

Protocol

Particle size distribution by centrifugal sedimentation (CPS)

1. Method

The CPS Disc Centrifuge separates particles by size using centrifugal sedimentation in a liquid medium. The sedimentation is stabilized by a slight density gradient within the liquid. The particles sediment within an optically clear and rotating disc (maximum speed: 24000 [rpm]). The particle concentration is measured by transmitted light intensity: when particles approach the outside edge of the rotating disc, they scatter a portion of a light beam that passes through the disc. The change in light intensity is continuously recorded, and converted by the operating software into a particle size distribution using Stokes law and assuming spherical particles. The measurable size ranges from 5 [nm] to 40 [μm]. Dilute suspensions, on the order of 0.01 – 1.0 [wt%], are prepared, using suitable wetting and/or dispersing agents. An ultrasonic treatment is useful in breaking up loosely-held agglomerates. Only 100 [μL] of suspension are required to carry out the measurements.

2. Equipment

- Instrument: CPS Disc Centrifuge Model DC 24000 (more info from <http://www.cpsinstruments.com>);
- 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 (26×6 [mm]);
- Magnetic stirrer;
- Ultrasonication bath: Wisag, 5 [minute], 150-300 [W];
- Horn for ultrasonic treatment: Telsonic Ultrasonics, model DG-100, 15 [min], 150 [W];
- Two solutions of saccharose (Merck 1.07687, 8 [wt%] and 24 [wt%]);
- A standard suspension of PVC (size: 0.377 [μm]);
- Dodecane (cap fluid);
- A syringe of 5 [mL] for the dodecane injection;
- Syringes of 1 [mL], for the standard and the sample injection.
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3. Preparations of the samples

General recommendations

- *The CPS must not be used with acetone or chlorinated solvents.*
- 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;
- Mild diluted suspension must be prepared, cloudy but not opaque;
- Samples of γ -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 $< 1 \mu\text{m}$ (ZrO_2 , Fe_2O_3 , BaTiO_3 , TiO_2 , $\text{ZnO}\dots$) are well dispersed using a solution of PAA 0.01 [wt%] ($R = \text{NH}_3/\text{PAA} = 1.5$), at a concentration between 0.01 to 1 wt% (0.004 g to 0.40 g of powder in 40 mL of PAA 0.01 [wt%]);
- 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.

Example of preparation: BaTiO₃, mean particle size 200 [nm]

- Weigh the empty plastic vessel, with a precision of 1 [mg]; carefully write down the result W_T [g].
- Weigh 0.020 [g] of BaTiO_3 powder with precision 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 40 [g]. Weigh with precision 1 [mg]. Write down the result W_{sol} [g].
- Insert the stirring rod into the suspension, 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 CPS

Procedure definition

- Start the software CPS-v95
- Select “Procedure definition”
- Fill the “Sample parameters”

Sample parameters	SiO₂ Klebosol	γ-alumina NanoTek	BaTiO₃ NBT36
Maximum diameter [μm]	0.5	1	3
Minimum diameter [μm]	0.01	0.01	0.1
Particle density [g/cm^3]	2.2	3.6	5.8
Particle refractive index	1.49	1.77	2.4
Particle absorption*	0.01	0.01	0.01
Non-sphericity factor	1	1	1

* Particle absorptions are higher than theoretical values to avoid anomalous “fine” tails to the distribution, probably due to non-sphericity of the particles¹.

1. Bowen P. Particle Size Distribution Measurement from Millimeters to Nanometers and from Rods to Platelets. *Journal of Dispersion Science and Technology*. 2002;23(5):631.

- Fill the “Calibration standard parameters”
 - o A PVC standard is used to perform a calibration before each measurement
 - o Enter the “Peak diameter” of the standard: 0.377 [μm]
 - o Half height peak width: 0.1 [μm]
 - o Particle density: 1.385 [g/mL]
- Fill the “Fluid parameters”
 - o The sedimentation is stabilized by a gradient of sucrose (Merck 1.07687)
 - o Fluid density: 1.045 [g/mL]
 - o Fluid refractive index: 1.344
 - o Fluid viscosity: 1.2 [cps]
- Give a name to the method in “New name”
- Define the parameters for the presentation of the results like below

Display mode: Weight	Display curves: Differential
Y-axis scaling: Height	Show grid Horizontal Vertical
Peak detection sensitivity 05 Height 10 Window	Display operating date: Yes
Distribution table: none	X-axis scale: Log

- Then, click on “Save and exit”

Start the disc

- Switch on the CPS measuring unit at the back 1 hour before starting the measurements.
- Open the door of the apparatus, and check the disc is clean and empty. Check the Teflon part is correctly placed.
- Select “Choose procedure” on the screen, and choose the procedure in the list. Then click on “Change to selected procedure”.
- Click on START on the screen: the disc velocity is automatically calculated and depends on the size range. It is also possible to select the disc velocity manually by choosing “Manual” on the screen, and displacing the scroll bar.

Prepare the gradient

- Prepare two solutions of sucrose (8 [wt%] and 24 [wt%]). Place them close to the peristaltic pump
- Check the pump tubes are correctly fixed.
- Insert the right tube of the peristaltic pump in the solution at 8 [wt%] of sucrose, and the left tube in the solution at 24 [wt%] of sucrose. Place the syringe at the outlet of the pump to an empty beaker. Turn on the cursor to 40 [mL], then switch on the pump, and turn the second button to RUN to purge the pump.
- When the purge is finished, turn the button on RESET.
- Place the cursor of the pump on 16 [mL] (which is the volume of the disc), place the syringe at the outlet of the pump inside the disc, and turn the button on RUN. The disc is filled with a gradient made from the two sucrose solutions.
- When the disc is filled, take the syringe out of the disc.

- Put 0.5 [mL] of dodecane in the disc with the 1 [mL] syringe. Dodecane is a cap fluid, and helps maintaining the gradient inside the disc.
- The gradient is stable during 8 hours

Operation of CPS

- On the screen, select “Operate Analyser”, and follow the instructions
 - o Introduce Sample ID, then click on Start
 - o Inject 100 [μL] of the standard with a 1 [mL] syringe in the disc and press the space bar *at the same time*
 - o Then inject 100 [μL] of the sample with a 1 [mL] syringe in the disc and press the space bar *at the same time*
 - o An optimal concentration is obtained when the blue curve is in the middle of the screen
- Once the measurement is finished, click on Next Sample.
- It is important to wait until all the particles have been counted (measurement at 0 on the screen), before starting a new measurement.
- If no new measurement has to be carried out, stop the disc by clicking on STOP on the screen.
- Open the door of the disc. Remove the suspension using the syringe. Rinse numerous times with water. Dry the interior of the disc with clean paper (Kimweep), then with isopropanol on a paper. Close the door of the disc, and switch off the CPS measuring unit at the back.
- Clean the peristaltic pump tubes with water: insert the two inlet tubes in a beaker of 100 [mL] full of ultra pure water, and place the syringe at the outlet of the pump to an empty beaker. Turn on the cursor to 40 [mL], and turn the second button to RUN.
- Then dry the tubes with air: remove the two inlet tubes from the beaker of water, and with the cursor on 40 [mL], go to RUN again.

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

Print the results

- Select “Retrieve distribution”
- Select your procedure with “Choose Procedure”, then the sample measurement, and click on “View”. Then click on “Print”, and choose a printer.

Export the results

- Select “Retrieve distribution”
- Select your procedure with “Choose Procedure”, then the sample measurement, and click on “View”. Then click on “Print” and choose PdfCreator. Save as [Powder-Lotn°-CPS-Experimentn°-Operator.pdf](#).
- Go to C:\Program Files\CPSV95
- Choose your procedure and copy the two files done for the same measurement as [Powder-Lotn°-CPS-Experimentn°-Operator.raw](#).

Data storage

- Copy the PDF report and the RAW files.
- 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°/CPS/Data](#) and [PDF](#).

Data treatment

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