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Contrasting manufactured nano objects emitted during maintenance of common particle generators with originally synthesized particles

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The production of engineered nanoparticles is rapidly growing and thus is the risk for unintentional human exposure increasing.

Workplace exposure measurements during handling of nanomaterials were recently reviewed (Kuhlbusch, 2011). Often production processes are monitored for emissions of manufactured nano objects (MNOs) in the particle size range <1µm. Less studied processes are cleaning and maintenance of particle synthesizing equipment.

In this work we characterized particle emissions during maintenance of common particle generators (a Spark Discharge Generator, SDG, and a High Temperature furnace, HT) and contrasted them to the originally synthesized particles, which we denote "*as-produced*". Both generators were operated upstream a sintering furnace, which was used to process the particles to a near-spherical shape.

Online characterization of as-produced particles, from the synthesizing process, was carried out with a Scanning Mobility Particle Sizer (SMPS) and filter sampling for analysis with transmission electron microscopy. The sampling during the emission measurements was carried out close to the expected emission zone by using an Aerodynamic Particle Sizer (APS, 3321, TSI Inc.) and a Condensation particle counter (P-trak, 8525, TSI inc.) for particle number concentration. Filters for scanning electron microscopy (SEM) analysis were collected. In addition a Laser Vaporization Aerosol Mass Spectrometer (LV-AMS, Aerodyne Inc.) was used for highly time-resolved chemical identification of both the as-produced and emitted particles.

The emissions in terms of mass and surface area were dominated by particles >1µm. SEM analysis revealed that the particles were highly agglomerated and were consisting of nanometer sized structures, figure 1.

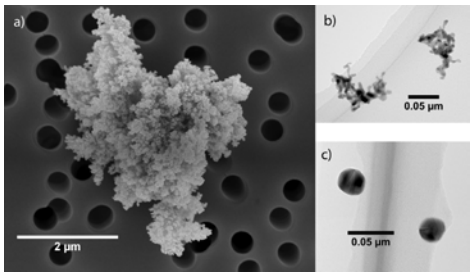

Figure 1. a) Typical emitted agglomerate with nanostructures related to sintered particles. b) Aggregates formed by the SDG. c) Sintered particles

The chemical identification of the emitted particles showed that they were dominated by the metal elements used during the particle synthesis sessions prior to the maintenance. The nano meter structures, of which the agglomerates consisted, could in terms of size and shape, be related to both the originally as-produced aggregates and the sintered particles.

By considering the geometric mean diameters of the as-produced (~0.03 µm) and of the emitted (1.8 µm) particles it is evident that they, respectively, overlap with the lower and the upper maxima of the pulmonary deposition curve (Multiple Path Particle Dosimetry, MPPD), figure 2.

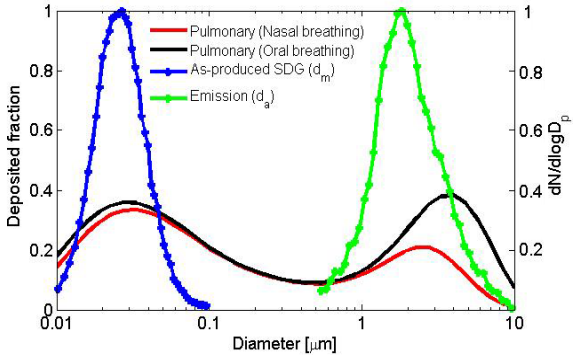

Figure 2. Two pulmonary deposition curves (MPPD) shown together with typical particle number size distributions (normalized) of as-produced particles and emitted particles during maintenance of the generators.

The fate of the emitted "*super-agglomerates*" after deposition in the lung fluid is unknown. If only kept together by van der Waals forces de-agglomeration is possible and thus the emitted agglomerates may have the same possible effects as free as-produced nanoparticles. This work shows the importance of including measurements of particles >1µm in assessments of emissions and exposure to manufactured nano objects since the agglomerates contribute significantly to the total emitted particle surface area, a key factor in particle toxicology.

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Kuhlbusch, T., Asbach C., Fissan H., Gohler D. and Stintz, M. (2011) *Particle and Fibre Toxicology*, **8**