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Size distribution of powders in the range 1 µm - 100 µm : a comparison of static digital image analysis and laser diffraction.

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ABSTRACT

Automated image analysis of particles under controlled orientation is becoming a challenging technique for laser diffraction in the field of sizing of particles above 500nm. Thanks to optimal particle dispersion and fully automated microscopic imaging, it is now possible to gather individual measurements on tens of thousands of particles within a minute.

In this paper, results obtained from both techniques are compared on a selection of powders in the range between 1µm and 100 µm.

For spherical and opaque materials both instruments give very similar results, but when shape or optical properties enter into play discrepancies are evident at both ends of the size distribution. Image analysis certainly offers enhanced robustness with respect to poorly calibrated material, since it allows to develop exploratory statistics and in particular to remove the influence of outliers on the general trend of a size distribution.

1 INTRODUCTION

Though it is based on a complex theory of interaction between monochromatic light and individual particles, laser diffraction (LD) has gained much attention and is considered as a reference technique for the analysis of fine particulate materials, particularly in the range between 1µm and 100 µm. The quality of laser diffraction analyses, their sensitivity to geometrical or optical properties and their reconciliation with other sizing techniques is often discussed but hardly contested because of the lack of alternative methods. On the other hand, optical as well as electron microscopy based techniques are often regarded as qualitative inspection tools but are considered as poorly representative and unproductive for daily use in an analytical laboratory.

The advent of fully automated microscopic particle imagers, coupled with dedicated image analysis software has brought a drastic improvement in terms of both quality and accuracy of measurements. Static image analysis (SIA) is now capable of picturing tens of thousands of particles in a minute and given the particles are under controlled orientation and adequately measured, the SIA output will guarantee a very good correlation with sieving [1].

The intention of this paper is to explore the correlation between both techniques (LD and SIA) on a selection of powders with variable geometrical as well as optical properties.

2 MATERIALS AND METHODS

2.1 Selected powders

A series of four different materials has been selected for this study in order to explore the influence of variable shapes, size ranges and optical properties on the final size distribution curve.

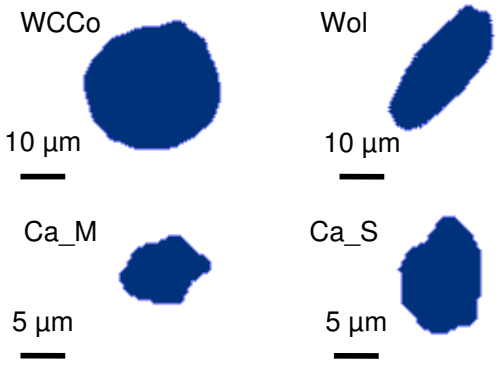

Fig.1. Selected particles representative of the powder samples used in this study.

WCCo is a sample of tungsten carbide/cobalt powder in the range between 20µm and 45µm as specified by the manufacturer from laser diffraction (Cilas) analyses. Particles are roughly spherical and opaque to light.

Wol is a sample of synthetic wollastonite ($CaSiO_3$) in the range between 1µm and 50µm. Wollastonite crystals are monoclinic, have a fibrous habit and refractive indices varying between 1.628 and 1.642.

Ca_M is a sample of calcitic filler obtained from milling limestone down to 80 µm.

Ca_S is a sample of a similar filler obtained from hydrocycloning fines produced during limestone crushing. Particles are typically under 80 µm.

Calcite particles are trigonal and strongly birefringent with refractive indices going from 1.656 to 1.485.

Figure 1 illustrates selected particles representative of each powder.

2.2 Laser Diffraction (LD)

For the purpose of this study, laser diffraction analysis has been performed using a Mastersizer 2000 instrument coupled to a Hydro 2000S wet dispersion unit, both from Malvern.

The optimization of the pump / stirrer rate was achieved by determining how the reported particle size changes as the pump speed is increased. The sample concentrations were set so as to allow reproducible scattering to be obtained without observing multiple scattering (about 15% of obscuration rate). Time and energy of ultrasound were optimized to enable full particle dispersion. Conversion of scattering patterns into particle size distributions (deconvolution step) were done by means of the Fraunhofer theory. The Mie theory was also used when it appeared more suitable.

2.3 Static Image Analysis (SIA)

Static image analysis has been performed using the Alpaga 500 Nano coupled with the VDD270 vacuum dispersion device, both from Occhio Instruments.

Using this principle, particles are allowed to settle down onto a circular glass plate forming the bottom of a cylindrical chamber. When they are at rest, the circular glass plate is moved in front of a collimated violet LED light and pictures of individual particles are captured with a 1392*1040 pixels video camera fitted with a telecentric lens. A typical resolution of 480nm is achieved at maximum magnification.

Digital image analysis is being performed in real time in order to give for each individual particles a series of size and shape parameters. It has been shown that although most image analyzers use the equivalent disk diameter (D_O) as a measure of size, the inscribed disk diameter (D_{IN}) is best suited to find a perfect correlation with sieves when analyzing particles lying on a rest plane [1].

Size and shape distribution curves can be recomputed at any time from the individual particle measurements. They can be expressed as number fractions or apparent volume fractions. They can be displayed with any user defined series of virtual sieves or size classes.

3 RESULTS

3.1 Tungsten carbide / Cobalt powder

Figure 2. illustrates the size distribution curves obtained from both LD and SIA for the WCCo powder. SIA results are shown as “sieving diameters” (D_{IN}) although “equivalent disk diameters” (D_O) would give very similar results because of the spherically shaped particles (fig.1).

Both techniques indicate a very narrow size range. Measurements obtained from LD show a slight shift towards larger sizes, but this is not confirmed by the laser diffraction data provided by the manufacturer indicating that discrepancies between LD instruments might be larger than between SIA and LD for spherical opaque powders (Tab.1).

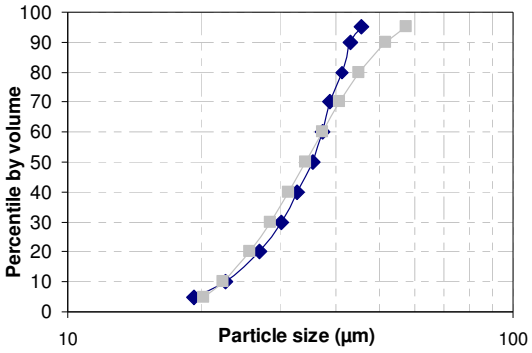

Figure 2: Comparison of cumulative size distributions obtained from laser diffraction LD (■) and image analysis SIA (▲) for the WCCo powder.

	SIA	LD	LD *Manufacturer*
D_2^V [µm]			22.19
D_5^V [µm]	19,19	20,21	
D_{20}^V [µm]	26.88	25.70	
D_{50}^V [µm]	35.52	34.13	33.15
D_{80}^V [µm]	41.28	45.21	
D_{95}^V [µm]	45.6	57.57	44.71
N	24250	N.A.	N.A.

Table 1. Volume weighted Xth percentiles (D_X^V) of the size distributions obtained from both SIA and LD on a WCCo powder (N : number of analyzed particles)

3.2 Wollastonite powder

Figure 3. illustrates the size distribution curves obtained for the Wollastonite powder. Table 2 summarizes the main volume weighted percentiles corresponding to these curves.

The fibrous shape habit of most particles (fig.1) has a tremendous influence on the size distribution curves as can be seen from the difference between LD and SIA (using the D_{IN} diameter). Because SIA relies on the analysis of particles resting on a plane perpendicular to the optical axis, it leads to less dispersion in the results. It should be noted that from the SIA dataset, one could as well produce distributions of lengths or aspect ratios. As an indication of the shape of wollastonite particles, the median aspect ratio as measured from SIA corresponds to 4:1.

Both Fraunhofer and Mie theories were used to deconvolve the laser diffraction results, leading to reasonably similar size distribution curves. Mie was computed for different plausible values of refractive and absorption indices. The best fit being obtained for a refractive index of 1.64 and an absorption index of 0.01.

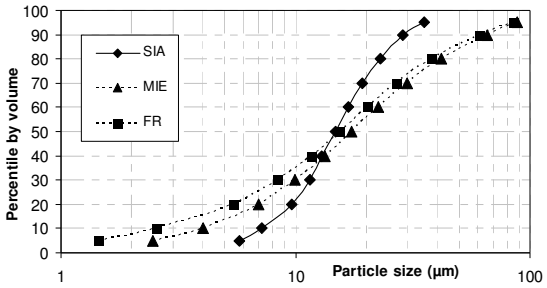

Figure 3 : Cumulative size distributions obtained for the wollastonite powder from SIA (plain line), LD Mie and LD Fraunhofer (dotted lines).

	SIA	LD *Fraunh.*	LD *Mie*
D_5^V [µm]	5.76	1.44	2.44
D_{20}^V [µm]	9.60	5.44	6.94
D_{50}^V [µm]	14.88	15.42	17.25
D_{80}^V [µm]	23.04	38.24	41.91
D_{95}^V [µm]	35.52	84.29	88.54
N	33 721	N.A.	N.A.

Table 2. . Volume weighted Xth percentiles (D_X^V) of the size distributions obtained from both SIA and LD on a Wollastonite powder.

3.3 Calcite fillers

Figure 4 illustrates the size distribution curves obtained for the Ca_M filler (milled limestone). From the image analysis results of 31536 particles it is easy to realize that only very few particles are above 65 µm. These particles can be considered as statistical outliers and consequently removed from the dataset in order to better visualize the size distribution of the remaining particles. The difference between the raw and the filtered size distribution is very significant as can be seen from the percentile values of table 3 after removal of only 11 particles out of 31536 !

Figure 5 displays the results obtained on the Ca_S (hydrocycloned limestone) filler

Two distribution curves are displayed for each SIA analysis, the first one by taking into account all measured particles and the second one by removing notable outliers in the distribution.

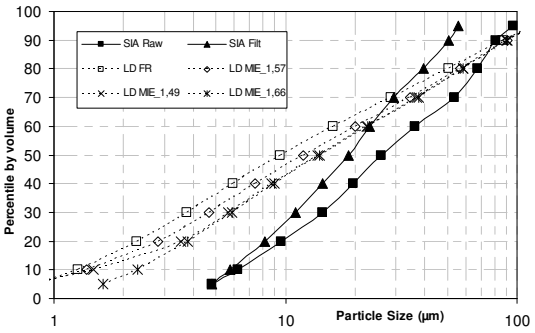

Figure 4: Cumulative size distributions obtained for the milled limestone filler (Ca_M) from SIA with and without outliers (plain line), from LD Fraunhofer and LD Mie using extreme (1,49; 1,66) or average (1,57) refractive indices for calcite (dotted lines).

	SIA *raw*	SIA *filtered*	LD *Fraunh*	LD *Mie*
D_5^V [µm]	4.8	4.8	0.85	0.84
D_{20}^V [µm]	9.6	8.16	2.33	2.81
D_{50}^V [µm]	25.92	18.72	9.87	11.92
D_{80}^V [µm]	67.29	39.55	52.38	56.85
D_{95}^V [µm]	96.36	55.62	120.95	121.19
N	31536	31525	N.A.	N.A.

Table 3. Volume weighted Xth percentiles (D_X^V) of the size distributions obtained for the Ca_M filler from SIA with the raw data or after outlier removal and from Fraunhofer or Mie based LD with a 1,57 refractive index.

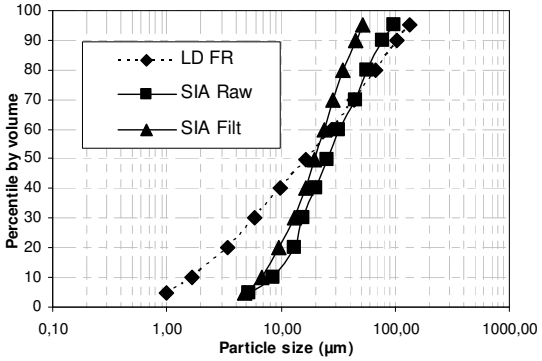

Figure 5: Cumulative size distributions obtained for the hydro-cycloned limestone filler (Ca_S) from SIA with and without outliers (plain lines) and from Fraunhofer based LD (dotted line).

	SIA *raw*	SIA *filtered*	LD *Fraunh*	LD *Mie*
D_5^V [µm]	5.28	4.80	0.99	1.97
D_{20}^V [µm]	12.96	9.60	3.39	5.40
D_{50}^V [µm]	25.44	19.68	16.56	23.34
D_{80}^V [µm]	57.37	34.65	67.12	75.69
D_{95}^V [µm]	97.87	52.15	135.63	146.32
N	31878	31862	N.A.	N.A.

Table 3. Volume weighted Xth percentiles (D_X^V) of the size distributions obtained for the Ca_S filler from raw SIA data or after outlier removal and from Fraunhofer or Mie based LD with a 1,57 refractive index.

4 DISCUSSION

The systematic comparison of laser diffraction and static image analysis on a selection of powders with variable shapes and optical properties is very instructive. It has already been tempted by several authors, but the exact operation mode for image analysis were unclear and the measured parameter was an equivalent disk diameter (D_O) ([2]

When analyzing well calibrated spherical opaque particles the correlation between SIA and LD is very strong. The slight difference between both techniques appears to be in the range of what is observed among LD instruments from different manufacturers.

When the analysis refers to a poorly calibrated material, the discrepancy between SIA and LD results is striking. A first reason is certainly the presence of outliers (i.e. occasionally very large particles). SIA is based on tens of thousands individual particle measurements. Just as for any statistical analysis, this allows for user interaction and immediate computation of size distribution curves with or without user-specified outliers. LD on the other hand is affected by the presence of outliers. The curve fitting principles used in the deconvolution theory generate a continuum of large particles that are inexistent.

Results obtained from both limestone fillers clearly demonstrate that LD also extends the size distribution towards the lower sizes. One could argue that SIA is blind to particles smaller than 3 pixels in width (1.44 µm) but this argument does not explain the discrepancies between LD and SIA in the small size range (< 10 µm). In order to shift the size distributions towards lower values and make SIA correspond to LD, one would need an enormous amount (> 90% by number) of very fine (1-10 µm) material. It seems impossible that this has been overlooked by SIA.

The argument that fines were not correctly dispersed in the SIA system cannot be completely dismissed on the basis of the analytical results.

However, experience shows that vacuum dispersion is very efficient and works even for very fine material.

On the other hand, the existence of a secondary peak corresponding to very fine sizes (around 4 µm) is a common artifact in LD size analyses.

The elongated morphology of wollastonite particles confirms the extension of LD size distributions towards both the larger and smaller sizes. SIA of oriented particles reveals that the largest particles have a width (sieve size) of 35 µm for a length of 140 µm. LD indicates a maximum size of 85 µm which is an average between width and length. This probably confirms a randomized orientation of the particles in the flow plane passing in front of the laser. But, here again, LD extends the size range towards lower sizes that are absolutely not present in the SIA analysis.The wollastonite fibers appear much more calibrated in width (sieve size) from SIA compared to LD. SIA results are more plausible with respect to the crystalline nature of the material.

5 CONCLUSIONS

Static image analysis (SIA) based on maximum inscribed discs diameters proves to be an extremely powerful and robust method for the analysis of particles above 1 µm. Previous work had already demonstrated the perfect correlation with sieve size distributions [1]. This work shows that SIA based on tens of thousand of particles also proves to be competitive with laser diffraction (LD) both in terms of efficiency and accuracy.

SIA even provides superior results when the powder sample is made of non-spherical particles or particles with complex optical properties. More importantly, when a powder sample contains discontinuities in the size range and typically when some small large particles are present, SIA provides the user with intelligent statistical tools to eventually remove extreme values. On the other hand, the LD deconvolution procedure appears to be fooled by very large particles and extends the size range at both extremities.

The availability of dedicated image analysis instruments clearly opens the way to unexplored problems in powder characterization. One should not forget to mention that SIA not only provides accurate size distributions in number or in volume, but also a wealth of data about individual particle morphologies.

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