Response of Laser Diffraction Particle Sizer to Anisometric Particles

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Abstract

This study deals with the size measurement of non-spherical particles by the laser diffraction technique. Size analyses of three sets of identical metallic bodies (cubes, tablets and cylinders) were performed by means of a Malvern 2600 instrument. The results prove that under the operating conditions chosen and in the case of anisometric objects, the mean total surface area is not measurable either because the Malvern software, strictly valid for spheres, is not applicable to such particles or because the particles adopt preferential orientations in the measurement cell. Further, a way of processing diffraction data is proposed in order to determine two characteristic dimensions of identical anisometric particles. It is based on the measurement of the minimum and maximum projected surface areas of the particles. The experimental results obtained with our particles show the procedure to be reliable.

1 Introduction

Recently, industrial interest in accurate particle size analysis has become very important owing to its direct relevance to many process applications. In fact, particle size analysis concerns industries producing and handling particulate solids, namely industrial crystallization, where the control of crystal size is often essential.

Responding to the growing industrial demand, recent years have seen significant developments in various particle size analysis methods. The laser light-scattering technique is recognized as a fast, versatile technique for size analysis in an on-line process environment. Unfortunately, problematic scientific issues limit the development of laser light-scattering particle sizing instruments in hostile environment, owing to the three fundamental assumptions inherent to diffraction size measurements:

1. All the particles in suspension are assumed to scatter a portion of the incident light independently of each other (i.e. single scattering).
2. Theoretical interpretation of measured light intensities does not require the knowledge of the optical properties of the particles and the liquid.
3. Particles are assumed to be spherical.

The condition of "single scattering", implied by the first assumption, is generally achieved in practice by keeping the solid load in suspension sufficiently low (maximum 1% v/v). Measurements made at high particle concentration must be corrected for multiple scattering effects if the true size is to be obtained [1]; these corrections are about to be incorporated in computer software [2]. Under certain circumstances, the optical properties of both solid and liquid critically affect the distribution of light energy received at the detector of the laser sizer; without correction for this effect, the true particle size would not be obtained. The simplified theory of Fraunhofer does not take these properties into account, in contrast to the rigorous Mie theory [3]. Newly marketed laser diffraction particle sizers use this latter theory. Finally, the assumption of spherical particle shape is difficult to justify because real disperse systems to be investigated consist mainly of non-spherical particles.

The objective of this experimental study is to analyse precisely how the laser diffraction technique responds to particles of non-spherical shapes. This problem of general interest has been mainly tackled by theorists [4-6]. The particles used in this study are metallic cubes, tablets and cylinders; these shapes are close to those of typical crystals. The size analysis of these objects, performed by means of a Malvern 2600 commercial system, is presented and an interpretation of these data intended for shape analysis is described.

2 Theory of Laser Diffraction Sizing

2.1 Measurement Principle

In instruments based on the laser diffraction technique, light emitted from a helium-neon laser ($\lambda = 0.6328$ μm) is expanded and illuminates the particle field as shown in Figure 1.

The particles present in the cell will either absorb or scatter incident light according to their size, shape and refractive index. The scattered light is subsequently collimated by a Fourier transform lens and focused on to an axisymmetric detector positioned at a distance from the lens equal to its focal length, f. It consists of a set of 31 concentric semi-circular light-sensitive diodes, corresponding to 31 size ranges, radially arranged at increasing distances S from the central diode; ring detectors increase in thickness with increasing distance from the centre of the detector. The undiffracted light is focused on the central detector. A measurement usually records and averages a large

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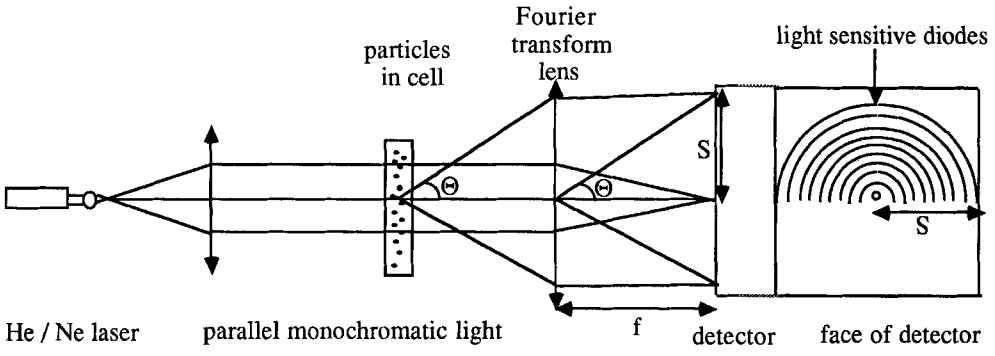


Fig. 1: Schematic diagram of laser diffraction particle sizing system.

number of sweeps for each detector element. In this way a composite diffraction pattern developed from all the contributing particles is recorded as a function of the scattered angle, Θ, with $\Theta \# S/f$ when Θ is small.

For example, the light energy distribution of the diffraction pattern for a field of monodisperse spherical particles of radius a is shown in Figure 2.

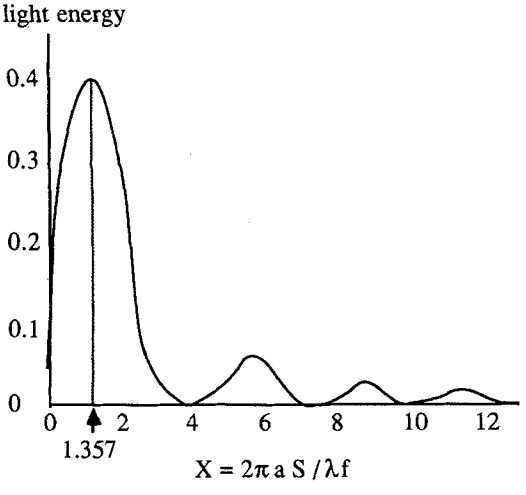


Fig. 2: Energy distribution of spherical particles of radius a.

The first maximum occurring at

$$X = 2\pi aS/\lambda f = 1.357 \quad (1)$$

corresponds to approximately 80% of the total light energy.

For a suspension containing a collection of particles of various sizes, the light energy falling on any ring in the focal plane is the sum of the contributions from individual particles. The latter scatter light at different angles so that the diffraction pattern becomes more complicated and no longer shows sharp minima at certain diffraction angles. The total light energy distribution for a suspension containing a collection of particles of different sizes may be expressed in matrix form as

$$L(j) = W(i).\ T(i, j) \quad (2)$$

where $L(j)$ is the light energy falling on ring j, $W(i)$ is the weight fraction of particles in the size range i and $T(i, j)$ is the scattering matrix for spherical particles containing the coefficients which define the light energy distribution, similarly to Figure 2, for each particle size range.

Eq. (2) is solved by assuming a value for $W(i)$ and calculating a theoretical value for $L(j)$ using the appropriate $T(i, j)$ matrix for a given set of experimental parameters. This theoretical $L(j)$ is compared with the experimentally measured value and the weight distribution is then iteratively adjusted until the sum of the squared errors in $L(j)$ reaches a minimum:

$$\min|\ \Sigma\ L(j) - W(i).\ T(i, j))^2|\ . \quad (3)$$

The relative weight distribution is determined by inverting the $T(i, j)$ matrix. Hence, the success of this measuring technique depends on two factors: the accuracy of the inversion step and the accuracy of the light-scattering model.

The inversion procedure, which translates the recorded scatter pattern into a crystal size distribution, must be both fast and reliable. Unfortunately, the inversion routine of the Malvern software is not divulged. Concerning the light-scattering model, the Malvern 2600 system uses either the Fraunhofer diffraction or the so-called "anomalous diffraction" software to interpret light-scattering measurements. Both theories are approximations to the rigorous Mie theory, which requires a prior knowledge of both the relative refractive index, m (ratio of the refractive index of the particles to that of the fluid medium), and the coefficient of light absorptivity of the particles in suspension. The rigorous Mie theory, which is applicable to scattering by particles of size comparable to or larger than λ, considers the reflected, refracted and diffracted components of the scattered light and consequently arrives at expressions which are a function of both particle size and relative refractive index m. In the limiting case of particles larger than λ and for low scattering angles (the Malvern 2600 detector covers the range from 0° to 11°), the contributions of reflective and refractive scatters are small and the Fraunhofer diffraction theory is adequate to describe the diffraction pattern when photons undergo one or no scattering events before leaving the medium. This simplified theory assumes that the particles are plane and perfectly opaque and consequently that there is a large difference in refractive index between the particles and the surrounding medium. When particles are not opaque, it is then necessary to take the value of m into account. When m is close to unity, as in the case of crystals in solution, it is possible for light to travel through the particle and to undergo a phase change without amplitude change, if there is no light absorption. The transmitted light interferes with the diffracted light to produce the so-called anomalous diffraction pattern. The light energy distribution, shown in Figure 2, is then modified. First, the location of the first peak depends on the value of $|m - 1|$ and tends towards 1.357 when $|m - 1|$ is high. Second, at some values of $|m - 1|$, the second peak can be almost as high as the first, whereas in Fraunhofer diffraction the second peak is always much smaller than the first (Figure 2). The present Malvern software, used in the 2600 apparatus, based on anomalous diffraction, sets m to

an arbitrary real value, possibly that of the latex spheres used to calibrate the equipment [7].
When laser diffraction was first used for particle sizing, it was applied to solid particles and droplets in air under conditions where $|m-1|$ was large; the Fraunhofer theory was applied and a small correction for anomalous diffraction was necessary only for small particle sizes. Owing to the extension of laser diffraction sizing to liquid-liquid and solid-liquid systems, the Mie theory, with the knowledge of the true value of m, must be applied [3].

2.2 Influence of the Particle Shape on Light Scattering

Light-scattering devices are usually confined to particles of spherical shape whereas in numerous fields of research particles are mainly non-spherical.
For both Fraunhofer and anomalous diffraction theories, the scattered light energy is proportional to the particle cross-sectional area. The cross-sectional area of a particle is combined with its diffraction pattern by a Fourier integral [8]. This means that the intensity distribution of the scattered light in the Fraunhofer plane and the light intensity in the object plane are Fourier reciprocal and be converted into each other by a set of Fourier coefficients. According to *Gebhart* [8], the diffraction equation of any object consists of two parts: an intensity factor and an angular function. Whereas the intensity factor is a function of the projected area of the particle only, the angular distribution changes with particle shape. This means that the total amount of light scattered due to diffraction is a function of the projected area of a particle, regardless of its shape. However the particle contour modifies the angular distribution of the diffracted light. The limit of the forward lobe of diffraction reflects the rough contour of a particle in a reciprocal manner and thus contains information about its projected area. Details of the contour are mainly stored at angular ranges outside the diffraction lobe and in Fourier coefficients of higher order. Hence microstructures of the particle contour tend to shift diffracted light to larger scattering angles.

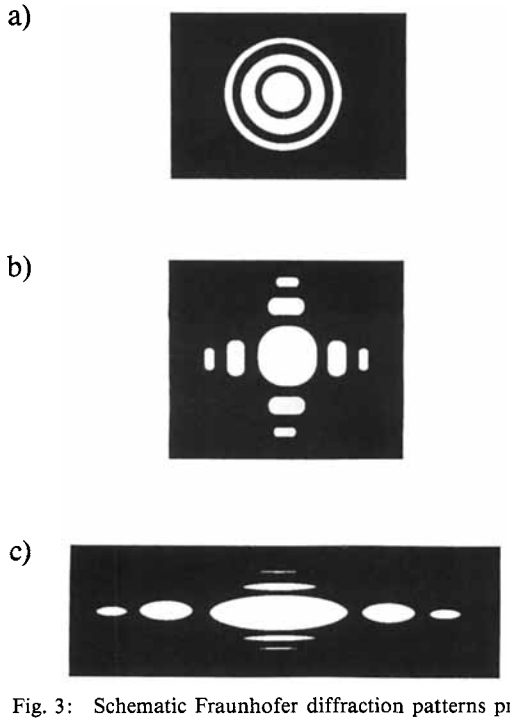


Fig. 3: Schematic Fraunhofer diffraction patterns produced by (a) a circular aperture, (b) a squared aperture and (c) a rectangular aperture.

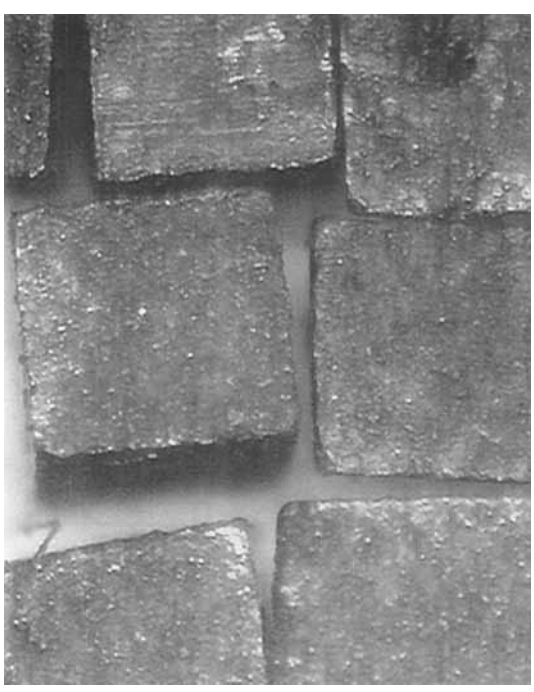
The effect of particle shape on light scattering is lower if the flux of scattered light is a function of the projected area of the particle. However, when a particle is moving in the sensing volume, its projected area depends on its orientation. When convex particles are randomly orientated in the path of the laser beam, the Cauchy theorem assumes that their mean geometrical projection area is one quarter of their total surface area provided that the instrument gives a projected area response.
In order to illustrate the effect of particle shape on the scattering pattern observed in the focal plane, Figure 3 shows schematic Fraunhofer diffraction patterns of (a) a circular aperture, (b) a squared aperture and (c) a rectangular aperture [9].
They all consist of a central bright spot characteristic of the shape of the aperture. For the circular aperture, the spot is surrounded by alternate bright and dark concentric rings so that the proportion of light falling on any semi-circular photodetector is independent of the orientation of the aperture. In the other two cases, the recording of diffracted light will depend on the orientation of the aperture in front of the laser beam owing to the geometry of the detector.

3 Experimental

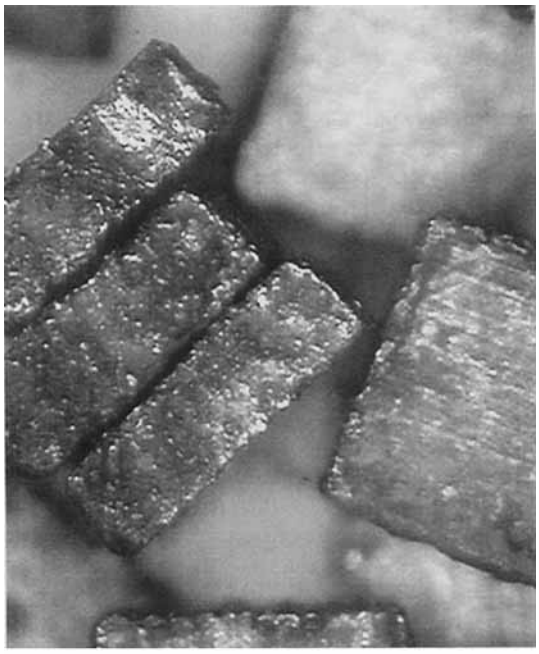
In order to detect the influence of the particle shape on the laser light-scattering sizing technique, three sets of identical unbreakable regular-shaped particles were analysed in this study.

3.1 Experimental Conditions and Results

The experiments were carried out using a Malvern 2600 laser diffraction sizer with a 1000 mm focal length lens giving a nominal size range of 19.3-1880 µm. The volume and the optical length of the measurement cell were 14 cm^3 and 14.3 mm, respectively. The particles were maintained in suspension in water by means of propeller. The materials used consisted of three sets of identical tailor-made steel particles: cubic grains, squared tablets and elongated particles of circular section (Figure 4). The dimensions of these objects are given in Table 1.



b)



c)

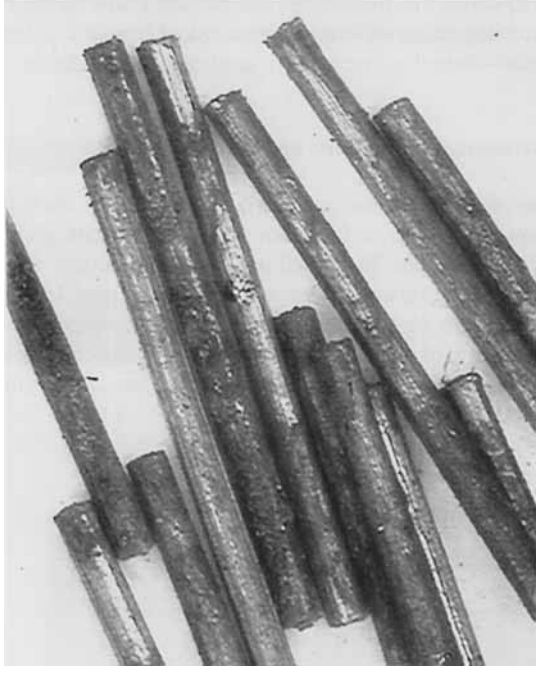
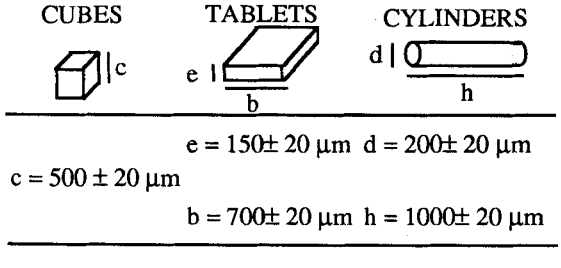


Fig. 4: Photographs of (a) cubic grains, (b) square tablets and (c) elongated particles of circular section.

The widths of the size distributions, about ±20 μm on average, are due to manufacturing defects.

Table 1: Dimensions of the particles.



Analyses were performed according to a standard procedure. For each measurement, Table 2 gives light energy values recorded on each detector.

Table 2: Scattering signatures.

	Detector Light Energy Values		
	Cubes	Tablets	Cylinders
0 (hole)	0.32	0.18	0.10
1	−149.71	29.83	−18.37
2	−0.18	81.73	−1.32
3	30.92	107.36	8.79
4	7.97	104.70	9.06
5	39.06	111.05	18.17
6	22.28	90.13	19.66
7	3.92	63.74	18.87
8	5.95	47.72	23.39
9	−6.12	32.11	24.06
10	1.28	31.01	25.93
11	3.84	32.86	25.59
12	11.02	35.41	26.27
13	3.15	26.62	24.80
14	1.09	18.47	21.96
15	3.63	17.42	18.32
16	4.31	21.13	14.55
17	3.27	15.54	11.55
18	3.67	15.22	11.31
19	2.81	16.17	13.83
20	4.02	13.07	17.09
21	3.43	12.54	18.23
22	4.38	11.59	16.11
23	4.72	11.11	13.48
24	5.09	11.10	14.19
25	5.85	10.65	16.46
26	6.69	10.89	15.11
27	7.77	10.91	13.63
28	9.09	10.95	15.08
29	10.63	11.16	13.85
30	12.06	11.56	13.92
31	13.86	11.92	12.58

The number size distributions (q_0) vs. the diffraction diameter (x) are presented in Figure 5. They were calculated from the volume size distributions, given directly by the apparatus, according to the following relationship:

$$q_0(\bar{x}_i) = \frac{q_3(\bar{x}_i)/\bar{x}_i^3}{\sum_j (q_3(\bar{x}_j)/\bar{x}_j^3)} \cdot 100 \qquad (4)$$

where $q_0(x_i)$ is the number percentage in sizeband $[x_i, x_{i+1}]$, $q_3(x_i)$ the volume percentage in sizeband $[x_i, x_{i+1}]$ and $\bar{x}_i$ the arithmetic mean of the limits of the sizeband.

3.2 Exploitation of the Results

The exploitation of the results is concerned, on the one hand, with the applicability of the Cauchy theorem and, on the other, with an extension of the diffraction data treatment to shape analysis:

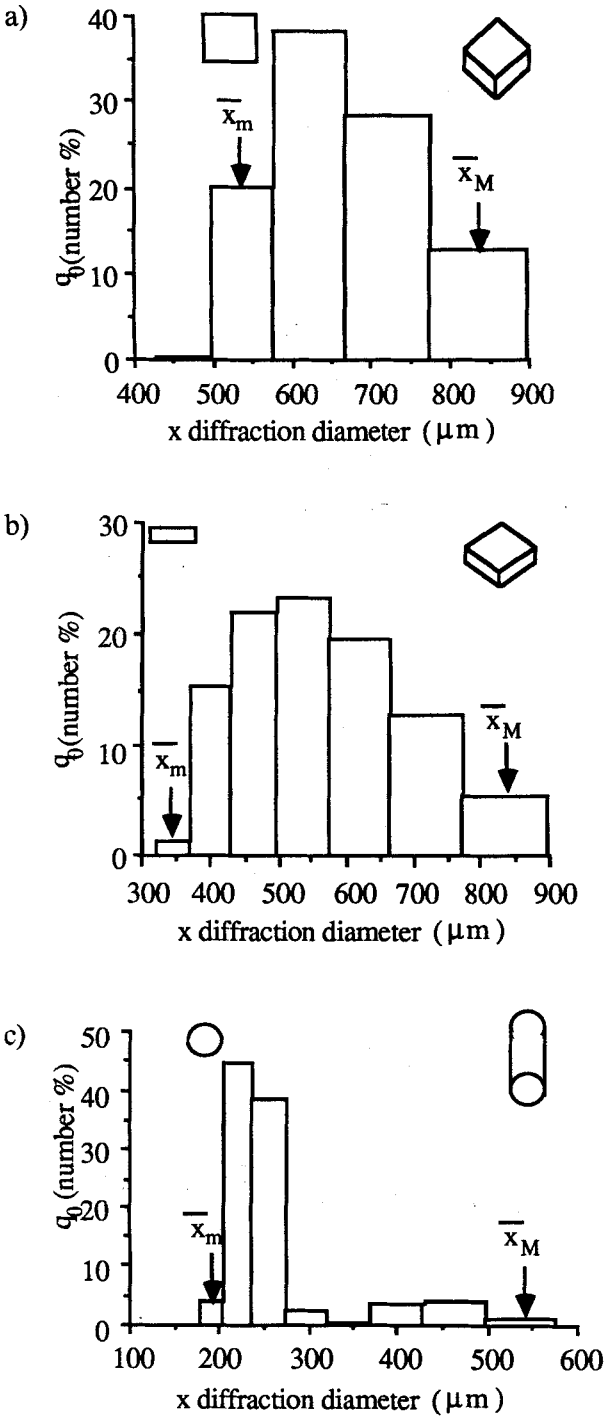


Fig. 5: Number size distributions as a function of diffraction diameter of (a) cubic particles, (b) square tablets and (c) cylindrical particles.

1. The determination of a particle size distribution by the laser light-scattering technique makes use of the Cauchy theorem, mentioned in Section 2.2, that gives the mean total surface area, A_c:

$$A_c = 4\pi \left[\sum_i q_0(\bar{x}_i)\bar{x}_i/100) \right]^2 . \quad (5)$$

It is possible to examine the applicability of this theorem by calculating, for each particle shape, the ratio of the mean total surface area, $A_{c\,mea}$, evaluated from the experimental number size distributions by applying the Eq. (5), to the real total surface area of the particles, $A_{c\,calc.}$, easily evaluated knowing the dimensions and the geometry of the objects. This ratio has been found to be 0.91, 0.69 and 0.30 for cubes, tablets and cylinders, respectively, although it should theoretically be equal to unity if the assumption of Cauchy was proved. Hence the values of this ratio are appreciably different from unity for tablets and elongated particles: their total surface is therefore noticeably underestimated, by 31% and 70%, respectively. Such results show that, under the operating conditions chosen and in the case of anisometric particles, the mean total surface area is not measurable by applying the Cauchy theorem either because the Malvern software, strictly valid for spheres, is not applicable to such particles or because particles adopt preferential orientations in the measurement cell. In practice, it is difficult to prove the latter assumption. Although the flow is turbulent, the large density difference between solid and liquid media may generate preferential orientations of the particles.

2. Since the anisometric particles analysed consist of identical bodies, the exploitation of their size distribution measured by the laser diffraction technique can yield some information other than the mean particle size. For example, it is possible to determine two characteristic dimensions of the particles knowing their shape and the mean diffraction diameters ($\bar{x}_m$ and $\bar{x}_M$) defined in Figure 5. The cases of tablets and cylinders have been considered; the case of cubes has been mentioned for information only.

The following relationships between the characteristic dimensions of the particles and the minimum, A_m, and maximum, A_M, projected surface areas have been established for:

– cubes:

$$A_m = c^2 \quad (6)$$

$$A_M = 3\,c^2\sqrt{2}/2 \quad (7)$$

– square tablets:

$$A_m = b.e \quad (8)$$

$$A_M = b^2 \cos\left[\text{arctg}\left(\frac{e\sqrt{2}}{b}\right)\right] + \sqrt{2}\,b.e \sin\left[\text{arctg}\left(\frac{e\sqrt{2}}{b}\right)\right] \quad (9)$$

– cylinders of circular section:

$$A_m = \pi d^2/4 \quad (10)$$

$$A_M = d.h \cos\left[\text{arctg}\left(\frac{\pi d}{4h}\right)\right] + \frac{\pi d^2}{4} \sin\left[\text{arctg}\left(\frac{\pi d}{4h}\right)\right] . \quad (11)$$

In the three cases, the minimum, A_m, and maximum, A_M, projected surface areas are taken as equal to

$$A_m = \frac{\pi \bar{x}_m^2}{4} \quad (12)$$

and

$$A_M = \frac{\pi \bar{x}_M^2}{4} \quad (13)$$

where $\bar{x}_m$ and $\bar{x}_M$ are the arithmetic mean diffraction diameters evaluated from the size distributions. These relationships express that the Malvern sizer gives a projected minimum and maximum area response.

The values of the characteristic dimensions calculated by solving the set of two equations (Eqs. (6) and (7) for cubes, Eqs. (8) and (9) for tablets and Eqs. (10) and (11) for cylinders) are reported in Table 3. The differences between the sizes calculated

with this method and the true values are of the same order of magnitude as the tolerances on the dimensions (about ±20 μm).

Table 3: Comparison between calculated and true dimensions.

	Geometry		
	Cube	Tablet	Cylinder
Calculated dimensions (μm)	$\bar{c} = 493$	$\bar{b} = 729$ $\bar{e} = 132$	$\bar{d} = 191$ $\bar{h} = 1182$
True dimensions (μm)	$\bar{c} = 500$	$\bar{b} = 700$ $\bar{e} = 150$	$\bar{d} = 200$ $\bar{h} = 1000$

4 Conclusion

The examination of the size distributions of identical sets of anisometric particles (tablets and cylinders), measured by laser diffraction technique using a Malvern 2600, leads to the following conclusions:

– Under the operating conditions chosen, the mean total surface area of the particles is not measurable by applying the Cauchy theorem either because the Malvern software, strictly valid for spheres, is not applicable to such particles or because the particles adopt preferential orientations in the measurement cell.

– Two characteristic dimensions of the particles can be calculated with reliability knowing their geometry and the minimum and maximum diffraction diameters directly given by the size analysis.

From this study, it is clear that there is a necessity to improve the development of laser diffraction particle sizers in order to extend the measurement to non-spherical particles. In order to calculate the scattering of distributions of non-spherical particles, the most reliable way is to use the "T matrix" method [11]. The software would then offer the possibility of selecting the scattering "T matrix" corresponding to the geometry of the analysed particles. This matrix depends only on the physical properties of the scattering object, shape, size and refractive index. This technique is particularly suitable for the investigation of the scattering of randomly orientated bodies. The drawbacks of the method are the complexity of the computer implementation and the longer computation times required. Nevertheless, the recent rapid increase in readily available computer power will make the use of such a theory more and more common. However, the exact calculation of the scattering by distributions of highly irregular-shaped particles does not appear to be possible in the near future.

5 Symbols and Abbreviations

a	radius of spherical particle
A_c	mean total surface area
A_m	minimum projected surface area
A_M	maximum projected surface area
b	width of tablets (μm)
c	edge of cubes (μm)
d	diameter of cylinders (μm)
e	thickness of tablets (μm)
f	focal length of the lens (mm)
h	height of cylinders (μm)
$L(j)$	light energy falling on ring j
m	relative refractive index
q_0	number percentage
q_3	volume percentage
S	radius of the detector ring (mm)
T	scattering matrix
$W(i)$	particle weight fraction in size range i
x	diffraction diameter (μm)
$\bar{x}_m$	minimum mean diffraction diameter (μm)
$\bar{x}_M$	maximum mean diffraction diameter (μm)
λ	wavelength of the incident beam (μm)
Θ	scattering angle (°)

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