Protocol
Particle size distribution with the X-Ray Disc Centrifuge (XDC)

1. Method

Particles suspended in a liquid medium which has a density lower than that of the particles will eventually settle to the bottom. In either the gravitation or centrifugation settling mode, large particles move faster than small ones. Hence particles separate on the basis of their size and this method of particle size analysis yields excellent results of even complex mixtures. The concentration gradient that is produced results in good resolution. The settling phenomena are accurately described by Stokes' Law with the assumption of a spherical particle morphology. Based on a homogeneous start, the exact equations are solved for the size versus cumulative mass undersize distribution. X-ray detection ensures accurate and quantitative measurement.

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

Below is the amount of powder to disperse in an aqueous solution with dispersant to prepare 40 [g] of suspension:

Alumina: 2.0 [g]
Barium titanate 0.5 [g]
Titanium dioxide: 0.5 [g]
Silicon dioxide: 1.7 [g]

The amount of powder depends on the X-ray absorption coefficient and varies with the atomic mass of the cationic constituents.

(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 it is reasonable with respect to the measurement time.

b. Single samples

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

c. Sample series

If you characterise a series of several samples, prepare 1 dispersion per sample and perform 1 or 2 repetitions.

3. Equipment

- Measurement device: Brookhaven X-Ray Disc Centrifuge BI-XDC (more info from http://www.bic.com/BI-XDC.html)
- Horn for ultrasonic treatment: Telsonic Ultrasonics, model DG-100, 15 [min], 150 [W].
- Analytical balance (precision 10 [mg])
- 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
- Magnetic stirring rod (26×6 [mm])
- Thermocouple or thermometer
- Magnetic stirrer
- Glass crystallizer vessel to cool down sample to 25°C

4. Dispersion of particles for measurement in XDC

(a) Powders - Example

Alumina

- Weigh the empty plastic vessel, with a precision of 10 [mg]; carefully write down the result W_T [g].
- Weigh 2.0 [g] of alumina 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. Shake well.
- 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

(b) Suspensions - Example

Silica (amorphous)

A suspension with a particle volume concentration of less than 2% is required in order to avoid hindered settling. The concentration should be still high enough to absorb X-Rays and give sufficient signal to noise ratio. Assuming the density is 2.2 (measured by He pycnometry), the required particle mass concentration $C_{mass} = (\rho \times C_{vol})/((\rho \times C_{vol})+(100-C_{vol}))$ is $(2.2\times2)/((2.2\times2)+(100-2)) = 4.3$ [wt%].

To prepare a diluted suspension with a mass concentration of 4.3 [wt%] from the supplied suspension of 30 [wt%], it is necessary to dilute by a factor $f = 30/4.3 = 7$.

- Weigh the empty plastic vessel, with a precision of 10 [mg]; carefully write down the result W_T [g].
- Shake well the container containing the concentrated silica suspension and add 5.7 ± 0.0 [g] (=40/*f*) of suspension to the plastic vessel. Add ultrapure water to the container such that the total mass of diluted suspension is 40 [g]. Weight with precision 10 [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 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 with stirring until temperature of 25 [°C] has been reached

5. Operation of XDC

- The key at the front of instrument should be turned OFF
- Switch on the instrument
- The disc should be full of liquid dispersant
- The detector should be placed in front of the disc: if not press the yellow button to do so
- Carefully close the front-door
- Turn the key to the ON position in order to initiate the X-ray production
- Allow the instrument to warm up for 30 min to 1 hour
- Start the software
- Open a old analysis file and press “CLEAR” on screen
- Introduce the analysis parameters: Select Modelling utility
    - Introduce data in the fields named Sample, Operator and Notes
    - Select Scan Mode X
    - Select the speed (maximum 9990 rpm if using high speed disc)) and time in order to cover the appropriate size range
    - Check the size range
    - Press SAVE

Parameters	**SiO_2 Klebosol PL 150H50**	**SiO_2 Klebosol PL 1508-35**	**γ-alumina NanoTek**	**$BaTiO_3$ NBT36**
Scan Mode	X	X	X	X
Disc Speed [rpm]	10001	9990	2000	1500
Particle Density [$g.cm^{-3}$]	1.70	1.70	3.40	5.80
Run Time [min]	120	120	120	30
Temperature [℃]	25.0	25.0	25.0 ℃	25
Spin Fluid	Aqueous	Aqueous	Aqueous	Aqueous
Spin Fluid Volume [mL]	25.0	25.0	25.0	25.0
Spin Fluid Density [$g.cm^{-3}$]	0.997	0.997	0.997	0.997
Spin Fluid Viscosity [cP]	0.911	0.911	0.911	0.911

- After pre-heating the instrument: select START on the computer screen and follow instructions
- Select START in order to measure the baseline at 0%, write down the value and select CONTINUE.
- Turn the key to OFF
- Displace the detector by pressing the yellow button HEAD

- Use a 30 [cm^3] syringe with a plastic tube attached to the outlet in order to remove the liquid from the disc.
- Dry the disc with paper
- Draw 25 [cm^3] of suspension initially thermostated at 25 [°C] into the syringe. Remove all the bubbles by pumping the liquid in and out several times.
- Transfer the suspension into the disc by applying the plastic tube horizontally to the left inside the disc.
- Apply single-face tape only on the disc outlet to maintain the suspension inside.
- Carefully close the front-door of the instrument
- Place the detector in front of the disc by pressing the yellow button HEAD
- Turn the key ON
- Press the MIX button
- On the computer screen: select OK then START in order to measure the lower baseline. Select CONTINUE
- On the instrument, press MIX and immediately after press START
- Once the measurement is finished and the raw data displayed on the computer screen, stop the engine by pressing the red button (STOP).
- Press MIX
- Turn the key to OFF
- Press the yellow button to displace the detector
- Remove the tape on the disc
- Remove the suspension using the syringe
- Rinse numerous times with water using the MIX button to rotate the disc.
- The disc is considered clean once the baseline value at 0% is back to same as measured prior to introducing the suspension for the measurement.
- If no new measurement is to be carried out: make sure the key is turned to OFF, the detector is in front of the disc then switch off at the back of the instrument.

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

Print the results

- Go to the FILE menu and select SAVE.
- In the graphic window, select the “Cum & Diff“ presentation for the graph.
- Go to the FILE menu, select PRINT OPTIONS for selecting the items to be included in the print-out, and press PRINT to obtain the results.

Export the results

- Go to the FILE menu, select DATABASE, select the file of interest and click EXPORT FILES. Save as Powder-Lotn°-XDC-Experimentn°-Operator.dat.
- Go to FILE/Printer setup. Choose PdfCreator, and save as Powder-Lotn°-XDC-Experimentn°-Operator.pdf.

Data storage

- Copy the PDF report and the DAT files.

- Go to \\Ltppc40\powderfiles. Copy the folder *Powderfiles*. Paste it in your project folder, and change its name into Powder-Lotn°.
- Paste the DAT and PDF files respectively in the folders Project/Powder-Lotn°/XDC/Data and PDF.

Data treatment

- Go to \\Ltppc40\powderfiles. In the folder Project/Powder-Lotn°, open the Excel sheet "Powdersheet.xls"
- Click on the *XDC* button, and follow the instructions given in the Excel sheet.