

Protocol

Particle size distribution by Photon Correlation Spectroscopy (PCS)

1. Method

The instrument measures the fluctuations in light intensity due to the Brownian motion of the particles in order to deduce the particle size. The measurable size ranges from 2-3 [nm] to 500 [nm] – 1 micrometer. Dilute suspensions, on the order of 0.0001 to 1.0 [%] v/v 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. Just a few minutes are required for the sample and cell to equilibrate with the actively controlled temperature environment inside the instrument. Please note that avoiding dust is essential to carry out these measurements. It is often necessary to filter¹ the solution of dispersant used for preparing the various dilutions and to wash all vessels in order to avoid the presence of dust. This is particularly important for particles with sizes below 50 [nm].

2. General recommendations for particle size distribution measurement

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.

(a) Recommended Concentrations

The amount of powder to disperse in a given volume of an aqueous solution (with dispersant) should be the same whatever the nature of the powder if plenty of sample is available. We recommend preparing 10 [g] of a concentrated suspension containing 250 [mg] of particles and applying a 15 [min] sonication treatment in order to ensure optimum dispersion. Then depending on the sample characteristics and the signal intensity this suspension will be diluted from 10 times to 1000 times for performing the PCS measurements.

If less than 250 [mg] of powder is available, a solution of 25 [mg] of powder per [g] should be prepared and dispersed using an ultrasonic bath for 5 [min]. Then depending on the sample characteristics and the signal intensity this suspension will be diluted from 10 times to 1000 times for performing the PCS measurements. If the result of the measurements shows the presence of agglomerates², then the PCS is probably not a suitable method and another instrument should be used instead.

(b) Samples

a. Unknown samples

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 this is reasonable regarding the measurement time.

b. Single samples

To characterise well-known single samples, prepare 2 dispersions and repeat 3 times the measurement for each sample.

¹ 20 nm filters, for example Whatmann Anopore

² Multi-modal distributions with significant differences in modal sizes (bigger than a factor of two)

c. Sample series

To characterise a series of similar samples, prepare 1 dispersion per sample and perform 1 or 2 repetitions.

3. Equipment

- Measurement device: Brookhaven BI-9000AT (more info from <http://www.bic.com>);
- Brand new polystyrene vessel of 50 [ml] volume with lid (external diameter 35 [mm], height 70 [mm], for instance Semadeni reference 2278);
- Spatula for powder samples, plastic pipette for liquid samples;
- Stirring rod (26×6 [mm]);
- Disposable, acrylic square cells are used for aqueous and simple alcohol suspensions;
- Glassround cells with reusable Teflon stoppers are used for aggressive solvent suspensions;
- Ultrasonication horn: Telsonic Ultrasonics, model DG-100, 15 [min] , 150 [W];
- Ultrasonication bath: Wisag, 5 [min], 150-300 [W];
- Magnetic stirrer
- Analytical balance (precision 0.1 [mg]);
- Micropipette of 100 [μL], 1000 [μL] and 10 [ml] for preparing dilutions of concentrated samples.

4. Protocol

Preparation of samples

The ideal concentration range for the measurement is 0.1-10 [mg]/[g]. The suspension should be translucent.

(a) Powders

Alumina

If at least 250 [mg] of powder are available, 10 [g] of concentrated suspension should be prepared to avoid statistical sampling errors:

- Weigh the empty plastic vessel, with a precision of 0.1 [mg]; carefully write down the result W_T [g].
- Weigh 250 [mg] of alumina powder with precision 0.1 [mg]. Write down the result W_P [g]. Add PAA solution (mol. Wt 2000, $R=NH_3/AA=1.5$) of 0.1 [wt%] into the vessel until the total mass of suspension is 10 [g]. Weight with precision 0.1 [mg]. Write down the result W_{sol} [g].
- Insert the stirring rod into the suspension and close the vessel with the lid. Shake well.
- Remove the lid and place the vessel into a water bath with ice cubes placed 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].
- Place the vessel onto a magnetic stirrer.

If less than 250 [mg] of powder are available, prepare a concentrated suspension with 25 [mg] of powder per [g] of solution – below is the example with 1 [g] of suspension, if using larger or smaller quantities, please apply the adequate ratio:

- Weigh the empty plastic vessel, with a precision of 0.1 [mg]; carefully write down the result W_T [g].
- Weigh 25 [mg] of alumina powder with precision 0.1 [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 1 [g]. Weigh with precision 0.1 [mg]. Write down the result W_{sol} [g].
- Insert the stirring rod into the suspension and close the vessel with the lid. Shake well.
- Place the vessel into the ultrasonic bath so that the suspension is immersed in the bath.
- Apply sonication for 5 [min].
- Place the vessel onto a magnetic stirrer.

Once the concentrated suspension has been prepared, dilutions need to be carried out in order to perform the characterisation, start with lowest dilution and increase the dilution if the number of counts measured by the instrument is higher than 500 kcps:

Dilution about 10 times (2.5 [mg]/[g]):

- Use a new disposable acrylic square cell
- Use a 1000 [μ L] pipette with a new tip, pump 150 [μ L] of concentrated suspension (25 [mg]/[g]) and transfer into the cell
- Use a 10 [ml] pipette with a clean tip, pump 1.5 [mL] of ultrapure water and transfer into the cell
- Immerse the portion of the cell containing the suspension in the ultrasonic bath and apply sonication for 30 [sec]. The cell is ready for the measurement (see Operations below).

Dilution about 100 times (0.25 [mg]/[g]):

- Use a new disposable acrylic square cell
- Use a 100 [μ L] pipette with a new tip, pump 15 [μ L] of concentrated suspension (25 [mg]/[g]) and transfer into the cell
- Use a 10 [ml] pipette with a clean tip, pump 1.5 [mL] of ultrapure water and transfer into the cell
- Immerse the portion of the cell containing the suspension in the ultrasonic bath and apply sonication for 30 [sec]. The cell is ready for the measurement (see Operations below).

Dilution about 1000 times (0.025 [mg]/[g]):

- Use a new disposable acrylic square cell
- Use a 10 [μ L] pipette with a new tip, pump 1.5 [μ L] of concentrated suspension (25 [mg]/[g]) and transfer into the cell
- Use a 10 [ml] pipette with a clean tip, pump 1.5 [mL] of ultrapure water and transfer into the cell
- Immerse the portion of the cell containing the suspension in the ultrasonic bath and apply sonication for 30 [sec]. The cell is ready for the measurement (see Operations below).

Barium titanate

The protocol is the same as above for the alumina.

(b) Suspensions

Silica

To prepare 10 [g] of a diluted suspension with a concentration of 25 [mg]/[g] (corresponds to 2.5 [wt%]) from the supplied suspension of 30 [wt%] (corresponds to 300 [mg]/[g]), it is necessary to dilute by a factor $f = 30/2.5 = 12$.

- Weigh the empty plastic vessel, with a precision of 0.1 [mg]; carefully write down the result W_T [g].
- Shake well the container containing the concentrated silica suspension and add 0.833 ± 0.0 [g] ($=10/f$) of suspension to the plastic vessel. Add ultrapure water to the container such that the total mass of diluted suspension is 10 [g]. Weigh with precision 0.1 [mg]. Write down the results $W_{conc.sol}$ [g] and W_{sol} [g].
- Insert the stirring rod into the suspension and close the vessel with the lid. Shake well.
- Remove the lid and place the vessel into a water bath with ice cubes placed 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 5 [min].
- Place the vessel onto a magnetic stirrer.

Once the concentrated dilution has been prepared, further dilutions need to be carried out in order to perform the characterisation, start with lowest dilution and increase the dilution if the number of counts measured by the instrument is higher than the range 100-2000:

Dilution about 50 times (0.50 [mg]/[g]):

- Use a new disposable acrylic square cell
- Use a 100 [μ L] pipette with a new tip, pump 30 [μ L] of concentrated suspension (25 [mg]/[g]) and transfer into the cell
- Use a 10 [ml] pipette with a clean tip, pump 1.5 [mL] of ultrapure water and transfer into the cell
- Immerse the portion of the cell containing the suspension in the ultrasonic bath and apply sonication for 30 [sec]. The cell is ready for the measurement (see Operations below).

Dilution about 100 times (0.25 [mg]/[g]):

- Use a new disposable acrylic square cell
- Use a 100 [μ L] pipette with a new tip, pump 15 [μ L] of concentrated suspension (25 [mg]/[g]) and transfer into the cell
- Use a 10 [ml] pipette with a clean tip, pump 1.5 [mL] of ultrapure water and transfer into the cell
- Immerse the portion of the cell containing the suspension in the ultrasonic bath and apply sonication for 30 [sec]. The cell is ready for the measurement (see Operations below).

Operations

- Switch on the instrument (using the main switch or behind instrument).
- Type the username: ZetaPlus. There is no password.
- Click twice the icon ""Brookhaven Instruments Corp (Win32)".
- Select by clicking twice (careful, sometimes slow to open the software)
 - o BIC Dynamic Light Scattering Software = DLS, which enables rigorous particle size distribution analysis
 - o One can hear a "clic" which indicates the laser has started
 - o Before starting a measurement a delay of minimum 5 minutes must be respected to stabilize the laser and the temperature in the cell
- Close the 4 windows.
- Select the menu "FILE", then "Database", double click on the file name you want to start with, then select exit.

- Select the menu “FILE”, then “Load Configuration”, select the configuration name, then select ok.
- **1st window:**

Parameters - example for silica

Sample ID	SiO ₂ 45nm
Operator ID	FJ
Notes	Klebosl 1508-35-mesure 2- dilué 100×, pH 10
Temperature	25°C (it is advised to work at room temperature to improve the sample stability, but this can be changed if necessary)
Liquid	aqueous (⇒ viscosity, refractive index are automatic)
Angles	90° (fixed)
Wavelength	660nm (fixed)
Self-beating	Select
Refractive index	1.46 0
Measured baseline	Select
Dust filter	Deselect unless necessary
Other parameters	Unchanged

- o Once completed, click OK

Layout

- o Channel spacing: ratio
- o Channels requested: 200
- o Extended channels: Channels 4, Multiplier 4
- o Delay range (microseconds) – adjust depending on the correlation function
Can start with First delay: 0.5
Last delay: 1.000 +05

Duration

- o Choose a measurement time with Elapsed time: 2 minutes
- **2nd window:** results
 - o Layout: choose diameter by volume, deselect data smoothing.
 - o Cursor – results during measurement.
 - o Summary – table of distribution (frequency and cumulative).
- **3rd window:** fitting the correlation function
 - o This window should be monitored during the measurement, the blue curve (model) should fit the best and as early as possible the red dots (measurement).
- **4th window:** number of counts (kcps) recorded by the detector per time unit. This provides indications about the signal homogeneity as a function of time (ideally between 100 and 2000). If several points are away from the straight line formed by the others, it means that the suspension is “dusty”. In such an event, either select “dust filter” as parameter in the **1st window** or prepare another dilution using filtered water.
- Place the cell inside the instrument and close the door
- On computer select the menu “ZetaPals”, then select “Maximize Light Intensity”,
- Click Clear in the 1st window
- Click Start (duration 2 minutes based on default configuration) (green button)
 - o Check the **3rd window** for fit quality and the **4th window** for homogeneity of the signal.

- In the 1st window, the count rate should be below 500 kcps to avoid multiple scattering. To check that there is no multiple scattering, prepare 2 suspensions, one being two times more diluted than the second. The count rate measured must be exactly two times less. If not, it indicates an effect of multiple scattering due to a too high concentration. The sample must be diluted until a factor two in the count rate is obtained between two samples with a concentration which differs with a factor two.
- Select the menu “FILE”, then “Save Configuration Function as”

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

- To open a file already saved, or change the model used for processing the results:
 - Close the 4 windows
 - Select the menu “FILE”, click Database, file, file name
 - Select the menu “ISDA”, click Non-negatively-Constrained Least Squares: Regularized (Contin.) Current model – new graph window
 - Layout – Diameter by volume, detect data smoothing – click OK

Print the results

- Select menu “File” – Report print options
 - ISDA summary: select Contin,
 - ISDA graph: Contin – Layout – Diameter by volume, deselect data smoothing.
- Select “Menu: File – Print (careful deselect "generate colour output", no colour cartridge available)

Export the results

- Go to the menu “ISDA”, click Non-negatively-Constrained Least Squares: Regularized (Contin.). Click on “Copy for Spreadsheet” and paste it into a wordpad sheet. Save this sheet as [Powder-Lotn°-PCS-Experimentn°-Operator.txt](#).
- Go to FILE/Printer setup, and choose PdfCreator. Then go again to the FILE menu and select PRINT, and OK. Save as [Powder-Lotn°-PCS-Experimentn°-Operator.pdf](#).

Data storage

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

Data treatment

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

6. Particle sizing software

For simple measurements, one can use Particle sizing software instead of DLS

- Select the menu “File”, then “Database”, double click on the file name you want to start with, then select exit.
- Select “Setup/Incident power setting/optimize incident power at start of each measurement”, then OK.
- In the bottom of the page, click on “Parameters”, and fill the table as described with the example of silica.

Sample ID	SiO ₂ 45nm
Operator ID	FJ
Notes	Klebosol 1508-35-mesure 2- dilué 100×, pH 10
Temperature	25°C (it is advised to work at room temperature to improve the sample stability, but this can be changed if necessary)
Liquid	aqueous (⇒ viscosity, refractive index are automatic)
Angles	90° (fixed)
Wavelength	660nm (fixed)
Batch	1
Run duration	1 minute
Refractive index	1.46
	0
Dust cut off	30
Auto save results	Select

- Click on “Runs”, and select the number of measurements: 10
- Click on “Clear”
- Click on “Start”
- During the measurement:
 - o Click on “Dust filter On”, and compare with “Dust filter Off”. The difference must be less than 10 [%]. If more, the preparation of the sample must be improved, by filtering and more cleanliness.
 - o the “Avg count rate” should be below 500 kcps to avoid multiple scattering. To check that there is no multiple scattering, prepare 2 suspensions, one being two times more diluted than the second. The count rate measured must be exactly two times less. If not, it indicates an effect of multiple scattering due to a too high concentration. The sample must be half diluted again, until a factor two in the count rate is obtained between two following samples.
 - o The “Polydispersity” indicates the broadness of the size distribution. Below 0.05, the particle size distribution is quasi monodisperse.
 - o Choose “Setup/MSD/Output format”: volume
 - o On the graph, one can follow
 - Lognormal*: distribution derived from the correlation function
 - MSD*: size distribution in the sample
 - Corr. Funct.*: the correlation function

Print the results

- File/Print options: choose Results summary, MSD summary, and single page. Then, choose File/Print report.

Export the results

- File/Database. Choose the measurement of interest, click on “Copy for Spreadsheet” and paste it into a Excel sheet. Save this sheet as [Powder-Lotn°-PCS-Experimentn°-Operator.xls](#).
- Go to FILE/Printer setup, and choose PdfCreator. Then go again to the FILE menu and select Print report, and OK. Save as [Powder-Lotn°-PCS-Experimentn°-Operator.pdf](#).

Data storage

- Copy the PDF report and the XLS file.
- 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°/PCS/Data](#) and [PDF](#).

Data treatment

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

7. Comments

If large particles have been detected, they might consist of either dust or agglomerates which survived the sonication treatment.

- In the presence of dust, the concentrated suspension should not be sedimenting. It is therefore necessary to work with extra precautions for ensuring cleanliness and prepare a dilution of the concentrated suspension using clean and filtered water (ultrapure water is usually suitably filtered – For 250 nm particles, it is necessary to filter on 20 nm pores).
- When performing several measurements on the same sample without removing the cell from the instrument, the agglomerates will not be detected anymore after some time due to their sedimentation below the laser level: from then on only the fines will be measured. Sedimentation within the concentrated suspension may also be observed visually.
 - o It is recommended to prepare a concentrated suspension with twice as much dispersant (higher concentration) or half the powder for the same mass of liquid in order to allow more polymer molecules to adsorb onto the surface of the particles and improve the stability of the suspension.
 - o If agglomerates are still present, the sample indeed contains hard agglomerates and another instrument should be used for characterising the particle size distribution, this method being mostly suitable to characterise narrow particle size distributions with sizes less than 1 µm.