3 Spray chamber setup

The spray experimenzs were carried out in a glovebox equipped with a high efficiency particulate air (HEPA) filter and a ventilation unit (Mecaplex, Grenchen, Switzerland) The dimensions of the glovebox are 94 x 55 x 67 cm (b, l, h), which should represent the near breathing zone of a consumer. The setup ensures a low particle background to simulate an untreadted aerosol, as it is inhales by consumers. Figure one shows a schematic illustration of the glovebox setup.

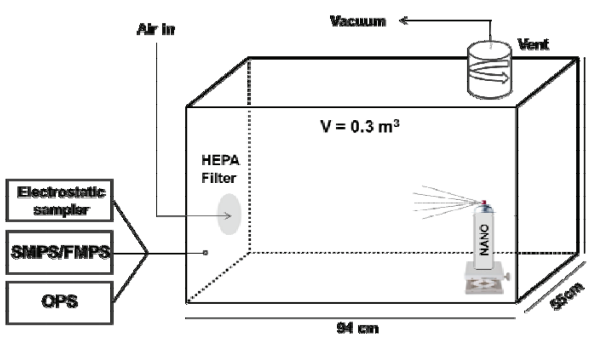

Figure 1: Schematic illustration of the glovebox setup.

Important parameters for exposure modeling are the size distribution relevant for lungs uptake, which means from about 20 µm down to a few nanometer, and the particle number concentration of the nanoparticles released from the sprays. Thus, an optical particle sizer (OPS) the upper size range (>300 nm) and a scanning mobility particle sizer (SMPS) or fast mobility particle sizer (FMPS) for the lower size range (<500 nm) are employed. Since a SMPS needs about 3 min per size scan, a fast mobility particle sizer FMPS (ca 1 second per size scan) is preferred to monitor the transient behavior during spray formation and aerosol aging. In parallel an electrostatic sampler was employed which allows a sampling of single particles on transmission electron microscopy (TEM) grids for subsequent electron microscopy analysis to achieve information on size (via image analysis), morphology and chemistry of the nanoparticles and agglomerated in the generated spray aerosols.

In the work of Lorenz [10,11] the transfer lines connecting the glovebox with the instruments were made of Tygon and just one lenghth of tubing was used during all measurements. During this work, two different tubing materials and different tubing length were tested to estimate the particle loss within the tubings. The first tubing materials was also Tygon, the second one was a conductive silicon tubing. Due to charges on the nanoparticles higher losses in the Tygon tubing is expected than in the conductive silicon tubing.

A critical literature review [10,12-15] pointed out that the particle number concentration as well as the particle size was always mesured for one fixed position of the spray inside the spray chamber. But for generating data, which should represent realistic spray scenarios different spray disatances, directions and also different spray heights with respect to the instrumentation must be taken into account.

For this reason during this work different spray scenarios where readjusted always in matters of real spray sceanarios. Cosmetic sprays for expample, like an antiperspirant spray is sprayed in a much lower distance to the consumer than it is the case for a cleaning or an impregnation spray. In this way realistic data for later exposure modeling can be generated.

Figure 2 shows the experimental setup which was used for the experiments.

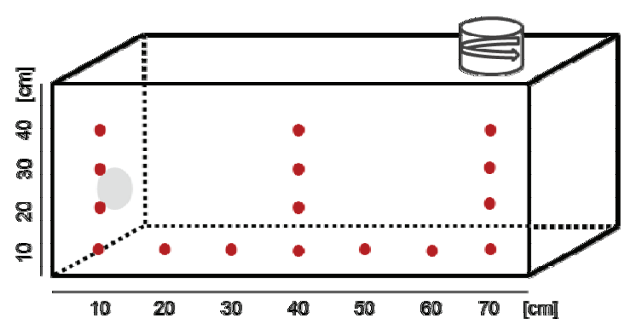

Figure 2: Experimental setup generating data of spatial distribution of nanoparticles. The red dotes represent the different spray positions.

Spray experiments where done at different positions but also in different directions. Meaning the spray was in a first test positioned in a way that the spray nozzle was directed towards the instrument (faced positon). In a second test the spray bottle was turned 180° so that the nozzle was directed towards the back side of the glovebox (advert position). For this experiments the silver nanoparticle suspension was therefore sprayed with a the propellent spray dispenser and with the pump spray dispenser. In this way also informations about the different spray dispensers can be obtained.

4 RESULTS

Experimental studies using different tubing materials and tubing length show, that for an spray duration of 10 seconds using the propellent gas dispenser the particle number concentration measured within the glovebox using a Tygon tubing was 5.9*10^4 #/cm^3. Wherby when using the conductive silicon tubing with the same length tan the Tygon tubing the particle number concentration was 6.8*10^4 #/cm^3. For the Tygon tubing also different tubing length was tested. The experiments show that for a spray duration of 1 second using again the propellent gas spray dispenser and a tubing length of 20 cm (minimum length which is needed to connect the box to the instruments) the particle number concentration is 2.4*10^4 #/cm^3. By increasing the tubing length up to 110 cmm the particle number concentration decreases to 1.7*10^4 #/cm^3. These first results show, that the tubing has an important influence on the measured particles number concentrations.

For the spatial resolution experiemnts the following results are obtained. Both for propellent gas sprays as for pump sprays it can be observed that the particle number concentration in a faced spray position is for a near inhalation zone (spray positions near to the instrument) round about 5 times higher than the one of a remote inhalation zone. When the spray bottle 180° around it can be observed that the concentration for the advert spray experiments is much lower than the one for the faced spray experiments. The particle size lies above 130 nm after 9 minutes and exceeds therefore the critical value of 100 nm, as a nanoparticle is defined. The particle size distribution looks for both spray scenarios more or less the same. This is again the case for both vessel types.

What can also clearly be seen is that the particle number concentration which is generated by a propellent gas spray is round about 50 times higher when spraying the same amount of suspension than it is when using a pump spray dispenser. Also the particle size is round about half as much when the suspension is sprayed with a propellent gas spray as with a pump spray.

These experiments deliver us first considerations that propellent gas sprays are the more critical than pump sprays due to the smaller particles generated during the spray process and due to the higher particle number concentration. With these results a first hypothesis concerning the dispenser dependet particle size drawn up by Hagendorfer [9] can be confirmed. Figure 3 shows this hypothesis.

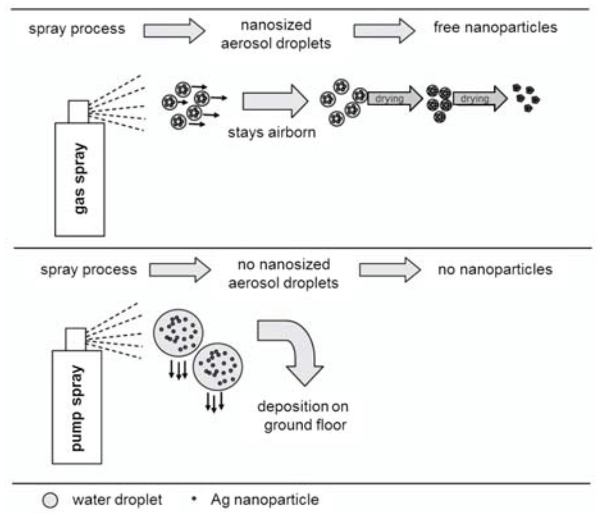

Figure 3: Scheme of understanding of the spray process, subsequent nanoparticle transport and release using a propellant gas spray or a pump spray dispenser.

5 CONCLUSION

The experiments with standardized silver nanoparticle sprays, and standardized spray equipment pointed out that the particle number concentration and particle size distribution strongly depend on several influencing factors, e.g. the spray position/direction and distance relative to the instrument, and on the spray vessel. Also the experimental setup, e.g. the tubing material connecting the instruments can have a certain influence on the measured particle number concentration. Next to the here mentioned criteria, also other factors such as temperature and humidity inside the spray chamber, the spray duration and the actually sprayed amount of the suspension can have a significant influence on the generated results. First experiments in a larger spray chamber already showed that the dimension of the chamber can have a significant influence on the residence time of the generated spray but needs to be further investigated. Thus, all these parameters need to be standardized for a critical evaluation of the spray simulation setup. Only a well characterized and standardized setup allows a reliable evaluation of real consumer spray products.

Another next step of this study will focus on a further investigation of the behavior of the spray aerosol under real-life environment, which means in interaction with other particles (dry) or aerosols (gas, droplets or solids) mixed to the generated spray aerosols. Therefore, standardized aerosols will be introduced for defined interaction with the generated spray aerosols to study the influence on the nanoparticle behavior and agglomeration processes. In a later phase, also addition toxicological studies investigating the interaction of nanoparticles with lung cells are planned. All data should build the basis for guidelines proposed to perform simulation experiments and generate data for an appropriate consumer exposure modeling.

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