Modern Laser Diffraction for Particle Size Analysis, an Introduction

September 7, 2017
Perspective

ViewSizer 3000
nanotrack analysis (NTA)
surface charge (zeta potential)
protein aggregation

CAMSIZER XT, CAMSIZER
digital image analysis
additive manufacturing

LA-960
battery materials
powdered metals
polymers

LA-350
laser diffraction
oxides
food

camsizer

LA-100
dynamic light scattering
surface charge (zeta potential)
water treatment

SZ-100
water treatment

Resolution of mixture components

Diameters, microns

10^{-4} 10^{-3} 10^{-2} 10^{-1} 10^{0} 10^{1} 10^{2} 10^{3} 10^{4}
Why Particle Size?

Size affects material behavior and processing across a number of industries.

<table>
<thead>
<tr>
<th>Industry</th>
<th>Industry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ceramic</td>
<td>Construction</td>
</tr>
<tr>
<td>Oil/rubber</td>
<td>Chemical</td>
</tr>
<tr>
<td>Battery</td>
<td>Pharmaceutical</td>
</tr>
<tr>
<td>Electricity</td>
<td>Food/Drink</td>
</tr>
<tr>
<td>Automobile</td>
<td>Paper/Pulp</td>
</tr>
<tr>
<td>Mining</td>
<td>Ink/Toner</td>
</tr>
</tbody>
</table>
Application: Pigment Hiding Power

Operator dependent, need to wait for drying.

Operator independent, no need to wait for drying.
Core Principle

Investigate a particle with light and determine its size.
When a Light beam Strikes a Particle

Some of the light is:
- Diffracted
- Reflected
- Refracted
- Absorbed and Reradiated

- Small particles require knowledge of optical properties:
  - Real Refractive Index (bending of light, wavelength of light in particle)
  - Imaginary Refractive Index (absorption of light within particle)
  - Refractive index values less significant for large particles
- Light must be collected over large range of angles
LA-960 Optics
Diffraction Pattern
Light

Expressed in just in y-direction

\[ E = E_0 \sin(ky - \omega t) \]
\[ H = H_0 \sin(ky - \omega t) \]

Oscillating electric field

Oscillating magnetic field

(orthogonal to electric field)

Complements of Lookang @ weelookang.blogspot.com
Light: Interference

Look at just the electric field.

\[ E = E_0 \sin(kx - \omega t + \phi) \] \hspace{1cm} \text{Oscillating electric field}

\[ E = E_0 \sin(kx - \omega t) \] \hspace{1cm} \text{Second electric field with phase shift}
Path Length Difference

Path length difference is $s \sin(\theta)$

Detector (far away)
Use models to interpret data

Scattering data typically cannot be inverted to find particle shape.

We use optical models to interpret data and understand our experiments.
Laser Diffraction Models

Large particles -> Fraunhofer
More straightforward math
Large, opaque particles as 2-D disks
Use this to develop intuition

All particle sizes -> Mie
Messy calculations
All particle sizes as 3-D spheres
Fraunhofer Approximation

\[
(S_1)^2 = (S_2)^2 = \alpha^4 \left[ \frac{J_1(\alpha \sin \Theta)}{\alpha \sin \Theta} \right]^2
\]

\[
I(\Theta) = \frac{I_0}{k^2 \alpha^2} \alpha^4 \left[ \frac{J_1(\alpha \sin \Theta)}{\alpha \sin \Theta} \right]^2
\]

dimensionless size parameter \( \alpha = \frac{\pi D}{\lambda} \);

\( J_1 \) is the Bessel function of the first kind of order unity.

Assumptions:
\( a) \) all particles are much larger than the light wavelength (only scattering at the contour of the particle is considered; this also means that the same scattering pattern is obtained as for thin two-dimensional circular disks)

\( b) \) only scattering in the near-forward direction is considered (\( Q \) is small).

Limitation: (diameter at least about 40 times the wavelength of the light, or \( \alpha \gg 1 \))*

If \( \lambda = 650 \text{nm} \) (0.65 \( \mu \text{m} \)), then 40 \( \times \) 0.65 = 26 \( \mu \text{m} \)

If the particle size is larger than about 26 \( \mu \text{m} \), then the Fraunhofer approximation gives good results.
Fraunhofer: Effect of Particle Size

- 50 micron diameter
- 100 micron diameter

Scattering angle vs. scattering intensity ($I(\theta)$)
Diffraction: Large vs. Small

LARGE PARTICLE:
- Peaks at low angles
- Strong signal

SMALL PARTICLE:
- Peaks at larger angles
- Weak Signal
- Narrow Pattern - High intensity
- Wide Pattern - Low intensity
Poll

How many of you work with particles with sizes over 1 mm?

How many of you work with particles with sizes over 25 microns?

How many of you work with particles with sizes less than 1 micron?
Mie Scattering

\[ I_s(m, x, \theta) = \frac{I_0}{2k^2r^2} \left( |S_2|^2 + |S_1|^2 \right) \]

Use computer for the calculations!

\[ S_1(m, x, \theta) = \sum_1^\infty \frac{2n+1}{n(n+1)} \left\{ a_n\pi_n + b_n\tau_n \right\} \]

\[ S_2(m, x, \theta) = \sum_1^\infty \frac{2n+1}{n(n+1)} \left\{ a_n\tau_n + b_n\pi_n \right\} \]

\[ a_n = \frac{m\psi_n(mx)\psi'_n(x) - \psi_n(x)\psi'_n(mx)}{m\psi_n(mx)\xi'_n(x) - \xi_n(x)\psi'_n(mx)} \]

\[ b_n = \frac{\psi_n(mx)\psi'_n(x) - m\psi_n(x)\psi'_n(mx)}{\psi_n(mx)\xi'_n(x) - m\xi_n(x)\psi'_n(mx)} \]

\[ \pi_n = \frac{P_n^1(\cos \theta)}{\sin \theta} \]

\[ \tau_n = \frac{d}{d\theta} \left( P_n^1(\cos \theta) \right) \]

\[ \xi, \psi: \text{Ricatti-Bessel functions} \]

\[ P_n^1: 1^{\text{st}} \text{ order Legendre Functions} \]
Critical Variables

The equations are messy, but require just three inputs which are shown below. The nature of the inputs is important.

\[ x = \frac{\pi D}{\lambda} \]

Decreasing wavelength is the same as increasing size. So, if you want to measure small particles, decrease wavelength so they “appear” bigger. That is, get a blue light source for small particles.

\[ m = \frac{n_p}{n_m} \]

We need to know relative refractive index. As this goes to 1 there is no scattering.

\[ \theta \]

Scattering Angle
Refractive Index

Real part-change in wavelength

Imaginary part-absorption in particle

$n = 2 - 0.05i$

$n = 1$ (for air)
By using blue light source, we double the scattering effect of the particle. This leads to more sensitivity. This plot also tells you that you need to have the background stable to within 1% of the scattered signal to measure small particles accurately.
Example Results

Data from very small particles.

30, 40, 50, 70 nm latex standards
Effect of Size

As diameter increases, intensity (per particle) increases and location of first peak shifts to smaller angle.

As diameter increases, intensity (per particle) increases and location of first peak shifts to smaller angle.
Mixing Particles? Just Add

The result is the weighted sum of the scattering from each particle. Note how the first peak from the 2 micron particle is suppressed since it matches the valley in the 1 micron particle.
Comparison, Large Particles

For large particles, match is good out to through several peaks.
Comparison, Small Particles

For small particles, match is poor. Use Mie.
Glass Beads and Models

<table>
<thead>
<tr>
<th>Data Name</th>
<th>Graph Type</th>
<th>Refractive Index (R)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard Glass Beads Mie</td>
<td>[STD-GLASSBEADS</td>
<td>STD-GLASSBEADS( 1.510 - 0.000i),</td>
</tr>
<tr>
<td>Standard Glass Beads Fraunhofer</td>
<td>[Fraunhofer Kernel</td>
<td>Fraunhofer Kernel( 0.000 - 0.000i)</td>
</tr>
</tbody>
</table>

Graph Type: D(v,0.1) D(v,0.5) D(v,0.9)
- Red: 8.98783(μm) 13.47741(μm) 18.8536
- Blue: 2.58072(μm) 3.62044(μm) 22.3174
## CMP Slurry

<table>
<thead>
<tr>
<th>Data Name</th>
<th>Graph Type</th>
<th>Refractive Index (R)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CMP Slurry Mie</td>
<td>Red</td>
<td>2.20-0.0i [2.20-0.0i(2.200 - 0.000i), Water (1.333)]</td>
</tr>
<tr>
<td>CMP Slurry Fraunhofer</td>
<td>Blue</td>
<td>Fraunhofer Kernel [Fraunhofer Kernel (0.000 - 0.000i)]</td>
</tr>
</tbody>
</table>

![Graph](image)
Analyzing Data: Convergence

1. Initial Raw Flux
2. Calculate Modified Flux
3. Compute Flux Difference

..
Other factors

Size, Shape, and Optical Properties also affect the angle and intensity of scattered light

Extremely difficult to extract shape information without *a priori* knowledge

Assume spherical model
Pop Quiz

What particle shape is used for laser diffraction calculations?

A. Hard sphere
B. Cube
C. Triangle
D. Easy sphere
Pop Quiz

What particle shape is used for laser diffraction calculations?

A. Hard sphere  
B. Cube  
C. Triangle  
D. Easy sphere

Either gets full credit!
Measurement Workflow

Prepare the sample
Good sampling and dispersion a must!
May need to use surfactant or admixture
Measurement Workflow

Prepare the system

Align laser to maximize signal-to-noise

Acquire blank/background to reduce noise
Measurement Workflow

Introduce sample

Add sample to specific concentration range

Pump sample through measurement zone

Final dispersion (ultrasonic)
Flexible Sample Handlers

- Wide range of sample cells depending on application
- High sensitivity keeps sample requirements at minimum
- Technology has advanced to remove trade-offs
How much sample (wet)?

*It depends on sample, but here are some examples.*

**Larger, broad distributions require larger sample volume**

**Lower volume samplers for precious materials or solvents**

<table>
<thead>
<tr>
<th>Sample Handlers</th>
<th>Dispersing Volume (mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aqua/Solvo Flow</td>
<td>180 - 330</td>
</tr>
<tr>
<td>MiniFlow</td>
<td>35 - 50</td>
</tr>
<tr>
<td>Fraction Cell</td>
<td>15</td>
</tr>
<tr>
<td>Small Volume Fraction Cell</td>
<td>10</td>
</tr>
</tbody>
</table>

Note: Fraction cell has only magnetic stir bar, not for large or heavy particles

**Bio polymer**
- Median (D50): 114 µm
- Sample Amount: 1.29 mg

**Colloidal silica**
- Median (D50): 35 nm
- Sample Amount: 132 mg

**Magnesium stearate**
- Median (D50): 9.33 µm
- Sample Amount: 0.165 mg
How much sample (dry)?

It depends on sample ……
Larger, broad distributions require larger sample quantity

Can measure less than 5 mg (over a number of particle sizes).

<table>
<thead>
<tr>
<th>Material</th>
<th>Median (D50)</th>
<th>Sample Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bio polymer</td>
<td>114 µm</td>
<td>1.29 mg</td>
</tr>
<tr>
<td>Colloidal silica</td>
<td>35 nm</td>
<td>132 mg</td>
</tr>
<tr>
<td>Magnesium stearate</td>
<td>9.33 µm</td>
<td>0.165 mg</td>
</tr>
</tbody>
</table>

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Method Workflow

First determine RI
Choose solvent (water, surfactants, hexane, etc.)
Sampler selection: sample volume
Pump & stirrer settings
Concentration
Measurement duration
Does the sample need ultrasound?
  Document size-time plot
  Disperse sample, but don’t break particles
Check for reproducibility
Determine Refractive Index

Real component via literature or web search, Becke line, etc.
Measure sample, vary imaginary component to see if/how results change
Recalculate using different imaginary components, choose value that minimizes R parameter error calculation
Concentration

High enough for good S/N ratio
Low enough to avoid multiple scattering
Typically 95 – 80 %T
Measure at different T%, look at d50 result, Chi Square calculation
Ultrasonic Dispersion

Adding energy to break up agglomerates – disperse to primary particles, without breaking particles
Similar to changing air pressure on dry powder feeder
Typically set to 100% energy, vary time (sec) on
Investigate tails of distribution
  High end to see if agglomerates removed
  Small end to see if new, smaller particles appear (breakage)
Test reproducibility, consider robustness

Note:
  Do not use on emulsions
  Can cause thermal mixing trouble w/solvents - wait
  Use external probe if t > 2-5 minutes
Dispersion vs. Breakage

Theoretical

Actual

Size

Stability

Size

Increasing energy

Increasing energy

Higher air pressure or longer ultrasound duration
Dispersion vs. Breakage

Dispersion and milling can be parallel rather than sequential processes

Theoretical

Actual
Effect of Air Pressure: MCC

Graph Type:  
Remarks 1:  
Median Size:  
Air:  
- small nozzle 58.57821(µm) High  
- small nozzle 64.59890(µm) Mid  
- small nozzle 65.93757(µm) Low

- [%] vs Diameter(µm)
LA-960 Method Expert

Method Expert guides user to prepare the LA-960 for each test

Results displayed in multiple formats: PSD, D50, R-parameter
Measurement Workflow

Measurement

Click “Measure” button

*Hardware* measures scattered light distribution

*Software* then calculates size distribution
Reproducibility– Mg Stearate dry, 2 bar

<table>
<thead>
<tr>
<th>Graph Type</th>
<th>Remarks</th>
<th>Median Size</th>
<th>Air</th>
</tr>
</thead>
<tbody>
<tr>
<td>small nozzle</td>
<td>8.25422(μm)</td>
<td>Mid</td>
<td></td>
</tr>
<tr>
<td>small nozzle</td>
<td>8.20483(μm)</td>
<td>Mid</td>
<td></td>
</tr>
<tr>
<td>small nozzle</td>
<td>8.20709(μm)</td>
<td>Mid</td>
<td></td>
</tr>
<tr>
<td>small nozzle</td>
<td>8.23608(μm)</td>
<td>Mid</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>D50</th>
<th>D10</th>
<th>D90</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.254</td>
<td>4.58</td>
<td>14.898</td>
</tr>
<tr>
<td>8.205</td>
<td>4.568</td>
<td>14.678</td>
</tr>
<tr>
<td>8.207</td>
<td>4.579</td>
<td>14.583</td>
</tr>
<tr>
<td>8.236</td>
<td>4.595</td>
<td>14.722</td>
</tr>
</tbody>
</table>

Mean: 8.226 4.581 14.720
Standard Deviation: 0.024 0.011 0.132
COV (st dev/mean)*100: 0.268 0.242 0.896
## Cement Dry

<table>
<thead>
<tr>
<th></th>
<th>D10</th>
<th>D50</th>
<th>d90</th>
</tr>
</thead>
<tbody>
<tr>
<td>Portland Cement 1</td>
<td>3.255</td>
<td>11.152</td>
<td>24.586</td>
</tr>
<tr>
<td>Portland Cement 2</td>
<td>3.116</td>
<td>11.183</td>
<td>24.671</td>
</tr>
<tr>
<td>Portland Cement 3</td>
<td>3.112</td>
<td>11.128</td>
<td>24.92</td>
</tr>
<tr>
<td>Average</td>
<td>3.161</td>
<td>11.154</td>
<td>24.726</td>
</tr>
<tr>
<td>Std. Dev.</td>
<td>0.082</td>
<td>0.027</td>
<td>0.173</td>
</tr>
<tr>
<td>CV (%)</td>
<td>2.6</td>
<td>0.24</td>
<td>0.70</td>
</tr>
</tbody>
</table>
## Cement Wet

*Measure in isopropyl alcohol (IPA) (not water)*

<table>
<thead>
<tr>
<th></th>
<th>D10</th>
<th>D50</th>
<th>d90</th>
</tr>
</thead>
<tbody>
<tr>
<td>Portland Cement 1</td>
<td>2.122</td>
<td>11.81</td>
<td>27.047</td>
</tr>
<tr>
<td>Portland Cement 2</td>
<td>2.058</td>
<td>11.696</td>
<td>26.743</td>
</tr>
<tr>
<td>Portland Cement 3</td>
<td>1.999</td>
<td>11.614</td>
<td>27.001</td>
</tr>
<tr>
<td>Average</td>
<td>2.06</td>
<td>11.707</td>
<td>26.93</td>
</tr>
<tr>
<td>Std. Dev.</td>
<td>0.062</td>
<td>0.098</td>
<td>0.164</td>
</tr>
<tr>
<td>CV (%)</td>
<td>3.0</td>
<td>0.84</td>
<td>0.61</td>
</tr>
</tbody>
</table>
### Instrument to instrument variation

#### 20 instruments, 5 standards

<table>
<thead>
<tr>
<th>Sample</th>
<th>CV D10</th>
<th>CV D50</th>
<th>CV D90</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS202 (3-30µm)</td>
<td>2%</td>
<td>1%</td>
<td>2%</td>
</tr>
<tr>
<td>PS213 (10-100µm)</td>
<td>2%</td>
<td>2%</td>
<td>2%</td>
</tr>
<tr>
<td>PS225 (50-350µm)</td>
<td>1%</td>
<td>1%</td>
<td>1%</td>
</tr>
<tr>
<td>PS235 (150-650µm)</td>
<td>1%</td>
<td>1%</td>
<td>2%</td>
</tr>
<tr>
<td>PS240 (500-2000µm)</td>
<td>3%</td>
<td>2%</td>
<td>2%</td>
</tr>
</tbody>
</table>

These are results from running polydisperse standards on 20 different instruments.
### Instrument to instrument variation

**Industrial Samples**

<table>
<thead>
<tr>
<th></th>
<th>Dmean</th>
<th>D5</th>
<th>D10</th>
<th>D50</th>
<th>D90</th>
<th>D95</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average (nm)</td>
<td>155</td>
<td>112</td>
<td>119</td>
<td>152</td>
<td>193</td>
<td>208</td>
</tr>
<tr>
<td>Std. Dev. (nm)</td>
<td>0.8</td>
<td>0.8</td>
<td>0.7</td>
<td>1.0</td>
<td>1.1</td>
<td>0.7</td>
</tr>
<tr>
<td>CV (%)</td>
<td>0.5</td>
<td>0.7</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
<td>0.3</td>
</tr>
</tbody>
</table>

e 8: Instrument to instrument variation across four LA-950 systems for Formulation 1.

<table>
<thead>
<tr>
<th></th>
<th>Dmean</th>
<th>D5</th>
<th>D10</th>
<th>D50</th>
<th>D90</th>
<th>D95</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average (nm)</td>
<td>193</td>
<td>136</td>
<td>147</td>
<td>187</td>
<td>247</td>
<td>264</td>
</tr>
<tr>
<td>Std. Dev (nm)</td>
<td>1.5</td>
<td>0.5</td>
<td>0.4</td>
<td>0.6</td>
<td>0.4</td>
<td>1.1</td>
</tr>
<tr>
<td>CV (%)</td>
<td>0.8</td>
<td>0.4</td>
<td>0.3</td>
<td>0.3</td>
<td>0.2</td>
<td>0.4</td>
</tr>
</tbody>
</table>

e 9: Instrument to instrument variation across four LA-950 systems for Formulation 2.
Diffraction Drawbacks

Volume basis by default

Although excellent for mass balancing, cannot calculate number basis without significant error

No shape information
Benefits

Wide size range
  Most advanced analyzer measures from 10 \textit{nano} to 5 \textit{milli}

Flexible sample handlers
  Powders, suspensions, emulsions, pastes, creams

Very fast
  Allows for high throughput, 100’s of samples/day

Easy to use
  Many instruments are highly automated with self-guided software

Good design = Excellent precision
  Reduces unnecessary investigation/downtime

First principle measurement
  No calibration necessary

Massive global install base/history
Q&A

Ask a question at labinfo@horiba.com

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Thank-you