Addressing the issue of wetting and clustering by means of SPES technolgoy: Water suspension of powders

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INTRODUCTION

A quantitative multiparametric analysis of powders suspended in water is discussed as a case study of typical issues caused by surface activity and wetting properties of grains, with the consequent aging/aggregation processes bringing to irregular, internally mixed clusters that are difficult to be recognised and understood. Classizer™ ONE, through the SPES patented method, allows to get insight into these typical issues when handling dry powders suspended in liquids.

Powders of industrial interest are composed by microscopic and sub-microscopic grains with properties that strongly depend on the chemical/mineralogical composition and size. More generally, the suspending liquid can be a mixture of components and additives with physical and chemical role against instabilities and clustering. Shelf life, manufacturing processes, handling are influenced by optimizing the suspending liquid and the specific powder.

From a physical point of view, size is by far the most relevant parameter influencing optical signals exploited to characterize powders. Nevertheless, refractive index, shape and internal mixing affect the signals, thus introducing relevant discrepancies with the geometrical size. Moreover, a non-spherical, non-ideal object cannot be associated to one size, making "sizing" ultimately an ill-posed problem. Therefore, dealing with internally mixed powder grains has remarkable impact on application performances. Even the apparently simplest task to recover a reliable particle size distribution becomes critical. Classizer™ ONE provides the information needed to fill in the gap and achieve a better comprehension of the powder under study.

PARTICLE ANALYSIS METHOD

Among the methods currently adopted for particle sizing, optical ones have unique advantages. Therefore, they have brought light scattering into the forefront of analytical methods in many scientific and industrial applications. Unfortunately, the number of parameters typically affecting the scattering properties of a given particle is such that the basic measure of the scattering power (or even the power removal from a light beam -extinction- from one particle) is far from being enough to recover something more than a rough estimate of its size. Things change appreciably when considering a collection of many scatterers, with the immediate drawback of introducing the need for mathematical inversion and ill- posed problems to interpret resulting data.

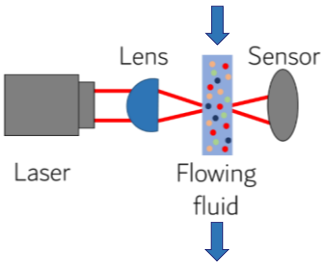
EOS Classizer™ ONE – front view

EOS Classizer™ ONE particle analyser is based on the patented Single Particle Extinction and Scattering (SPES) method. It introduces a step forward in the way light scattering is exploited for single particle characterization.

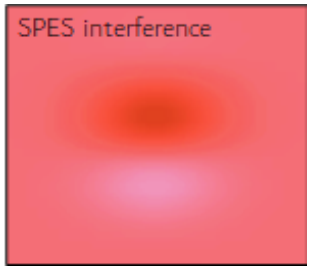
EOS Classizer™ ONE provides data well beyond the traditionally optical approaches. EOS Classizer™ ONE discriminates, counts, and analyses single particles through their optical properties. It provides the user with several pieces of information such as: particle size distribution of the single populations, absolute and relative numerical concentrations, particle stability, information about optical particle structure and oversize. Classizer™ ONE works offline and online/real-time, enabling to verify consistency of intermediate and final formulations with target QbD, SbD, and Quality Control target expectations.

SPES TECHNOLOGY IN A NUTSHELL

The patented Single Particle Extinction and Scattering (SPES) method is based on a self-reference interferometric measurement of the scattered wavefront in the forward direction by a single illuminated particle.

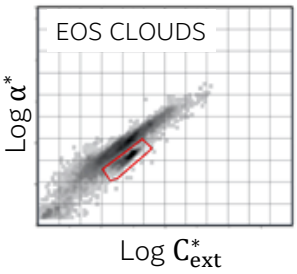


Particles are driven by a laminar fluid flow (liquid or gas depending on the application/CLASSIZER™ version) through the waist region of a tightly focused laser beam.



The intense transmitted beam interferes with the faint scattered wavefront in the far field, thus superimposing the two waves with the same curvature. This causes the interference pattern to exhibit intensity modulations on the spatial scale of the beam itself.

Two scattering features are sampled to follow the evolution of the intensity modulations during the passage of each single particle through the beam: i) the beam attenuation, given by the particle which removes a small fraction of the incoming power; ii) the fringes given by the partially constructive interference, which depth is proportional to the amplitude of the complex forward scattered field S(0). These two features are directly related to the real and imaginary components of S(0), $\Re\mathrm{e}\ S(0)$ and $\Im\mathrm{m}\ S(0)$, accordingly to the Optical Theorem [H. C. van de Hulst, Light Scattering by Small Particles, 1981]. On the other side they are also related to **the Extinction Cross Section** $\mathbf{C^*_{ext} = \frac{k^2}{4\pi}\Re e\ S(0)}$ **and the Polarizability** $\boldsymbol{\alpha^* = k^3\ \alpha = \Im m\ S(0)}$, where $k = 2\pi n/\lambda$ is the wave number in the medium with refractive index n at wavelength λ. Whatever the choice, two independent parameters **are thus retrieved for each detected, validated, and counted particle** thanks to a robust Pulse Shape Analysis scheme and proprietary algorithms. No need is there of adopting ill-posed problems, like inversion or deconvolution. At will, other optical parameters could be alternatively retrieved, eg. particle optical thickness ϱ.



In a few minutes SPES/ CLASSIZER™ ONE creates the unique **EOS CLOUDS**: a 2D histogram which is the optical fingerprint of the sample. Heterogeneous samples produce different clouds for each particle population simultaneously. They can be selected, analyzed, and compared. Statistical approaches as PCA are possible for extracting additional valuable information typically inaccessible with current instrumentation.

Added-value information is provided thanks to **SPES** and **EOS Classizer™ ONE** unique data and analysis libraries:

- **Optical Classification,** Absolute **Particle Size Distribution, Numerical Concentration** of each single population irrespectively of polydispersity/composition.

- Quality Control of particle **porosity, wetting**, **aspect ratio**, **payload**, **impurities**, **scraps**, and **shelf-life without intermediate steps** (purification/filtration).

- Measurement of **particle behavior and formulation stability** directly in real **heterogeneous non-filtered target biological, industrial, or environmental fluids**.

- Hi-Resolution **Continuous Flow Analysis**, also coupling SPES information with other analytical devices as CF3 separators, small chemical reactors, and pilot line.

- Statistical approaches as **Oversize Measure** and **PCA** for Hi-Quality Batch-2-Batch analysis and out-of-specifics identification in product formulation and production.

EOS Classizer™ ONE, based on patented SPES method, is the ideal solution for improving formulations and for verifying product consistency with the target Quality-by-Design final expectations.

Depending on the system configuration and sample, EOS Classizer™ ONE covers a dynamic range of 0.1 – 20 µm, concentration range of 1E5-1E7 ptc/mL @ 0.5-5ccm. External sample manager and autosampler are available.

This document presents representative examples of applications of EOS Classizer™ ONE and does not cover all the cases where the patented SPES method solves the particle identification, classification, and characterisation of challenges in heterogeneous samples and complex liquids. EOS software release SW1.4.39 is used for the data analysis and generation of the figures.

For a general introduction to SPES data with standard samples, as polystyrene spheres, please refer to the Application Note AN001/2021, available for free online at EOS website: www.eosinstruments.com/publications/

APPLICATION EXAMPLES

EOS Classizer™ ONE is exploited to characterize water suspensions of powders composed of different materials, typically representing some cases of general interest in complex fluids. In all cases the results are remarkably influenced by the non-homogeneous internal structure of the clusters, affecting the optical properties needed to characterize the single particles.

Here we report three case studies of water suspension of typical powders:

1) clusters formed by standards latex spheres by adding salt to screen the electrostatic stabilization layer.

2) TiO_2 clusters showing a fast instability when suspended in water due the high electrostatic surface activity and limited wetting of the grain surface.

3) Carbon Black aggregates (soot) showing a behaviour similar to point 2); the strong absorption is shown to compete with the minute internal structure of these fluffy objects, mimicking a much less absorbing medium with even more remarkable consequences on the sample characterization.

1) Polystyrene clusters

Figure *1* shows SPES data for a water suspension of polystyrene (PS) spheres 100 nm in diameter undergoing

aggregation, 20 minutes after adding a $MgCl_2$ water solution to bring the system out of equilibrium. Data from thousands of clusters are collected in a few minutes. Grey tones are proportional to relative numerical particle concentration. Number concentration is not of interest here, so that we mainly focus at studying the features of the SPES CLOUDS and the size distributions, as two main features to understand the powder behaviour in water.

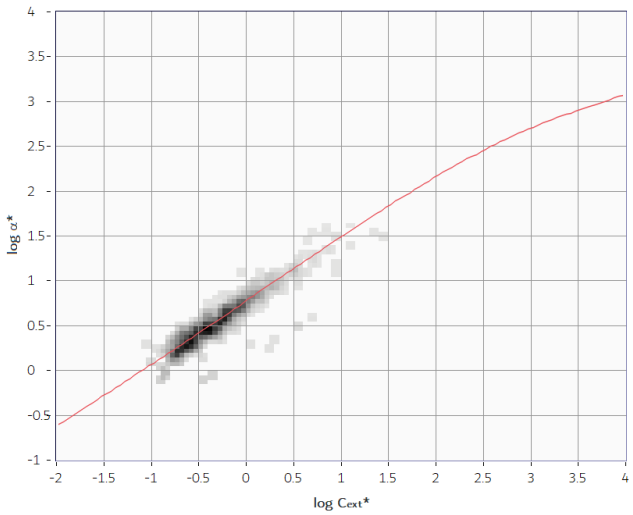


Figure 1 EOS CLOUDS histogram for clusters formed by PS spheres 100 nm in diameter. Red line corresponds to particles with a refractive index n = 1.39, appreciably smaller than the PS value, n = 1.59

Experimental results are automatically compared to conventional dielectric spheres (Mie theory) by fitting to data the best RI, here resulting n = 1.39 in clear disagreement with the expected PS RI, n = 1.59. Notice that here we can safely assume the grains to be as purely dielectric (no absorption). The discrepancy is definitely due to the internal structure of each measured object, composed by PS spheres and water irrespectively of size. The actual optical response is then appreciably changed, and an "effective" RI can be measured to be remarkably smaller than the PS one. Now, each particle can still be sized basing on the effective RI assuming ideal spherical shape. EOS Classizer™ ONE provides the user with the Numerical Particle Size Distribution and other statistical values as AVG, CV, and quantiles (see Figure *2* and Table *1*). Nevertheless, the user is informed about the criticality this measure is endowed with by the strong discrepancy of the measured and expected RI values thanks to the specific features of the EOS Classizer™ ONE. We limit observing that the criticality is simply introduced by the natural missing "size" definition of a complex cluster with internal mixing. Different effective sizes can be introduced depending on the measurement approach and the particle size inversion approach. Examples are the hydrodynamic radius obtained with DLS; gyration radius obtained with SALS/MALS, spherical equivalent radius obtained with OPC, extinction equivalent one obtained with obscuration.

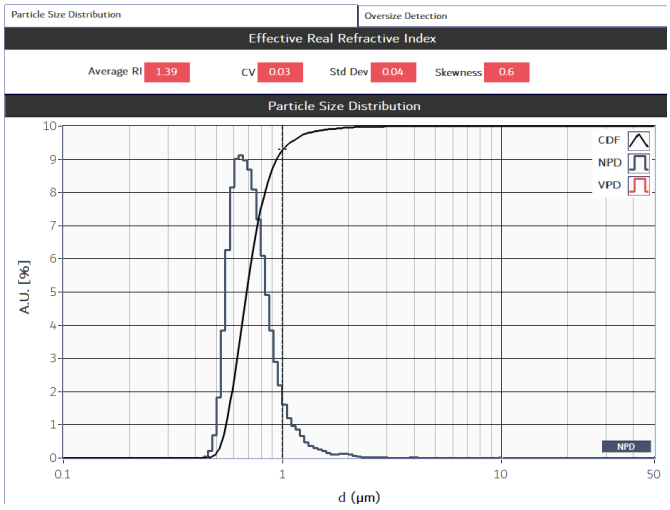


Figure 2 Numerical Particle Size Distribution obtained from data in Figure 1. Average particle diameter retrieved by EOS Classizer™ is 0.75 µm @ measured n=1.39. Mie scattering model is considered for particle sizing.

Particle Size Distribution | Oversize Detection

Estimate of Oversize Measured/Scaled

Dimensional Class	Meas Num Conc [ptc/mL]	Scaled Num Conc [ptc/mL]	Relative Num Conc [%]	Expert Advise on Statistics
overall	6.73E+5	6.73E+5	100%	-
> 0.5 µm	6.66E+5	6.66E+5	99%	-
> 0.7 µm	3.36E+5	3.36E+5	50%	-
> 1.0 µm	5.45E+4	5.45E+4	8%	-
> 2.0 µm	3.08E+3	3.08E+3	0%	-
> 5.0 µm	1.81E+2	1.81E+2	0%	-
> 10.0 µm	0.00E+0	0.00E+0	0%	-

Table 1 Oversizers obtained from data reported in Figure 1.

2) TiO_2 clusters

In Figure *3* we report the results obtained by simply dropping some TiO_2 powder into pure water and gently shaking. By fitting the RI to data, a value n = 1.52 is found, still much smaller than the bulk value n = 2.4. This is reasonably due to the surface activity of the grains, likely forming shallow structures, chains, or even fractal-like aggregates. As in the previous case, the effective RI is smaller than the bulk one.

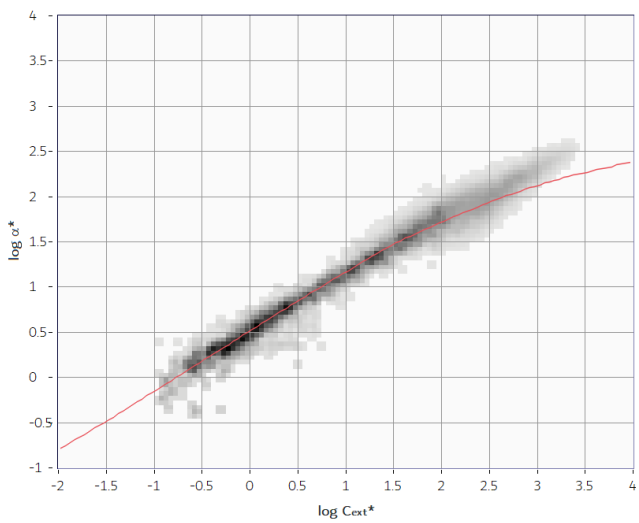


Figure 3 Titanium Oxide powder simply put into pure water. The sample is characterized by an effective RI n=1.52, as evidenced by the red line (adapted from Mie theory). This is well below the expected n=2.4

In Figure *4* the corresponding size distribution shows rampant polydispersity over almost two decades. The corresponding oversize analyses is reported in Table *2*. The effect is evident of clustering due to the low wetting of TiO_2 crystals and the consequent ease of sticking.

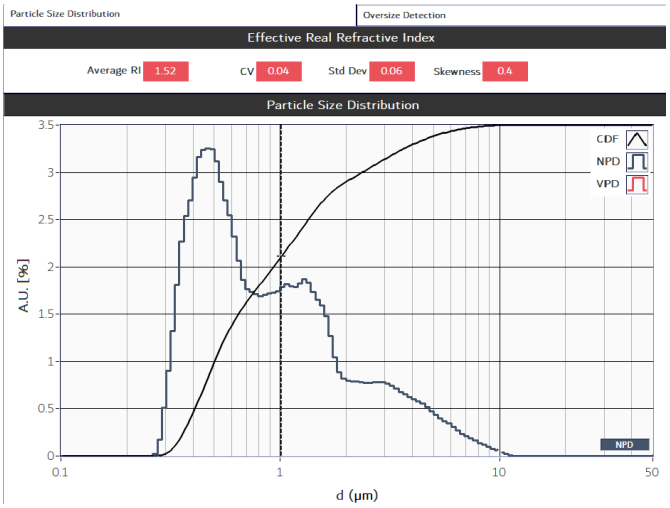


Figure 4 EOS CLOUDS extracted from data reported in Figure 3 show evidence of a heterogeneous suspension composed by objects highly polydisperse in size.

Particle Size Distribution | Oversize Detection

Estimate of Oversize Measured/Scaled

Dimensional Class	Meas Num Conc [ptc/mL]	Scaled Num Conc [ptc/mL]	Relative Num Conc [%]	Expert Advise on Statistics
overall	8.09E+5	8.09E+5	100%	-
> 0.5 µm	5.84E+5	5.84E+5	72%	-
> 0.7 µm	4.37E+5	4.37E+5	54%	-
> 1.0 µm	3.29E+5	3.29E+5	41%	-
> 2.0 µm	1.41E+5	1.41E+5	17%	-
> 5.0 µm	2.84E+4	2.84E+4	4%	-
> 10.0 µm	5.81E+2	5.81E+2	0%	-

Table 2 Oversize analysis results for the population in Figure 4.

The same suspension can clearly be prepared more carefully. We provide evidence that EOS Classizer™ ONE allows to monitor and quantify the quality of the suspension by simply comparing the result with the previous ones. Data reported in Figure *5* and *Figure 6* have been obtained after treating the suspension with ultrasounds. Results prove a remarkable effect on the sample after ultrasonic treatment, as it is well known. Clusters clearly break up, as it is evident from both the smaller sizes and higher RI, n = 1.74. This is in accordance with the smaller structures, that will reasonably be more compact and therefore contain more material and less water within a given volume, namely a larger density. Increasing density then means larger polarization and larger RI. Moreover, two populations are found instead the one observed before. They can be studied separately with the EOS Classizer™ ONE software, as described below.

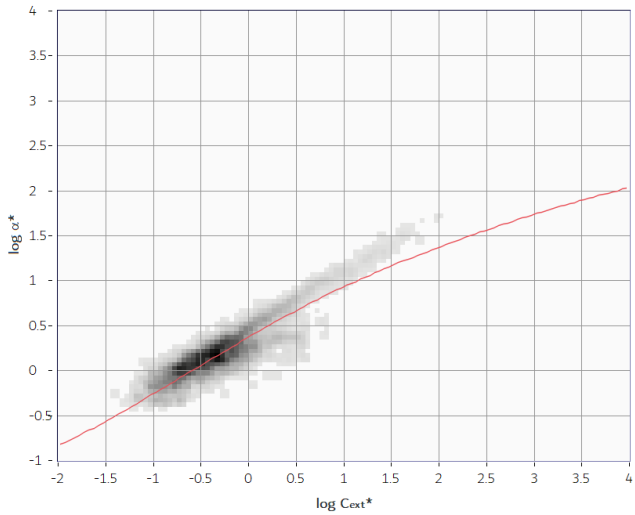


Figure 5 EOS CLOUDS obtained after sonicating the sample analyzed in Figure 3. The adapted Mie theory represented by the red line indicates an effective RI n = 1.74, much higher than before, but still below the bulk one.

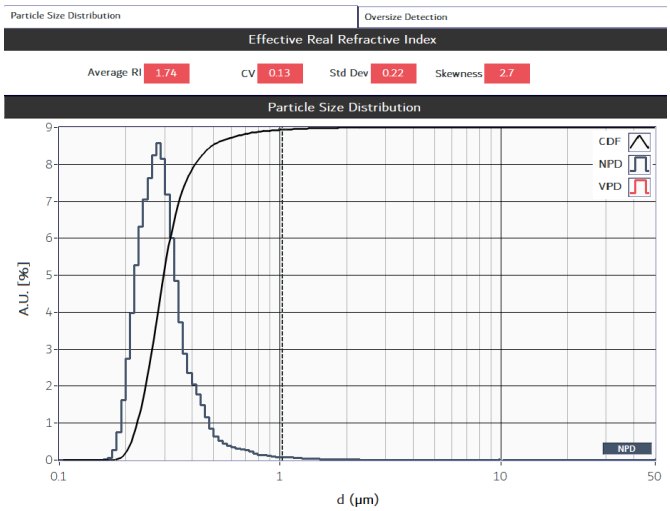


Figure 6 PSD obtained by fitting to data in Figure 5 the effective RI (Mie theory). The distribution is much less extended, and the average size reduced to 310 nm.

Figure *7* shows the theoretical curve (red line) fitted to the experimental data within the lower population. The resulting RI is now just n = 2.4, as expected by assuming spherical grains composed by bulk material. The spherical approximation here is more than acceptable here, since the TiO_2 grains, although not perfectly spherical, are still well isometric. This proves that the lower population is formed by single grains that did not interact, a feature that is not found at all in the measurement of Figure *3*. On the contrary, the upper population is still compatible with internally mixed clusters that maintain the refractive index measured above. They likely did not break up upon sonication or may have formed again thanks to the fast-aging processes they undergo.

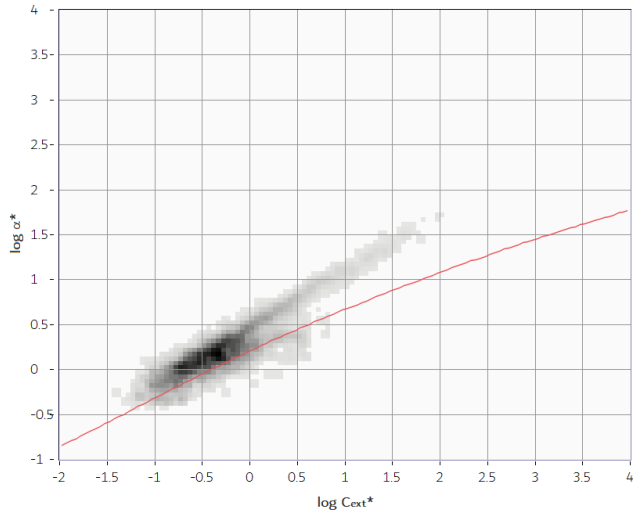


Figure 7 Comparison of the lower portion of the EOS CLOUDS to the expected Mie theory for the bulk material, with RI n = 2.4.

3) Black Carbon

As another example of a powder with very high surface activity we report the results of measurements performed with clusters composed of black carbon (soot). After suspending a dry powder in pure water we immediately treat the sample with 30 min ultrasonic bath and measured immediately (see Figure *8*) and after 20 hours (Figure *9*). As it can be clearly seen the change is rampant, as it is evident by comparing the EOS CLOUDS. As expected, even after breaking up the largest clusters the sample undergoes an aggregation process that forms larger structures. Moreover, we can clearly assess a very strong absorption of the samples, especially from the data in Figure *8*: this is clearly suggested by the remarkably small polarizability (vertical axis) for a given extinction (horizontal axis). No dielectric material would fit this population. As a limit case, notice the EOS CLOUDS reported in Figure *7* for the bulk TiO_2, one of the largest RI for dielectric materials. Therefore, the automatic inversion is now impossible (the system automatically returns a precise caveat). By imposing the refractive index to n=1.5+i0.1 we obtain the red line in Figure *9***Errore. L'origine riferimento non è stata trovata.** and the PSD reported in Figure *10*. The same curve is compared to data in Figure *11*, showing a reasonable fit for lower sizes (lower left part of the EOS CLOUD) but with relevant discrepancy for the largest (upper left). In Figure *12***Errore. L'origine riferimento non è stata trovata.** and Figure *13* we compare the same data reported in Figure *9* to the reference curve automatically fitted to data by the software, by (wrongly) assuming a pure dielectric material. The comparison between the EOS cloud and the red line serves as a strong caveat here. This is a typical example where a sample with rampant absorption can be wrongly interpreted as a dielectric one because of peculiar scattering features of particles endowed with such a complex internal mixing (in this case likely similar to fractal aggregates).

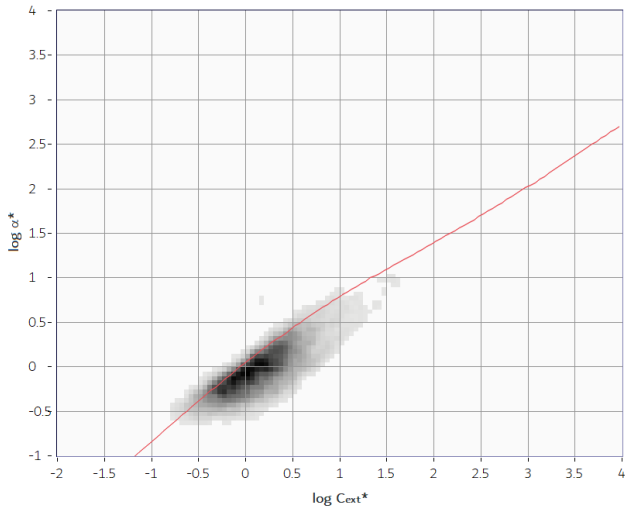


Figure 8 Data obtained with a suspension of black carbon immediately after sonication. Data cannot be fitted by any curve for a dielectric material, thus indicating the strong absorption the sample. The red line is the best fit for particles endowed with absorpt.

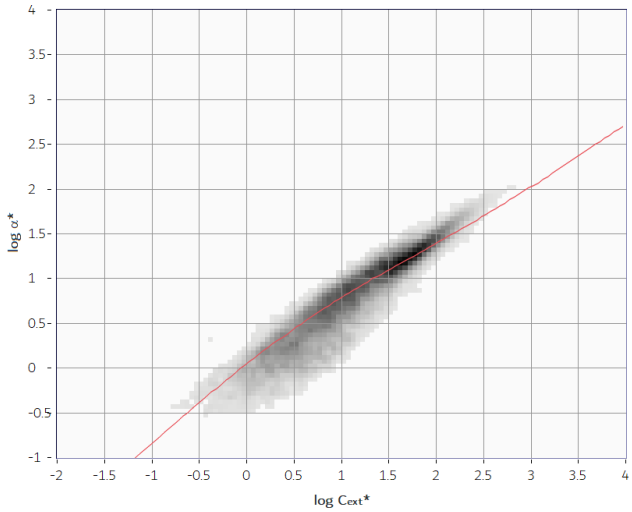


Figure 9 Data obtained with a suspension of black carbon 20 hours after sonication. The red line is the manual best fit for particles endowed with absorption, n=1.5+i0.1, that only shows a slight discrepancy for larger sizes (upper right part of the EOS CLOUDS).

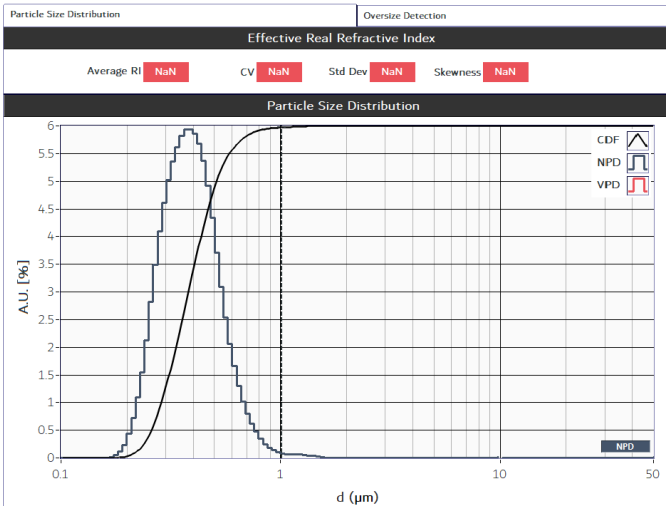


Figure 10 PSD obtained by fitting the complex refractive index to data in Figure 8. The value n=1.5+i0.1 is considered the best fit.

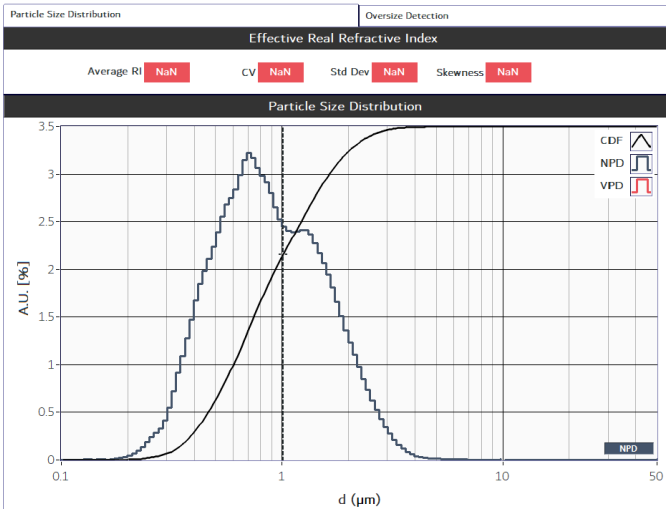


Figure 11 PSD obtained by fitting the complex refractive index to data in Figure 9 (n=1.5+i0.1). Notice that a relevant discrepancy is there at the largest sizes in Figure 9, hidden in the PSD.

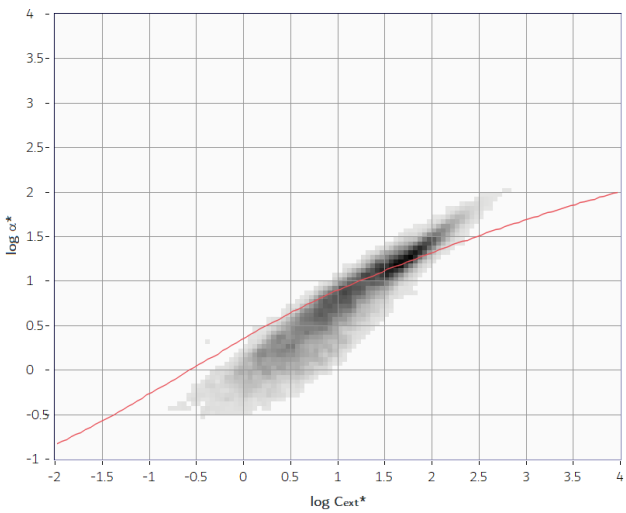


Figure 12 The same data reported in Figure 9 compared to the automatic fitted curve obtained assuming pure dielectric material. The discrepancy is rampant.

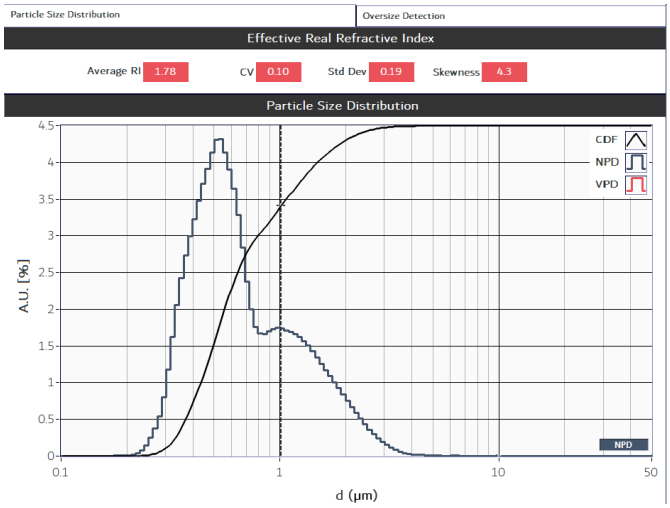


Figure 13 PSD obtained by automatically fitting the data in Figure 12. A value of n = 1.78 is obtained. Notice that the discrepancy evidenced by the EOS CLOUD in Figure 12 cannot be assessed from just the PSD.

CONCLUSIONS

The capability of EOS Classizer™ ONE and SPES patented method in discriminating single particle basing on their optical properties is of capital importance with heterogeneous, internally mixed systems. In particular, the advantage is rampant and unique when particles have to be analysed to tailor the effectiveness of the product formulation or to study features like stability, surface activity, wetting, as well as the behavior of one component among the others, etc.

The independent measurements of different EOS CLOUDS for each component within a heterogeneous formulation or a complex mix of interacting particles can be of utmost importance and utility to identify the undergoing processes, like aging, starting from the optical properties of the single particles, as it occurs here for aggregates. The results of this analysis can effectively prove changes in particle behavior stability, and properties due to the surrounding media.

SPES data provide physical and statistical information, as particle size distribution, effective refractive index, and numerical concentration, as well as insight into the particle internal structure. Applications range from the study of the behaviour of particles in target heterogeneous media to tailor the formulation, to the improvement of wetting properties of the grains depending on the preparation and the surrounding medium. Oversize analysis can be performed accurately separating different populations, also in presence of impurities. Scraps and out-of-spec can be monitored in intermediate and final formulation.

RELEVANT PUBLICATIONS AND REFERENCES

Presentation of Single Particle Extinction and Scattering (SPES) method for particle analysis
AN001-2021 Analysis of Polymeric Particles via SPES Technology – a general introduction to SPES method

AN006-2021 Multiparametric Classification of Particles as a Pathway to Oversize Analysis in Complex Fluids via SPES Technology

Potenza MAC *et al.*, «Measuring the complex field scattered by single submicron particles », AIP Advances 5 (2015)

Example of CFA application of SPES technology
AN002-2021 Continuous SPES Flow Analysis CFA-SPES

Example of PCA application of SPES technology
AN005-2022 Multiparametric Principal Component Analysis of Heterogeneous Samples via SPES Technology

Classizer™ ONE with Sample Manager Autosampler
AN008-2022 Automatic Liquid Sample Management, Dilution, and System Cleaning with EOS Sample Manager

AN009-2022 Standardize SPES Operative Procedure of Liquid Samples Analysis via EOS Autosampler

Example of SPES application to aggregates
AN003-2021 Addressing the Issue of Wetting and Clustering by Means of SPES Technology

Potenza MAC *et al.*, «Single-Particle Extinction and Scattering Method …», ACS Earth Space Chem 15 (2017)

SPES application to non-spherical particles
AN004-2021 Addressing the Classification of Non-Spherical Particle by means of SPES Technology

Simonsen MF *et al.*, «Particle shape accounts for instrumental discrepancy in ice …», Clim. Past 14 (2018)

Example of SPES application to emulsions w/o payload in environmental waters
AN012-2021 Monitoring the Fate of a Lipid/ZnO Emulsion in Environmental Waters

Examples of SPES application to particle analysis and behavior characterization in biotech applications
AN007-2021 Quantitative Classification of Particles in Biological Liquids via SPES Technology

Sanvito T *et al.*, «Single particle extinction and scattering optical method unveils in real…", Nanomedicine 13 (2017)

Potenza MAC *et al.*, «Single particle optical extinction and scattering allows real time quantitative…», Sci Rep (2015)

Example of SPES application to oxide particles, abrasives, and industrial slurries w/o impurities
Potenza MAC *et al.*, «Optical characterization of particles for industries», KONA Powder and Particle 33 (2016)

AN002-2021 Analysis of Abrasives via SPES Technology

Example of SPES application to ecotoxicity analysis
Maiorana S *et al.*, «Phytotoxicity of wear debris from traditional and innovative brake pads», Env Int., 123 (2019)

Example of SPES application to aerosol analysis
Mariani F *et al.*, «Single Particle Extinction and Scattering allows novel optical …», J Nanopart Res 19 (2017)

Cremonesi L *et al.*, «Multiparametric optical characterization of airborne dust …. », Env Int 123 (2019)

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