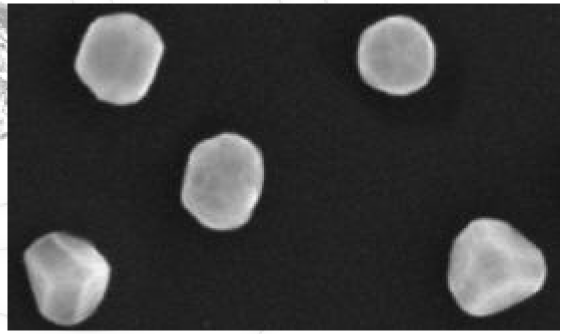

Size and Zeta Potential of Colloidal Gold Particles

Mark Bumiller
mark.bumiller@horiba.com

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Colloid Definition

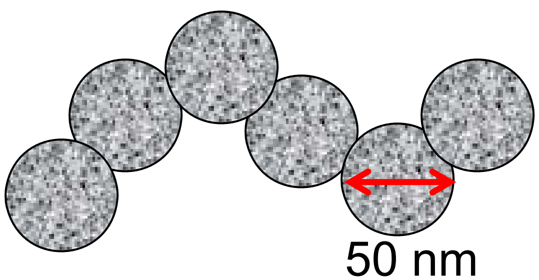
Two phases:
•**Dispersed phase** (particles)
•**Continuous phase** (dispersion medium, solvent)
May be solid, liquid, or gaseous
Size range 1 nm – 1 micron
High surface area creates unique properties

		Dispersed Medium		
		Gas	Liquid	Solid
Continuous Medium	Gas	**NONE** (All gases are mutually miscible)	**Liquid Aerosol** Examples: fog, mist, clouds	**Solid Aerosol** Examples: smoke, air particulates
	Liquid	**Foam** Examples: whipped cream	**Emulsion** Examples: milk, mayonnaise, hand cream	**Sol** (suspension) Examples: paint, pigmented ink
	Solid	**Solid Foam** Examples: aerogel, styrofoam, pumice	**Gel** Examples: gelatin, jelly, cheese, opal	**Solid Sol** Examples: cranberry glass, ruby glass

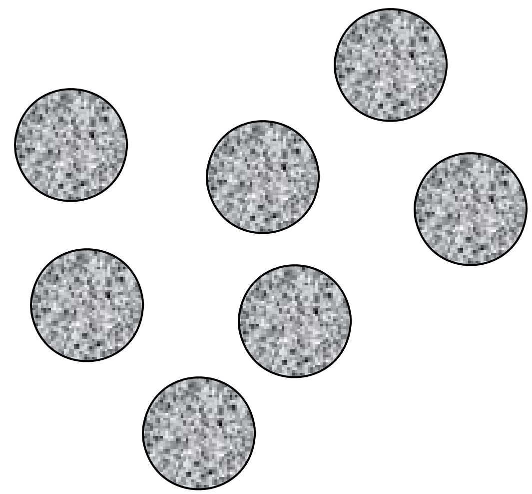
Nanoparticle Definition

Nanoparticle: size below 100 nm

SSA = $6/\rho D$



ultrasound



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

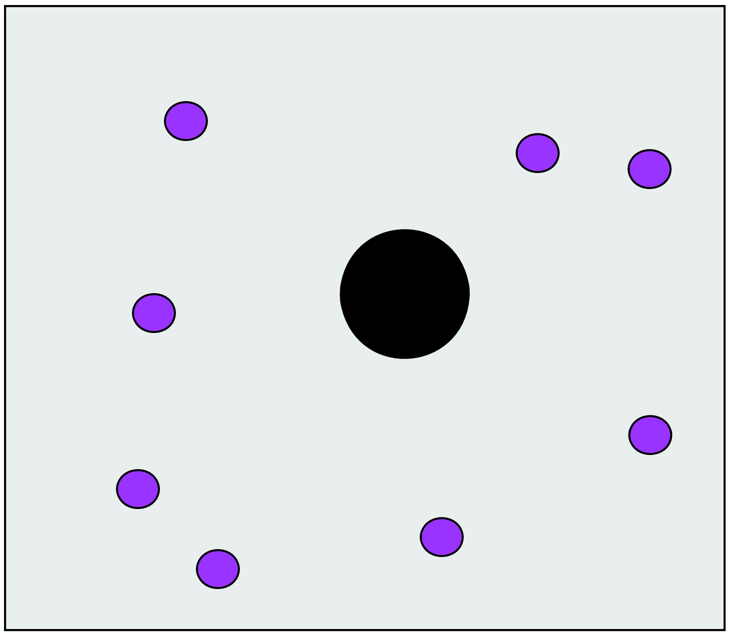
SZ-100: Nanoparticle Analyzer

- Size: .3 nm - 8 µm
  - 90° and 173°
- Zeta potential: -200 - +200 mV
  - Patented carbon coated electrodes
- Molecular weight: $1x10^3$ - $2x10^7$ g/mol
- Optional titrator

•Nanoparticles
•Colloids
•Proteins
•Emulsions
•Disperison stability

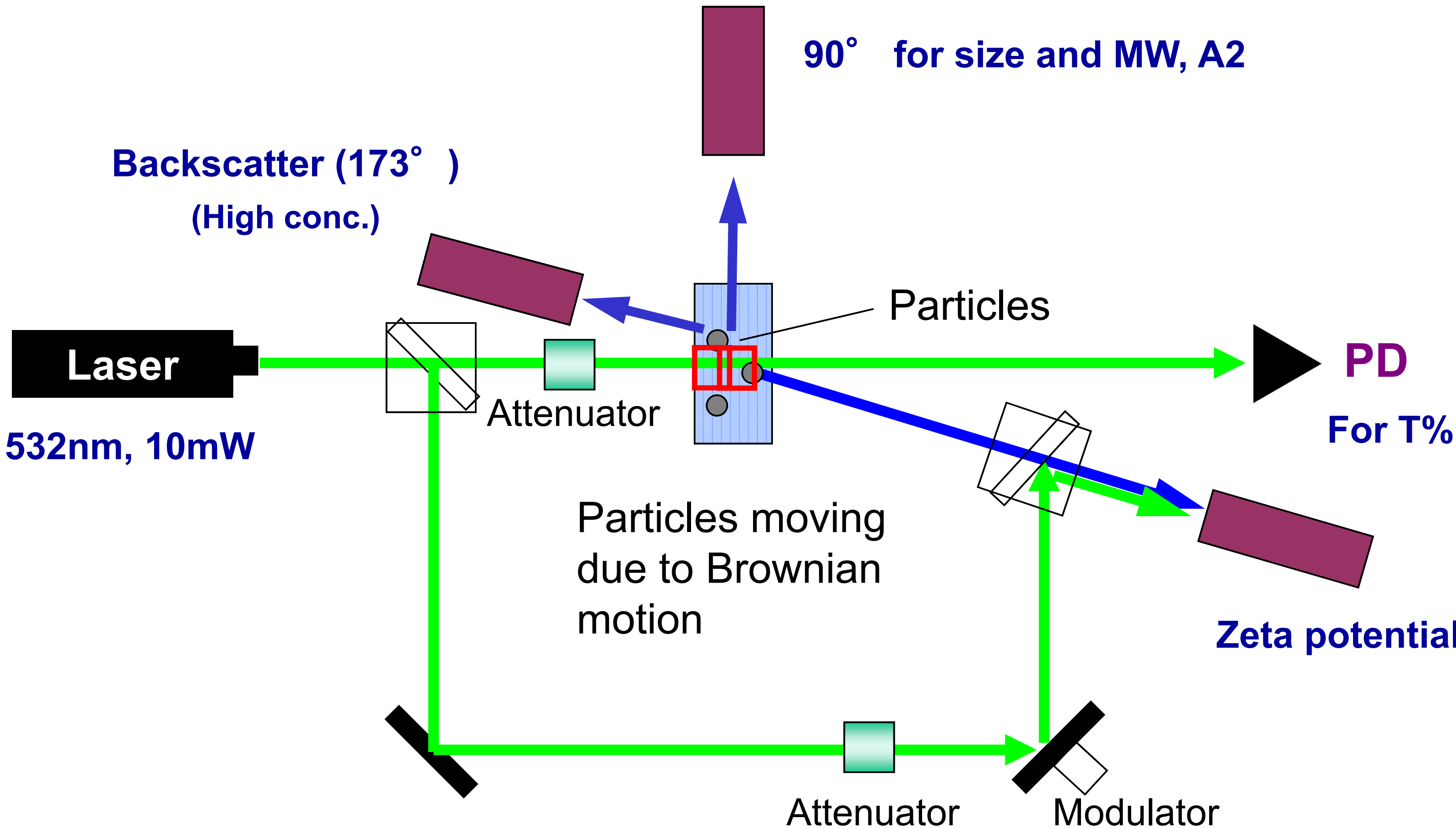
Dynamic Light Scattering

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

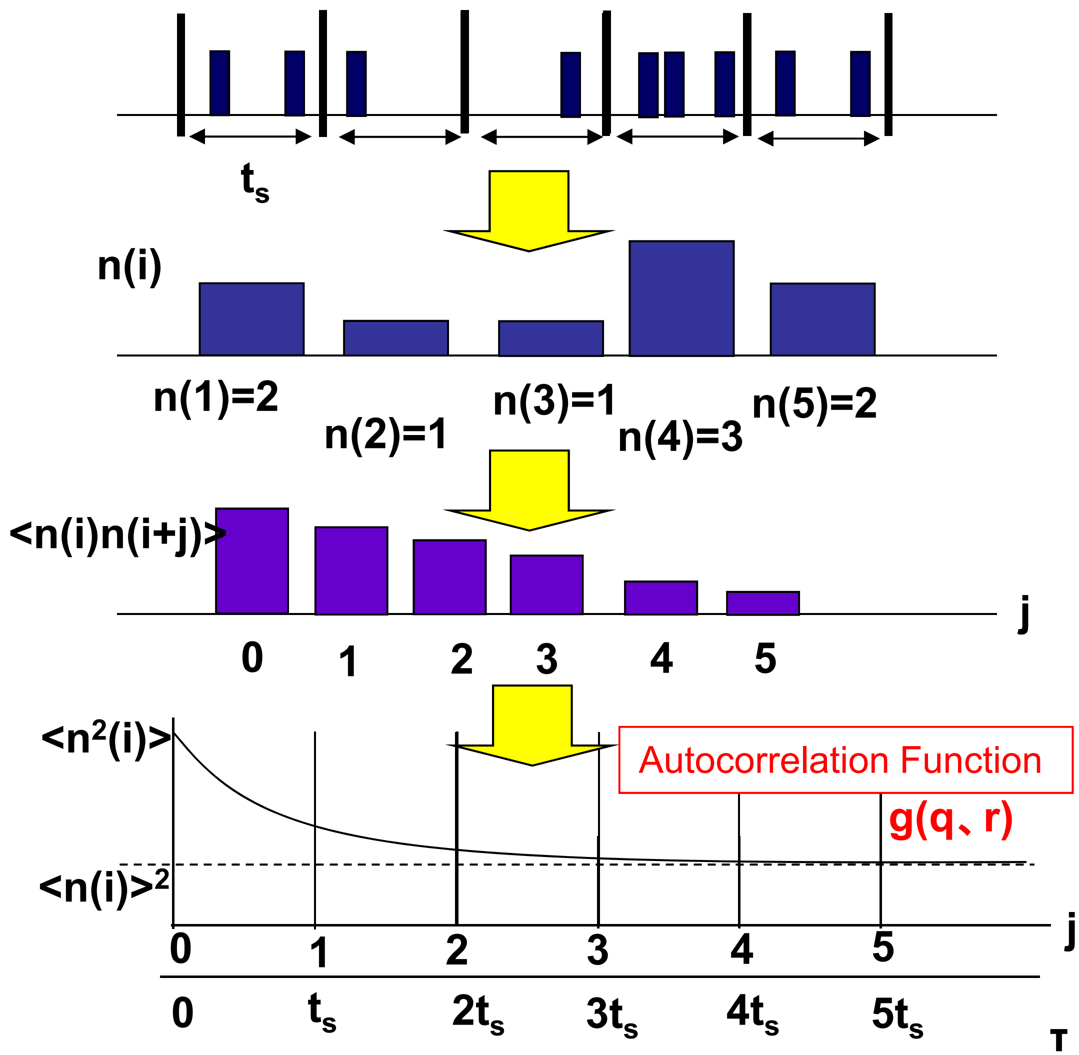


Particle moves due to interaction with liquid molecules
Small – faster
Large - slower

SZ-100 Optics



SZ100 Measurement Principle



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

Relaxation time

$$\left\langle \left| \gamma(t) - \gamma(t+\tau)\right)^2 \right| \right\rangle \cong 6D\tau$$

Particle's moving distance

Diffusion constant

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

Relaxation time

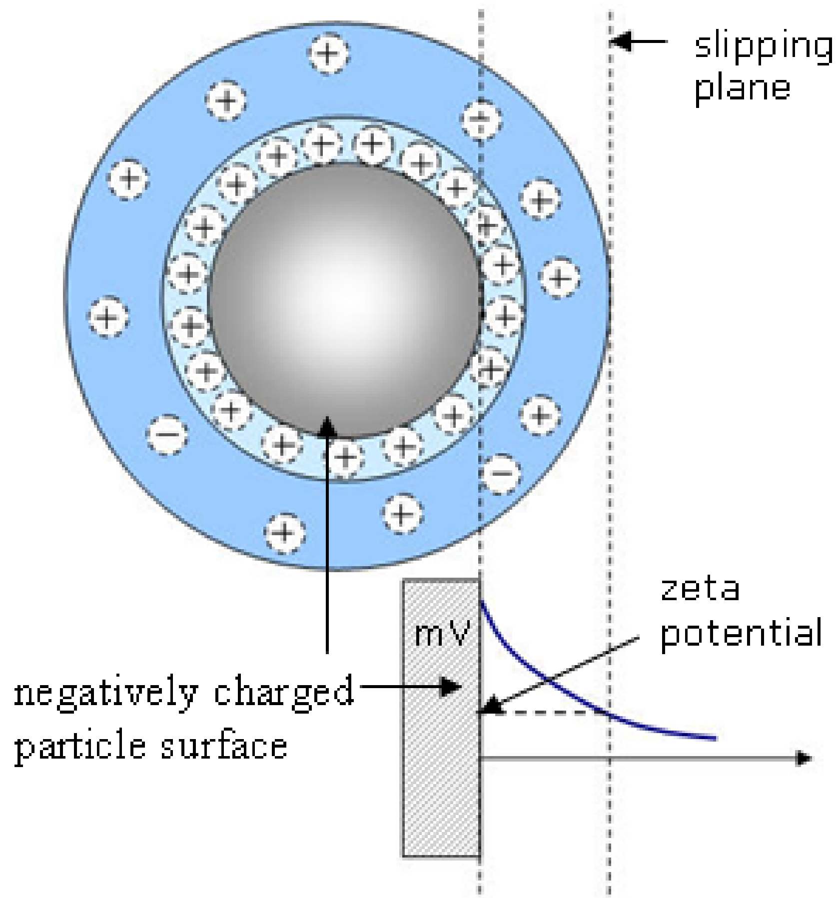
Particle radius

q: Scattering vector η: Viscosity

k_B: Boltzmann constant

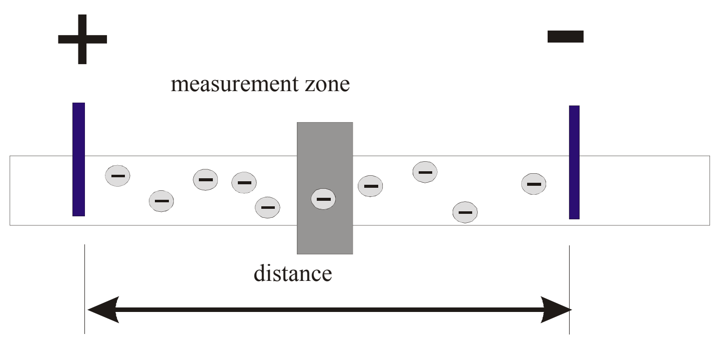
Zeta Potential

- 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 = potential (mV) at slipping plane

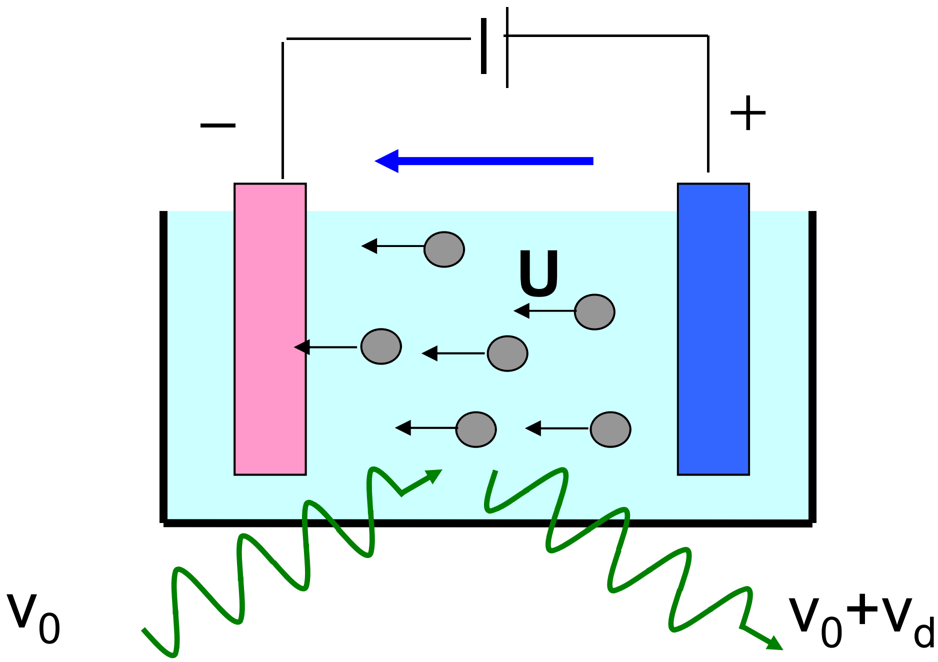


Zeta Potential: Measurement

- 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



Particle motion causes Doppler shift
Frequency → mobility
Mobility → zeta potential

Mobility

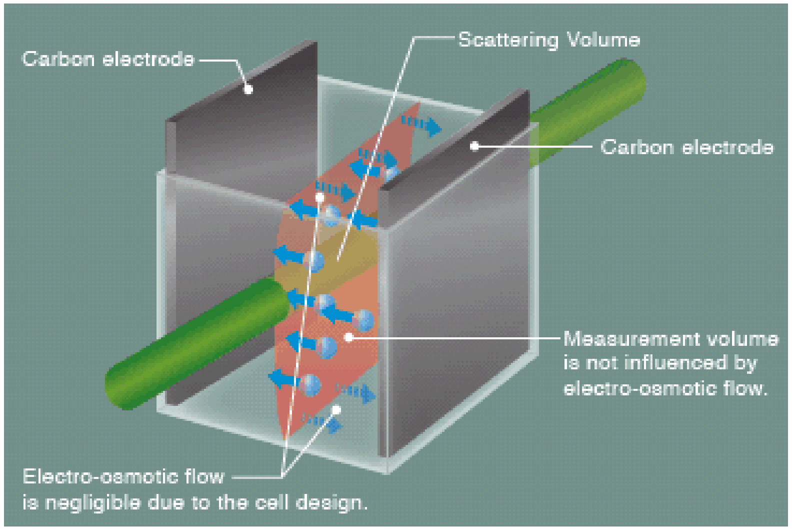
$$U = \frac{\lambda \Delta \nu_d}{2En\sin(\theta/2)}$$

Zeta potential

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

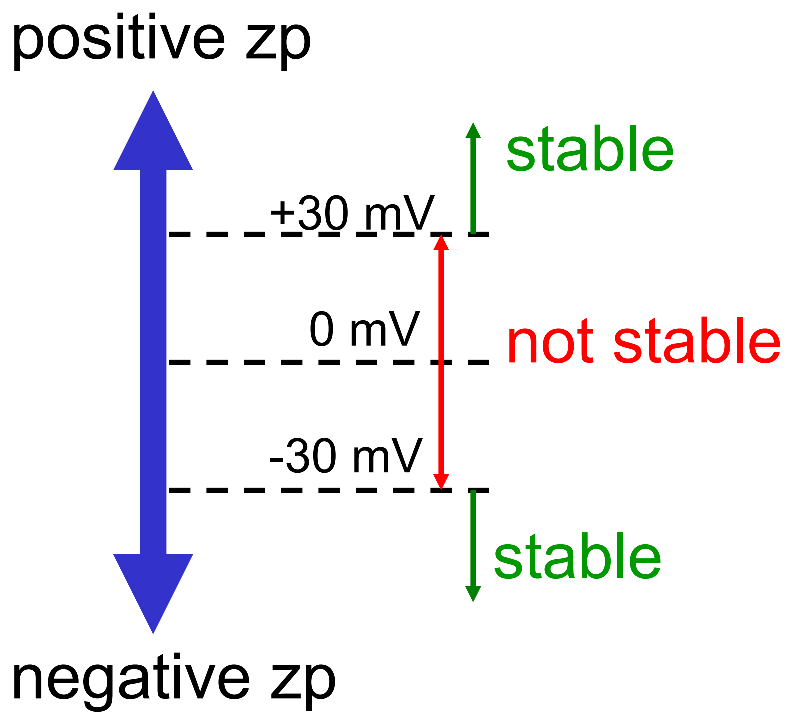
Measurement Details

- 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



Zeta Potential Predicts Stability

Different guidelines



Sample Dependency

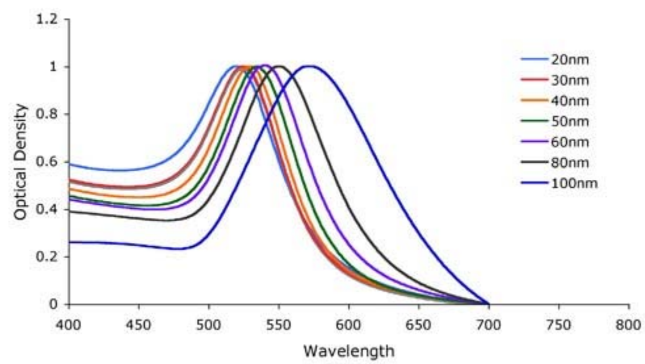
- Oil/water emulsions > 10 mV
- Polymer latices > 15 mV
- Oxides > 30 mV
- Metal sols > 40 mV

Colloidal Gold: Not so New

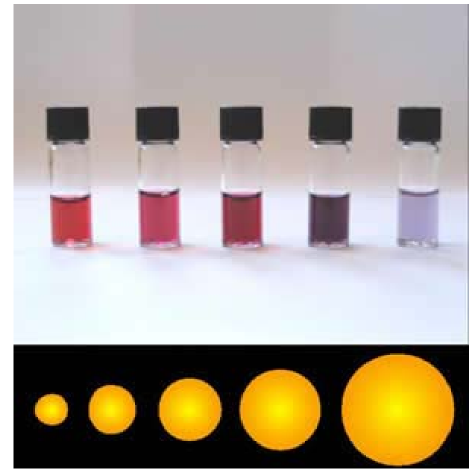
- Lycurgus cup 4th century AD
- Faraday experiments in 1857 “Experimental relations of gold (and other metals) to light”
- Mie in 1908 “Contributions on the optics of turbid media, particularly colloidal metal solutions”

Applications: Colloidal Gold

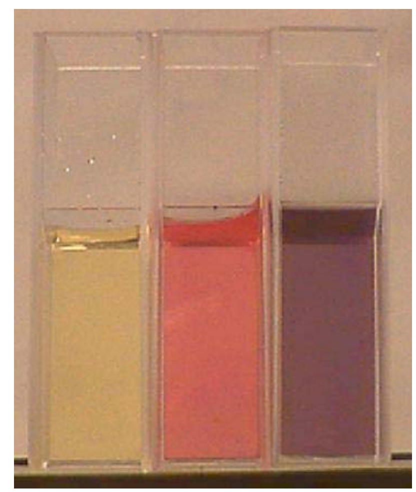
- Some properties change with size*
- Electronics
- Sensors
- Probes
- Diagnostics
- Drug Delivery
- Catalysis



*graph from to Cytodiagnostics.com

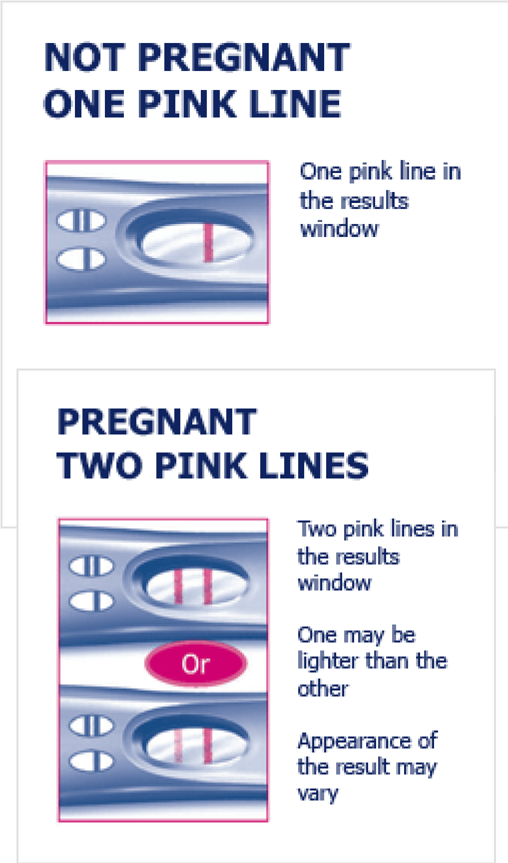


Red → Blue



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 gonadotropic hormone

Gold Nanoparticle Standards

●Nano-materials; Gold colloid

Au Colloid	RM8011(10 nm), 8012(30 nm), 8013 (60 nm)
Hydrodynamic Dia.	13.5 nm, 32.4 nm, 58.4 nm

<u>Conditions</u>

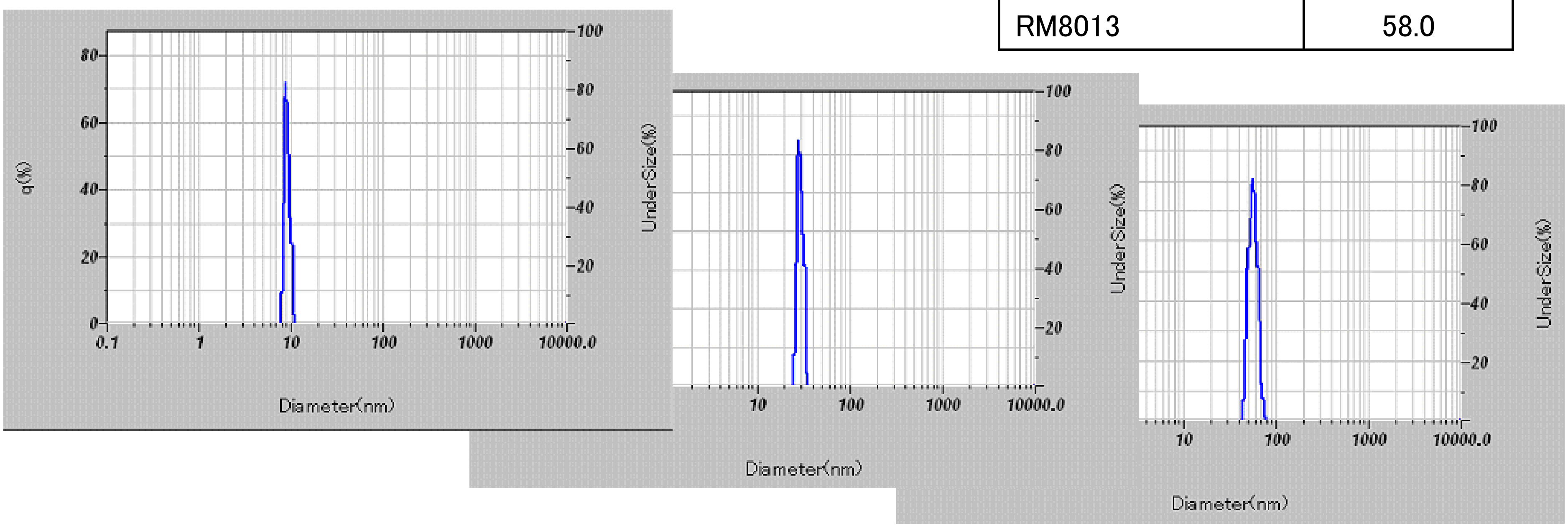
Temperature; 25 C degree

Solvent; Water

Refractive Index; 1.333

Distribution base; Scattering light

	Z ave. (nm)
RM8011	13.0
RM8012	32.0
RM8013	58.0



NIST Gold Nanoparticle RMs

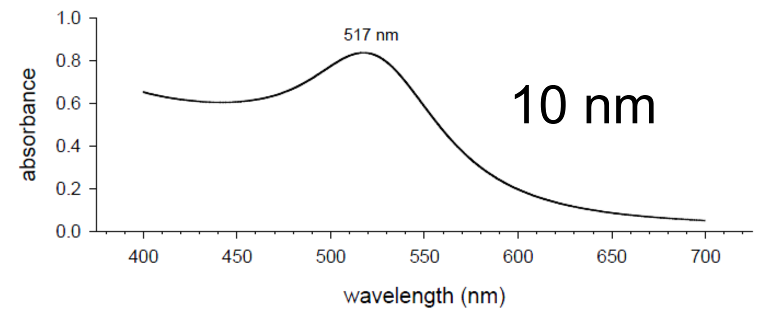
National Institute of Standards & Technology

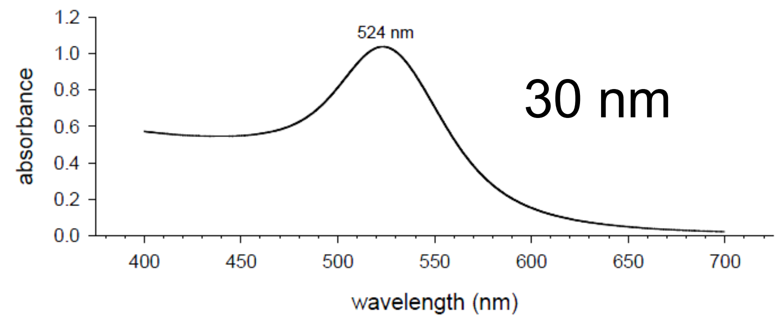
Report of Investigation

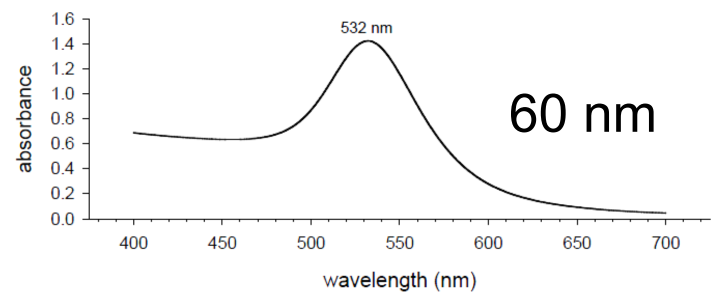
Reference Material 8011

Gold Nanoparticles, Nominal 10 nm Diameter

Technique	Analyte Form	Particle Size (nm)
Atomic Force Microscopy	dry, deposited on substrate	8.5 ± 0.3
Scanning Electron Microscopy	dry, deposited on substrate	9.9 ± 0.1
Transmission Electron Microscopy	dry, deposited on substrate	8.9 ± 0.1
Differential Mobility Analysis	dry, aerosol	11.3 ± 0.1
Dynamic Light Scattering	liquid suspension	13.5 ± 0.1
Small-Angle X-ray Scattering	liquid suspension	9.1 ± 1.8



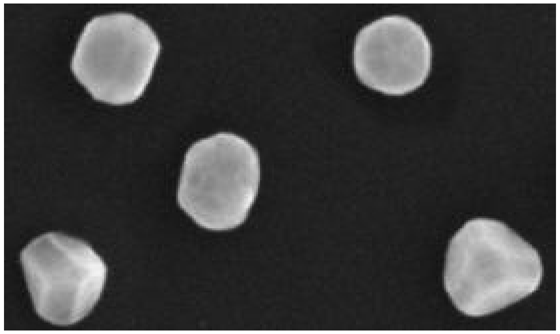




ASTM Interlaboratory Study RM 8011

Material	Average [1]	Standard Deviation of the lab averages	Repeatability Standard Deviation	Reproducibility Standard Deviation	Repeatability Limit	Reproducibility Limit	Number of Reporting Laboratories
	$\bar{x}$	$s_{\bar{x}}$	s_r	s_R	r	R	n
Sample A-combined	15.8	4.2	2.0	4.7	5.7	13.1	13
Sample B-combined	31.2	3.6	2.0	4.1	5.7	11.5	13
Sample C-combined	59.8	5.0	5.0	6.8	13.9	19.2	13
Sample D-combined	8.0	2.4	0.9	2.6	2.6	7.2	12
Sample E-combined	6.7	1.8	0.9	2.0	2.6	5.6	12

NIST Colloidal Gold



NIST Certificates

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	
173º scattering angle	28.6 ± 0.9
90º 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	
173º scattering angle	56.6 ± 1.4
90º scattering angle	55.3 ± 8.3
Small-Angle X-ray Scattering	53.2 ± 5.3

SZ-100 Results

8011		
HORIBA	**Average**	**St dev**
Sample 1	13.4 nm	1,8
Sample 2	12.6nm	1,9
ASTM	**Z ave**	**st dev**
Combined	15.8 nm	4,2

8012		
HORIBA	**Average**	**St dev**
Sample 1	31.5nm	3,9
Sample 2	32.4 nm	5,9
ASTM	**Z ave**	**st dev**
Combined	31.2 nm	3,6

8013		
HORIBA	**Average**	**St dev**
Sample 1	57.6 nm	3,5
Sample 2	58.4 nm	3,9
ASTM	**Z ave**	**st dev**
Combined	59.8 nm	5,0

Colloidal Gold, Real World Data*

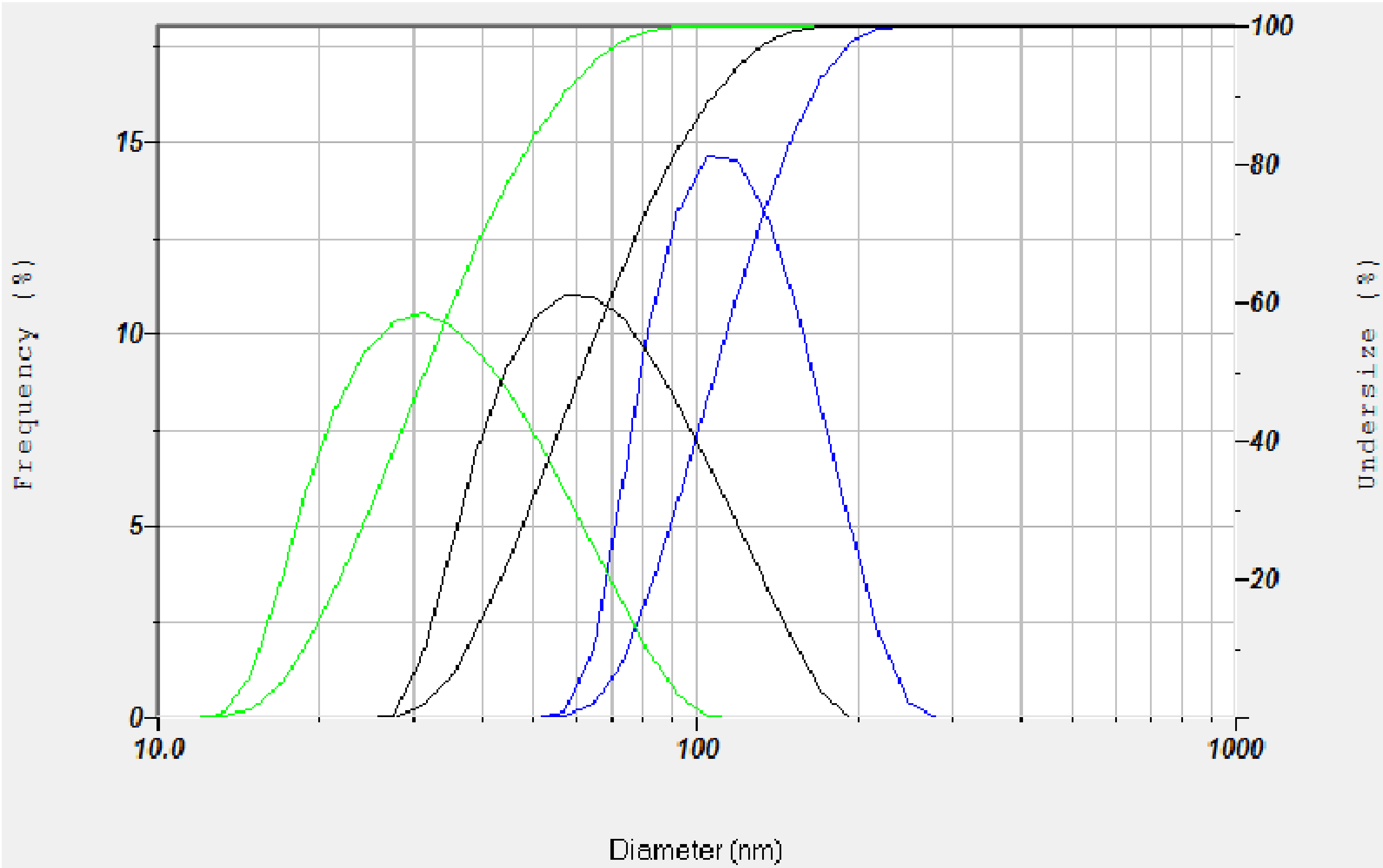
Summary Table
(Three Measurements of Each Sample)

	Sample ID	Zeta Potential, mV		Z-Average Diameter, nm	
		Avg. of 3 repeats	S.D.	Avg. of 3 repeats	S.D.
Sample 1	20 nm Gold NP	-54.4	0.1	29.5	0.1
Sample 2	50 nm Gold NP	-39.1	0.3	57.9	0.2
Sample 3	100 nm Gold NP	-59.5	2.7	106.2	0.5

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

cytodiagnostics

Colloidal Gold, Real World Data*



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Colloidal Gold, Real World Data *

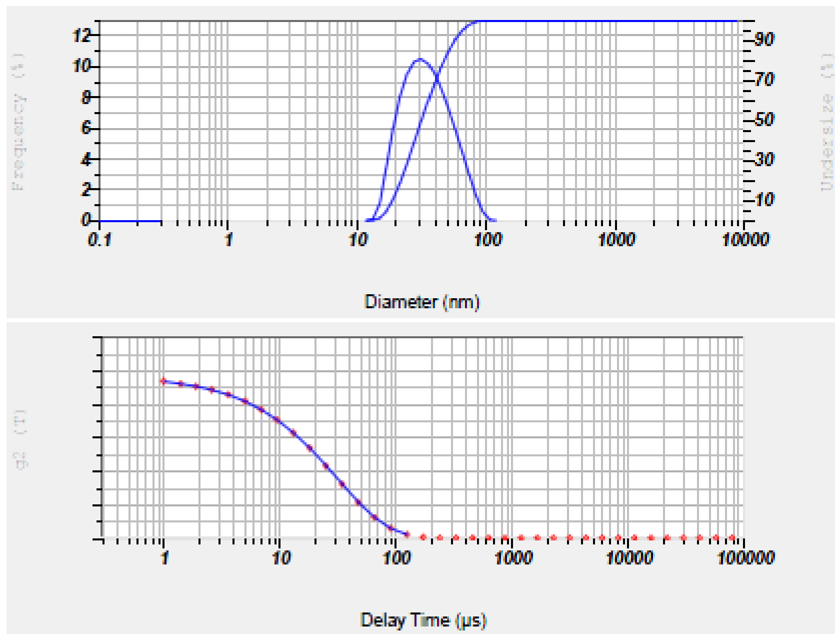
Measurement Results

Sample Name	:	20nm Gold NP
Date	:	Wednesday, November 23, 2011 12:53:41 PM
Measurement Type	:	Particle Size
Scattering Angle	:	173
Temperature of the holder	:	24.9 °C
Form Of Distribution	:	Standard
Representation of result	:	Scattering Light Intensity
Count rate	:	3869 kCPS

Calculation Results

Cumulant Operations

Z-Average	:	29.4 nm
PI	:	0.094



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Colloidal Gold Real World Data*

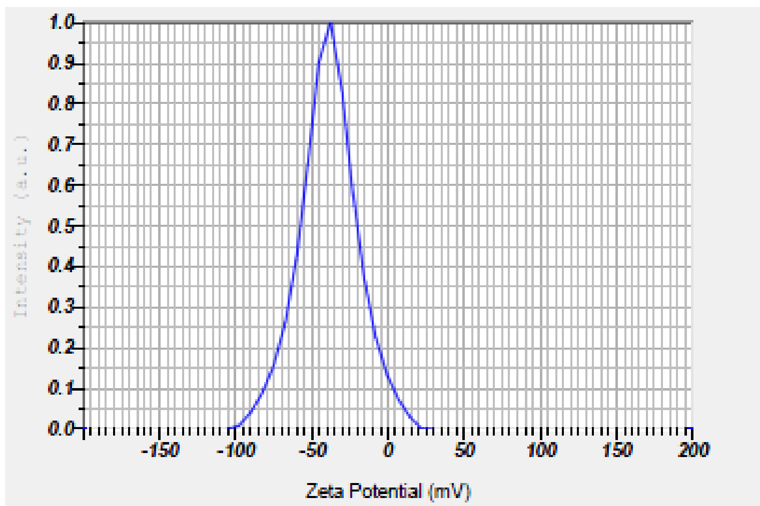
Zeta Potential

Measurement Results

Sample Name	: 50nm Gold NP
Date	: Wednesday, November 23, 2011 2:51:34 PM
Measurement Type	: Zeta Potential
Temperature of the holder	: 25.0 °C
Electrode Voltage	: 3.4 V

Calculation Results

Zeta Potential (Mean)	: -38.9 mV
Electrophoretic Mobility mean	: -0.000302 cm^2/Vs



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Colloidal Gold for Sale

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742031 ALDRICH

Gold nanoparticles

100 nm diameter, OD 1, stabilized suspension in citrate buffer

DOWNLOAD MSDS (PDF)

Synonym: AU NP, Gold Colloid

Linear Formula Au | Molecular Weight 196.97 | EC Number 231-791-2 | MDL number MFCD00003436

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Au

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Properties

Related Categories	79: Au, Materials Science, Nanomaterials, Nanopowders and Nanoparticle Dispersions, New Products for Materials Research and Engineering More...
concentration	~3.8E+9 particles/mL
OD	1
diameter	100 nm
M_w/M_n	<0.2
UV absorption	λ_{max} 564-574 nm

Price and Availability

SKU-Pack Size	Availability	Price (USD)	Quantity
742031-25ML	Ships on 08/07/12 - FROM		
742031-100ML	Ships on 08/07/12 - FROM		

Bulk orders?

ADD TO CART

Description

Application

This material is highly monodisperse (<12% variability in size and shape), and provides significantly improved surface reactivity. Applications include Surface Enhanced Raman Lables[1], Sensing/Detection[2], Biological Targeting[3], Plasmonics[4] and Electronics[5].

Packaging

25, 100 mL in glass bottle

Legal Information

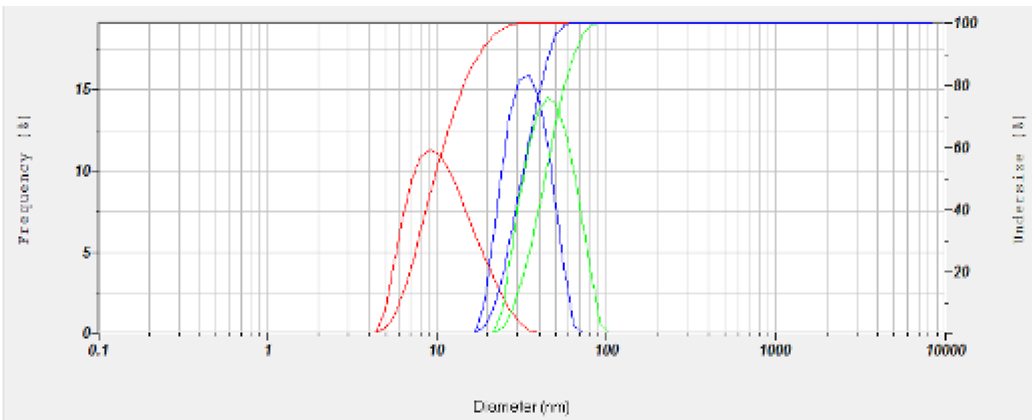
Product of CytoDiagnostics, Inc.

Colloidal Gold, Real World Data *

Summary Table
(Three Measurements of Each Sample)

	Sample ID	Z-Average Diameter, nm	
		Avg. of 3 repeats	S.D.
Sample 1	258-106	27.1	0.1
Sample 2	272-004	10.9	0.6
Sample 3	272-008	37.7	0.1

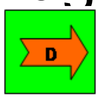
Overlay of 3 Samples

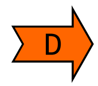


Blue: 258-106
Red: 272-004
Green: 282-008

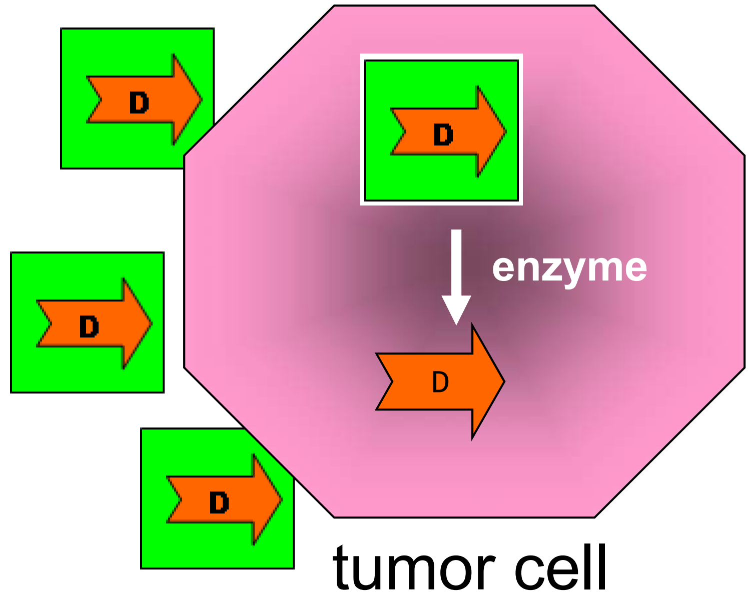
* Un-named customer at their request

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 Modified with a Genetically Engineered Nitroreductase: Toward a Novel Enzyme Delivery System for Cancer Prodrug Therapy, Vanessa V. Gwenin, Chris D. Gwenin, and Maher Kalaji *Langmuir*, **2011**, *27* (23), pp 14300–14307

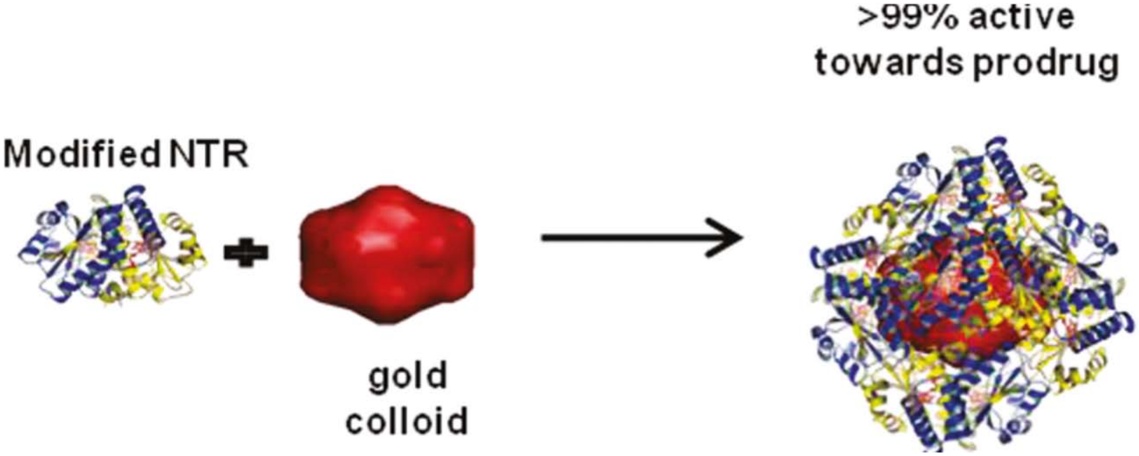
Colloidal Gold: Drug Delivery*

- 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 Modified with a Genetically Engineered Nitroreductase: Toward a Novel Enzyme Delivery System for Cancer Prodrug Therapy, Vanessa V. Gwenin, Chris D. Gwenin, and Maher Kalaji *Langmuir*, **2011**, *27* (23), pp 14300–14307

Colloidal Gold: Drug Delivery*

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



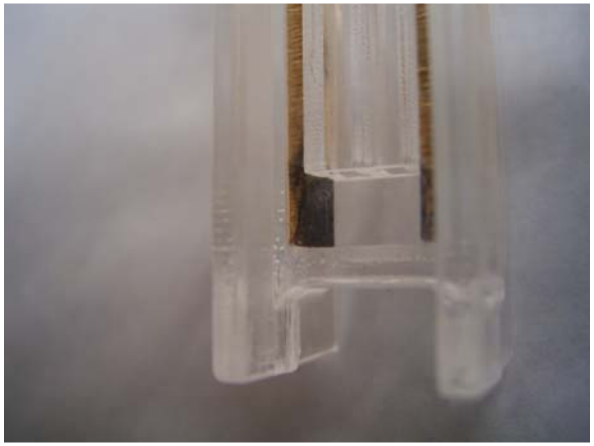
		Molar ratio of enzyme to gold colloid				
		90:1	180:1	270:1	360:1	450:1
His-NfnB-gold colloid	Size (nm)	53.5	57.5	82.6	69.7	75.4
	Zeta-potential (mV)	-43	-31.7	-30.7	-33.3	-30.4
Cys-NfnB-gold colloid	Size (nm)	56.3	59.8	61.1	69.8	69.7
	Zeta-potential (mV)	-23.4	-25.3	-26.0	-27.7	-34.2

less ordered

more ordered

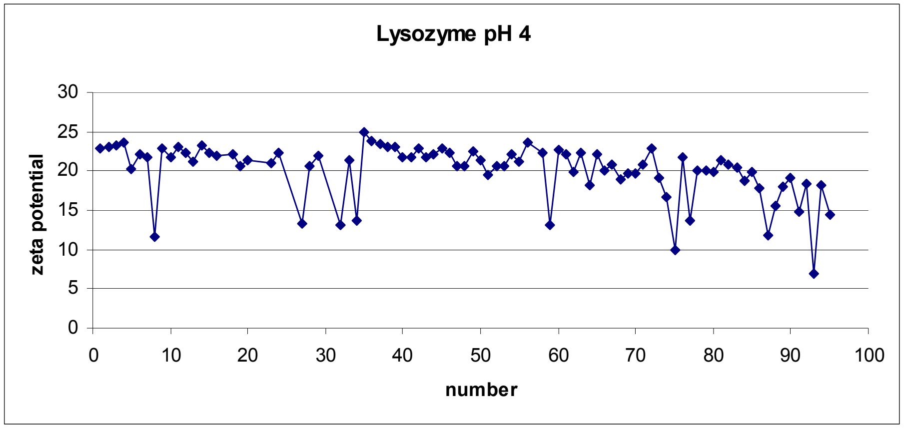
Colloidal Gold Modified with a Genetically Engineered Nitroreductase: Toward a Novel Enzyme Delivery System for Cancer Prodrug Therapy, Vanessa V. Gwenin, Chris D. Gwenin, and Maher Kalaji *Langmuir*, **2011**, *27* (23), pp 14300–14307

Zeta Potential Cells

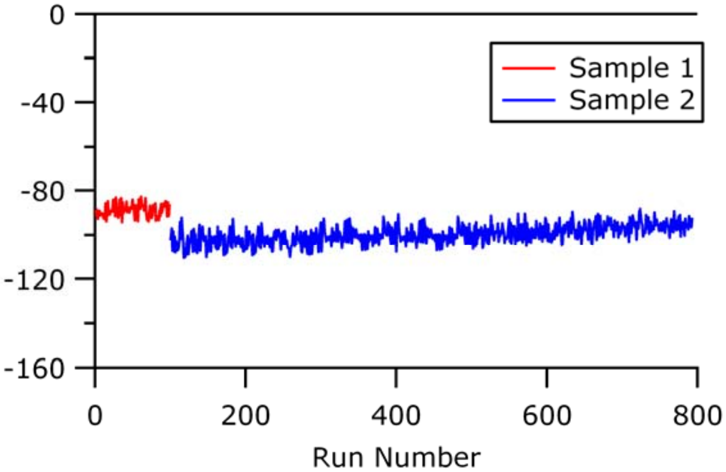


Gold coated electrodes (ruined)

Carbon coated electrodes



Lysozyme protein



800 measurements with one cell

Explore the future

HORIBA

Resources: www.horiba.com/particle

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View application notes, webinars, etc.

Thank-you