Determination of Particle Size Distributions by Laser Diffraction

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The paper deals with the main principles of the determination of particle size distribution using Mastersizer 2000, Malvern Instruments Ltd., UK. Using several problems as examples we have demonstrated that the method is not a routine one and that the measurement procedure is not limited to entering a sample into the dispersion unit and pressing the button. Furthermore, we have shown that the sample preparation method and, therefore, the accuracy of results conclusively depend on the physical and chemical properties of the analyzed materials.

Key words: *Particle size distribution, Mastersizer 2000, Laser diffraction and Light scattering.*

1. INTRODUCTION

The interest for particle size measurements arises from fact that the properties of dispersed materials are strongly correlated with their particle size and uniformity. From academic and industry researches to the control and production optimization of raw materials, medicaments, food and other products, there is a growing for a fast and accurate on-line method for the determination of particle size distribution. Due to its simplicity and accuracy, the laser diffraction method is nowadays the primary method for the examination of the size distribution in disperse systems such as soles and emulsions. The measurement procedures on modern laser diffraction devices (LD) are fast and fully automated; they are reproducible and can be standardized for certain systems. However, in order to obtain reliable data about the analyzed particle systems it is crucial to understand and take into account several important factors, such as the nature of the material, the instrument, measurement methodology and the verification of results.

2. BASICS OF THE LD METHOD

The LD technique is based on the fact that the spatial distribution of scattered light is a function of the particle size of the analyzed sample. The phenomenon of light diffraction on particles is complex, but it can be vividly presented. As a stone hits the water surface, the concentric rings of waves appears.

The waves near the site of impact are intense - higher, while the wave height decreases as moving away. Larger stones will create higher waves in comparison with smaller stones. Waves will also be more intense and clearly separated in the case of larger stones [1].

Generally speaking, a similar occurs when a particle is illuminated as is shown on fig. 1: for smaller particles the diffraction images are more diffuse. Basically, the LD method measures the intensities of diffraction rings and the distance between them (declination angles from the direction of incident light) [2]. It would be an easy method if an additional phenomenon does not occur. Besides diffraction during the illumination of particles other phenomena such as: reflection, refraction, absorption and re-radiation occur.

The phenomena that happen on illuminated particles are called light scattering, shown on figure 2. In contrast to diffracted light, which is emitted at small angles relative to incident light, scattering is more complex because the scattered light is emitted in all directions. The spatial distribution of scattered light is commonly called the scattering pattern of a particle.

The scattering pattern depends on ratio of particle diameter (D) and the wave length of incident light (λ); accordingly, the scattering pattern will change not only with a change in the size of particles but also as result of a change in the wave length λ. Depending on the D/λ ratio it can be distinguished among the Fraunhofer, Mie and Rayleigh scattering.

The Fraunhofer scattering occurs if particle size is at least 5 to 6 times larger the λ. The Rayleigh scattering occurs when the particle size is considerably

smaller then λ (e.g. 10 times) while Mie scattering occurs if the D/λ ratio is around one. The ratio of light scattered forward and behind is considerably smaller in case of Mie then from Fraunhofer scattering, whereas in the Rayleigh scattering, the amount of scatte-

red light forward and backward is almost the same. Since detectors do not recognize light if it is diffracted or scattered as a result of another phenomenon, all these facts must be taken into account when analyzing a scattering pattern.
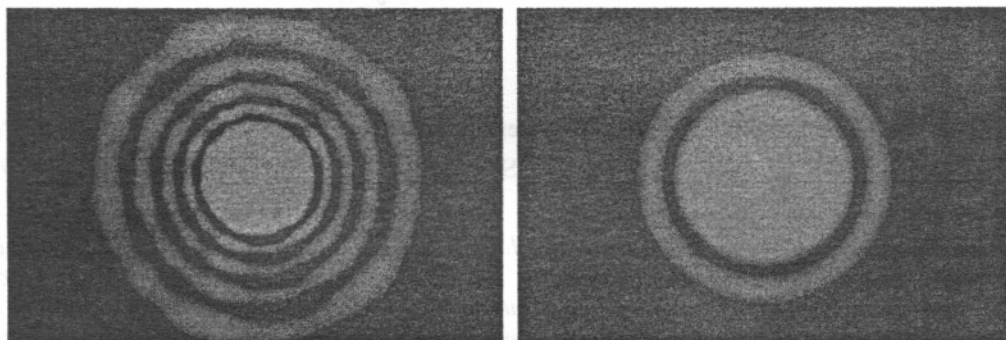

Figure 1 – Diffraction images from larger particle (left) compared to a smaller particle (right).

The solution to this problem is provided by Mie's theory or Mie's solution (1908). Its simplified form is presented in equation (1), where I is the scattered light intensity, E is the flux of the incident light per unit area, k and K are the constants, D is the diameter of the particles, J1 is the Bessel function of the first order, the first kind, θ is the scattering angle and m is the complex refractive index [1].

For the calculation of the scattering pattern intensities, there are three key physical parameters: particle diameter (D), the scattering angle (θ), which is measured on detectors, and the optical parameter (m) i.e. the complex index of refraction which contains a real and an imaginary part

Consequently, it is clear that if the optical parameters are unknown correct results based on theory

$$I(\theta) = E \{\underline{k^2 D^4 [J1]^2} \; \theta^\perp + [K_1 \; \theta]^l + [K_2 \; \theta]^3 + [K_3 \; \theta]^5 + \underline{k^4 D^6 (m-1)^2} \; \theta^6 / 8\pi\} \qquad (1)$$

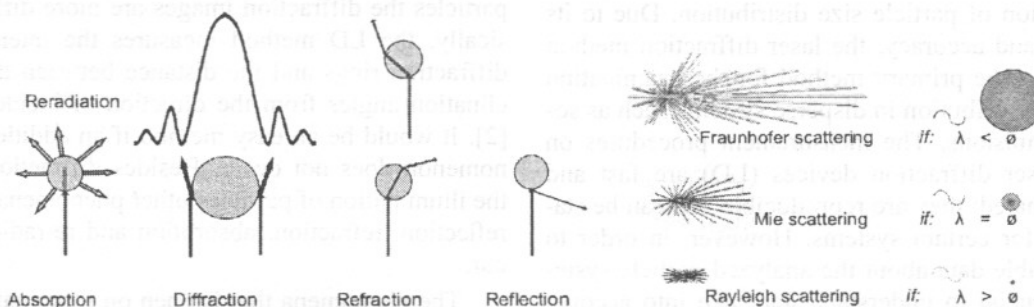<center>Fraunhofer term   Rayliegh term</center>

Figure 2 – The phenomenon occurs upon illumination of particle. The light scattering types depending on the ratio of the particle size to the wavelength of incident light.

can not be obtained. In Mie's solution only in Rayleigh term figures optical parameters so if this member of the equation is negligible it can be excluded from the account so that the optical parameters would not be needed for analysis. This is the case when the particles are very large, so that the scattering angles become small. This analysis is known as the Fraunhofer's analysis or approximation, as noted above, and it can be applied to particles where the ratio D/λ greater than 6. All smaller particles can be analyzed using full Mie's equation where is necessary knowing of optical parameters. In practice, the wavelength of

the light source devices range from 633 to 900 nm [1] so that only particles larger than 4.5 µm can be analyzed by Fraunhofer's approximation, and smaller by Mie's theory. For Malvern's device, Mastersizer 2000 critical size is about 3 µm [3].

Optical parameter m is expressed in the form of two terms, the real and imaginary. The real refractive index is often named as n, and imaginary as n_i. Both of the refraction indices depend on wavelength λ and temperature. The real refractive index (RI) of a substance is the ratio of the speed of light in the reference environment (which is usually a vacuum) and in the substance (the particle). For LD measuring parti-

cles must be dispersed in a fluid: either in the liquid (water, alcohol, etc.) or a gas (usually air). In this case, the reference environment is the medium in which particles are dispersed. On interface boundary, between particle and fluid, a change of direction of light at angle of refraction occurs. This angle is determined by Snell law. The imaginary refractive index (IRI) is a measure of the strength of absorption loss and it is also called the coefficient of attenuation (extinction)

k. In determining the size of submicron particles, both indices are important. On the basis of these, the software processes the recorded data in order to obtain more accurate results. By setting the optical parameters of the particle and environment, the operator sets the so-called optical model. The problem is that for most systems these optical parameters are not known, particularly for new materials, while in multiphase systems the situation is even more complicated.
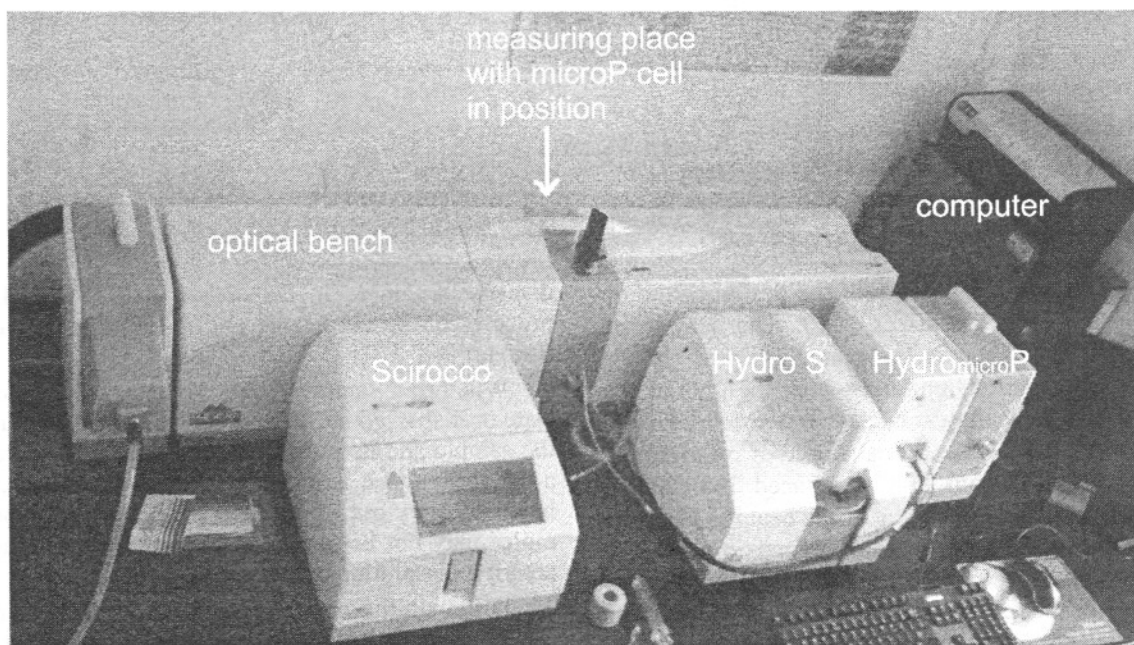

Figure 3 - Instrument for the LD analysis the Mastersizer 2000, Malvern Instruments, UK: an optical instrument and measuring cells Scirocco, HydroS and HydroμP.

Smaller particles scatters light of a lower intensity to larger angles, while the larger particles scattered light of the relatively stronger intensity toward smaller angles. Since the intensity of scattered light to the front decreases with decreasing particle size, thereby the sensitivity of the device is reduced and there is a limit of detection of particles below a certain size, for example at $\lambda = 750$ nm is 400 nm. However, current devices have a limit of detection to a few tens of nanometers (Malvern Mastersizer 2000, HORIBA Instruments The particle LA-950V2). This limit is far beyond the range of detection of the LD method. In order to make progress in this field it is necessary to include some other techniques are necessary that are complementary with the LD method, and they differ from manufacturer to manufacturer, though all of them are based on the same principle [1]. By adding the a detector for the light scattered sideways and backwards information is gathered on the relative intensity of the light scattered forward in other directions. On the basis of these data, it can be measured whether particles produce Rayleigh or Fraunhofer scattering. If the forward scattering is weaker, and the

back scattering is intense then it Rayleigh scattering occurs. Again, for a full analysis should be more information and additional sources of light are introduced in order to obtain the spectrum of light scattering of other wavelengths to be simultaneously analyzed. However, different spectra are obtained from the light of the same λ, which is differently polarized; accordingly filters are introduced to separate the light polarized horizontally and vertically. When particles of 450 nm are illuminated by a light source of 633 nm wavelength, the Rayleigh scattering will be produced. If particles are illuminated by the light of 450 nm λ, Mie's scattering will occur.

Figure 3 shows the Mastersizer 2000 instrument which makes part of the equipment in our laboratory. The system for the LD analysis consists of an optical instrument, the sample dispersion units HydroS, HydroμP, Scirocco and a computer with an appropriate software package. The dispersion unit Hydro is used for dispersing particles in liquids, while the unit Scirocco is used for dispersing dry particles in air. An optical instrument is coupled with these units and the computer.
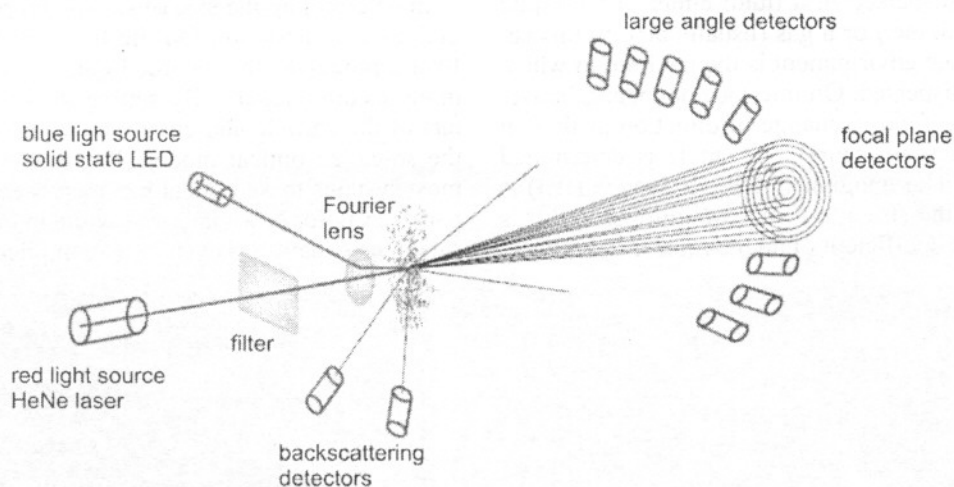
Figure 4 – Sketch of the LD instrument parts.

Figure 4 gives a scheme of the design of the optical instrument Mastersizer 2000. The sample particles dispersed in a suitable medium pass through the focused beam of light and scatter the light at characteristic spatial angles. Mastersizer 2000 uses two light sources: HeNe laser is a source of red light of a wavelength of 633 nm, and it is placed in the axis of the instrument. The diameter of the beam is 0.63 mm, the divergence is 1.5 mrad, and the maximum optical power of laser is 4 mW. The second light source, which is not in the axis, is the LED that emits blue light of a wavelength of 455 nm.

In addition to the conventional detector for small angles in the form of concentric rings located in front of the measuring zone in the axis of the device, there are additional side detectors for the light scattered at angles smaller than 90° and detectors for the light scattered at angles greater than 90°, to cover the range of measurement from 0.01 to 135°. The Fourier lens is placed behind the measuring zone, in contrast to the classical geometry of such devices, where the lens is in front of the measuring zone. This detection range has been extended to larger angles, which is essential for the accurate measurement of the scattering of submicron particles. The particle size range that can be measured by the instrument is from 0.02 to 2000 microns. The filter shown in Figure 4 is used to separate vertically and horizontally polarized light.

3. SAMPLE PREPARATION AND MEASUREMENT

The scheme 1 shows the preparation flow of an unknown sample. The preparation of the sample before placing it into the measuring system is essential for accurate results. More than half of the problems encountered in measurements of different samples are due to poor preparation. When the optimal way to disperse a sample in dispersion units is found, the process can be automated and measurements can be compared.

Whether a sample would be analyzed in the dry state or dispersed in a liquid depends on the nature of the sample and its purpose. If the product is stored in a dry form and it is in a dry form that it is used, it is better to carry out its analysis in that state. Some samples may not be dispersed in liquids due to the reactivity, dissolution or swelling.

Dispersibility of particles in liquids can be increased by adding surfactants and additives to neutralize the charge on the particle surface. These substances are added in minute amounts on the order of a drop per liter of dispersant. Large amounts may lead to the formation of bubbles in the system. The most commonly used surfactants are: Igepal, Teepol, Synperonic N, which are not ionic, Aerosol OT, sodium dodecilsulfat – anionic, and Hyamine 2389 – cationic. Common additives used for this purpose are sodium hexametaphosphate (kalgon), sodium pyrophosphate, sodium phosphate, ammonia, sodium oxalate, calcium chloride, and others [3].
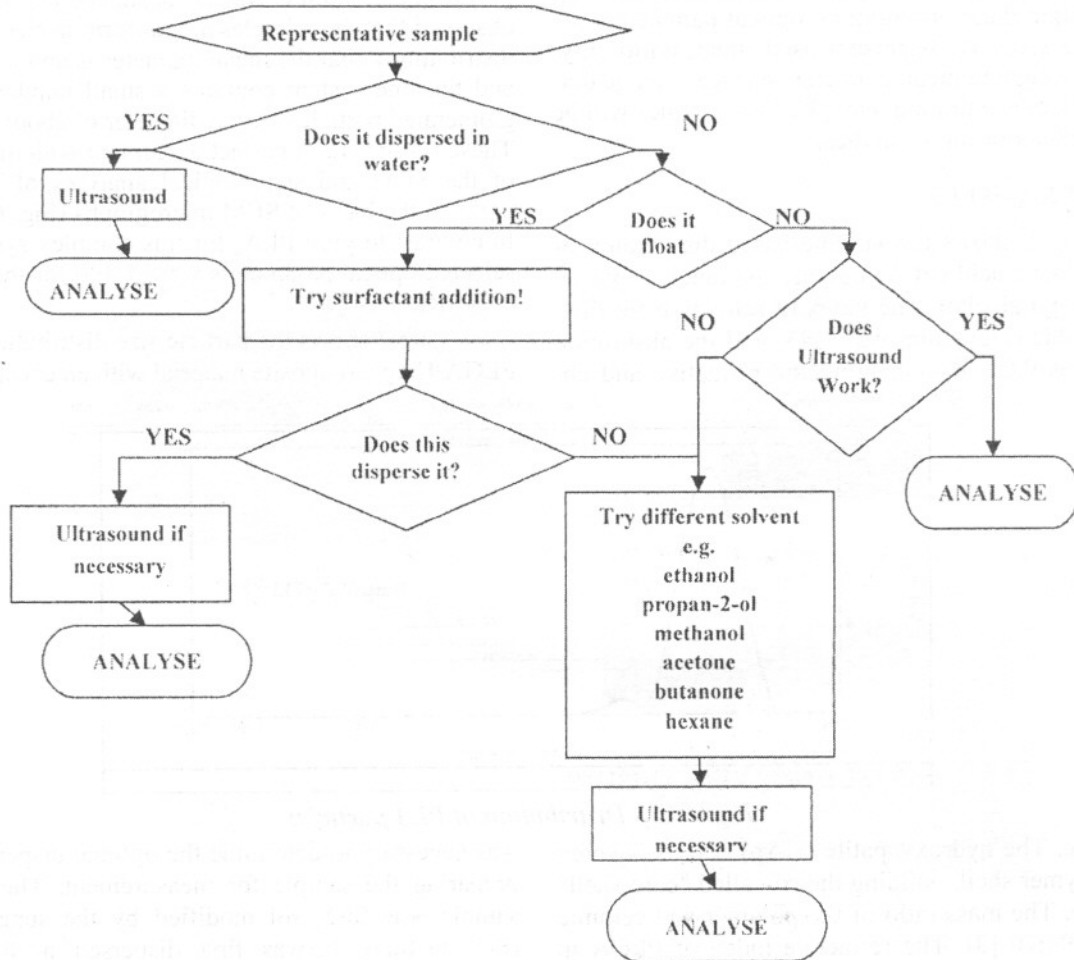
Three steps can be distinguished in sample measuring:

- The prepared and dispersed sample in an appropriate concentration is entered into the measuring zone of the instrument. The dispersion units are meant to serve this purpose. If the sample is unrepresentative or poorly dispersed, the basic measurements will not be accurate and, accordingly, any further analysis will not yield correct results.
- The function of an optical instrument is to record the spectrum of the light scattered from the prepared sample, i.e. the measurement. As already mentioned, a part of the instrument includes a series of individual detectors. Each collects scattered light of a certain angle. One recording co-

llected on the detectors shows the spectrum of light scattered when particles pass through the laser beam over a period of time. One shot would not be sufficient to show a representative reading. To overcome this problem, during each measurment, the instrument registers about 2000 shots,

one shot every millisecond, which is averaged to the final result.

Mie's theory assumes that the particles are perfect spheres. In practice this is usually not the case, making it difficult to determine the particle size. One of

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                    Representative sample
                            |
                            v
  YES              Does it dispersed in              NO
 +------           water?           ----------------+
 |                                                  |
 v                                                  v
Ultrasound                          YES      Does it        NO
 |               +----------------- float ----------+
 v               v                                  |
ANALYSE      Try surfactant addition!               |        Does          YES
                 |                          NO     Ultrasound --------+
                 v                                  Work?             |
  YES         Does this          NO                                  v
 +----------- disperse it? --------+                              ANALYSE
 |                                 |
 v                                 v
Ultrasound if              Try different solvent
necessary                        e.g.
 |                             ethanol
 v                            propan-2-ol
ANALYSE                        methanol
                               acetone
                               butanone
                                hexane
                                  |
                                  v
                             Ultrasound if
                              necessary
                                  |
                                  v
                              ANALYSE
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Scheme 1 - The proper preparation of the wet dispersion for measurement [3, 4].

the methods to achieve more accurate calculations of the particle size from the approximated results of the measurements is to compare them with the characteristic sizes of irregular particles [5, 6].

- When the measurement is complete, raw data are software analyzed using defined optical parameters or the Fraunhofer approximation. The laser diffraction method is suitable for use because the data collected by measuring can be software processed again by changing optical parameters.

To understand how to display the data, it is necessary to define the basic values that exist in the output data. Basically, the distribution statistics are expressed in derived diameters D [m, n]. The expression for calculating the diameter of the secondary and ot-

her moments of the particle size distribution is given in equation (2):

$$D[m,n] = \left[\frac{\sum V_i d_i^{m-3}}{\sum V_i d_i^{n-3}} \right]^{\frac{1}{m-n}}$$

(2)

The diameters of the particle D (v, 0.5), D (v, 0.1) and D (v, 0.9) are the standard data shown in the reports of the LD measurements, are marked as d (0.1), d (0.5) and d (0.9). D (v, 0.5) is the Mass Median Diameter of the volume of distribution (marked by a lowercase v). It is expressed in microns, and it indicates that 50% of the sample has a size smaller than that value, whereas 50% have a larger size. D (v, 0.1) indicates that 10% of the sample mass are particles in

sizes smaller than that value, while D (v, 0.9) indicates that 90% are smaller and 10% are larger than that value. Instead of the letter v, the letter s may stand for the distribution of surfaces; the letter l for the length of particles and the letter n for the numerical distribution of particles.

The result analysis report includes the following basic output data: obscuration, optical parameters used in the analysis, dispersant used, span, uniformity, volume-weighted mean diameter, surface average diameter, fit, concentration, etc. [3]. These values will be discussed in our future studies.

4. THE EXAMPLES

Figure 5 shows the volume-based distribution of the polylactic acid (PLA) polymer particles dispersed in isopropyl alcohol. The index of refraction for PLA used in this calculation was 1.43, and the absorption index was 0.01. By changing the refractive and ab-

sorption indices, the measurement results were drastically changed; in order to establish a proper optical model for this system, additional characterization methods were required.

Figure 6 (a) shows the distribution of the poly (lactic-co-glycolic acid) (PLGA) polymer spheres into which vitamin C was encapsulated [7]. It may be observed that the particles are uniform in size (narrow distribution), that the mean diameter is about 200 nm, and that the system contains a small number of agglomerated particles with a diameter of about 550 nm. These results are in perfect agreement with the results of the SEM and stereological analyses of the data done on the basis of SEM micrographs (Fig. 6 (b, c)). In contrast to pure PLA, for this complex system the selected optical parameters were 1.400 for the RI and 0 for IRI.

Figure 7 shows the particle size distribution of the PLGA/HAp composite material with an encapsulated

| d(0.1): | 0.066 | um | d(0.5): | 0.129 | um | d(0.9): | 0.259 | um |

Figure 5 - Distribution of PLA particles.

antibiotic. The hydroxyapatite (HAp) core is covered by a polymer shell, building the so-called "core-shell" structure. The mass ratio of the polymer and ceramic parts is 90:10 [8]. The refractive index of PLGA in this case is 1.40, and the absorption index is 0.001. The measurement was carried out immediately after the dispersion had been obtained by the precipitation of the polymer prior to stabilization. For the measurement, a mixture consisting mainly of water was used as the dispersant.

In these systems, problems may arise while measuring a dispersion of polymer particles because of their instability and tendency to swell and bind after several minutes. The formed agglomerates are iregular in shape and dimensions, which are several orders of magnitude larger than those of the primary particles. To overcome this problem it is necessary to find appropriate dispersant media.

Proper selection of dispersants – The LD method enables to determine the size distribution of the unmodified and modified silica (SiO$_2$) particles. The modification is done using three different methods: conventional, NC and SC sol–gel method [9–11]. It

was necessary to determine the optimal dispersant for preparing the sample for measurement. The chosen sample was SiO$_2$ sol modified by the supercritical (SC) method. It was first dispersed in the most commonly used medium – ethanol. The calculated median diameter of particles d(0.5) was 704 nm. That value was not in accordance with the previously recorded SEM micrographs, from which it was established that particles were smaller than 100 nm. In a second step, isopropyl alcohol was used as a dispersant and the calculated value of d(0.5) was 660 nm. When methanol was used as a dispersant, d(0.5) was 63 nm, which was consistent with the results obtained by using the previous characterization method. A comparative review of the particle size distribution of SiO$_2$ sol modified by the SC method, dispersed during the preparation for the measurement in ethanol, isopropyl alcohol and methanol, is shown in fig. 8. Based on the results, it was decided that all of the silane modified SiO$_2$ samples should be dispersed in methanol. The presented examples clearly illustrate the importance of choosing a proper dispersant during the preparation of the samples for measurement
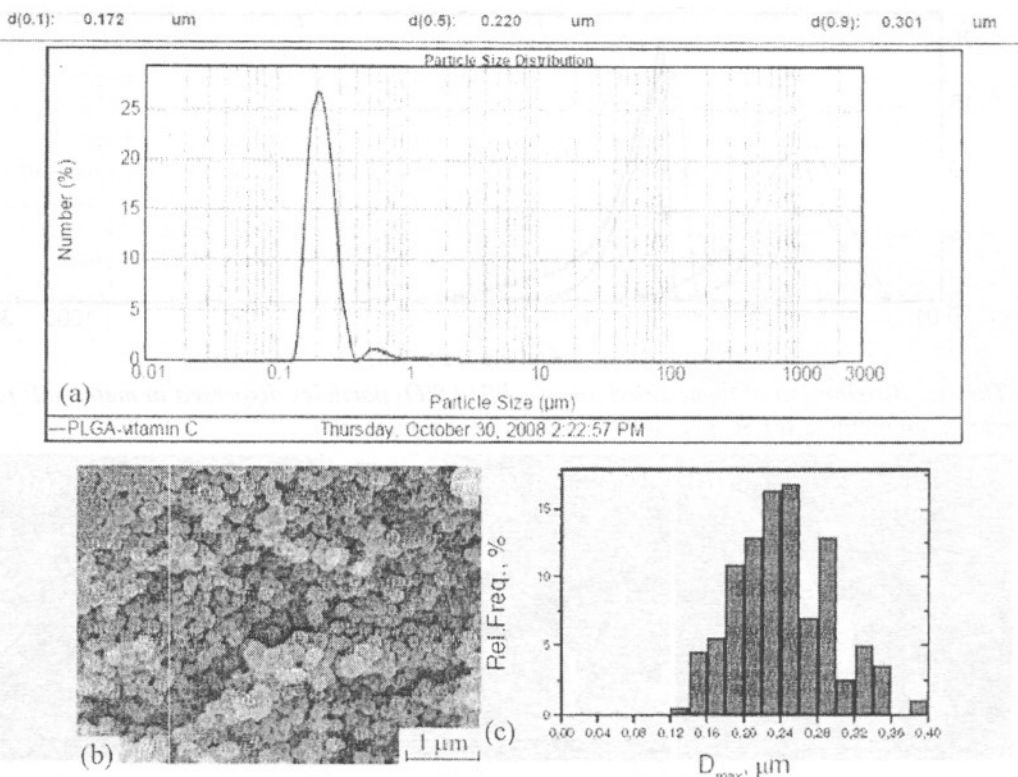
d(0.1): 0.172 um   d(0.5): 0.220 um   d(0.9): 0.301 um

Figure 6 - (a) The PSD of PLGA/vitamin C spheres, (b) SEM micrographs and (c) stereological analysis.

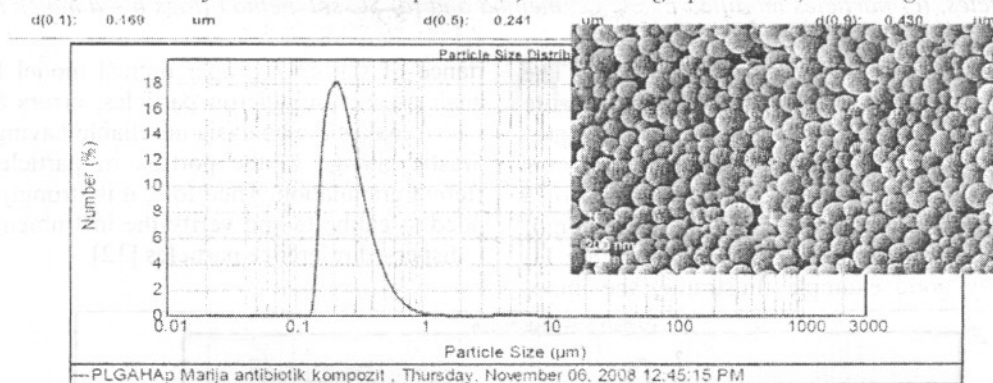d(0.1): 0.169 um   d(0.5): 0.241 um   d(0.9): 0.430 um

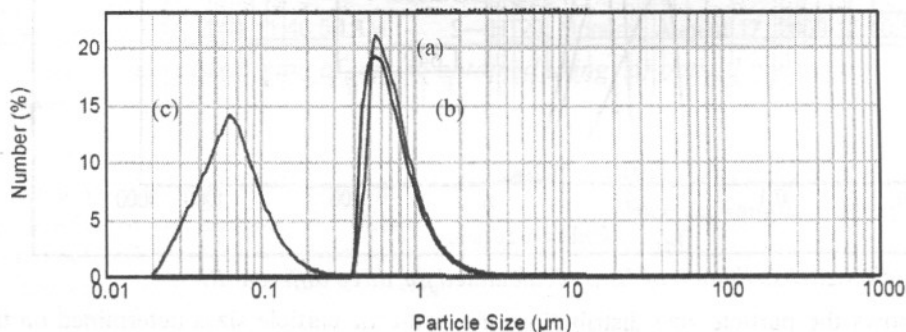Figure 7 - Distribution of the particle sizes of the PLGA/HAp composite with an antibiotic

Figure 8 – The size distribution of SiO₂ modified by the SC sol method, dispersed during the preparation in: (a) ethanol, (b) isopropyl alcohol and (c) methanol.

A comparison of the median particle size of the SiO₂ samples (unmodified and modified) dispersed in methanol (fig. 9) obtained by the LD method and the SEM micrographs (fig. 10) shows that the LD measurement was performed under optimal conditions.
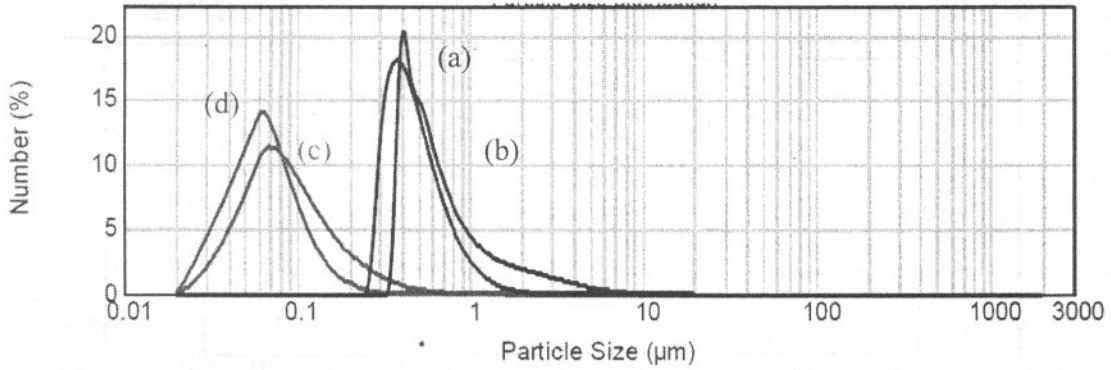
Figure 9 – The size distribution of unmodified and modified SiO₂ particles dispersed in methanol: (a) SiO₂, (b) conventional method, (c) SC gel method and (d) SC sol method.
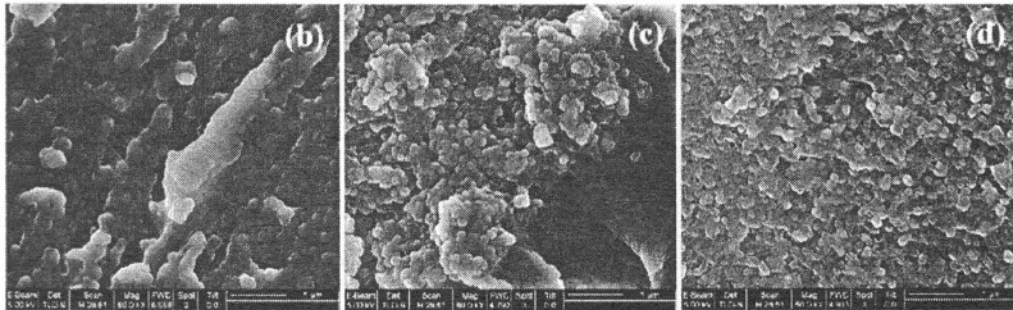

Figure 10 - SEM micrograph of the PMMA composite material comprising: (b) conventional modified nanoparticles, (c) particles modified by SC gel method and (d) SC sol method (tags b – d match marks from Figure 9).

Proper selection of the refractive index (RI) – The LD analysis was performed on the hydroxy apatite (HAp) particles synthesized by the chemical precipitation method. For HAp, the index of refraction is around 1.649. A change in the refractive index of a sample leads to different results, even in the region of the Fraunhofer diffraction, as it is shown in figure 11. This is a very good example illustrating the impo-rtance of setting a proper optical model for the LD analysis. For submicron particles, errors are greater, which makes the analysis unreliable having in mind a drastic change in the portion of particles with different granulation. Therefore, it is strongly recommended to calibrate and verify the instrument with poly – dispersed reference particles [12].
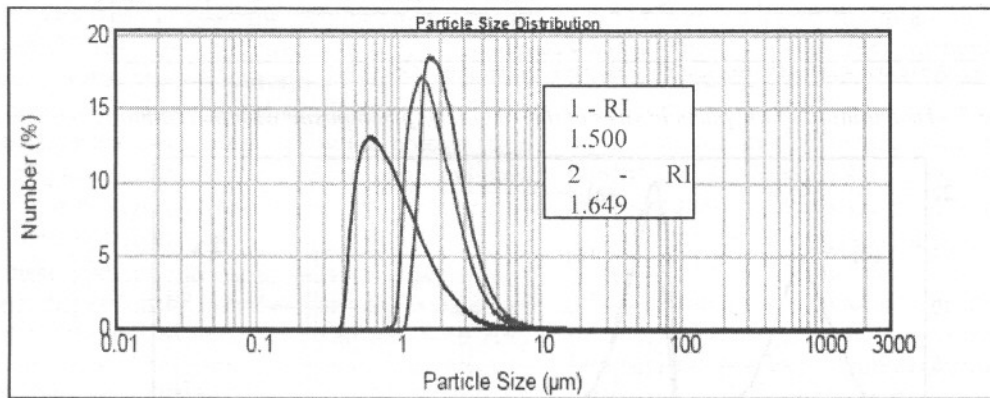

Figure 11 – Particle size distribution of HAp recalculated for three different RI

Figure 12 shows the particle size distribution of HAp synthesized by hydrothermal processing; in this case, the optical model was set to a refractive index of 1.649 and an absorption index equal to zero. The particle surface was modified with oleic acid; the dispersion medium was non-polar solvent n-heptane. The results of the LD method were in accordance with the particle sizes determined on the basis of the FE-SEM micrographs. According to the results, the volume based distribution d(0.5) was 134 nm and the number-based distribution 62 nm.

In the systems where the Fraunhofer approxima- tion can be used, the distribution of particle sizes can be determined without the exact knowledge of the

optical parameters. Fig. 13 shows the distribution of the bulk $LiFePO_4$ particles for which the refractive index is 1.6 and absorption index 0.02. Using the Fraunhofer approximation the significant portion of submicron particles occurs in sample where there are no. From the SEM images it can be clearly seen that the largest dimension of these is about 10 μm (the longest diagonal of the particles) and the smallest is about 3 μm; no submicron particles are present. These particles were synthesized by a hydrothermal treatment of the precipitates in the presence of PVP.
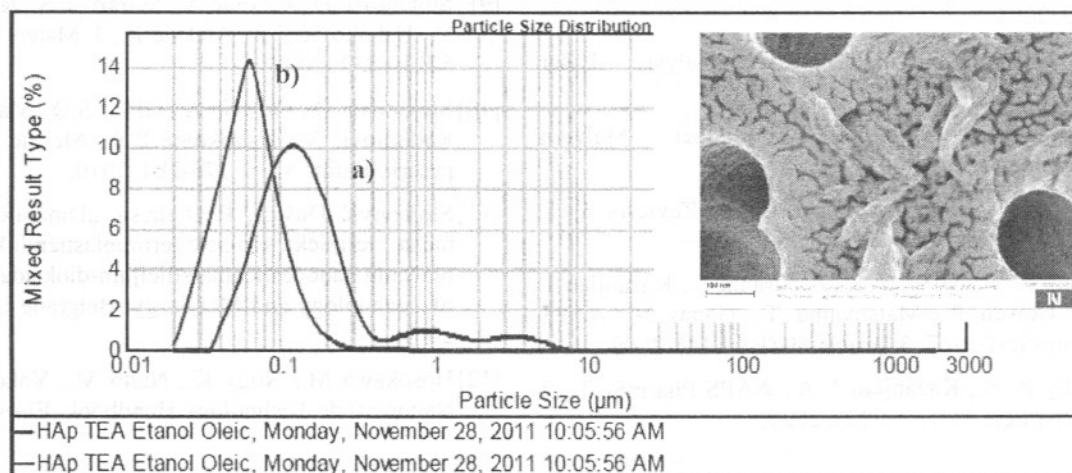

Figure 12 – Distributions of HAp nanoparticles modified with oleic acid dispersed in heptane: a) volume based and b) number based distribution.
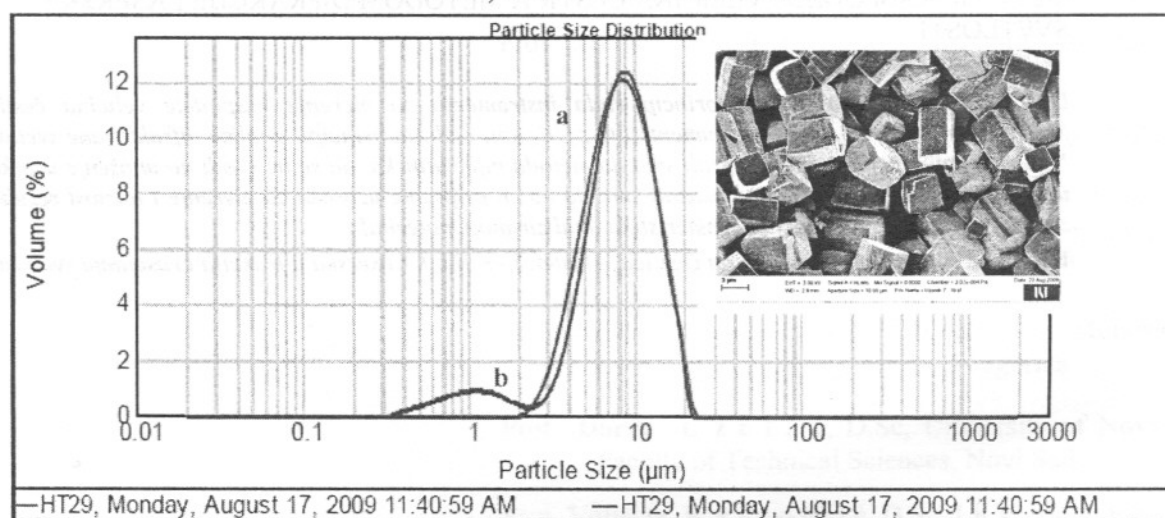

Figure 13 - Particle size distribution of olivine obtained using: a) optical parameters and b) Fraunhofer's approximation.

CONCLUSION

This paper explains the theoretical bases and basic operation principles of the instrument – Mastersizer 2000, manufactured by Malvern Instruments Ltd. – for laser diffraction measuring and particle size distribution analysis. We have used several examples to demonstrate that the method is not a routine one and that it largely depends on the sample preparation method and the understanding of basic physical and chemical characteristics of the sample (optical properties, surface properties, phase composition, solubility, reactivity etc.). Appropriate preparing and measuring conditions, accompanied with a proper optical model for a specific sample lead to the standardization of the method.

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REZIME

MERENJE RASPODELE VELICINA CESTICA METODOM DIFRAKCIJE LASERSKE SVETLOSTI

U ovom tekstu objašnjen je princip rada instrumenta za merenje raspodele veličina čestiica Mastersizer 2000, Malvern Instruments Ltd., UK, koji radi na principu analize difraktovane svetlosti. Na konkretnim primerima, pokazali smo da metoda nije rutinska, da se ne svodi na unošenje uzorka u uređaj i pritiskanje dugmeta. Pokazali smo da način pripreme uzoraka za merenje i tačnost rezultata zavise od fizičkih i hemijskih karakteristika analiziranog materijala.

Ključne reči: *Raspodela veličina čestiica, Mastersizer 2000, Laserska difrakcija i rasejanje svetlosti.*