Zeta Potential

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› Laser Doppler electrophoresis (electrophoretic light scattering)
› Phase analysis light scattering (PALS)
› Analysis options
› Data Interpretation
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› Data Interpretation

Phase Plots

› The phase plot shows the difference in phase between the measured beat frequency and a reference frequency as a function of time
Laser Doppler Electrophoresis

- A laser beam is passed through the sample in the capillary cell undergoing electrophoresis and the scattered light from the moving particles is frequency shifted.
- The frequency shift $\Delta f$ is equal to:

$$\Delta f = \frac{2v \sin(\theta/2)}{\lambda}$$

- $v$ = the particle velocity
- $\lambda$ = laser wavelength
- $\theta$ = scattering angle

Particle velocity $V=0$
- Scattered light has same frequency as incident laser

Particle velocity $V>0$
- Scattered light now has greater frequency than incident laser
Laser Doppler Electrophoresis

- Frequency of light is very high (10^{14} \text{Hz})
- Frequency shift can only be measured by an optical mixing or interferometric technique
- Use a pair of mutually coherent laser beams derived from a single source and following similar path lengths
- One of these beams must pass through the particle dispersion (this is called the scattering beam)
- The other beam (called the reference beam) is routed around the cell
- The scattered light from the particles is combined with the reference beam to create intensity variations

How Do These Intensity Variations Arise?
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Reference beam $F_1$

How Do These Intensity Variations Arise?

Reference beam $F_1$ and scattered beam $F_2$
How Do These Intensity Variations Arise?

Reference beam $F_1$ and scattered beam $F_2$

Let's combine them.
How Do These Intensity Variations Arise?

Reference beam $F_1$ and scattered beam $F_2$

The two waves interfere constructively at $A$ and destructively at $B$.
How Do These Intensity Variations Arise?

Reference beam $F_1$ and scattered beam $F_2$

The two waves interfere constructively at $A$ and destructively at $B$

$F_1 - F_2 = \Delta f$

The interference produces a modulated beam having a much smaller frequency equal to difference of $F_1$ and $F_2$

The Beat Frequency Is Focussed Onto The Detector

It is the intensity variations of the “beat” frequency which are detected
Optical Configuration of the Zetasizer Nano

Phase Plots

- The phase plot shows the difference in phase between the measured beat frequency and a reference frequency as a function of time.
Phase Plots

- The phase plot shows the **difference in phase** between the measured **beat frequency** and a **reference frequency** as a function of time.

![Phase Plot Diagram]

Determining the Sign of the Doppler Shift

- Determined by comparing the **beat frequency** with that of a **reference frequency**
- **Reference frequency** produced by modulating one of the laser beams with an oscillating mirror
- The mobility of the particles in an applied field produces a frequency shift away from that of the modulator frequency (320 Hz)
- This gives an unequivocal measure of the sign of the zeta potential
### Determining the Sign of the Doppler Shift

<table>
<thead>
<tr>
<th>Zeta Potential (mV)</th>
<th>Reference Frequency (Hz)</th>
<th>Measured Beat Frequency (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>320</td>
<td>320</td>
</tr>
<tr>
<td>+50</td>
<td>320</td>
<td>320</td>
</tr>
<tr>
<td>-50</td>
<td>320</td>
<td>320</td>
</tr>
</tbody>
</table>
### Determining the Sign of the Doppler Shift

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<tbody>
<tr>
<td>0</td>
<td>320</td>
<td>320</td>
</tr>
<tr>
<td>+50</td>
<td>320</td>
<td>370</td>
</tr>
<tr>
<td>-50</td>
<td>320</td>
<td>270</td>
</tr>
</tbody>
</table>
Phase Plots

- The phase plot shows the difference in phase between the measured beat frequency and a reference frequency as a function of time.
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**Phase Analysis Light Scattering**

› Very accurate determination of a frequency shift
› At least >100 times more sensitive than standard Fourier Transform (FT)
› PALS gives the ability to accurately measure samples that have low particle mobilities
  - high conductivity samples
  - high viscosity
  - non-aqueous applications
Phase Analysis Light Scattering

- The measured phase change is proportional to the mobility of the particles

- Phase = Frequency x Time

- Phase/Time = Frequency
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Analysis Options

› Three analysis models available:
  ▪ Auto Mode (default)
  ▪ General Purpose
  ▪ Monomodal
General Purpose

- General Purpose = FFR + SFR
- FFR = zeta potential mean (electrophoresis only)
- SFR = zeta potential distribution (electrophoresis and electro-osmosis)

General Purpose: Voltage Plot
General Purpose: Voltage Plot

FFR

General Purpose: Voltage Plot

FFR  SFR
General Purpose: Phase Plots

General Purpose: Phase Plots
General Purpose: Phase Plots

![Phase Plot Diagram](image)

Monomodal

- Monomodal = FFR only
- Zeta potential mean only
- No zeta potential distribution is determined
Monomodal: Voltage Plot

Monomodal: Phase Plot
Auto Mode

- Default measurement option
- Software determines the most suitable type of measurement to perform after measuring the sample conductivity

Measurement Sequence Flow Chart: Capillary Cell Auto Mode

- Check reference beam count rate
- Adjust attenuator so that sample scattering is <300kcps
- Measure sample conductivity
- <5mS/cm: General Purpose and 150V
- >30mS/cm: Monomodal and 10V
- <30mS/cm: Monomodal and 50V
Measurement Sequence Flow Chart: Capillary Cell Auto Mode

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Data Interpretation Overview

› The quality of the data obtained from the measurement is essential in determining how repeatable the answers will be
› In order to aid the interpretation of data, a number of report pages and record view parameters can be viewed

Recommended Reports

<table>
<thead>
<tr>
<th>Report Name</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zeta Potential</td>
<td>The zeta potential result obtained from the measurement</td>
</tr>
<tr>
<td>Zeta Quality</td>
<td>Incorporates a number of tests on a selected record</td>
</tr>
<tr>
<td>Expert Advice</td>
<td>Quality checks on a single record and trends 3 or more records</td>
</tr>
<tr>
<td>Phase</td>
<td>The phase difference between the measured beat frequency and the reference frequency plotted as a function of time</td>
</tr>
<tr>
<td>Frequency</td>
<td>The frequency spectrum obtained from the SFR part of the measurement</td>
</tr>
<tr>
<td>Voltage and Current</td>
<td>The voltage applied and the current detected in the cell over the duration of the measurement</td>
</tr>
</tbody>
</table>
Recommended Parameters

<table>
<thead>
<tr>
<th>Parameter Name</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zeta Potential Mean</td>
<td>The mean zeta potential value</td>
</tr>
<tr>
<td>Zeta Potential Width</td>
<td>The standard deviation of the zeta potential distribution</td>
</tr>
<tr>
<td>Conductivity</td>
<td>The conductivity of the sample determined from the measurement</td>
</tr>
<tr>
<td>Attenuator</td>
<td>The attenuator position used during the measurement</td>
</tr>
<tr>
<td>Quality Factor</td>
<td>A signal to noise based parameter derived from a phase analysis during the FFR stage of the measurement</td>
</tr>
<tr>
<td>SFR Spectral Quality</td>
<td>A signal to noise based parameter that is derived from the frequency analysis during the SFR stage of the measurement</td>
</tr>
<tr>
<td>Effective Voltage</td>
<td>The voltage requested during the measurement</td>
</tr>
<tr>
<td>Zeta Runs</td>
<td>The number of sub runs used in the measurement</td>
</tr>
</tbody>
</table>

Zeta Quality Report Overview

- The zeta quality report incorporates a number of tests on any selected record
- If any of the tests fall outside specified limits, a warning message is displayed together with advice of possible reasons for the warning
- If none of the tests fail, a “Result Meets Quality Criteria” message is displayed
# Zeta Quality Report

<table>
<thead>
<tr>
<th>Test</th>
<th>Description</th>
<th>Possible Reasons</th>
<th>Possible Action</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quality of the phase data</td>
<td>Is the Quality Factor &lt; 1?</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sample concentration too low</td>
<td></td>
<td>Increase sample concentration</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Increase number of sub runs</td>
</tr>
<tr>
<td></td>
<td>Sample concentration too high</td>
<td></td>
<td>Decrease sample concentration</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Increase number of sub runs</td>
</tr>
<tr>
<td></td>
<td>High conductivity causing sample/electrode degradation</td>
<td></td>
<td>Use the diffusion barrier method</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Ensure Monomodal is used</td>
</tr>
<tr>
<td></td>
<td>Zeta potential of sample is close to zero</td>
<td></td>
<td>Confirm by adjusting the sample pH and see whether the zeta mean changes</td>
</tr>
</tbody>
</table>

## Phase Plot: Good Quality General Purpose

![Phase Plot](image-url)
Phase Plots: Poor Quality General Purpose

Phase Plot: Good Quality Monomodal
## Zeta Quality Report

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<th>Test</th>
<th>Description</th>
<th>Possible Reasons</th>
<th>Possible Action</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quality of the zeta potential distribution data</td>
<td>Is the Spectral Quality Factor &lt; 1?</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Possible Reasons**

- Sample concentration too low
- Sample concentration too high
- High conductivity causing sample/electrode degradation
- Manually reduce voltage

**Possible Action**

- Increase sample concentration
- Decrease sample concentration
- Increase number of sub runs
- Use the diffusion barrier method
- Ensure Monomodal is used
Frequency Plots: Good Data

Frequency Plots: Poor Data
### Zeta Quality Report

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<th>Possible Reasons</th>
<th>Possible Action</th>
</tr>
</thead>
<tbody>
<tr>
<td>Attenuator position used</td>
<td>Checks whether attenuator position 11 was used during measurement</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

#### Results and Data Example 1

- Zeta means low but stable – data quality poor (quality factors < 1) - sample close to zero?
- Attenuator used position 7 suggesting that sample concentration is not a problem
- Conductivity high – Monomodal used – no zeta potential distribution obtained - 50 sub runs used per measurement (manually set)
Results and Data Example 2

- Zeta means low, zeta deviations very large - Sample close to zero? Data quality poor?
- Attenuator used position 11, mean count rates very low - sample concentration too low or too high?
- Conductivity very low – deionised water used? 100 sub runs used per measurement and phase data (quality factor) and distribution data (SFR Spectral Quality) very poor

Results and Data Example 3

- Zeta means low but stable – Sample close to zero? Data quality poor?
- Attenuator used position 7 suggesting that sample concentration is not a problem
- Conductivity high – Monomodal used – no zeta potential distribution obtained – number of sub runs used per measurement is high quality factors obtained > 1
Many thanks for your attention

Any questions?