Detecting the Mass of Pigment Particles - Towards a Universal Size Standard

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Introduction

We present a novel approach that introduces mass as a fundamental metric for characterizing the size and structure of pigments and nanoparticles, offering the potential to establish a new standard for particle size determination. Leveraging measurement techniques developed in aerosol sciences, we apply them to uniquely analyze pigment particles in an application-oriented manner.
ENMs are produced at a massive scale, ranging from 10^3 to 10^7 tons per year. The physical properties of individual particles, aggregates, fibers, etc., profoundly influence the application performance of these materials. Traditional methods for characterizing physical dimensions are either expensive and time-consuming (e.g., TEM imaging) or limited to equivalent diameters. For instance, laser diffraction size analysis requires the refractive indices for a wide range of color pigments and struggles to accurately measure non-spherical or aggregated particles.
Moreover, various material properties are mass-based metrics, facilitating the calculation of other essential values. For instance, using skeletal density (g/cm^3) or specific surface area (m^2/g), one can derive absolute particle volume or surface area and key performance indicators like the number of particles per gram or particles per dollar. Additionally, we measure the mobility diameter, enabling the calculation of particle bulk densities, fractality, porosities, and more.
To introduce this potential of this measurement concept we present results of three commercially available iron red pigments, three Carbon Blacks, and a coated iron yellow pigment. First, we give some background information on the relation between particle mass and diameter, collectively defining the particle structure, and briefly discuss the experimental setup.

Background: Mass plus diameter equals structure

The structure of a particle population is encoded in the relation between mass and diameter of the individual particles. The scaling relation between particle mass (m) and the particle diameter (d) can be expressed by

$$\boldsymbol{m} = k \cdot \boldsymbol{d}^{\mathrm{fi}} \quad (1)$$

with a constant (k) and the fractal index (fi). While a fractal index of three indicates scaling of a solid object, a fractal index below three (and above two, which would indicate plate-like scaling) signifies the scaling of an increasingly more porous material (see Figure A1). In the context of color pigments, the fractal index describes the branching of the aggregates itself and varies for every material. To visualize that, let's have a look at the effective density, i.e. the density of a particle with mass m and diameter d assuming sphericity. Inserting Equation 1 for the diameter gives

$$\boldsymbol{\rho_{eff}} = \frac{6}{\pi} \cdot \frac{\boldsymbol{m}}{\boldsymbol{d^3}} = \frac{6k^{-3/\mathrm{fi}}}{\pi} \cdot \boldsymbol{m}^{1-\frac{3}{\mathrm{fi}}} \quad (2)$$

The scaling for three structurally different particle types is illustrated in Figure 1. Solid particles with a fractal index of three exhibit a constant effective density (in this special case equal to the skeletal density). The effective densities of aggregated particles, here exemplary for columns and spheres (Figure 1), decreases with increasing mass, indicating a fractal index below three. The stronger the decrease, the lower the fractal index and the higher the aggregation level of the particles.
femtoG uses the electrical mobility analysis to measure the geometric dimensions of a particle. Unlike other diameter estimates the mobility diameter it is not affect by the material density and refractive index. The mass is an intrinsic property of a particle, unlike any equivalent diameter it does not require any prior assumption and is independent of the measurement method. Therefore, the particle mass is well-suited to serve as a standard for the particle size.

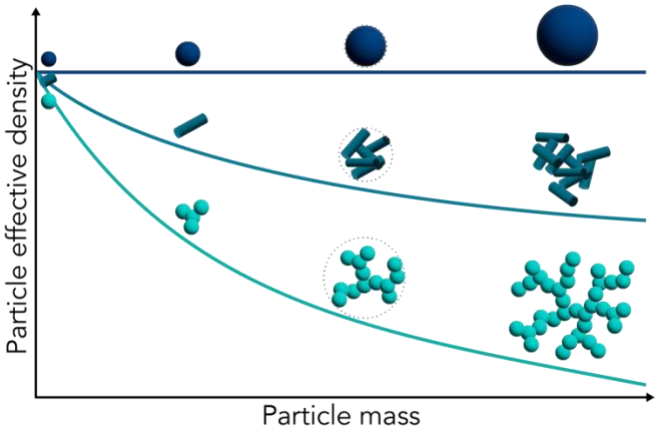

Figure 1: Particle effective density as a function of particle mass for three structurally different particle types: Solid spheres (top), aggregated columns (middle), and aggregated spheres (bottom). Gray circles indicate a diameter estimate for visual guidance. *Note: Same skeletal density assumed. Particle mass axis is logarithmic.*

Methods

Our approach employs the newly developed Mass & Mobility Aerosol Spectrometer[1] (M2AS, Cambustion Ltd., UK) in combination with particle dispersion systems, enabling the rapid measurement of size distributions for both absolute particle mass and a diameter (electrical mobility) within five to 15 minutes.

Powder analysis is initiated by an aerosolization of the powder material. Here we suspended 0.2 g of a pigment in 100 ml ultrapure water. The particles were deagglomerated by a finger-type ultrasound probe until an energy input 100 J/ml was reached. Subsequently, the suspension was nebulized and the droplets were dried to retrieve the initial pigment particles. By producing small droplet and working with dilute suspensions re-agglomeration during the drying process can be prevented.

The aerosol particles produced this way are guided into the M2AS. In this instrument, first particles are electrically charged before, secondly, being exposed to a combination of centrifugal and electrostatic forces allowing the separation of particles by their mass to charge ration. In a third step the particle electrical mobility ("*diffusivity*") in air is determine by combining electrostatic and drag force. In the fourth and last step, the particles are counted, and the electric current is recorded. By scanning through the entire population, the (number-weighted) distribution of absolute particle mass and mobility diameter is obtained.

Base data and the femtoG fingerprint

Figure 2 shows an exemplary data set for an iron(III) oxide. The measured particle concentration (black diamonds, left axis) in air is plotted as function of the absolute particle mass (bottom axis) and the

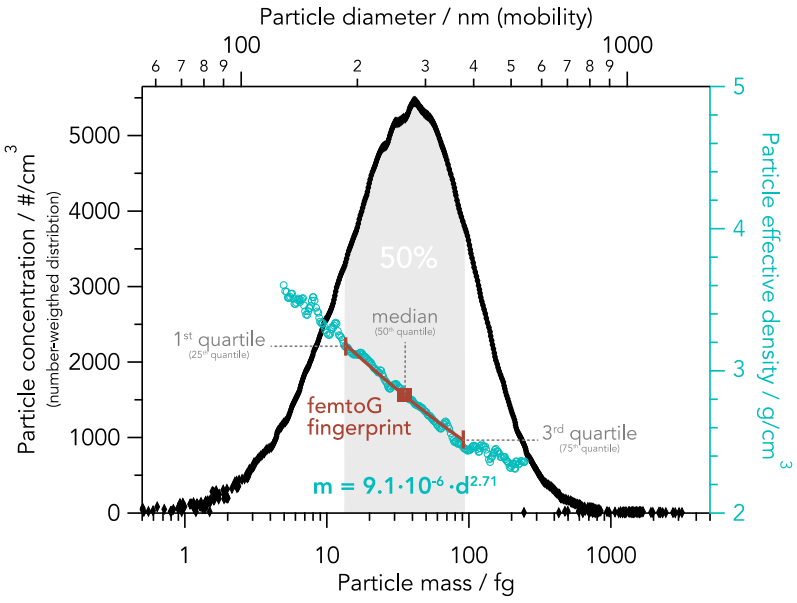

Figure 2: Data overview and femtoG fingerprint of an iron(III) oxide: Number-weighted particle concentration (black, left axis) and particle effective density (turquoise, right axis) against particle mass (lower axis) and particle diameter (upper axis). The relation between mass and diameter (eq. 1) is given in the lower center. The inner 50% of the particle distribution (particles falling into the interquartile range) is highlighted in gray. The femtoG fingerprint is indicated in red.

[1] Manufacturer's website: The Mass & Mobility Aerosol Spectrometer

particle diameter (upper axis), which were measured simultaneously. The link between particle mass and diameter is given by the equation on the lower center (turquoise, cf. Equation 1) and allows for the calculation of the effective density (turquoise open symbols, right axis). Various insights are hidden in such a multiparameter data set.

First the median value of the mass distribution (m_{50}) and diameter distribution (d_{50}), respectively, can be obtained. The m_{50} is 31 fg (femtogram, 10^{-15} g) and the d_{50} is 274 nm. This leads to a median effective density (ρ_{50}) of 2.9 g/cm^3. This density is below the true material density of iron(III) oxide of 5.1 g/cm^3, since the particles are not spherical, but structured particles. The effective density (turquoise, right axis) declines exponentially with increasing particle mass and diameter. This behavior is characteristic for aggregated particles. With increasing aggregation level and size more void volume is incorporated in the particle structure and therefore effective particle density declines. The correlation between mass and diameter (Figure 2 lower center) implies the particle mass is proportional to the diameter to the power of 2.71. As a reminder, for a solid sphere this fractal index is three (Figure 1) and for plates it would be two. The fractal index gives insights into the fractality (~dimensionality) of the aggregate structure.

Based on this data set, different data products can be derived. For example, by integrating the number-weighted distribution the total number of particles in one gram of powder can obtained. The here analyzed product contains 1.8 ·10^{13} particles per gram. Which allows to answer the question: What is the particle concentration in a powder? Other paint and coating related parameters like the area of a mono-particle layer per gram or porosity are also easily retrieved.

To quickly compare different particle types (powders) in size and structure, we retrieve a representative interval of the density curve – the femtoG fingerprint. It is defined as the particle effective density curve against particle mass between the first and third quartile of the number-weighted particle distribution (red in Figure 2). The bars indicate the quartiles spanning the interquartile range of the particle mass and diameter distribution, while the square indicates the median. Therefore, it represents the inner 50% of particles (particles falling into the interquartile range) and their associated structure in the form of the density decay. In the following section we apply the femtoG fingerprint to distinguish the aggregation level of similar pigments.

Case study: Investigating the aggregation level of color pigments

Our approach links the scaling of the mass and the size allowing for the determination of particle structure. In this case study we investigated three iron red pigments and three furnace blacks with different particle structures. In the center of Figure 3 we present the fingerprints of the investigated

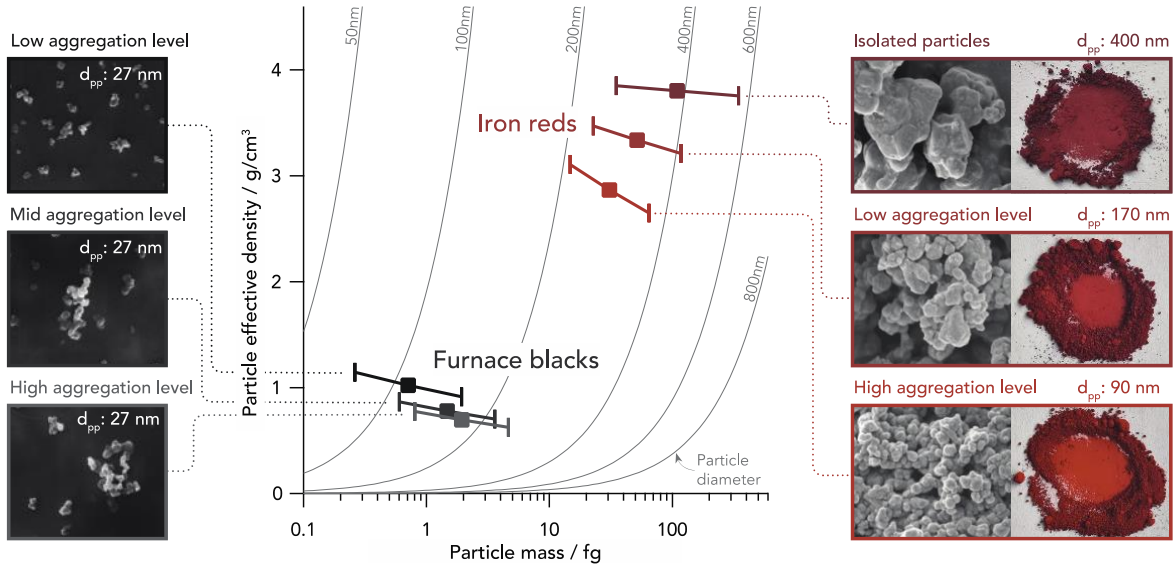

Figure 3: femtoG fingerprints of three iron red pigments (iron(III) oxide) and three color furnace blacks (center). Gray lines indicate constant (electric mobility) diameters. The three color furnace blacks with same primary particle size (d_{pp}, 27nm, determined by electron microscopy) but varying aggregation level are accompanied by transmission electron microscopy images (left). The three iron red pigments of varying primary particle size (top to bottom: 400nm, 170nm, and 90nm, determined by electron microscopy) and varying aggregation level are accompanied by scanning electron microscopy images and pictures of the product (right). *Note: The equivalent particle diameter refers to information given in product data sheet published by the manufacturer.*

samples. The iron red pigments (iron(III) oxide) show median masses between 110 fg and 31 fg and densities between 3.7 g/cm^3 and 2.9 g/cm^3, respectively. This decreasing trend towards lower effective density coinciding with the trend towards lighter particles suggests a trend of increasing aggregation level. This suggestion is confirmed by the decreasing fractal index, i.e. the increased slope of the density decay. These observations could be validated with electron microscopy presented on the right. Using the primary particle size provided in the product specifications, and knowing the material density, one can calculate the mass of a primary particle (m_{pp}). By comparing the theoretical m_{pp} with the measured m_{50}, the median number of primary particles in an aggregate can be estimated. With a decrease in primary particle diameter from 400 to 90nm the number of constituent particles increase from one and 16 particles for the investigated iron red pigments (Table 1). In the end, these structural differences contribute to the change in color of the products (Figure 3 right).

Table 1: Summary of key performance indicator for the analyzed color pigments: Median mass (m_{50}), median (electric mobility) diameter (d_{50}), median effective density (ρ_{50}), fractal index (fi), number of aggregates per gram (N_{agg}), area of a particle monolayer per gram (A_{mono}), and median number of particles per aggregate[1] (N_{pa}).

Sample	Structure	m_{50} / fg	d_{50} / nm	ρ_{50} / g/cm^3	fi	N_{agg} / 10^{13}/g	A_{mono} / m^2/g	N_{pa} / #
Iron red 1	Isolated particles	110	380	3.7	2.97	2.2	1.2	1
Iron red 2	Low aggregation	49	320	3.3	2.85	1.9	0.91	3
Iron red 3	High aggregation	31	270	2.9	2.71	1.8	1.7	16
Furnace black 1	Low aggregation	0.71	110	1.0	2.69	46	11	37
Furnace black 2	Mid aggregation	1.5	150	0.78	2.69	28	9.7	79
Furnace black 3	High aggregation	1.9	170	0.65	2.67	22	9.1	100

For the furnace blacks also an increasing aggregation level was observed associated with a decrease in effective density (cf. electron microscopy images on Figure 3 left). Yet, the aggregation trend in the furnace black pigment series coincides with an increasing median particle mass. This different behavior in contrast to the iron red pigments is owed to the fact, that the primary particle size of the furnace blacks is the same. Therefore, a higher aggregation level coincides with on average higher partilce masses In the case of the furnace blacks.
Concluding, the presented method can detect changes in aggregation level. In addition, in the case of the same particle material, the trends between effective density and particle mass allow for the qualitative description of a primary particle influence. More key performance indicators of the individual samples are listed in Table 1. Ultimately, changes in the fingerprint allow for resolving the impact of a particular process on the particle structure and the effect thereof on the key performance indicators.

Case study: Differentiating two particle populations

A particular analytical challenge are pigment systems that contain more than one component. For example, an iron yellow pigment with improved thermal stability. This product consists of rod-like iron(III) oxide-hydroxide (Fe(III)OOH) particles that have been coated with aluminum-phosphate ($AlPO_4$). Both components have different refractive indices and different material densities. Without known optical properties any laser particle sizing method will give wrong results. The undefined particle densities affect the validity of sedimentation sizing methods. Further, the particles are rod-shape according to manufacturer imposing an additional challenge for the diameter determination. The here presented analysis based on the particle mass is not affected by these points.
Figure 4 shows the measured particle concentration (black diamonds, left axis) and particle effective density (turquoise open symbols, right axis) as a function of the particle mass. The (number) distribution shows two distinct modes. The heavier particles with the mode around 115 fg, respectively 516 nm (axis not shown), are the iron(III) oxide-hydroxide particles. Similar to the discussed iron(III) oxide red pigment, the effective density declines with increasing particle mass and diameter indicating that the rod-like particles are aggregated. The lighter particles with a mode mass of 3.8 fg, respectively 185nm (axis not shown), are isolated aluminum-phosphate particles that are not coating the iron(III) oxide-hydroxide core. The constant effective density indicate that the particles are not aggregated.

[1] Using the primary particle size (d_{pp}) provided by the manufacturer based on electron microscopy (Figure 3) and using the skeletal material density.

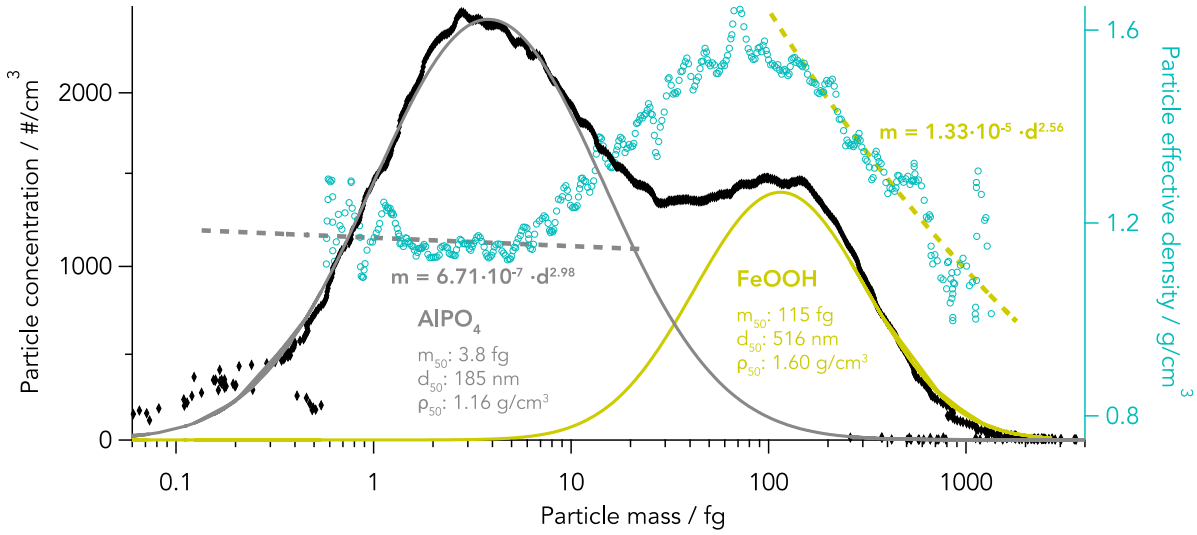

Figure 4: Analysis of a aluminum-phosphate coated Fe(III)OOH yellow pigment. Particle concentration (black diamonds, left axis) and particle effective density (turquoise open symbols, right axis) against particle mass. The two particle modes were each fitted with a lognormal distribution. The particle effective density was fitted by two exponentials in each range where one of the distributions dominates and associated to the corresponding particle population. In addition, median values (mass, diameter, effective density) and the mass-diameter relation (Equation 1) is given for each effective density fit per population.

The total particle number and mass of both particle population can be determined by a bimodal lognormal fit followed by integration per mode. In total, one gram of powder material contains $1.5 \cdot 10^{13}$ particles. Thereof 70% (in number) are isolated aluminum-phosphate particles. Since they are light, they only contribute to 10% of the total mass. This is a subset of the total aluminum-phosphate content of 26% (in mass) which was added by the producer. This implies that 40% of the coating material does not adhere to the iron(III) oxide-hydroxide core.

Conclusion: Potential of the new method

The parallel and rapid analysis of the particle mass and a particle diameter provides a new and intrinsically precise approach to characterize color pigments. This aerosol-based analysis method is independent from the optical properties of the pigment particles. Complex particle structure also does not affect the particle mass and is even resolved in the analysis by the diameter analysis and resulting effective density. With this, laser and sedimentation sizing method can be complemented. As our approach relies on a constant aerosol flow, it is also ideally suited to be used for monitoring at e.g. a production facility.

A whole new concept is the particle number per gram, which can simpler be described as “particle concentration in a powder”. This quantity is helpful for health and safety assessment, and particularly useful to quantify unwanted material, such as non-attached coating material. This could even be extended for a deeper investigation, when applying a varying dispersion intensity to assess the strength of coatings or the adherence of powders in general.

Lastly, the particle mass is a fundamental particle property that is independent of the measurement and therefore well-suited to become a new reference for the particle size.

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Auxiliary figures

Figure A1 illustrates the relationship between particle mass and diameter given in Equation 1. A fractal index of three represents the scaling behavior of a solid object (left in Figure A1). A fractal index below three indicates an increasing amount of void volume enclosed by a particle with increasing size. The larger the proportion of void volume gain the lower the fractal index. On logarithmic axes, as in Figure A1, the fractal index from Equation 1 is pictured by the slope of the mass to diameter relation.

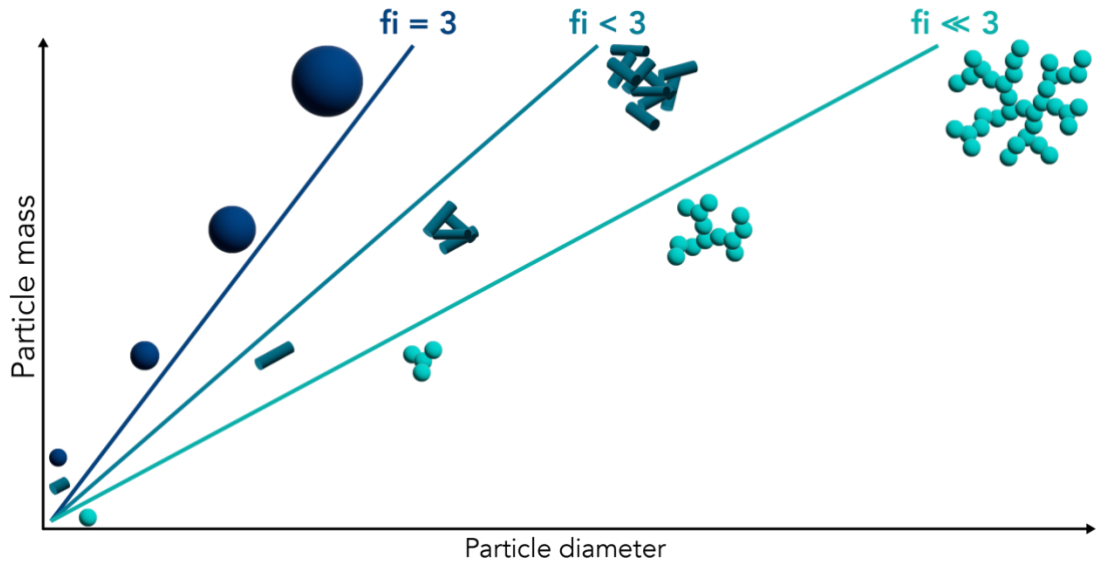

Figure A1: Particle mass as a function of particle diameter for three structurally different particle types: Solid spheres (top), aggregated columns (middle), and aggregated spheres (bottom). The fractal index fi, representing the slope of line in this presentation, is given above each line. *Note: Same skeleton density assumed. Axes are logarithmic.*