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Nanoparticle aggregate volume determination by electrical mobility analysis: Test of idealized aggregate theory using aerosol particle mass analyzer measurements

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Abstract

The nanoparticle aggregate volumes are determined from the mobility diameter using the idealized aggregate (IA) theory proposed by Lall and Friedlander [(2006). On-line measurement of ultrafine aggregate surface area and volume distributions by electrical mobility analysis: I. Theoretical analysis. *Journal of Aerosol Science*, *27*, 260]. The use of IA theory makes it possible to account for aggregate number and size of primary particles and aggregate orientation in the electric field. The theory is tested using an aerosol particle mass analyzer (APM) which determines particle mass based on particle motion in a centrifugal and electrical force field. Unlike electrical mobility analysis, the APM mass measurements are independent of particle morphology because the centrifugal force is directly proportional to the mass. The aggregate volumes based on IA theory are compared with the aggregate volumes measured by the APM. The comparison is made for iron oxide (density = 5.7 g/cc) and carbon (density = 2 g/cc) aggregates, both generated by laser ablation. A differential mobility analyzer (DMA) was used to classify the aggregates corresponding to mobility diameters of 80, 100, and 120 nm. For each mobility diameter, the aggregate volume was calculated from IA theory; the primary particle diameter was measured by electron microscopy. The aggregate mass for each mobility diameter was measured directly by the APM without the use of IA theory. The aggregate volume was determined from the mass measured by the APM and the primary particle density. The agreement between the DMA and APM aggregate volume measurements was good for both materials studied. The results support the application of IA theory. In a further application of IA theory, literature data for DMA–APM measurements of the ultrafine atmospheric aerosol were used to calculate the fraction of aggregates.

Keywords: Carbon; Iron oxide; Aggregates; Aerosol; Aerosol particle mass analyzer (APM); Differential mobility analyzer (DMA); Migration velocity; Electrical mobility diameter; Ultrafine atmospheric aerosol (UAA); Effective density; APM transfer function; Laser ablation

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1. Introduction

Ultrafine particles (smaller than about 0.1 μm) are often generated by flame reactors (Pratsinis, 1998), and are emitted from combustion sources such as diesel engines (Chung, Lall, & Paulson, 2008; Neer & Koylu, 2006; Wentzel, Gorzawski, Naumann, Saatho, & Weinbruch, 2003) and other high-temperature processes (Mädler, Kammler, & Mueller, 2002) in the form of fractal-like aggregates composed of solid nanoparticles. There is need for the online measurement of ultrafine aggregate volume and mass. Conventional offline filter based gravimetric methods such as those used in emission standard testing (Burtscher, 2005; Kittelson, 1998) require long sampling times for ultrafine particles. Moreover, most instruments for online measurement of ultrafine particle distribution functions, for example, differential mobility analyzers (DMAs), are calibrated for spherical particles. These calibrations hold for compact particles but lead to serious errors when applied to aggregates.

Early studies on the use of DMA for measuring chain aggregate size distributions were made by Kasper (1982a, 1982b) and Wen, Reischl, and Kasper (1984a, 1984b). Kasper (1982a, 1982b) measured the slip coefficients of iron oxide chain aggregates in the transition regime which enables the use of aggregate mobility equivalent diameter as a function of the number and size of primary particles that compose the aggregate. Wen et al. (1984a, 1984b) proposed a relation between the chain aggregate charging efficiency and the number and size of primary particles that compose the chain aggregates. The charging efficiency was tested for iron oxide aggregates with primary particle radius between 20.5 and 40.5 nm. Other studies on aggregate morphology measurement involved the use of DMA in combination with other instruments such as low pressure impactor (Kütz & Schmidt-Ott, 1990; Schleicher, Kunzel, & Burtscher, 1995; van Gulijk, Marijnissen, Makkee, Moulijn, & Schmidt-Ott, 2004). Rogak, Flagan, and Nguyen (1993) proposed the use of projected surface area equivalent diameter as the mobility diameter. Their analysis is widely used for separating aggregates with a known surface area and thereby determining surface area distributions. There still remains need to establish a relationship between aggregate volume (or mass) and mobility diameter. Due to lack of such a relationship, extensive transmission electron microscope (TEM) analysis of over 1000 aggregates was often used to determine the volume of mobility classified aggregates (Park, Kittelson, & McMurry, 2004a; Park, Kittelson, Zachariah, & McMurry, 2004b).

Lall and Friedlander (2006) developed idealized aggregate (IA) calibrations for interpreting DMA data for aggregates and thereby determining number, surface area and volume distributions, if the primary particle size is known. The method was based on the aggregate drag calculations of Chan and Dahneke (1981) and aggregate charging efficiencies proposed by Wen et al. (1984a, 1984b). The method applies to IAs composed of uniform primary particles in the free molecule size range such that each primary particle is equally exposed to the surrounding gas. This is a reasonable approximation for aggregates with low fractal dimension ($D_f < 2$). The IA model represents the analog for aggregates that spheres are for irregular compact particles. The IA method relates the number and the radius of primary particles that compose the aggregates to the mobility diameter. The relation is obtained by equating aggregate migration velocity to that of spheres with the same mobility diameter. In this way the ultrafine aggregate number, surface area and volume distributions can be calculated from DMA measurements *corrected for aggregate drag and charging efficiency*. The aggregate mass distribution can be calculated, if the primary particle density is known.

The IA theory was tested experimentally using low fractal dimension silver aggregates generated by an evaporation/condensation method (Lall, Seipenbusch, Rong, & Friedlander, 2006). The primary particle diameter was 18.5 nm. The aggregate number distributions with respect to volume were calculated using the IA theory. In a separate set of experiments, the aggregates were sintered to form spheres. The number distributions with respect to sintered aggregate volumes were calculated using the standard DMA calibrations for spheres. Lall et al. (2006) found good agreement between number distributions with respect to aggregate volume measured before and after sintering: these should be the same because the aggregate volume remains unchanged during sintering. The aggregate volumes based on the standard DMA calibration for spherical particles were significantly overpredicted.

The IA theory is also useful in converting the DMA number distribution with respect to mobility diameter ($\mathrm{d}N/\mathrm{d}\log(d_m)$ vs. d_m) to number distribution with respect to aggregate volume ($\mathrm{d}N/\mathrm{d}\log(v)$ vs. v). The number distribution with respect to volume (or mass) is independent of particle morphology. The method can be applied to aerosols composed of low fractal aggregates with uniform primary particles such as certain diesel exhaust emissions (Chung et al., 2008; Neer & Koylu, 2006) and a part of the ultrafine atmospheric aerosol (UAA).

In this paper, we provide further support for the IA method using measurements that are independent of aggregate morphology and orientation. The mass measured by an aerosol particle mass analyzer (APM) does not depend on particle