

Protocol Zeta Acoustosizer

1. Method

Zeta Acoustosizer measures zeta potential, and also particle size distribution, using an acoustophoresis method. Compared to the electrophoresis method (Zeta Pals), this technique presents the advantage of working at much higher concentration (1.0 to 40 [wt.%]), so that industrially relevant suspensions can be investigated. At least 160 [mL] of suspension are required, held in a cell containing a stirrer, a pH probe and a conductivity meter. In this technique an alternating electric field of a known frequency is applied to the suspension which causes the particles to oscillate at the same frequency. The liquid in the shear plane around the particles moves, but due to differences in permittivity and density the movements are out of phase. This results in a cyclic longitudinal pressure variation in the suspending liquid, i.e. a sound wave. This acoustic wave is detected by the transducers. The amplitude of this acoustic signal and its phase difference is then recorded in the dynamic mobility spectrum, (frequency range 300 kHz to 11.5 MHz). From this spectrum a zeta potential and a particle size can be calculated.

2. Equipment

- Measurement device: AcoustoSizer II (more info from <http://www.chem.agilent.com>);
- pH buffer solutions (pH 4, 7 and 10);
- Solutions of HNO₃ 1 [M] and KOH 1 [M], for pH adjustment and pH titration;
- Brand new polystyrene vessel of 180 [mL] volume with lid (external diameter 55 [mm], height 100 [mm], for instance Semadeni reference 3722);
- Spatula for powder samples, plastic pipette for liquid samples;
- Stirring rod (26×6 [mm]);
- Ultrasonic horn: Telsonic Ultrasonics, model DG-100, 15 [min], 150 [W];
- Ultrasonic bath: Wisag, 5 [minute], 150-300 [W];
- Magnetic stirrer;
- Analytical balance (precision 0.1 [mg]);
- Centrifuge.

3. Preparation of the samples

- The concentration range for the measurement is very large: 1.0-40 [wt.%]. Suspensions at 2.5 [wt.%] are prepared as routine;
- The total volume of the suspension must be set at 160 [mL];

Example of preparation: Al₂O₃, mean particle size 300 [nm]

- Weigh the empty plastic vessel.
- Weigh 4.0 [g] of Al₂O₃ powder. Add HNO₃ 0.01 [M] solution into the vessel until the total mass of suspension is 160 [g].
- Insert the stirring rod into the suspension, place the vessel on the magnetic stirrer. Stir with medium speed.
- Insert the ultrasonic horn into the vessel and adjust at about 1 [cm] from 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. Operations

- Switch on the instrument;
- Make sure the measurement cell and the tubes are clean and dry (clean them if necessary);
- Place the tube into the peristaltic pump, and close it firmly;
- Close the conductivity cell;
- Place the measurement cell on its support (with the big mark in front), adjust the mixing bar;
- If necessary, a thermostated cell is available to work at different temperatures;
- Switch on the computer. Open the software "AZR2". Select solvent type: choose Polar when working with aqueous suspensions.

4.1 Calibration of the pH electrode

- Go to "Calibrate/Support Sensors/Next".
- Choose "pH probe", and "Next".
- Rinse the pH electrode. Dry it softly.
- Choose "Acid", and Next: Place the electrode in the pH buffer solution at pH 4. Check the value, or adjust it to 4, if necessary. Click on "Calibrate/OK". Then "Next".
- Rinse the pH electrode. Dry it softly.
- Choose "Neutral", and do the same with the pH buffer solution at pH 7.
- Rinse the pH electrode. Dry it softly.
- Choose "Basic", and do the same with the pH buffer solution at pH 10.
- Rinse the pH electrode. Dry it softly.
- Place it in the measurement cell.

4.2 Calibration of the ESA sensors

- Go to "Calibrate/ESA Sensors/Next".
- Fill the measurement cell with the standard solution A (Colloidal Dynamics, 0.25 [S/m] KSiW Solution "Polar calibration standard for acoustosizer and zeta probe" pH = 4.50 ± 0.25).
- Start the peristaltic pump (Power/Fwd: clockwise), and the mixing bar (350 [rpm]), adjust the speed at 4-5.
- Click on Measure. Wait until the calibration is finished (around 5 [min]). When the message "Calibration successful" appears, click on OK, and "Close".
- Stop the mixing and the pump. Transfer the calibration solution in its bottle A. Rinse the measurement cell and the tubes with ultra-pure water before replacing them in the apparatus.

4.3 Operations to do by the equipment manager

Every 6 months, the responsible should check the ESA sensor solution. To do so, go to "Tools/KSiWTest". Put the current solution A into the cell of measurement, and click on "Measure". Then remove the solution A, clean the cell with ultra-pure water, and add a new solution B. Click on "Measure". At the end of this measurement, the apparatus will say if the solution A is still ok, or should be replaced by solution B.

The temperature and conductivity electrodes should also be verified every 6 months.

4.4 Zeta measurement

- Go to “Data logging”.
- Add the name of the sample, and its characteristics: density, dielectric constant, concentration. These parameters can be saved for a future measurement with “Save as”. If sample properties have already been saved, click on “Open”, and choose the corresponding file.
- In “Solvent properties”, add the solvent characteristics (density, dielectric constant, viscosity and speed of sound).
If working in aqueous solutions, click on “Properties of water”, to fill automatically these values.
- Click on “ESA”, and “Zeta only”. The measurement will only give the zeta potential (time of measurement around 30 [s]). If this option is not validated, the measurement will add the measurement of the particle size distribution (around 3 [min]).
- Add comments (sample preparation...).
- In “Filename prefix”, save as **Powder-Lotn°-Zeta-Experimentn°-Operator**.

Add the suspension (160 [mL]) in the cell of measurement. Place the pH electrode inside, and start the stirring (velocity 350 [rpm]). Start the peristaltic pump (Power/Fwd: clockwise), adjust the speed at 4-5.

- Click on “Measure”. The apparatus applies different frequencies, and record a measurement every 30 [s]. A good mean value can be calculated from 10 measurements, thus 5 [min] of recording. An Excel sheet is automatically open with the measurement, and saved as defined by the operator.
- To stop the measurement (usually after 10 points), choose “Abort/Yes”.

4.5 pH titration

Example of titration of Al₂O₃ suspension at 2.5 [wt.%] with a solution of KOH at 0.5 [M].

**Remarks: right burette = blue tube: for basic solutions
 left burette = red tube: for acid solutions**

Click on “Burette control”

Purge the burette with the solution of titration

- In “Initial sample volume”, put 200 [mL]. Choose the right burette, and insert the corresponding tube in ultra pure water. Place the outlet tube to an empty beaker. Click on OK. Then choose “Number of washes: 10”.
- Click on “Wash syringe” Right.
- Repeat the operation with the solution of titration.
- Click on “Close”.

Click on “Titration”

- Add the name of the sample, and its characteristics: density, dielectric constant, concentration, or “open” your file.
- In “Titration type”, choose “Potentiometric series”.
- Choose “Zeta only”.

- Add comments (sample preparation...).
- In “Filename prefix”, save as [Powder-Lotn°-ZetaT-Experimentn°-Operator](#).

Click on Next. Add the suspension (160 [mL]) in the measurement cell. Place the pH electrode inside, and start the stirring (velocity 350 [rpm]). Start the peristaltic pump (Power/Fwd: clockwise), adjust the speed at 4-5.

In “Titration properties”, add the properties of

- “Base ID” (Blue): put the name (KOH) and its concentration (0.5 M)
- “Sample volume”: 157 [mL] (recalculated: 4 g of Al₂O₃ (d=3.9) and 156 g of water)
- Equilibrium delay: 30 [s]
- In “Titration”, fill Start pH, End pH, and pH increment

Put the outlet of the burette in the cell of measurement

- Click on “Titrate”, and OK: the measurement is starting.

4.6 Other titration

Example of titration with a solution of PAA at a concentration of 5.0 [wt.%].

Click on “Burette control”

Purge the burette with the solution of titration

- In “Initial sample volume”, put 200 [mL]. Choose one burette (Left or Right), and insert the corresponding tube in ultra pure water. Place the outlet tube to an empty beaker. Click on OK. Then choose “Number of washes: 10”.
- Click on “Wash syringe” Left or Right, depending on the burette chosen.
- Repeat the operation with the solution of titration.
- Click on “Close”.

Click on “Titration”

- Add the name of the sample, and its characteristics: density, dielectric constant, concentration, or “open” your file.
- In “Titration type”, choose “Concentration series”.
- Choose “Zeta only”.
- Add comments (sample preparation...).
- In “Filename prefix”, save as [Powder-Lotn°-ZetaT-Experimentn°-Operator](#).

Add the suspension (160 [mL]) in the measurement cell. Place the pH electrode inside, and start the stirring (velocity 350 [rpm]). Start the peristaltic pump (Power/Fwd: clockwise), adjust the speed at 4-5.

In “Auto Burette Control”, add the properties of

- “Titrant”: for example, PAA solution R=1.5
- “Titrant concentration”: choose [mol/L] or [wt.%], for example 5.0 [wt.%]

- Choose Left or Right syringe
- “Sample volume”: 160 [mL]
- Equilibrium delay: 30 [s]
- Total titrant volume: usually 10 to 40 [mL]
- Number of addition points: usually 10 to 20
- Initial dose: 0.01
- Choose “Equispaced titration” or “Log-spaced titration”
- These parameters can be saved for a future measurement with “Save as”

Put the outlet of the burette in the measurement cell.

- Click on “Titrate”, and OK: the measurement is starting.

4.7 Background measurement

- Centrifuge the suspension, and put the supernatant in the cell of measurement
- Go to “Background”
- In “Background file profile”, put the name of the background measurement
- Click on “Measure”

4.8 Stop the equipment

- Switch off the pump and the stirring.
- Put the pH electrode and the burette out.
- Rinse the pH electrode with ultra pure water. Store it in KCl solution.
- Clean the burette with ultra pure water. *It is very important to have a good cleaning of the burette which contained basic solutions (burette in glass).* Click on “Burette control”. In “Initial sample volume”, put 200 [mL]. Choose the burette (Left or Right), and insert the corresponding tube in ultra pure water. Place the outlet tube to an empty beaker. Click on OK. Choose “Number of washes: 10”. Click on “Wash syringe” Left or Right, depending on the burette chosen. Finally click on “Close”. Then do the same with air, to dry.
- Place the tubes 10 [min] in an ultrasonic bath. Then clean them with ultra pure water, and dry with air.
- Clean the cell of measurement with caution (use only ultra pure water).
- Finally put some ultra pure water in the cell of measurement. Go to “Tools”. Select “Check probe clean”, then “Measure”. When “Clean” appears on the screen, empty the cell of water.
- Put the tubes out of the pump, and open the cell of conductivity.

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

Analyse with the background

- Go to “Search file”, and choose a file to reanalyse it with the background

For a simple zeta measurement, choose “Background correction”, save as [Powder-Lotn°-Zeta-BG-Experimentn°-Operator](#), and “Analyse” by choosing the background file previously saved.

For a titration, select all the data in the left column, and put the background file in the right column. Click on “Link”, then OK, and “Analyse”. Save as [Powder-Lotn^o-ZetaT-BG-Experimentn^o-Operator](#)

Export the results

- Go to “C:/Program Files/AZR2/Probe1/spredsht”, or on the Desktop “AZR2 Datafiles”
- The Excel files [Powder-Lotn^o-Zeta-Experimentn^o-Operator.xls](#) are automatically saved.

Data storage

- Copy the XLS files.
- Go to \\Ltpc40\powderfiles. Copy the folder *Powderfiles*. Paste it in your project folder, and change its name into [Powder-Lotn^o](#).
- Paste the XLF files in the folder [Project/Powder-Lotn^o/ZetaPals/Data](#).

Data treatment

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