Introduction to Dynamic Light Scattering for Particle Size Determination
Sizing Techniques

- **Size**
  - Nano-Metric
  - Colloidal
  - Fine
  - Coarse

- **Apps**
  - Macromolecules
  - Suspensions and Slurries
  - Powders

- **Methods**
  - Electron Microscope
  - Acoustic Spectroscopy
  - Sieves
  - Light Obscuration
  - Laser Diffraction – LA-960
  - Electrozone Sensing
  - DLS – SZ-100
  - Sedimentation
  - Disc-Centrifuge
  - Image Analysis PSA300, Camsizer

- **Sizing Techniques**
  - 0.001 to 0.01
  - 0.1
  - 1
  - 10
  - 100
  - 1000
Two Approaches to Image Analysis

Dynamic:
particles flow past camera

Static:
particles fixed on slide,
stage moves slide

1 – 3000 um

0.5 – 1000 um
2000 um w/1.25 objective
Laser Diffraction

Laser Diffraction
- Particle size 0.01 – 3000 µm
- Converts scattered light to particle size distribution
- Quick, repeatable
- Most common technique
- Suspensions & powders
Laser Diffraction

Suspension

Silica
~ 30 nm

S.P.Area : 2.0183E+6 cm²/cm³
Mean Size : 0.02990(µm)
Variance : 5.0313E-6(µm²)
Median Size : 0.03013(µm)
Mode Size : 0.0302(µm)
Skewness : -0.2901

Powders

Coffee Results
0.3 – 1 mm
What is Dynamic Light Scattering?

- Dynamic light scattering refers to measurement and interpretation of light scattering data on a **microsecond** time scale.

- Dynamic light scattering can be used to determine
  - Particle/molecular size
  - Size distribution
  - Relaxations in complex fluids
Other Light Scattering Techniques

• **Static Light Scattering**: over a duration of ~1 second. Used for determining particle size (diameters greater than 10 nm), polymer molecular weight, 2\textsuperscript{nd} virial coefficient, $R_g$.

• **Electrophoretic Light Scattering**: use Doppler shift in scattered light to probe motion of particles due to an applied electric field. Used for determining electrophoretic mobility, zeta potential.
DLS Optics

Backscatter (173°) (High conc.)

Particles moving due to Brownian motion

Laser 532nm, 10mW

90° for size and MW, A2

Particles

Attenuator

PD For T%
Brownian Motion

Particles in suspension undergo Brownian motion (random thermal motion).

- Brownian Motion
  - Random
  - Related to Size
  - Related to viscosity
  - Related to temperature
DLS signal

- Random motion of particles leads to random fluctuations in signal (due to changing constructive/destructive interference of scattered light.)
Correlation Function

- Random fluctuations are interpreted in terms of the autocorrelation function (ACF), $C(\tau)$.

\[ C(\tau) = 1 + \beta \exp(-2\Gamma \tau) \]
Gamma to Size

\[ q = \frac{4\pi n}{\lambda} \sin\left(\frac{\theta}{2}\right) \]

- \( \Gamma \) decay constant
- \( D_m \) diffusion coefficient
- \( q \) scattering vector
- \( n \) refractive index
- \( \lambda \) wavelength
- \( \theta \) scattering angle
- \( D_h \) hydrodynamic diameter
- \( \eta \) viscosity
- \( k_B \) Boltzmann’s constant

Note effect of temperature!
What is Hydrodynamic Size?

- DLS gives the diameter of a sphere that moves (diffuses) the same way as your sample.
Hydrodynamic Size

- The instrument reports the size of sphere that moves (diffuses) like your particle.
- This size will include any stabilizers bound to the molecule (even if they are not seen by TEM).

Gold Colloids

<table>
<thead>
<tr>
<th>Technique</th>
<th>Size nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic Force Microscopy</td>
<td>8.5 ± 0.3</td>
</tr>
<tr>
<td>Scanning Electron Microscopy</td>
<td>9.9 ± 0.1</td>
</tr>
<tr>
<td>Transmission Electron Microscopy</td>
<td>8.9 ± 0.1</td>
</tr>
<tr>
<td>Dynamic Light Scattering</td>
<td>13.5 ± 0.1</td>
</tr>
</tbody>
</table>

SEM (above) and TEM (below) images for RM 8011
## Nanogold Data

<table>
<thead>
<tr>
<th>Run</th>
<th>Z-avg. Diameter, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run 1</td>
<td>50.5</td>
</tr>
<tr>
<td>Run 2</td>
<td>51.1</td>
</tr>
<tr>
<td>Run 3</td>
<td>49.2</td>
</tr>
<tr>
<td>Run 4</td>
<td>51.5</td>
</tr>
<tr>
<td>Run 5</td>
<td>49.7</td>
</tr>
<tr>
<td>Run 6</td>
<td>50.9</td>
</tr>
<tr>
<td>Avg.</td>
<td>50.5</td>
</tr>
<tr>
<td>St. Dev.</td>
<td>0.9</td>
</tr>
<tr>
<td>COV</td>
<td>1.7 %</td>
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</table>
## Nanogold Data

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<tr>
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<tbody>
<tr>
<td>1</td>
<td>10.5</td>
</tr>
<tr>
<td>2</td>
<td>10.6</td>
</tr>
<tr>
<td>3</td>
<td>10.2</td>
</tr>
<tr>
<td>4</td>
<td>10.5</td>
</tr>
<tr>
<td>5</td>
<td>10.3</td>
</tr>
<tr>
<td>Avg.</td>
<td>10.4</td>
</tr>
<tr>
<td>St. Dev.</td>
<td>0.2</td>
</tr>
<tr>
<td>COV</td>
<td>1.9 %</td>
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### Average Z-avg. Diameter:

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## Lab to Lab comparison

### Colloidal Silica

<table>
<thead>
<tr>
<th></th>
<th>Mean determined Z-average size (nm)</th>
<th>COV (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Dynamic Light Scattering with SZ-100, laboratory 1</strong></td>
<td>34.4</td>
<td>0.7</td>
</tr>
<tr>
<td><strong>Dynamic Light Scattering with SZ-100, laboratory 2</strong></td>
<td>34.6</td>
<td>0.3</td>
</tr>
</tbody>
</table>
Emulsion Polymers

IUPAC definition

Emulsion polymerization:

Polymerization whereby monomer(s), initiator, dispersion medium, and possibly colloid stabilizer constitute initially an inhomogeneous system resulting in particles of colloidal dimensions containing the formed polymer.
Polystyrene Latex Sample
Polydisperse Sample Cumulants

For a mixture of sizes, the autocorrelation function can be interpreted in terms of cumulants. This is the most robust method of analyzing DLS data.

\[ C(\tau) = 1 + \beta \exp(-2\Gamma \tau) \]

\[ C(\tau) = 1 + \beta \exp \left[ 2 \left( -\Gamma \tau + \left( \frac{\mu_2}{2!} \right) \tau^2 - \cdots \right) \right] \]

\[ \Gamma = D_m q^2 \]

"z-average size"

\[ D_{z,h} = \frac{k_B T}{3\pi \eta(T) D_m} \]

Polydispersity = \[ \frac{\mu_2}{\Gamma^2} \]
### SiO$_2$

<table>
<thead>
<tr>
<th>Run</th>
<th>Z-average Diameter (nm)</th>
<th>Polydispersity Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>473.2</td>
<td>0.127</td>
</tr>
<tr>
<td>2</td>
<td>479.5</td>
<td>0.066</td>
</tr>
<tr>
<td>3</td>
<td>478.8</td>
<td>0.077</td>
</tr>
<tr>
<td>4</td>
<td>487.7</td>
<td>0.039</td>
</tr>
<tr>
<td>Avg.</td>
<td>479.8</td>
<td>0.077</td>
</tr>
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</table>
Mixtures of Particles

Sum the autocorrelation functions
Polydisperse Sample (ILT)

A more general relationship can be given between the autocorrelation function and the size distribution. Let each size have a relation constant $\Gamma$. The scattering from each population is then given by $S(\Gamma)$. Now we have an integral equation. Solving for $S(\Gamma)$ gives us size distribution.

\[
C(\tau) = 1 + \beta \left| g^{(1)}(\tau) \right|^2
\]

\[
g^{(1)}(\tau) = \int S(\Gamma) \exp(-\Gamma \tau) d\Gamma
\]
Bimodal Sample

- **Nominal 20 nm and 500 nm latex run individually**
Bimodal Sample

- Mixed sample (in black)
Dust

- Dust: large, rare particles in the sample
- Generally not really part of the sample
- Since they are rare cannot get good statistics
Filtering

- Filter to remove dust. If particles are too large (D >50 nm for 0.1 µm filter), at least filter diluent.
- Filters available in sizes 20nm to 2µm
- We can also centrifuge the sample and extract the supernatant.
### Settling and DLS

The Natural limit for Dynamic Light Scattering: Gravitational Settling

Gravitational Settling occurs at about 1-3μm

<table>
<thead>
<tr>
<th>Particle Diameter (μm)</th>
<th>Movement due to Brownian Motion</th>
<th>Movement due to Gravitational Settling</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>2.36</td>
<td>&gt;&gt;</td>
</tr>
<tr>
<td>0.25</td>
<td>1.49</td>
<td>&gt;</td>
</tr>
<tr>
<td>0.50</td>
<td>1.052</td>
<td>&gt;</td>
</tr>
<tr>
<td>1.0</td>
<td>0.745</td>
<td>~</td>
</tr>
<tr>
<td>2.5</td>
<td>0.334</td>
<td>&lt;</td>
</tr>
<tr>
<td>10.0</td>
<td>0.236</td>
<td>&lt;&lt;</td>
</tr>
</tbody>
</table>

> 0.005

> 0.0346

> 0.1384

~ 0.554

< 13.84

<< 55.4
Why DLS?

- **Non-invasive measurement**
- Requires only **small quantities** of sample
- Good for **detecting trace amounts** of aggregate
- Good technique for **macromolecular sizing**
Nanoparticle Analyzer

• Single compact unit that performs size, zeta potential, and molecular weight measurements.
Q&A

Ask a question at labinfo@horiba.com

Keep reading the monthly HORIBA Particle e-mail newsletter!

Visit the Download Center to find the video and slides from this webinar.

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Thank-you