



Rationale for Data Evaluation of the Size Distribution Measurements of Agglomerates and Aggregates in Gases with Extended SMPS-Technology

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ABSTRACT

Engineered nanoparticles (ENP) very often occur in form of agglomerates built up from spherical primary particles and sintered aggregates. The properties of materials making use of ENPs depend on the distributions of the structural properties of agglomerated/aggregated ENPs. The amount and structural properties of accidentally released ENPs are also of interest with regard to their transport and environmental effects.

We report on the possibilities of using extended SMPS-technology with the addition of an Aerosol Particle Mass Analyzer (APM) and/or an Electrical Sensor (ES), as well as the results of recently developed sintering models, to describe the structures of agglomerates and aggregates. Proposals are made for suitable data evaluation procedures to yield accurate property distributions.

Keywords: Engineered nanoparticles; Sintering model; Aerosol Particle Mass Analyzer (APM); Electrical Sensor (ES); Agglomerate and aggregate characterization.

INTRODUCTION

Engineered nanoparticles (ENPs) are mainly produced in the liquid and in the gas phase. Due to unavoidable coagulation and unwanted or wanted sintering processes they often occur in form of loose agglomerates consisting out of primary particles touching each other in one point or sintered aggregates with stronger chemical bonds. In this paper we will not only consider loose agglomerates as has been done in the past (Lall and Friedlander, 2006a; Lall *et al.*, 2006b; Wang *et al.*, 2010), but we will consider data evaluation procedures for the structurally more complicated aggregates. Although the primary particles in agglomerates can have different shapes (spheres, fibers, plates) depending on the material and the synthesis process, very often they are spherical with diameters of a few nanometer to below 100 nm. The overall size of the formed loose agglomerates depends on the number of primary particles per agglomerate and the structuring of the primary particles within an agglomerate. The upper limit, which we consider here, is

determined by the limit of the Scanning Mobility Particle Sizer (SMPS)-technology at about 1 μm . An aggregate formed from such a loose agglomerate has a smaller overall size down to the size of a sphere with equal volume at the end of a sintering process. The structure of ENPs and their sizes are of great importance for the properties of the end products (Hülser *et al.*, 2011) and also after release for their behavior in the environment (Kuhlbusch *et al.*, 2011; Wang *et al.*, 2011, 2012).

Structure information and concentration size distributions are of greatest value for nanoparticle control during synthesis in the gas phase as well as for exposure assessment in the air. The concentration measures mainly of interest are the number, surface area and mass (volume) concentrations as function of particle size. There are several different size definitions of interest. Particle mass or volume related effects ask for the volume (mass) per particle as size indicator. The surface area per particle is less used as size indicator, although it is an important parameter for describing interface effects (catalysis and sensor technology). Very popular are equivalent sizes described as a diameter of a sphere, which shows the same behavior as the agglomerate/aggregate in the physical process used for measurement. For gas borne nanoparticles the electrical mobility diameter is of great importance, because popular sizing instruments are making use of the size dependent transport of charged particles in an electric field.

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EXISTING TECHNOLOGIES AND DATA EVALUATION PROCEDURES; NEEDED FURTHER DEVELOPMENTS

Existing Technologies and Data Evaluation Procedures

The most important tool for gas borne particle size distribution measurements thus far is the Scanning Mobility Particle Sizer (SMPS) or related instruments like the Fast Mobility Particle Sizer (FMPS), for which the calibration and data evaluation procedures are based on the assumption that the particles are spherical. In a SMPS spherical particles are bipolarly charged in a defined way. They are then fractionated according to their electrical mobility of one polarity, which is related to their electrical mobility diameter. In case of spherical particles the (electrical) mobility diameter of singly charged particles is equal to the geometric diameter. The fractionated particles are counted with a Condensation Particle Counter (CPC), in which the particles are enlarged to optically detectable sizes. The resulting number size distribution does not yet represent the airborne number size distribution, because it is biased by multiply charged particles and does not yet take into account charging probabilities. To obtain the correct number size distribution from the measured distribution, initially the higher than singly charged particles, which have the same electrical mobilities as singly charged particles are deducted from the corresponding mobility class of the distribution of singly charged particles, resulting in the corrected distribution of singly charged particles as function of mobility size (Hoppel, 1978; ten Brink *et al.*, 1983; Fissan *et al.*, 1983). With the known size-dependent probability of a particle acquiring a single elementary charge in the bipolar charger (Wiedensohler, 1988), the total number distribution as function of geometric diameter, equal to the electrical mobility diameter for spheres, is calculated.

In case of agglomerates/aggregates the mobility diameter dependent charge distribution changes, which affects the correction of the number concentration distribution. This will be discussed later. In SMPS and other similar instruments a CPC is used for counting. In the range where the CPC reaches near 100% detection efficiency the CPC signal is independent of the form of the particle and hence number concentrations of agglomerates/aggregates measured with an SMPS are only affected by the different charge distributions of spheres and agglomerates/aggregates.

In case of agglomerates/aggregates the measured mobility diameter is an equivalent diameter, which describes the transport behavior of the agglomerate/aggregate in an electric field. Only for processes, in which agglomerates/aggregates are transported in an electric field comparable to the one in the Differential Mobility Analyzer (DMA), the measurement delivers physically meaningful results. This diameter does not give direct information about the structure of the agglomerate/aggregate and does not allow the calculation of the surface area or volume of agglomerates/aggregates without other assumptions or models.

If we only deal with spherical primary particles and their agglomerates we can differentiate two types of measurement objects, loose agglomerates of single spheres with open structures (different fractal dimensions) and aggregates

(higher fractal dimension due to necking). Under certain circumstances it has been observed that the primary particles are of equal size, which eases the description of loose agglomerates. Their surface area and volume can be described by just two parameters, number of primary particles and primary particle size (independent of their fractal dimension), from which agglomerate properties like surface area $a_{aggl.}$ and volume $v_{aggl.}$ per agglomerate can be easily derived:

$$a_{aggl.} = N\pi d_p^2, \quad v_{aggl.} = \frac{1}{6} N\pi d_p^3 \quad (1)$$

N is the number of primary particles per agglomerate and d_p is the primary particle diameter. These equations do not apply for aggregates.

Lall *et al.* (2006a, b) developed a model, which allows data interpretation of SMPS-measurements for loose, chain like (low fractal dimension) agglomerates consisting out of equally sized primary particles of known size. They used existing models for the drag force and the friction coefficient of the described agglomerates, which allow equating the migration velocity of the agglomerate to that of a sphere. The resulting equation relates the number and size of primary particles of the agglomerate to the (mobility) diameter of a sphere with the same migration velocity for particles with unit charge.

The number of primary particles N in one agglomerate with the mobility diameter d_m can be computed as

$$N = \frac{12\pi\lambda}{c^* d_p^2 C_c(d_m)} d_m \quad (2)$$

where c^* is a constant regarding particle orientation for chain like agglomerates, λ is the mean free path of gas and $C_c(d_m)$ is the Cunningham slip correction factor.

The value of the model is limited because of the assumptions made with respect to the structure of the agglomerates (loose agglomerates with low fractal dimensions). In several cases of different synthesis methods it has been observed that loose agglomerates with similar low fractal dimension have been formed. Lall *et al.* (2008) produced similar loose iron oxide and carbon agglomerates using laser ablation. They were used to verify successfully their model for loose agglomerates. But still this model is not applicable for aggregates.

Thus far we discussed agglomerate properties. The starting point for getting distributions is the measured number distribution as function of mobility diameter, which is biased as with spheres by multiple charge effects caused by bipolar charging. For correction the bipolar charge distribution of the agglomerates has to be known. This information is still limited (Rogak and Flagan, 1992; Maricq, 2008; Xiao *et al.*, 2012). Lall *et al.* (2006a, b) used a model for bipolar agglomerate charging developed by Wen *et al.* (1984a, b) approximating agglomerate structure by long prolate spheroids. They claim that the Boltzmann distribution is a good approximation for the fraction of agglomerates with

charge q :

$$\eta_{agg} = \frac{e}{(\pi D_{qe} kT)^{1/2}} \exp\left(\frac{-q^2 e^2}{D_{qe} kT}\right) \quad (3)$$

e is the elementary charge, q is the number of charges per particle, k is the Boltzmann constant, T is the temperature and D_{qe} is the charging equivalent diameter of the agglomerate ($N \geq 10$), describing the diameter of a sphere with the same charge as the agglomerate.

Using the already introduced correction procedure for spheres (Hoppel, 1978; Fissan *et al.*, 1983; ten Brink *et al.*, 1983) Eq. (3) was used for the correction of the multiple charge effect and to determine the total concentration with the ratio of the charging efficiency for a singly charged agglomerate to that of a singly charged sphere. Starting with the corrected number distribution other distributions can be calculated with the known and already discussed properties of the agglomerates.

In this method the primary particle size has to be determined beforehand, which may be achieved using time-consuming, off-line techniques such as transmission electron microscopy (TEM) or small angle X-ray scattering measurement. Therefore a faster technique for determination of the primary particle size has been looked for. To get additional structure information an Electrical Sensor – ES has been added to a SMPS in parallel with a CPC (Wang *et al.*, 2010).

We call Electrical Sensor (ES) any instrument with an electrometer as the main component. The ES used here consists of a unipolar charger, a charge manipulator (ion trap) followed by an electrometer. Currently several slightly different instruments of this kind are commercially available. We will discuss the use of an Electrical Aerosol Detector (EAD) (Medved *et al.*, 2000), which was the first developed instrument of this kind. A similar instrument with slightly operational modifications (NSAM) has been used to measure lung deposited surface area concentrations (Fissan *et al.*, 2007; Asbach *et al.*, 2009; Shin *et al.*, 2009). With this extended SMPS-system the number and current distribution can be measured. In the size range where the number and current distribution is not affected by multiply charged particles, the current measured with the ES at a certain mobility diameter can be divided by the number concentration measured with the CPC. This quantity we call sensitivity S . The charge per particle n , a particle property, can then be determined:

$$n = S/(e \times Q) \quad (4)$$

e is the elementary charge, Q is the flow rate through the ES.

The resulting unipolar charge level of the particles is mainly caused by the unipolar charging process in the ES. There might be a slight dependency on other effects in the instrument (particle losses and incomplete mixing).

The charge per agglomerate depends among others on its electrical capacitance, which changes, when a spherical

particle is structured into a loose agglomerate with the same total volume. For a loose agglomerate with equally sized primary particles the capacity change depends on the primary particle size. Making use of this dependency, Wang *et al.* (2010) developed a semi-empirical model, which allows the on-line primary particle size determination for chain like agglomerates with low fractal dimensions from the measured values of charge per agglomerate. The developed model has been adjusted by making use of measured charge per particle data of spherical and loosely agglomerated silver particles. Several comparisons with TEM-measurements showed a rather good agreement of the mean primary particle sizes (Wang *et al.*, 2010; Liu *et al.*, 2012), Wang and Pui (2013). The used model does not show any material dependency (Shin *et al.*, 2009), but other materials may not form the ideal loose agglomerates with equally sized primary particles. The primary particle size is determined only for a limited size range of electrical mobilities. It is assumed that the determined primary particle size is valid for all agglomerates in the distribution. This assumption can be omitted, if we develop a charge correction procedure for the measured current distribution similar to the one for number concentrations taking into account the unipolar charge level of the particles (Kaminski *et al.*, 2012). With a known relationship between charge per agglomerate and primary particle size, the primary particle size distribution could be determined.

The measured primary particle size as well as the measured agglomerate number distribution are introduced into the Lall *et al.* (2006a) model. The agglomerate number concentration distribution as function of mobility diameter is corrected for the effect of the different charge distribution for chain like loose agglomerates compared with spheres using the Wen *et al.* (1984a, b) model. It delivers the number of primary particles per agglomerate. With the known primary particle size and the derived number of primary particles per agglomerate all the wanted geometric properties of the agglomerates (surface area, volume (mass)) can be determined. The measured number concentration corrected for multiple charge effects and the known geometric properties of the agglomerates then allow for the determination of the wanted distributions.

Needed Further Developments for Agglomerates/Aggregates

During sintering agglomerates transfer into aggregates and finally spheres. The techniques described thus far are not applicable to aggregates formed during sintering, which are measurement objects of interest in this paper. First the correction procedure for the measured number concentration as function of mobility diameter for aggregates will be discussed. For the transformation of the corrected number distribution as function of mobility diameter into number, surface area, volume (mass) concentration distributions as function of volume (mass) per aggregate, the volume (mass) per aggregate as function of mobility diameter is needed. This can be determined with a DMA and an APM in series. More possibilities will be discussed in the chapter on “Transformation of aggregate number - mobility size distribution into - volume- size distribution”. Eggersdorfer *et al.* (2012a, b) developed a sintering model, which describes

the structure with equivalent primary particle size and equivalent number of primary particles per aggregate and geometric parameter (surface area) changes during sintering as function of mobility diameter and the volume of the aggregate. We will demonstrate the use of this model to determine equivalent primary particle sizes and number of primary particles of aggregates, which then allow for the calculation of the surface area per aggregate. Finally the possibilities to replace the APM by an Electrical Sensor (ES), a much simpler, cheaper and smaller instrument will be discussed. During the course of the development of the different data evaluation procedures several assumptions will be made, because of lack of accurate models or missing model validations causing some uncertainties. Therefore in the end, we will put together the need for further developments improving the quality of the data evaluation procedures.

Determination of Number Concentration Distribution as Function of Electrical Mobility Diameter for Agglomerates/Aggregates

In the following we describe aggregates as loose agglomerates, but with equivalent primary particle size and number (Eggersdorfer *et al.*, 2012a, b). This includes loose agglomerates with their real primary particle size and number to begin with. The SMPS with CPC as detector delivers right away number concentration as function of mobility diameter biased by multiple charge effects. To perform the correction for agglomerates/aggregates similar to what is done with spherical particles one needs the bipolar charge distributions of agglomerates/aggregates as function of mobility diameter for any kind of structure. Unfortunately the information about these distributions in form of measurements and models is limited (Wen *et al.*, 1984a, b; Rogak and Flagan, 1992; Maricq, 2008; Xiao *et al.*, 2012)

To demonstrate the procedure and to discuss the importance of the correction we use the limited model for chain like agglomerates by Wen *et al.* (1984a, b). With the known charge distribution Eq. (3) the correction of the multiple charge effect can be performed the same way as for spheres. For correcting the change in charging probabilities, Eq. (5) with Eq. (3) and the bipolar charge distribution for spheres (Wiedensohler (1988) can be used, which then allows the calculation of the number concentration of the agglomerates.

$$n_{agg} = n_{sph} \frac{\eta_{sph}}{\eta_{agg}} \quad (5)$$

where n_{sph} and n_{agg} are the number distributions for spheres and agglomerates, respectively; η_{sph} and η_{agg} are the fractions of singly charged spheres and agglomerates, respectively. The ratio is plotted in Fig. 1, which is similar to Fig. 4 in Lall *et al.* (2006a, b).

The figure shows that the ratio to be used to calculate the total concentration in case of loose agglomerates deviates from the one for spheres the most (< 30%) for small and large agglomerates. It is also depending on primary particle size. If we describe aggregates as loose agglomerates with

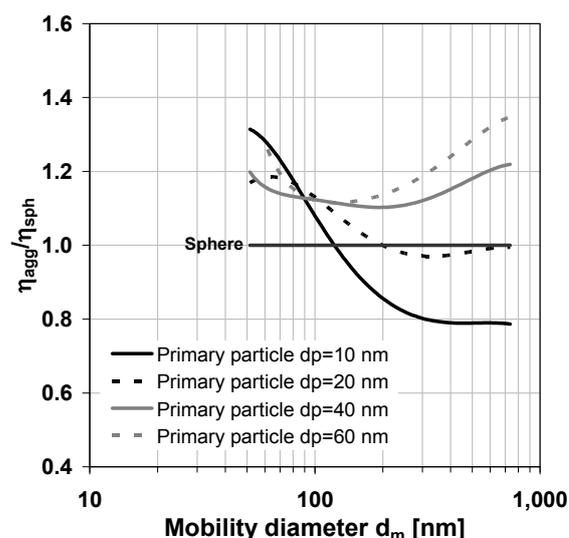


Fig. 1. Ratio of bipolar charging efficiencies for singly charged particles of loose agglomerates with different primary particle sizes and of spheres as function of mobility diameter (Wen *et al.*, 1984a, b; Lall *et al.*, 2006a, b).

increasing equivalent primary particle diameter and decreasing number of primary particles during sintering, as done in the sintering model (Eggersdorfer *et al.*, 2012a), which will be discussed later, we can expect that the charge correction becomes more and more similar to the known one of spheres.

If the bipolar charge distributions for loose agglomerates and aggregates are known from models or complete measurements, there is still the question, which charge distribution is relevant for the actually investigated aggregates, since their structure is not known yet. With the known charge distributions for different aggregates diagrams similar to Fig. 1 can be constructed. With the SMPS in combination with the ES the charge per aggregate of one polarity can be determined in a limited size range, which is not biased by multiple charge effects, if the unipolar charger in the ES is shut off. Only the electrometer is used. At the given mobility diameter with the known charging efficiency for a singly charged sphere the ratio of the charging efficiency for a singly charged aggregate and the sphere can be determined. This ratio introduced into a diagram similar to Fig. 1, but for different aggregates can be used to identify the corresponding charge ratio distribution and therefore the corresponding charge distribution of the investigated aggregate. The identified charge distribution can then be used in the same way as for spheres to eliminate the multiple charge effect and to calculate the total number concentration distribution.

Transformation of Number Concentration as Function of Mobility Diameter into a Distribution as Function of Volume or Mass per Aggregate

The discussed number concentration of aggregates as function of mobility diameter is of limited value, because the mobility diameter is only an equivalent diameter with relevance to particle processes in electric fields and also

diffusional processes. Also the number concentration may not be of interest as a measure. For other processes like transport or chemical reactions of agglomerates/aggregates the mass (volume) or the surface area per agglomerate/aggregate are more relevant. For very same reasons the mass (volume) and surface area concentrations as function of mass (volume) per agglomerate/aggregate are of interest. For determining the number concentration as well as the mass (volume) concentration as function of the mass (volume) of the agglomerate/aggregate the mass (volume) of the aggregate has to be known. This can only be done with an additional mass measurement. For the transformation of mass into volume or vice versa the material density of the aggregates has to be known. Liu *et al.* (2012) used the gravimetric method to measure the mass concentration of particles from a spark generator and to compare them with the total mass concentration derived from SMPS + ES-measurements determining the primary particle size and the number distribution of chain like loose agglomerates making use of the Lall *et al.* (2006a, b) model, which showed rather good agreement. Sampling of the fractionated aggregates on a filter and counting and weighing them is however very time-consuming and laborious, because of the lack of suitable online measurement techniques.

Practically the same, but more sensitive approach would be the determination of the amount of a chemical entity with known mass ratio in the agglomerate/aggregate by counting the fractionated particles on the filter and performing chemical analysis. The sensitivity depends on the chemical analysis technique used. Another way would be to sinter the aggregates until they become spheres. With the assumption that the aggregates do not lose mass during sintering, the measured particle diameter of the sintered agglomerate/aggregate allows the calculation of the volume (mass). But not all types of agglomerates can practically be turned into spheres and it is again an offline technique. The APM mounted behind a bipolar charger and a DMA, to fractionate the particles according to their mobility in a SMPS, allows a measurement of the mass (volume) of aggregates as function of mobility diameter additionally to the number distribution measurement. For a given mobility (DMA setting) the CPC

behind the APM gives the number concentration as function of particle mass. The mass distribution shows a distinct peak for singly charged particles. The corresponding mass at maximum is the representative mass for the agglomerates with the given mobility.

Once the mass or volume of the aggregate as function of mobility diameter is known, starting with the measured number concentrations as function of mobility diameter, the number concentration as function of volume per aggregate and the volume concentration as function of mobility diameter and volume per aggregate can easily be calculated.

Determination of Other Structural Parameters of Aggregates

The discussed number and volume distributions do not provide any information about the structure of the aggregates, which is described for loose agglomerates by their primary particle size and the number of primary particles per agglomerate and the resulting surface area. The Lall *et al.* (2006a, b) model describes the relationship between the measured parameters mobility diameter and primary particle size (by offline TEM-measurement or ES-measurement) and the derived number of primary particles per agglomerate. It is limited to ideal loose agglomerates with low fractal dimensions and equal primary particle size. During sintering aggregates are formed with necks until eventually the aggregate turns into a sphere. Assuming that no particle material evaporates, the volume of the aggregate remains constant during sintering (see Fig. 2).

The change in the structure from loose agglomerate to sphere causes a decrease of the mobility diameter. Recently Eggersdorfer *et al.* (2012a, b) developed a model describing the agglomerate and following aggregate changes in a sintering process. Aggregate sintering by viscous flow of amorphous materials (silica, polymers) and grain boundary diffusion of crystalline ceramics (titanium, alumina) or metals (Ni, Fe, Ag, etc.) was investigated. A scaling law was found between average aggregate projected area and equivalent number of constituent primary particles during sintering: from fractal-like agglomerates to aggregates and eventually compact particles (e.g., spheres). They defined

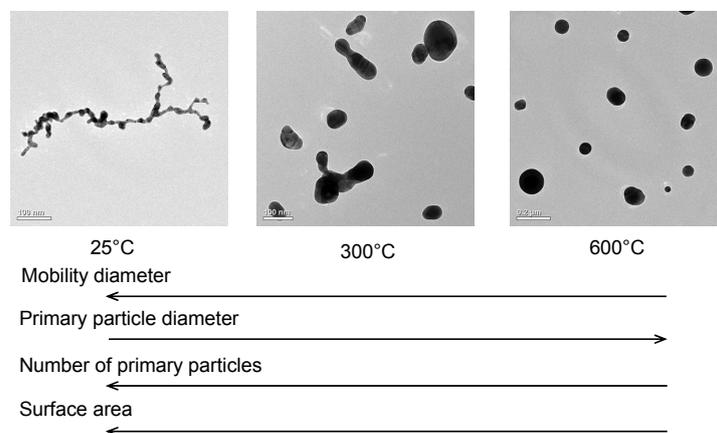


Fig. 2. Structure changes during sintering, volume per particle stays constant. The given parameters increase in the direction of the arrows.

equivalent primary particles for the description of (partly) sintered aggregates such that the sum of surface areas of the equivalent primary particles equals the aggregate surface area. They further derived a relationship between the size and number of equivalent primary particles per agglomerate/aggregate and the measured quantities mobility diameter and volume (mass) per agglomerate/aggregate. This is essentially a relation independent of time, material properties and sintering mechanisms.

The starting equation is the definition of the diameter d_{va} as ratio of volume to surface area

$$d_{va} = \frac{6v}{a} \quad (6)$$

with d_{va} as the equivalent primary particle diameter and v and a as volume and surface area of the agglomerate/aggregate. The equivalent primary particle number n_{va} of an agglomerate is

$$n_{va} = \frac{v}{\pi d_{va}^3 / 6} \quad (7)$$

The average projected area a_a of fractal-like agglomerates of monodisperse primary particles can be related to the real primary particle number n_p by a power law:

$$n_p = k_a \left(\frac{a_a}{a_p} \right)^{D_a} \quad (8)$$

where a_p is the projected area of a primary particle and k_a and D_a are parameters describing agglomerate structure that are extracted from experimental or numerical studies. k_a and D_a in this study are taken from Eggersdorfer *et al.* (2012a).

With the mobility equivalent diameter d_m of an agglomerate in the free molecular (Meakin (1988)) and transition regime (Rogak *et al.*, 1993)

$$d_m = \sqrt{\frac{4a_a}{\pi}} \quad (9)$$

d_{va} can be described as function of mobility diameter d_m and volume v (mass) per agglomerate or aggregate (Eggersdorfer *et al.*, 2012a, Eq. (8))

$$d_{va} = \frac{6v}{a} = \left(\frac{\pi k_a}{6v} (d_m)^{2D_a} \right)^{1/(2D_a-3)} \quad (10)$$

The equivalent primary particle diameter d_{va} as function of mobility diameter is plotted in Fig. 3 for different volumes v per aggregate. The curves describe the increase in equivalent primary particle size for constant volume aggregates during sintering from loose agglomerates to spheres. It allows the determination of the equivalent

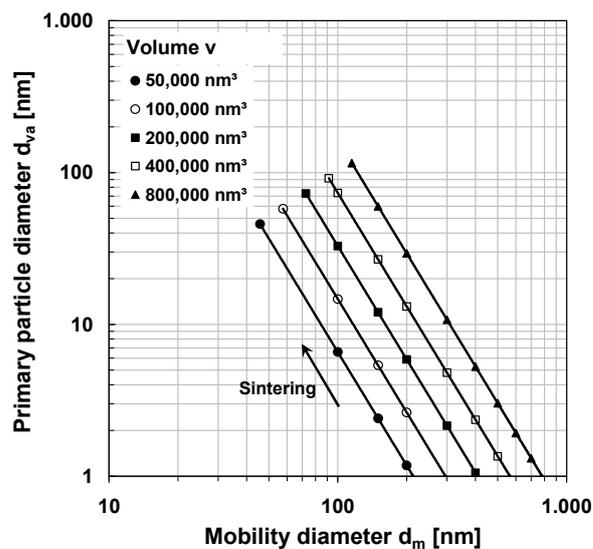


Fig. 3. Equivalent primary particle diameter as function of the mobility diameter for different volumes.

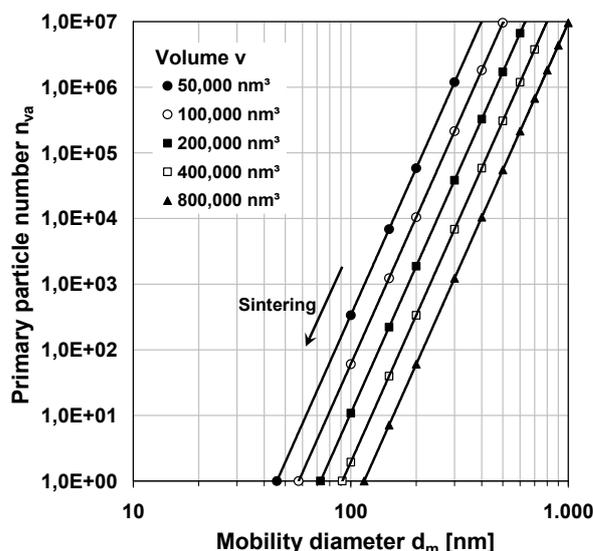


Fig. 4. Equivalent primary particle number as function of the mobility diameter for different volumes.

primary particle size from measured mobility diameter and volume (mass) of aggregate.

With Eq. (7) the equivalent number n_{va} of primary particles per aggregate can be calculated (Fig. 4). With known mobility diameter and equivalent primary particle size, the surface area of the aggregate can also be derived from Eq. (10):

$$a = \left(\frac{\pi k_a}{d_{va}^{(2D_a-2)}} \right) (d_m)^{2D_a} \quad (11)$$

Eggersdorfer *et al.* (2012a) argue that this surface area (see Fig. 5) is equal to the surface area measured with BET.

Eq. (12) allows the determination of the volume (mass) of aggregates (see Fig. 6):

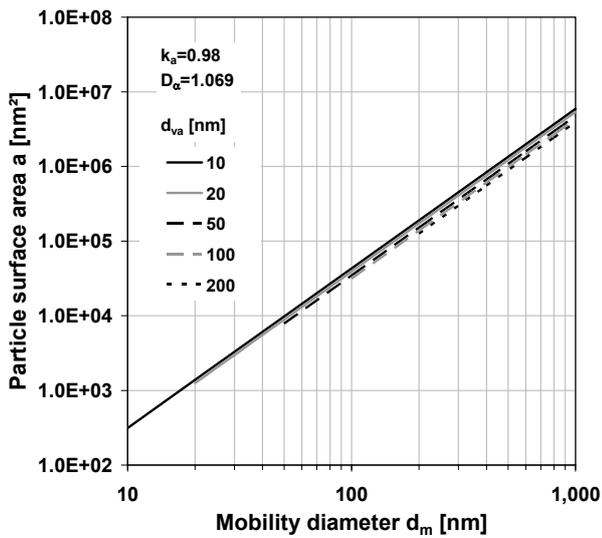


Fig. 5. Aggregate surface area as function of mobility diameter for different primary particle sizes (Eggersdorfer *et al.* (2012a) model).

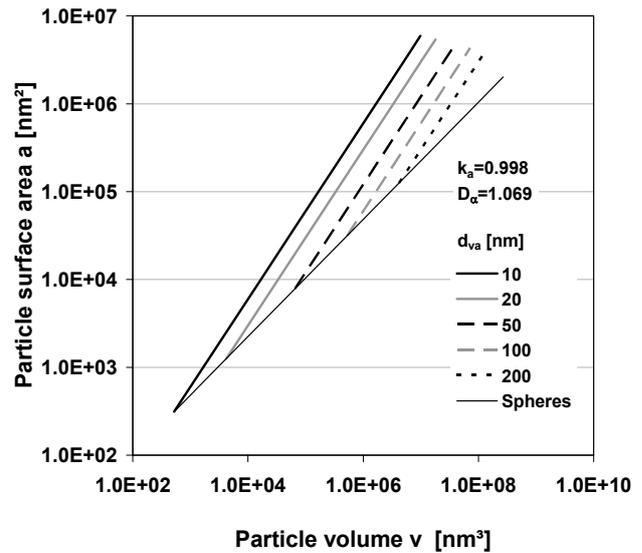


Fig. 7. Aggregate surface area as function of particle volume of aggregate (Eggersdorfer *et al.* (2012a) model).

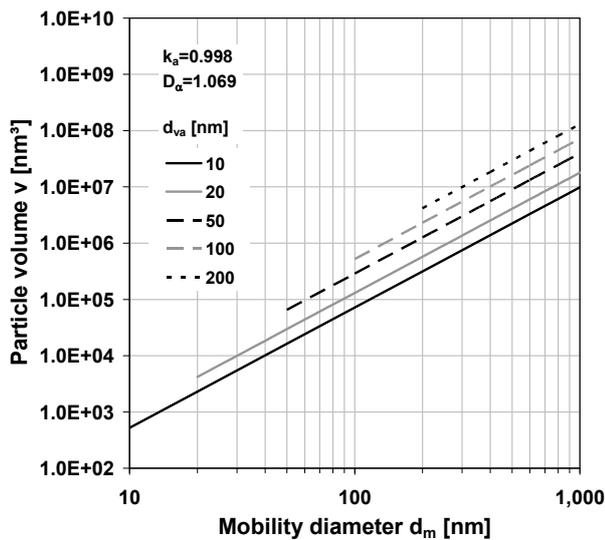


Fig. 6. Volume per aggregate as function of mobility diameter for different equivalent primary particle sizes (Eggersdorfer *et al.* (2012a) model).

$$v = d_{va} a/6 \quad m = \frac{d_{va} a \rho}{6} \quad (12)$$

It is interesting to note that the surface area per aggregate as function of mobility diameter (Fig. 5) shows only a weak dependency on the equivalent primary particle size. This becomes more dominant, if we look at the surface area per aggregate as a function of volume (mass) per aggregate (see Fig. 7).

Possibilities for Replacing APM by ES

The APM introduced into a SMPS allows the measurement of the mass of an agglomerate/aggregate as function of mobility diameter. With the determined mobility diameter

and the mass of an corresponding agglomerate/aggregate introduced into the sintering model for agglomerates/aggregates (Eggersdorfer *et al.*, 2012a) one can determine structural parameters, i.e., equivalent primary particle size and number of primary particles as well as the surface area per agglomerate/aggregate. The slope of mass (volume) per agglomerate/aggregate as function of mobility diameter delivers also information about the fractal dimension of the investigated agglomerates/aggregates (Eggersdorfer *et al.*, 2012c). For mass determination using an APM within a SMPS behind the DMA the operational parameters of the APM have to be adjusted to yield the maximal signal at each mobility diameter. This is a slow process and does therefore not allow online measurements. The APM is big, difficult to handle and expensive. On the other hand the cheap and simple ES delivers online a current and with the number concentration the sensitivity. For the replacement of the APM we need the relationship between the sensitivity and the mass per aggregate or the equivalent primary particle size. For SMPS + ES we developed a model (Wang *et al.*, 2010) to relate the charge per agglomerate to the primary particle size with several limitations described already in the introduction. It is also possible to base the data evaluation procedure for ES on the relationship between sensitivity and mass per aggregate, determined via calibrations performing parallel measurements of number concentration (SMPS), mass per aggregate (APM) and current (ES) of monodisperse aggregates.

We propose to perform sintering experiments. Loose agglomerates of metals, metal oxides or other kinds of particle material are produced in a furnace, a flame reactor or by an electric arc (Shin *et al.*, 2010; Liu *et al.*, 2012), and go through a coagulation chamber. The agglomerates/aggregates are fractionated with respect to electrical mobility with a DMA. The exiting agglomerates are led through another furnace and heated up. They sinter to form aggregates and finally spheres (see Fig. 2). During the sintering process

the temperature of the agglomerates/aggregates, their sensitivity and mobility diameter as well as their mass (volume) are measured. A complete set of these kinds of measurements is not available yet.

To evaluate feasibility of calibration and applicability of the calibration results we use available data resulting from separate measurements of sensitivity and mass per aggregate. This is causing some risk because of possible different experimental conditions. Using a similar set up as in Kim *et al.* (2007) for silver agglomerate synthesis and sintering, we performed measurements of the sensitivities using an SMPS with CPC and ES in parallel as detectors. In Fig. 8 the measured sensitivities for silver aggregates (loose agglomerates (room temperature), aggregates (200°C), spheres (600°C) are plotted as function of mobility diameter. The sensitivity increases with the mobility diameter and decreases when the particles are more compact. We observed that the sensitivities of partly sintered aggregates (exemplarily shown for a sintering temperature of 200°C) will be between the two limiting curves for loose agglomerates and spheres.

Unfortunately this result is limited to aggregates which do have the same changing fractal dimension during sintering as the ones used in the calibration procedure, because the sensitivity (charge per aggregate) is depending on the fractal dimension. Fortunately very often product agglomerates and aggregates even from different synthesis processes and from different materials do have similar fractal dimensions. For example, agglomerates formed by random Brownian motion, often referred to as Diffusion Limited Cluster Aggregation, were found to possess fractal dimensions around 1.8 in multiple studies (Meakin 1988; Cai *et al.*, 1995; Lattuada *et al.*, 2003; Sorensen, 2011). Also during sintering there fractal dimension compare very well independent of their original fractal dimension as agglomerate (Eggersdorfer *et al.*, 2012a).

Kim *et al.* (2009) performed APM-measurements of silver agglomerates and aggregates with a similar synthesis set up and determined the mass per aggregate as a function of mobility diameter at different sintering temperatures for silver aggregates (see Fig. 9). The mass increases with increasing mobility diameter. The slope describes the fractal dimension. It increases with increasing temperature. The mass per aggregate together with the corresponding mobility diameter allow the calculation of the equivalent primary particle diameter using the Eggersdorfer *et al.* (2012a) model. In the calibration experiment the mass per aggregate is related to the sensitivity. Using the APM-data from Kim *et al.* (2009) study and the measured sensitivity values for loose agglomerates, aggregates and spheres we constructed the corresponding calibration curves, sensitivity as function of particle mass per aggregate for different mobility diameters, shown in Fig. 10. The calibration curves for aggregates will be between the two curves (broken lines). One drawback can be seen. The factor of the change in mass of loose agglomerates shown is about 30, whereas for sensitivity the factor is about 7.5. The resolution for detecting mass changes is reduced for ES measurements. With ES we lose accuracy, but ES is easier to handle.

With the measured sensitivity at the known mobility

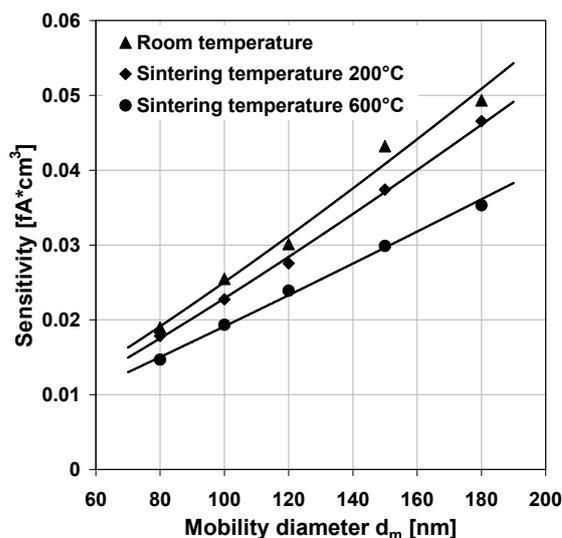


Fig. 8. Measured sensitivities for silver loose agglomerates (room temperature), aggregates (200°C) and spheres (600°C) as function of mobility diameter (Wang *et al.*, 2010).

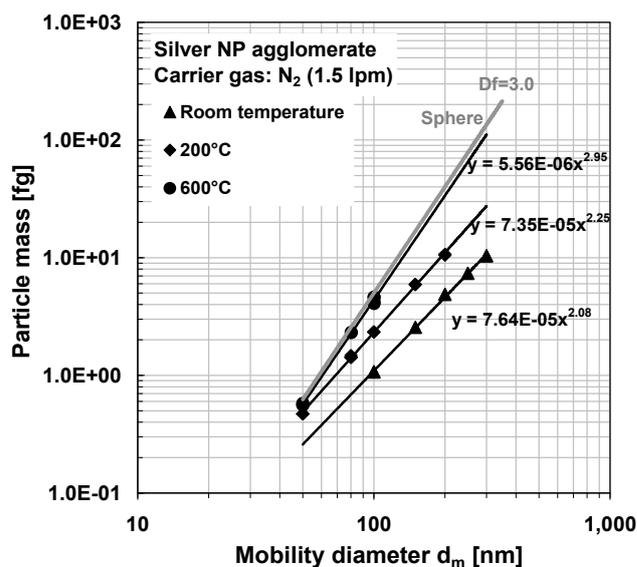


Fig. 9. Silver aggregate mass as function of mobility diameter for different sintering temperatures (from Kim *et al.* (2009)).

diameter and the relevant calibration curve the mass of the aggregate can be determined. With the derived mass per aggregate and using the Eggersdorfer *et al.* (2012a) model the structural parameters, equivalent primary particle size and number of primary particles as well as the surface area per aggregate can be determined.

The model can also be included in the calibration diagram. One can plot the sensitivity as function of the equivalent primary particle size for constant mobility diameter (see Fig. 11). The change of sensitivity of the ES-measurement with primary particle size is rather small (dotted lines). This is even less sensitive than the mass per aggregate determination.

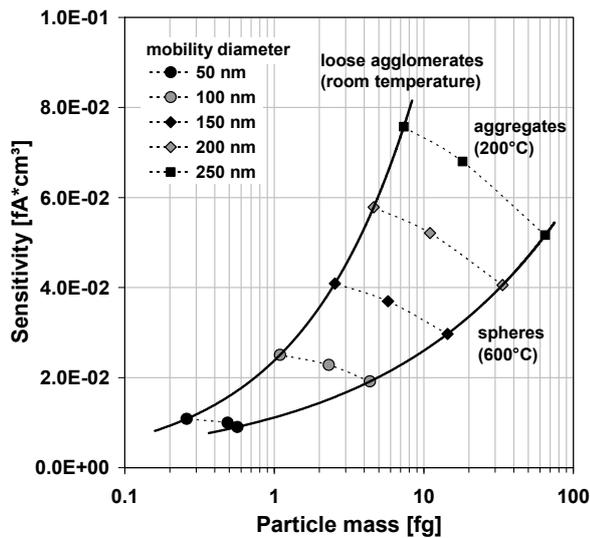


Fig. 10. Sensitivity as function of mass per particle for loose agglomerates and spheres. The calibration curves for aggregates will be between the two curves.

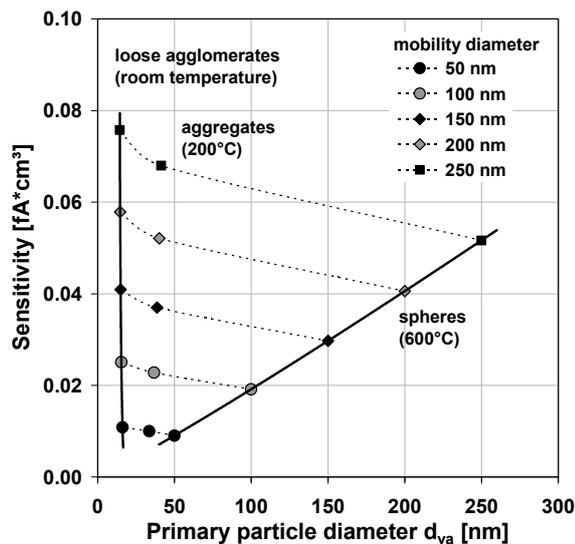


Fig. 11. Sensitivity as function of the primary particle diameter d_{va} for different mobility diameters.

Inserting the mass per aggregate (primary particle size) and the mobility diameter into the Eggersdorfer *et al.* (2012a) model yield the equivalent number and size of primary particles. These allow the calculation of all the other needed aggregate properties and the aerosol size distributions.

FURTHER RESEARCH NEEDS

For the correction of the measured number distributions for multiple charge effects with the different charge distributions of agglomerates and aggregates compared to spheres the bipolar charge distributions have to be known. If we want to correct the measured current (ES) we also need the unipolar charge distributions. Up to now the available information is limited, although several research

groups are working in this direction.

Software procedures have to be developed along the ones used for spheres, which take into account the changing bipolar and unipolar charge distributions for agglomerates and aggregates.

A key tool for the data evaluation of size distribution measurements of aggregates is the sintering model by Eggersdorfer *et al.* (2012a). This model has to be experimentally evaluated by performing sintering experiments of monodisperse loose agglomerates with different sizes with parallel measurements of mobility diameter and the volume per aggregate. The derived properties equivalent primary particle size, number of primary particles (TEM) and surface area (BET) at least for loose agglomerates has to be checked with independent methods. If possible, conclusions from the model calculations like independency of polydispersity of primary particle and fractal dimensions of starting agglomerates should be checked.

The use of the Electrical Sensor instead of APM for aggregate mass (or primary particle size) determination based on calibration is limited. The ratio "Sensitivity" derived from the ES and CPC signals is less sensitive and depending on the fractal dimensions, which can be different for loose agglomerates with same number of primary particles and primary particle size and therefore same volume and surface area (Eggersdorfer *et al.*, 2012b). The development of a unipolar charging model for aggregates would help to extend the application of this simple ES-measurement technique with respect to hardware, usage and data handling and interpretation to different fractal structures. This may include the need for an additional sensor, which indicates the fractal dimensions of the aggregate.

During the development of data evaluation procedures assumptions are made, which may cause errors. Checking and if necessary reducing assumptions improves the accuracy of the data evaluation procedures.

It should be noted that for accurate measurement, instruments should be applied to samples for which the underlying assumptions are valid. SMPS and the possible extensions described here are only valid for samples they are intended for. In industrial processes, particles are produced under controlled conditions and their structures are expected to be within a certain variety range. Calibration for such limited structure variations is possible, thus we suggest SMPS and its extension can be used for measurement and monitoring of industrial processes.

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