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A system to assess the stability of airborne nanoparticle agglomerates under aerodynamic shear

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ABSTRACT

Stability of airborne nanoparticle agglomerates is important for occupational exposure and risk assessment in determining particle size distribution of nanomaterials. In this study, we developed an integrated method to test the stability of aerosols created using different types of nanomaterials. An aerosolization method, that resembles an industrial fluidized bed process, was used to aerosolize dry nanopowders. We produced aerosols with stable particle number concentrations and size distributions, which was important for the characterization of the aerosols' properties. Next, in order to test their potential for deagglomeration, a critical orifice was used to apply a range of shear forces to them. The mean particle size of tested aerosols became smaller, whereas the total number of particles generated grew. The fraction of particles in the lower size range increased, and the fraction in the upper size range decreased. The reproducibility and repeatability of the results were good. Transmission electron microscopy imaging showed that most of the nanoparticles were still agglomerated after passing through the orifice. However, primary particle geometry was very different. These results are encouraging for the use of our system for routine tests of the deagglomeration potential of nanomaterials. Furthermore, the particle concentrations and small quantities of raw materials used suggested that our system might also be able to serve as an alternative method to test dustiness in existing processes.

1. Introduction

Increasing number of products based on nanotechnology are leading to an increasing potential for human exposure to nanomaterials in the workplace. Workers can be exposed to nanoparticles during manufacturing processes, use of products, transport, storage or waste treatment (Curwin & Bertke, 2011; Koivisto et al., 2012; Kuhlbusch & Fissan, 2006). The inhalation of nanomaterials poses potential health risks (Bourdon et al., 2013; Paur et al., 2011). Particle sizes and their state of agglomeration determine where they deposit in the lung structure (Rissler et al., 2012; Zhang & Kleinstreuer, 2011). The size of agglomerates may also influence toxicological mechanisms (Noël et al., 2012). Furthermore, nanoparticles deposited in lungs could by-pass their defense system and enter the circulatory system, which could adversely affect the

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cardiovascular system (Geiser & Kreyling, 2010; Oberdoerster et al., 2004). Information on the particle size distributions of nanomaterials is, therefore, important for assessing the deposition and likelihood of translocation across biological barriers.

The stability of nanomaterial agglomerates is another important material parameter in modeling nanomaterial release and associated human exposure. Most of the industrially important nanomaterials are initially produced in the form of powders. These powders can easily enter the airborne phase as single particles, aggregates, or agglomerates. The size of the agglomerates, however, is often outside the nano-range and can reach from several hundred nanometers to micrometers in diameter (Gomez, Irusta, Balas, Navascues, & Santamaria, 2014). The mechanisms of particle agglomeration, as summarized by Schneider and Jensen (2009), include physical interlock (rough surface, entangled surface shapes, or chain-like, branched structure), electric forces (Van der Waal, conductive/non-conductive), magnetic forces (ferromagnetic, induced magnetic) and soft bridging (sticky surface, liquid film, organic functional groups). Previous studies reported that the deagglomeration of such submicron clusters is dependent on the energy present in the process from which they are released and the turbulence of their transport in the air (Islam & Cleary, 2012; Yang, Chan, & Chan, 2014). Such processes have also been shown to release primary particles or smaller, nano-sized agglomerates (Froeschke, Kohler, Weber, & Kasper, 2003; Stahlmecke et al., 2009).

Agglomeration strength can be studied directly, by measuring the binding force between individual particles, or indirectly, by triggering deagglomeration using external forces such as impaction or shear. Binding energy between primary particles was studied using atomic force microscopy (Blum & Blum, 2009). In the inertial impaction method, nanoparticle (NP) agglomerates collided with a substrate at high velocities (Froeschke et al., 2003). By subsequently analyzing transmission electron microscopy (TEM) images of the agglomerates, their degree of fragmentation was determined as a function of their impact velocity. The aerosol generation methods in their study included spark discharge generation and flame synthesis. For silver NPs, the degree of fragmentation increased as collision velocity increased, but decreased with smaller primary particle size. Another fragmentation method is the application of shear-forces in the air by forcing the agglomerate aerosol through a critical orifice. Originally, this effect was described for micrometer-sized particles (Fonda et al., 1999). Compact particles were effectively separated from each other in the turbulent airflow conditions created by a large drop in pressure. A recent study described the deagglomeration of nano-sized agglomerates (Stahlmecke et al., 2009). The overpressure used to create different shear forces stayed below or equal to 140 kPa. The mean particle size of the materials tested decreased as the overpressure was increased; this was interpreted as deagglomeration.

Two key components are needed to investigate the stability of NP aerosols with regards to changes in their size and numbers: an aerosolization system, and a means of applying energy to the airborne particles so as to test their stability, as described above. Ideally, the aerosolization system should be able to produce an aerosol with stable particle concentration and size distribution for a reasonably long time. Furthermore, it should only require the use of small amounts of material so that even expensive, novel materials can be tested. Different aerosolization methods exist, such as the continuous drop method (Bach & Schmidt, 2008), the rotating drum method (Breum, 1999; Schneider & Jensen, 2008), the vortex shaker method (Morgeneyer, Le Bihan, Ustache, & Aguerre-Chariol, 2013), the magnetic stirrer setup (Stahlmecke et al., 2009) and the stirred fluidization system (Saleh et al., 2014). These systems can produce different particle number concentrations by controlling such experimental parameters as the feed rate, rotation speed, or shaking frequency. However, these setups also have some disadvantages. Aerosol stability is a key problem, as the few published time-series graphs for these systems attest (Morgeneyer et al., 2013). Furthermore, the amount of material needed for the continuous drop method (500 g), the rotating drum method (35 cm^3) (CEN, 2013) and the stirred fluidization method (200 g) makes these tests too expensive to be conducted for some nanomaterials. Recently, a modified rotating drum method based on a downscaled version of EN 15051 was developed, which uses much less powder (6 g) per test (Schneider & Jensen, 2008). Other aerosolization systems which employs relatively lower amount of raw material include the Venturi dustiness testing device (Evans, Turkevich, Roettgers, Deye, & Baron, 2013) and the low-mass dustiness tester that simulates the powder falling process (O'Shaughnessy, Kang, & Ellickson, 2011). The powder quantities used in these two methods are 10 mg and 15 mg. Finally, the friction in the magnetic stirrer setup can create static charges during aerosolization that have the potential to alter an aerosol's state of agglomeration.

To overcome the shortcomings of the traditional systems, we turned to the fluidized bed system—an aerosolization concept commonly used in modern powder technology and known for its simple, easily controlled operational characteristics (Ahmed Mahmoud, Nakazato, Nakajima, Nakagawa, & Kato, 2004). Until now, fluidized bed systems were used mostly with powders composed of micrometer-sized particles. In the present study, a process closely based on the fluidized bed concept was established to create stable aerosols from nanopowders. An orifice-based approach was then used to study the deagglomeration potential of airborne nanomaterials using a wide range of air turbulence levels induced by the pressure drop across the critical orifice. Different types of materials were tested to investigate the influence of such characteristics as their composition, surface coating, primary particle size, and shape.

2. Material and methods

An integrated system was developed, composed of an aerosolization device, transport tubing, a deagglomeration orifice, and a measurement chamber (Fig. 1). A special glass funnel was used to activate dry powders. The relatively thick funnel wall (2–3 mm) was designed to resist pressure differences of up to 400 kPa. Before the start of the test, the funnel was filled with dry powder via the top opening. An airflow is then passed through a nozzle (2.1 mm diameter) at the bottom of the