

Protocol

Particle size distribution by laser diffraction (Malvern Master Sizer)

1. Method

The technique of laser diffraction is based on the principle that particles passing through a laser beam will scatter light at an angle that is directly related to their size: large particles scatter at low angles, whereas small particles scatter at high angles. The laser diffraction is accurately described by the Fraunhofer Approximation and the Mie theory, with the assumption of spherical particle morphology. The measurable size ranges from 50 [nm] to 1000 [μm]. Concentrated suspensions, on the order of 1.0 [wt%], are prepared, using suitable wetting and/or dispersing agents. A small ultrasonic treatment is sometimes useful in breaking up loosely-held agglomerates. A few [mL] of suspension are required to carry out the measurements. This method is very attractive because only a few minutes are required for the sample analysis. Suspensions are mostly prepared with water, but other solvents can also be used (ethanol, isopropanol, or octane). It is possible to carry out the measurement on dry powders by adapting a specific equipment. The limitations of this method appear for small sizes (< 1 [μm], Mie theory), for non-spherical particles, and for materials with a low refractive index with respect to the dispersive medium.

2. Equipment

- Instrument: Malvern MasterSizer (more info from <http://www.malvern.com>);
- Hydro SM small volume sample dispersion unit;
- Analytical balance (precision 0.1 [mg]);
- Spatula for powder samples; plastic pipette for liquid samples;
- Brand new polystyrene vessel of 50 [ml] volume with lid (external diameter 35 [mm], height 70 [mm], for instance Semadeni reference 2278);
- Stirring rod (26 \times 6 [mm]);
- Magnetic stirrer;
- Ultrasonication bath: Wisag, 5 [min], 150-300 [W];
- Horn for ultrasonic treatment: Telsonic Ultrasonics, model DG-100, 15 [min], 150 [W];
- Plastic pipette of 3 [ml]

3. Preparations of the samples

(a) General recommendations

- Depending on the aim of the measurement, either measuring the sample in its best state of dispersion or under conditions as close as possible to the application (i.e. slurry with specific dispersant), the preparation of the dispersion will be different. In the present document we will focus on and provide recommendations for the first scenario;
- Samples of α -alumina (300 [nm]) are prepared by dispersing 10 [mg] of powder in 20 [mL] of diluted acid (HNO_3 0.01 [M]);
- Several ceramics with sizes < 1 [μm] (ZrO_2 , Fe_2O_3 , BaTiO_3 , TiO_2 , ZnO ...) are well dispersed using a solution of PAA 0.01 [wt%] ($R = \text{NH}_3/\text{PAA} = 1.5$), at a concentration of 1 [wt%] (0.40 [g] of powder in 40 [mL] of PAA 0.01 [wt%]);
- Cements often present sizes in the micrometric range, with a broad size distribution. They can also be dispersed using a solution of PAA 0.01 [wt%] ($R = \text{NH}_3/\text{PAA} = 1.5$), at a

concentration of 1 [wt%] (0.40 [g] of powder in 40 [mL] of PAA 0.01 [wt%]), or in isopropanol;

- With the first dispersion, carry out 3 repetitions in order to verify the colloidal stability of the suspension against time. Once a stable dispersion has been achieved: prepare 3 dispersions and perform 3 repetitions with each dispersion if it is reasonable with respect to the measurement time;
- If you characterise well-known single samples, prepare 2 dispersions and repeat 3 times the measurement for each;
- If you characterise a series of similar samples, prepare 1 dispersion per sample and perform 1 or 2 repetitions.

(b) Example of preparation: BaTiO₃, mean particle size 200 nm

- Weigh the empty plastic vessel, with a precision of 10 [mg]; carefully write down the result W_T [g].
- Weigh 0.40 [g] of BaTiO₃ powder with precision 10 [mg]. Write down the result W_P [g]. Add PAA solution (mol. Wt 2000, R=1.5) of 0.1 [wt%] into the vessel until the total mass of suspension is 40 [g]. Weigh with precision 10 [mg]. Write down the result W_{sol} [g].
- Insert the stirring rod into the suspension and close the vessel with the lid. Stir with medium speed.
- Remove the lid and place the vessel on the magnetic stirrer. Stir with medium speed. Insert the ultrasonication horn into the vessel and adjust at about 1 [cm] of the bottom of vessel.
- Apply sonication for 15 [min]
- Cool down the suspension in a water bath under stirring continuously until temperature of 25 [°C] has been reached

4. Operation of Malvern

- Switch on the instrument 1 hour before starting the measurement
- Clean the dispersion unit three times with ultra pure water, by increasing the stirring speed to 3500 several times
- Start the software Mastersizer-S
- Select “File”, then “Open sample file and record”. Select your Directory, and fill Filename: XXX.SAM, to create a folder in which all the measurements will be saved
- Select “Set up”, then “Analysis”
 - o Choose “Polydisperse” for the Analysis model
 - o Choose an active beam length of 2.4 [mm] for standard cell
 - o Fill the particle density of your material

<i>Example</i>	SiO₂	γ-alumina	BaTiO₃
Density (g/cm ³)	2.2	3.6	5.8

- Select “Set up”, then “Presentation”
 - o For an existing suspension, select the corresponding Code, and click on “Load”

<i>Example</i>	SiO₂	γ-alumina	BaTiO₃
Code	3NDD	3_RHD	3_TFD

- For a new sample, select “Request” in the “Custom” window
Choose an existing sample, or add a new sample, by giving a new Name, and its refractive index (Real and Imaginary numbers)
Choose an existing dispersant, or add a new dispersant, by giving a new Name, and its refractive index
Click on “Select”, then “Load”, and close the window
- Select “Measure”, then “Start sequence”
 - Introduce data in the fields Sample Name, and Notes
 - Increase the stirring speed of the dispersion unit to 1800. Check that there are no air bubbles
 - Click on OK
 - Start the Alignment by pressing the space bar
 - Check that the laser power is at least 72 [%]
 - Start the Blank by pressing the space bar 2 times
 - When it’s done, add the sample in the dispersion unit with a plastic pipette, until the absorbance is in the range 12 – 16 [%] (green range)
 - Start the Measurement by pressing the space bar 2 times
 - When it’s done, press the space bar to see the result
- If a new measurement has to be done on the same sample (repeatability), select “Measure”, then “Start sequence”
 - Click “Next” twice, to skip the Alignment and the Blank
 - Start the Measurement by pressing the space bar 2 times
 - When it’s done, press the space bar to see the result
- For a new measurement, clean the dispersion unit three times with ultra pure water, by increasing the stirring speed to 3000 several times, and repeat the sequence as described above
- If no new measurement is to be carried out:
 - Clean the dispersion unit three times with ultra pure water, by increasing the stirring speed to 3000 several times. Leave the dispersion unit full of ultra pure water.
 - Switch off the equipment

5. Presentation of the results, data storage and data treatment

Print the results

- Go to the FILE menu, select “Open sample file and record”, and choose the measurement of interest. Then, with a right click on the graph, it is possible
 - to adjust the graphic scale
 - to get only the measurement of interest by selecting “Current”
 - the size distribution is given by selecting Frequency, the cumulative distribution is obtained by selecting Oversize
- Go to the FILE menu and select PRINT, then select “Report” and OK.

- Go to FILE/Printer setup, and choose PdfCreator. Then go again to the FILE menu and select PRINT, then select "Report" and OK. Save as [Powder-Lotn°-Malvern-Experimentn°-Operator.pdf](#).

Export the results

- Go to the EDIT menu,
 - o select COPY, then SIZES. Open an Excel sheet, and copy it in column A.
 - o select COPY, then RESULT. Copy it in column B in the Excel sheet.
- Save this Excel sheet as [Powder-Lotn°-Malvern-Experimentn°-Operator.xls](#).

Data storage

- Copy the Excel sheet, and the PDF report.
- Go to \\Ltpc40\powderfiles. Copy the folder *Powderfiles*. Paste it in your project folder, and change its name into [Powder-Lotn°](#).
- Paste the XLS and PDF files respectively in the folders [Project/Powder-Lotn°/Malvern/Data](#) and [PDF](#).

Data treatment

- Go to \\Ltpc40\powderfiles. In the folder [Project/Powder-Lotn°](#), open the Excel sheet "Powdersheet.xls"
- Click on the *Malvern* button, and follow the instructions given in the Excel sheet.