Size and Zeta Potential of Colloidal Gold Particles

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Colloid Definition

Two phases:
- **Dispersed phase** (particles)
- **Continuous phase** (dispersion medium, solvent)

May be solid, liquid, or gaseous

Size range 1 nm – 1 micron

High surface area creates unique properties

<table>
<thead>
<tr>
<th>Continuous Medium</th>
<th>Dispersed Medium</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Gas</td>
<td>Liquid</td>
<td>Solid</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Gas</td>
<td>NONE</td>
<td>Liquid Aerosol</td>
<td>Solid Aerosol</td>
</tr>
<tr>
<td></td>
<td>(All gases are mutually miscible)</td>
<td>Examples: fog, mist, clouds</td>
<td>Examples: smoke, air particulates</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Foam</td>
<td>Emulsion</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Examples: whipped cream</td>
<td>Examples: milk, mayonnaise, hand cream</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Solid Foam</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Examples: aerogel, styrofoam, pumice</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Solid Sol</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Examples: cranberry glass, ruby glass</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- **Sol** (suspension)
Nanoparticle Definition

Nanoparticle: size below 100 nm

$SSA = \frac{6}{\rho D}$

50 nm

D from SEM ~50 nm
D from SSA ~60-70 nm
D from DLS ~250 nm

So: is this a nanoparticle?

Used ultrasound to disperse to primary particles or use weak acid to break bonds
D from DLS ~50 nm
SZ-100: Nanoparticle Analyzer

- Size: 0.3 nm - 8 µm
  - 90° and 173°
- Zeta potential: -200 - +200 mV
  - Patented carbon coated electrodes
- Molecular weight: $1 \times 10^3 - 2 \times 10^7$ g/mol
- Optional titrator

- Nanoparticles
- Colloids
- Proteins
- Emulsions
- Disperison stability
Dynamic Light Scattering

Particles in suspension undergo Brownian motion due to solvent molecule bombardment in random thermal motion. ~ 1 nm to 1 µm

Particle moves due to interaction with liquid molecules
Small – faster
Large - slower
SZ-100 Optics

Backscatter (173°)
(High conc.)

Particles moving
due to Brownian motion

Laser
532nm, 10mW

90° for size and MW, A2

for T%

PD

Attenuator

Modulator

Zeta potential

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SZ100 Measurement Principle

\[ \frac{1}{\tau_R} = -\lim_{\tau \to 0} \left\{ \frac{\partial \ln[g(q, r)]}{\partial \tau} \right\} \]

Relaxation time

\[ \left\langle |\gamma(t) - \gamma(t + \tau)|^2 \right\rangle \approx 6D\tau \]

Particle’s moving distance

\[ D = \frac{1}{q^2\tau_R} = \frac{k_B T}{6\pi \eta a} \]

Diffusion constant

Relaxation time

Particle radius

Autocorrelation Function

\[ g(q, r) \]

Particle’s moving distance

\[ \tau_R = \frac{1}{k_B T} \]

Viscosity

\[ k_B \] Boltzmann constant

\[ q \] Scattering vector
Zeta Potential

- If surface has + charge, then - ions attracted to surface
- + ions attracted to – ions, builds electric double layer
- Slipping plane: distance from particle surface where ions move with particle
- $ZP = \text{potential (mV) at slipping plane}$
Zeta Potential: Measurement

- Apply electric field
- Measure particle motion
- Direction tells + or –
  - + particles move to –
  - - particles move to +
- Speed tells amplitude
  - Get speed from frequency shift from motion of particles
Zeta Potential Measurement

$\nu_0 + \nu_d$

Particle motion causes Doppler shift
Frequency $\rightarrow$ mobility
Mobility $\rightarrow$ zeta potential

**Mobility**

$$U = \frac{\lambda \Delta \nu_d}{2EN \sin(\theta/2)}$$

**Zeta potential**

$$\zeta = \frac{3U \cdot \eta}{2\varepsilon \cdot f(ka)}$$
Measurement Details

- First measure conductivity
- Then decide applied electric field
  - Auto or manually
- Reverse electric field to avoid polarization & electroosmosis
- To avoid electroosmotic effect near cell walls
  - “Uzgiris” type cells avoid this problem

![Diagram](image-url)
Zeta Potential Predicts Stability

Different guidelines

positive zp

+30 mV stable

0 mV not stable

-30 mV stable

negative zp

Sample Dependency

- Oil/water emulsions > 10 mV
- Polymer latices > 15 mV
- Oxides > 30 mV
- Metal sols > 40 mV
Colloidal Gold: Not so New

- Lycurgus cup 4th century AD
- Faraday experiments in 1857 “Experimental relations of gold (and other metals) to light”
- Mie in 1908 “Contributions on the optics of turbid media, particularly colloidal metal solutions”
Applications: Colloidal Gold

- Some properties change with size*
- Electronics
- Sensors
- Probes
- Diagnostics
- Drug Delivery
- Catalysis

*graph from Cytodiagnostics.com
Gold Nanoparticles In Use

- Pregnant women have excess of hormone HcG*
- HcG binds to complementary DNA base pair sequence
- That lock for HcG key is attached to gold nanoparticles
- Those gold nanoparticles reflect light of specific color
- If HcG detected: line reflects red

*human gonadotropin hormone
Gold Nanoparticle Standards

- Nano-materials; Gold colloid

<table>
<thead>
<tr>
<th>Au Colloid</th>
<th>RM8011 (10 nm), 8012 (30 nm), 8013 (60 nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrodynamic Dia.</td>
<td>13.5 nm, 32.4 nm, 58.4 nm</td>
</tr>
</tbody>
</table>

Conditions
- Temperature: 25°C
- Solvent: Water
- Refractive Index: 1.333
- Distribution base: Scattering light

<table>
<thead>
<tr>
<th></th>
<th>Z ave. (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RM8011</td>
<td>13.0</td>
</tr>
<tr>
<td>RM8012</td>
<td>32.0</td>
</tr>
<tr>
<td>RM8013</td>
<td>58.0</td>
</tr>
</tbody>
</table>
NIST Gold Nanoparticle RMs

National Institute of Standards & Technology

Report of Investigation
Reference Material 8011
Gold Nanoparticles, Nominal 10 nm Diameter

<table>
<thead>
<tr>
<th>Technique</th>
<th>Analyte Form</th>
<th>Particle Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic Force Microscopy</td>
<td>dry, deposited on substrate</td>
<td>8.5 ± 0.3</td>
</tr>
<tr>
<td>Scanning Electron Microscopy</td>
<td>dry, deposited on substrate</td>
<td>9.9 ± 0.1</td>
</tr>
<tr>
<td>Transmission Electron Microscopy</td>
<td>dry, deposited on substrate</td>
<td>8.9 ± 0.1</td>
</tr>
<tr>
<td>Differential Mobility Analysis</td>
<td>dry, aerosol</td>
<td>11.3 ± 0.1</td>
</tr>
<tr>
<td>Dynamic Light Scattering</td>
<td>liquid suspension</td>
<td>13.5 ± 0.1</td>
</tr>
<tr>
<td>Small-Angle X-ray Scattering</td>
<td>liquid suspension</td>
<td>9.1 ± 1.8</td>
</tr>
</tbody>
</table>
# ASTM Interlaboratory Study RM 8011

<table>
<thead>
<tr>
<th>Material</th>
<th>Average 1</th>
<th>Standard Deviation of the lab averages</th>
<th>Repeatability Standard Deviation</th>
<th>Reproducibility Standard Deviation</th>
<th>Repeatability Limit</th>
<th>Reproducibility Limit</th>
<th>Number of Reporting Laboratories</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample A-combined</td>
<td>15.8</td>
<td>4.2</td>
<td>2.0</td>
<td>4.7</td>
<td>5.7</td>
<td>13.1</td>
<td>13</td>
</tr>
<tr>
<td>Sample B-combined</td>
<td>31.2</td>
<td>3.6</td>
<td>2.0</td>
<td>4.1</td>
<td>5.7</td>
<td>11.5</td>
<td>13</td>
</tr>
<tr>
<td>Sample C-combined</td>
<td>59.8</td>
<td>5.0</td>
<td>5.0</td>
<td>6.8</td>
<td>13.9</td>
<td>19.2</td>
<td>13</td>
</tr>
<tr>
<td>Sample D-combined</td>
<td>8.0</td>
<td>2.4</td>
<td>0.9</td>
<td>2.6</td>
<td>2.6</td>
<td>7.2</td>
<td>12</td>
</tr>
<tr>
<td>Sample E-combined</td>
<td>6.7</td>
<td>1.8</td>
<td>0.9</td>
<td>2.0</td>
<td>2.6</td>
<td>5.6</td>
<td>12</td>
</tr>
</tbody>
</table>

1. **Average**: The average value of the measurements made by each laboratory.
NIST Colloidal Gold

Technique Size nm
Atomic Force Microscopy 8.5 ± 0.3
Scanning Electron Microscopy 9.9 ± 0.1
Transmission Electron Microscopy 8.9 ± 0.1
Differential Mobility Analysis 11.3 ± 0.1
Dynamic Light Scattering 13.5 ± 0.1
Small-Angle X-ray Scattering 9.1 ± 1.8

Technique Size nm
Atomic Force Microscopy 24.9 ± 1.1
Scanning Electron Microscopy 26.9 ± 0.1
Transmission Electron Microscopy 27.6 ± 2.1
Differential Mobility Analysis 28.4 ± 1.1
Dynamic Light Scattering 173° scattering angle 28.6 ± 0.9
90° scattering angle 26.5 ± 3.6
Small-Angle X-ray Scattering 24.9 ± 1.2

Technique Size nm
Atomic Force Microscopy 55.4 ± 0.3
Scanning Electron Microscopy 54.9 ± 0.4
Transmission Electron Microscopy 56.0 ± 0.5
Differential Mobility Analysis 56.3 ± 1.5
Dynamic Light Scattering 173° scattering angle 56.6 ± 1.4
90° scattering angle 55.3 ± 8.3
Small-Angle X-ray Scattering 53.2 ± 5.3

NIST Certificates

SZ-100 Results

<table>
<thead>
<tr>
<th>Technique</th>
<th>Average</th>
<th>St dev</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>13.4 nm</td>
<td>1.8</td>
</tr>
<tr>
<td>Sample 2</td>
<td>12.6 nm</td>
<td>1.9</td>
</tr>
<tr>
<td>ASTM</td>
<td>Z ave</td>
<td>st dev</td>
</tr>
<tr>
<td>Combined</td>
<td>15.8 nm</td>
<td>4.2</td>
</tr>
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</table>

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<tr>
<th>Technique</th>
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<tbody>
<tr>
<td>Sample 1</td>
<td>31.5 nm</td>
<td>3.9</td>
</tr>
<tr>
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<td>5.9</td>
</tr>
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<tr>
<td>Sample 1</td>
<td>57.6 nm</td>
<td>3.5</td>
</tr>
<tr>
<td>Sample 2</td>
<td>58.4 nm</td>
<td>3.9</td>
</tr>
<tr>
<td>ASTM</td>
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<td>59.8 nm</td>
<td>5.0</td>
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Colloidal Gold, Real World Data*

*thank-you to Cytodiagnostics, www.cytodiagnostics.com

### Summary Table
(Three Measurements of Each Sample)

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Zeta Potential, mV</th>
<th>Z-Average Diameter, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Avg. of 3 repeats</td>
<td>S.D.</td>
</tr>
<tr>
<td>Sample 1</td>
<td>20 nm Gold NP</td>
<td>-54.4</td>
</tr>
<tr>
<td>Sample 2</td>
<td>50 nm Gold NP</td>
<td>-39.1</td>
</tr>
<tr>
<td>Sample 3</td>
<td>100 nm Gold NP</td>
<td>-59.5</td>
</tr>
</tbody>
</table>
Colloidal Gold, Real World Data*

*thank-you to Cytodiagnostics, www.cytodiagnostics.com
Colloidal Gold, Real World Data *

*thank-you to Cytodiagnostics, www.cytodiagnostics.com
Colloidal Gold Real World Data*
Zeta Potential

*thank-you to Cytodiagnostics, www. cytodiagnostics.com
Colloidal Gold for Sale

**Properties**

- **Related Categories:** 7th Au, Materials Science, Nanomaterials, Nanoparticles and Nanoparticle Dispersions, New Products for Materials Research and Engineering
- **Concentration:** 3.0E+9 particles/mL
- **OD:** 1
- **Diameter:** 100 nm
- **Mw:** 62,000
- **UV Absorption:** λmax 564-574 nm

**Price and Availability**

- SKU: 742601-100ML
  - **Availability:** Ships on 08/01/12 - FROM
  - **Price (USD):** $x
  - **Quantity:** 1

**Description**

- **Application:** This material is highly monodisperse (<12% variability in size and shape), and provides significantly improved surface reactivity. Applications include Surface Enhanced Raman Spectroscopy (SERS), Sensing/Detection, Biological Targeting, Plasmonics, and Electronics.
- **Packaging:** 25, 100 mL in glass bottle
- **Legal Information:** Product of CyoDiagnostics, Inc.

**Explores the Future**

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Colloidal Gold, Real World Data *

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Z-Average Diameter, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Avg. of 3 repeats</td>
</tr>
<tr>
<td>Sample 1</td>
<td>258-106</td>
</tr>
<tr>
<td>Sample 2</td>
<td>272-004</td>
</tr>
<tr>
<td>Sample 3</td>
<td>272-008</td>
</tr>
</tbody>
</table>

* Un-named customer at their request
Colloidal Gold: Drug Delivery*

- Cancer therapy delivers drug to all rapidly dividing cells
- Prodrugs delivered in inactive form
- Once delivered, metabolized in vivo into active metabolite
- Study: Immobilize prodrug activating enzyme onto colloidal gold particles
- Enzymes: genetically modified nitroreductase from E. coli; NfnB and Cys-NfnB

Colloidal Gold: Drug Delivery*

- Start with 50nm gold particles
- Incubate with varying molar equivalents (90:1, 180:1, 270:1, 360:1, and 450:1) of purified recombinant Cys-NfnB or His-NfnB overnight at 4C
- Analyzed on SZ-100 for particle size and zeta potential

Colloidal Gold: Drug Delivery*

- **Base particle**
  - Size 51 nm
  - Zeta potential -52 mV
- **NfnB ~ 5 nm**
- **Combined ~ 60 nm**

Zeta Potential Cells

- Gold coated electrodes (ruined)
- Carbon coated electrodes

Lysozyme protein

800 measurements with one cell
Resources: www.horiba.com/particle

- Receive news of updates
- View application notes, webinars, etc.

Thank-you