femtoG
Unveiling structure

APPLICATION NOTE

Detecting the size and structure of iron oxide and furnace black pigments

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What is the size of an iron red pigment particle?

Iron(III)-oxide is a red pigment, but particle size affects its final appearance. Larger primary particles result in a more bluish color, and with decreasing particle size, the color shifts to a more yellowish red. The pictures show three Fe_2O_3 pigments with the same chemical composition but differ in color due to different particle sizes.

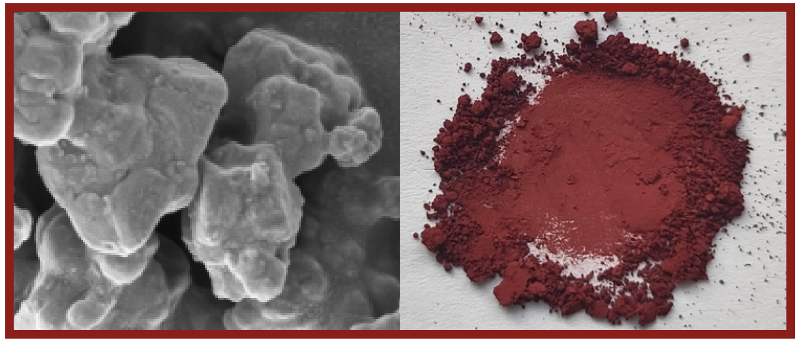
According to the producer, the average diameter of the primary particles (d_{PP}) is 400, 170 and 90 nm. Like all equivalent diameters, these numbers refer to spherical particles, but the SEM images clearly show that this is a simplified approach. Further, the pigments show different levels of aggregation, making the size analysis more challenging.

Existing sizing methods have their individual limitations. Laser diffraction, dynamic light scattering, etc. can only give accurate data on the particle size, if the optical properties are known. If the refractive index changes with size, no accurate particle diameter can be determined. Sedimentation analysis or analytical ultracentrifugation does not provide a solution to this problem either. These methods can only accurately determine the sinking velocity of a particle and calculate the stokes-diameter (stokes) from it. This requires knowledge of the effective particle density. This number is rarely known. Usually, the true material density (here, 5.0 g/cm^3) is used instead, which results in a constant underestimation of the particle size.

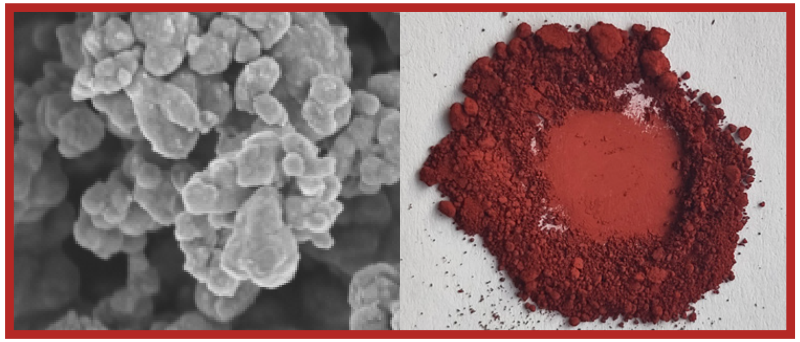
Further, it must be considered that no single diameter can accurately describe the size of irregular-shaped particles.

→ The mass of a particle is independent of such limitations.

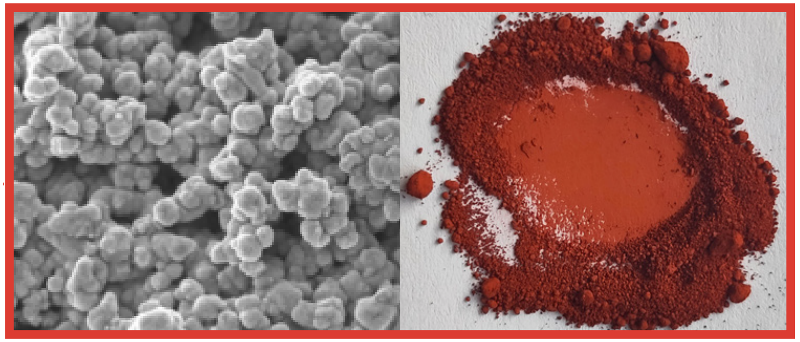
Isolated particles d_{pp}: 400 nm



Low aggregation level d_{pp}: 170 nm



High aggregation level d_{pp}: 90 nm



What is a particle?
Importance of sample preparation

The preparation of a sample material prior to any particle size analysis defines which structural level will be detected. Many dispersion methods aim to deagglomerate a powder to an extent that the smallest dispersible unit can be investigated. It must be noted that such a "smallest dispersible unit" does not always exist. The dispersion method and the energy input define the outcome of the analysis and must be considered in the data analysis.

The following two deagglomeration settings were used to deagglomerate and aerosolize the pigments so that their mass and diameter could be analyzed.

Wet dispersion for Fe_2O_3

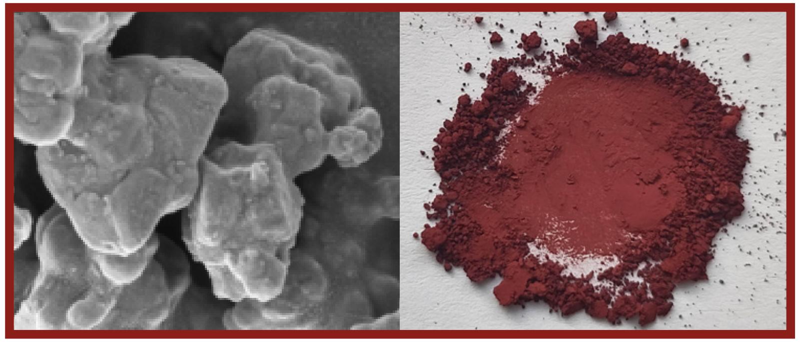
Suspension in water → ultrasonification @ 200 J/ml → Spray dispersion

Dry dispersion for Carbon Black

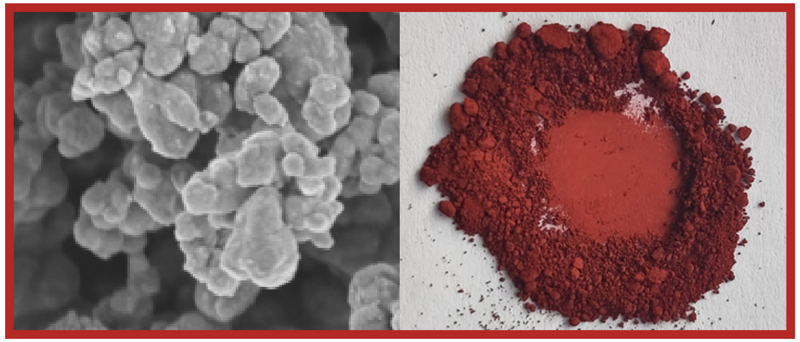
Powder → Aerosolization → Deagglomeration in Venturi nozzles

Note: Several other deagglomeration methods and dispersion fluids (hexane, acetone, …) are also applicable.

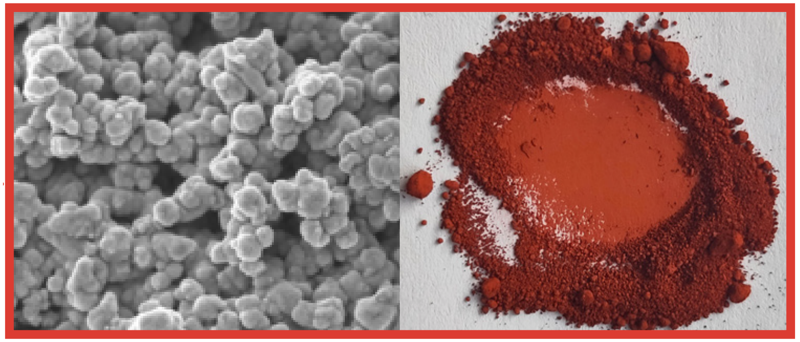
Isolated particles d_{pp}: 400 nm



Low aggregation level d_{pp}: 170 nm



High aggregation level d_{pp}: 90 nm

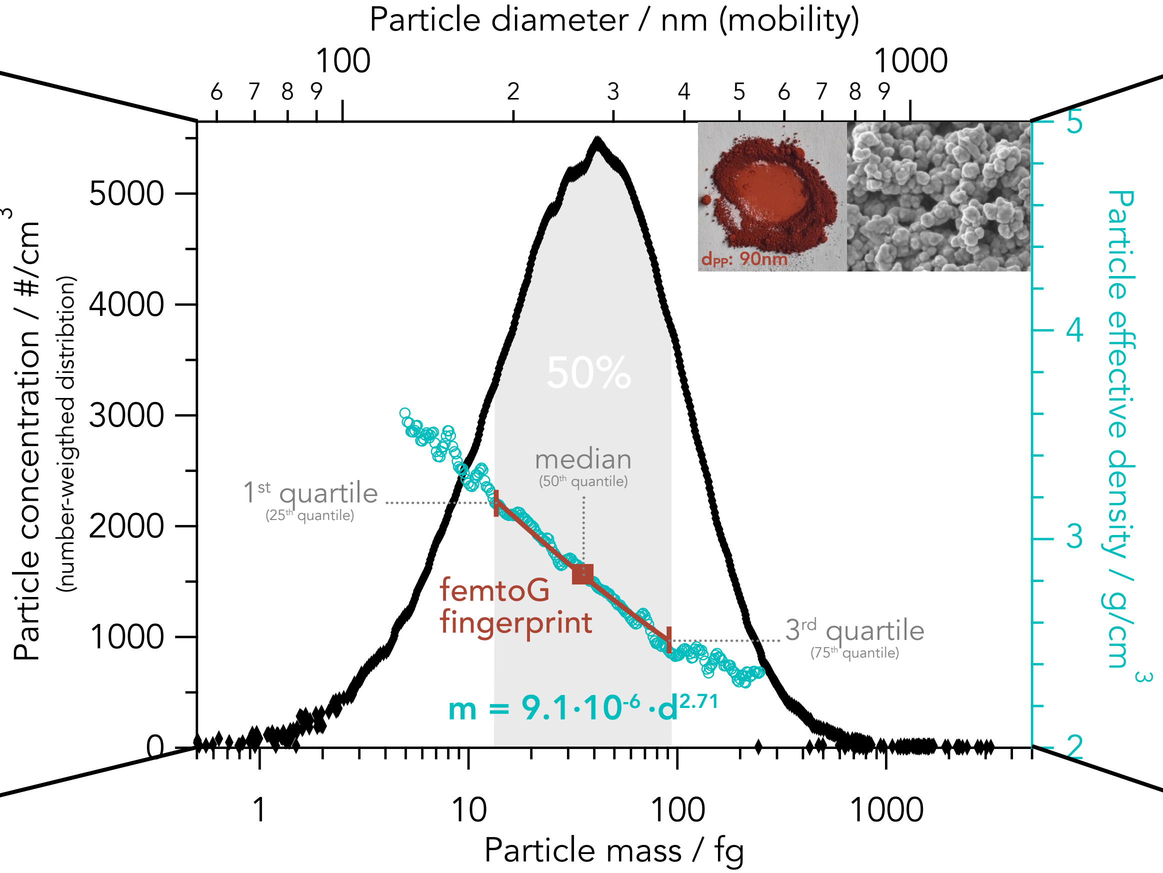


Mass and diameter of a Fe_2O_3 pigments: Full data set

An equivalent diameter is measured based on the drag-force coefficient in air. As such, it only scales with the geometric dimensions of a particle and is independent of the material density or optical properties.

The femtoG method relies on counting particles dispersed in a gas flow. By scanning through different set points, a number-weighted distribution of the particle mass and diameter is obtained.
This scan consists of 600 data points and requires 10 min, during which 4.7 mio. single particles were counted

Next to the usual average and median values, the total particle number in one gram of material can be obtained by integrating the mass distribution.
→ One gram of powder contains $1.8 \cdot 10^{13}$ particles .

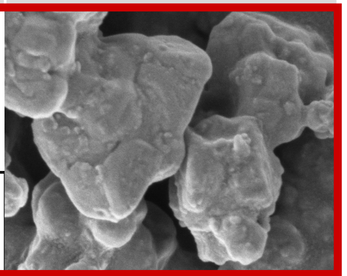
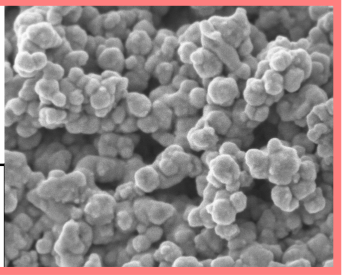


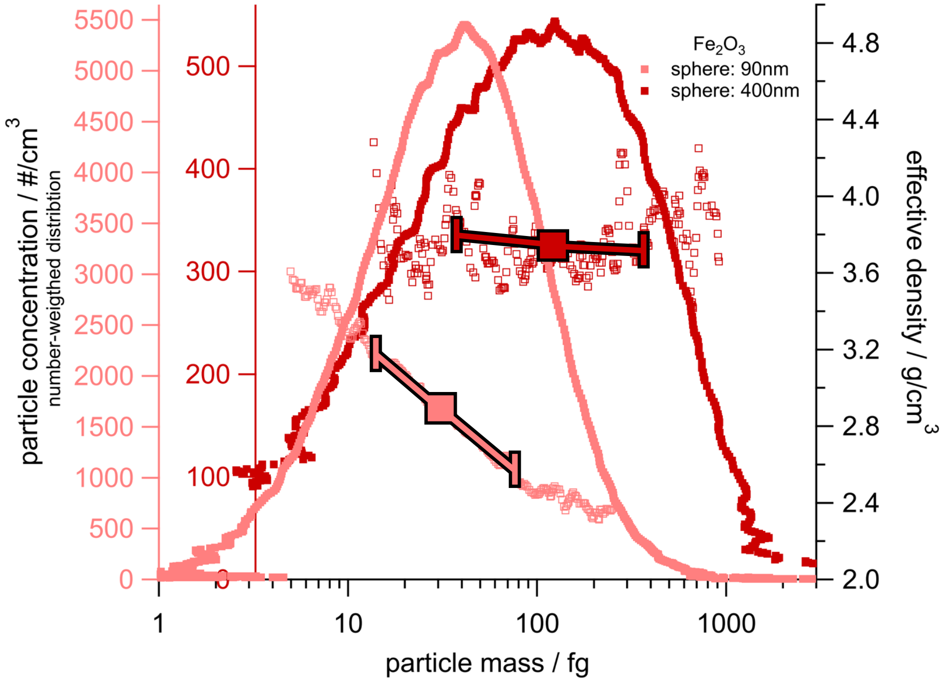
The link between mass and diameter of a particle is the particle density. Fe_2O_3 has a true material density of 5.0 g/cm³, but non-spherical or aggregated particles incorporate some void volume in the particle structure. The effective particle density is, therefore, reduced.

For structured particles, the density declines with increasing size. This gives information on the material structure. For aggregated particles, the scaling exponent is equal to the fractal dimension

The mass is a fundamental and intrinsic property of every single particle. It is independent of the material density, chemistry or optical properties. The particles are electrically charged and separated by a combination of centrifugal and electrostatic forces. The charging state is known, and from it the absolute particle mass can be determined in femtogram / 10^{-15} g.

Comparison of two Fe_2O_3 pigments

Median mass	Median diameter	Particles per gram	«Fractal»-index	SEM image
400nm sphere @ 5.0 g/cm³ m_{sphere}: 167 fg → **isolated «spherical» particles**				
109 fg	380 nm	$2.2 \cdot 10^{12}$ /g	2.97	
90nm sphere @ 5.0 g/cm³ → m_{sphere}: 1.9 fg → **fractal-like aggregate**				
31 fg	274 nm	$18 \cdot 10^{12}$ /g	2.71	



The fine Fe_2O_3 (d_{PP}: 90nm) has significantly lighter, smaller and less densely packed particles than the coarser Fe_2O_3 (d_{PP}: 400nm). By combining different aspects, more information on the particle structure can be gained than by simply comparing d_{50} and d_{90} values.

The coarse pigment has an almost constant effective density of 3.8 g/cm³ (mass~$dia^{2.97}$), which is close to the true material density of 5.0 g/cm³. The apparent particle porosity, responsible for the reduced density, is around 25% and can be attributed to the non-spherical shape of the particles. A hypothetical spherical particle of d_{PP}: 400nm at a density of 5.0 g/cm³ has a mass of 169 fg, close to the here reported median mass (m_{50}) of 109 fg. The d_{50} of 380nm matches the size data from the manufacturer, even though it is a different equivalent diameter. This product consists of isolated and non-aggregated particles that are not spherical but have a fractal-index close to it.

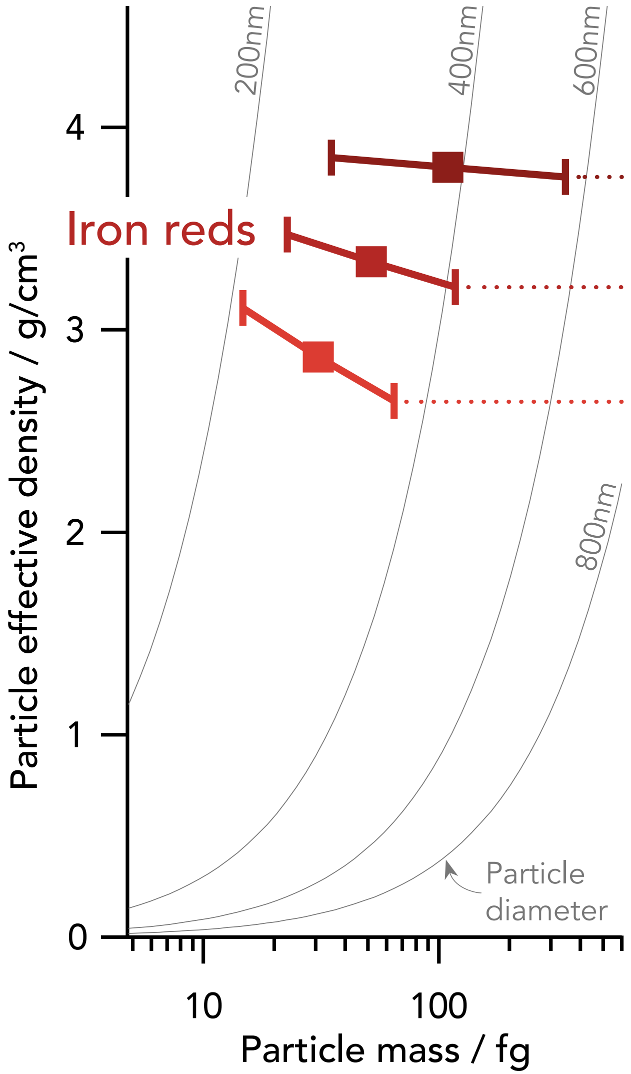
The fine Fe_2O_3 is different from that. The theoretical m_{sphere} for d_{PP}: 90nm is 1.9 fg, which is a fraction of the observed m_{50}. The mass is proportional to $dia^{2.71}$ and (not dia^3), which leads to a decreasing particle density with increasing size, a correlation characteristic for aggregated products. At the median of the q0-distribution, an aggregate consists of approximately 16 primary particles.

Particle structure of Fe_2O_3

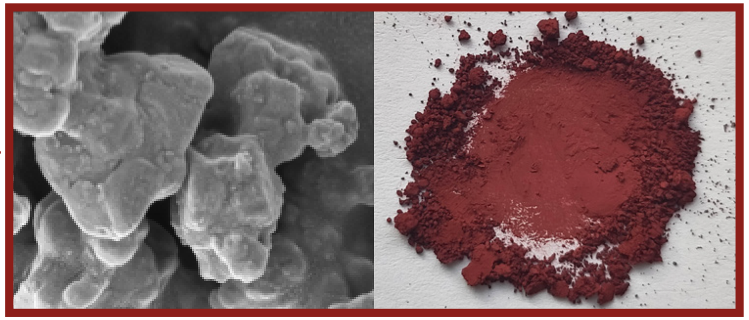
The fingerprint plot is a method to rapidly compare the structure of different materials by plotting the eff. density over the particle's mass at defined points of the mass distribution. Here, the median value and the 50%-interquartile range are chosen. The grey lines indicate the particle diameter.

The three different Fe_2O_3 differ in particle size and structure, as seen in the SEM images. With increasing primary particle size, there is a trend towards less aggregated particles and lower pore volumes with a higher degree of sphericity. The steepness of the curve represents the latter.

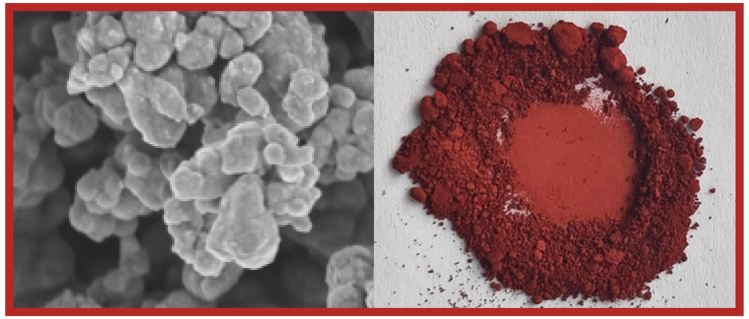
Electron imaging techniques can deliver qualitative information on the material structure, although they are time-consuming and expensive. Quantitative information requires the simultaneous analysis of particle mass and diameter.



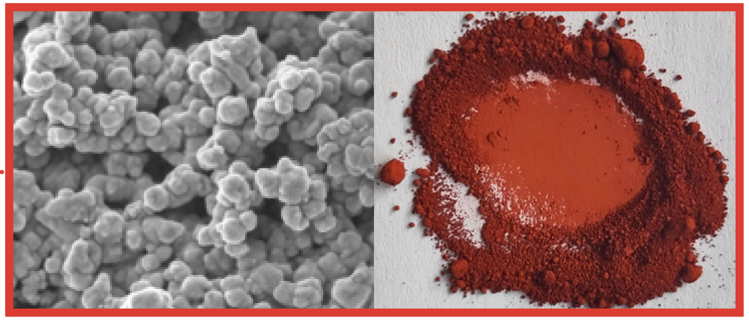
Isolated particles d_{pp}: 400 nm



Low aggregation level d_{pp}: 170 nm



High aggregation level d_{pp}: 90 nm



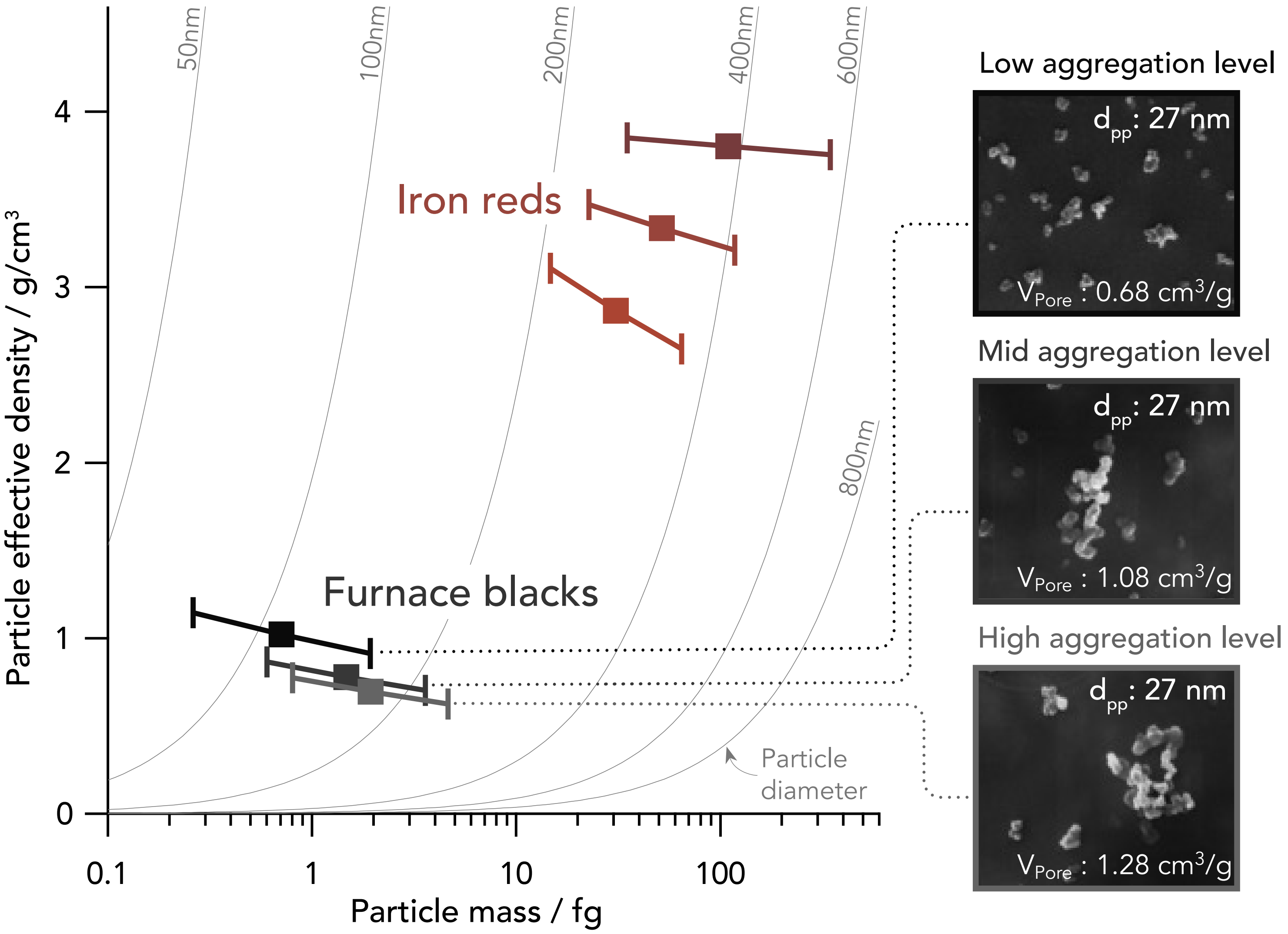
Particle structure of furnace blacks

A different pattern in the fingerprint plot can be observed for three different furnace blacks. Their d_{PP} is 27 nm for all three products, but they differ in the number of primary particles per aggregate (~ aggregation level).

From top to bottom, the m_{50} increases while the density decreases. This is a result of the higher aggregation level. Such a change in the particle structure is typically observed by an increase in the oil absorption number (~pore volume; V_{Pore}) and by a lower powder density.

All three furnace blacks are produced under the same conditions, so the aggregate formation follows the same parameter. Hence, the products have the same fractal index of 2.67.

Similar to the Fe_2O_3 data, such changes can be observed by electron imaging techniques but require considerably more resources and time.



Disclaimer

The analysis and results presented in this application paper pertain specifically to samples evaluated during this study. While the described technology offers a novel approach to determining the size and structure of color pigments and is generally applicable to any pigments, the specific results may vary depending on the batch of the sample analyzed, as well as the feedstock and processing conditions used. Therefore, the findings and conclusions should not be generalized to all pigments without further validation on different batches, feedstocks, and processing conditions. The data and conclusions presented herein are provided for informational purposes only and should not be interpreted as guarantees or warranties of performance for other samples or under different conditions. In no event shall femtoG be responsible or liable for any direct, indirect, punitive, incidental, special, or consequential damages whatsoever arising out of or connected with the use of, misuse of, or reliance upon such results or analysis.