Synthesis and Characterization of Gold Nanoparticles

(2016/03/14 revised)

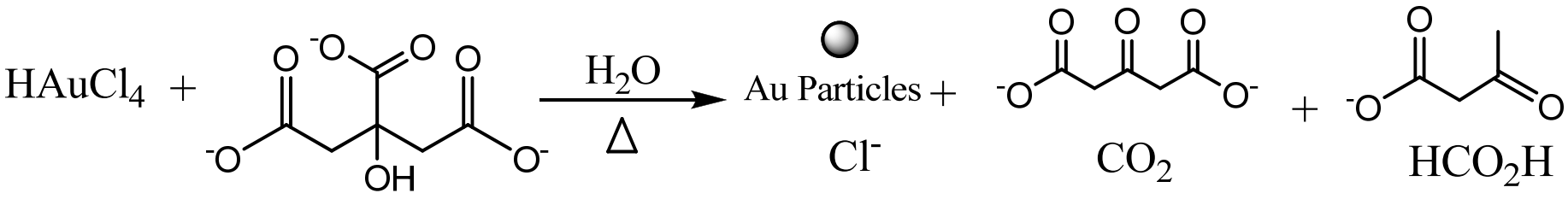
Collect

Apparatus	Amount	Apparatus	Amount
Wash with aqua regia in hood:			
50 mL round-bottomed flask	1	Cuvettes	2
Condenser	1	Stir bar (TA)	1
Sand bath container	1	Timer (TA)	1
Extension clamp (small)	1	Rubber tube	2
Extension clamp (large)	1	Dropper	1
Latex gloves	2	2 mL Measuring pipet	Shared
Linen gloves	2	15 mL Transfer pipet	Shared

***Clean the top of hot plate with wet cloth first**

Objective

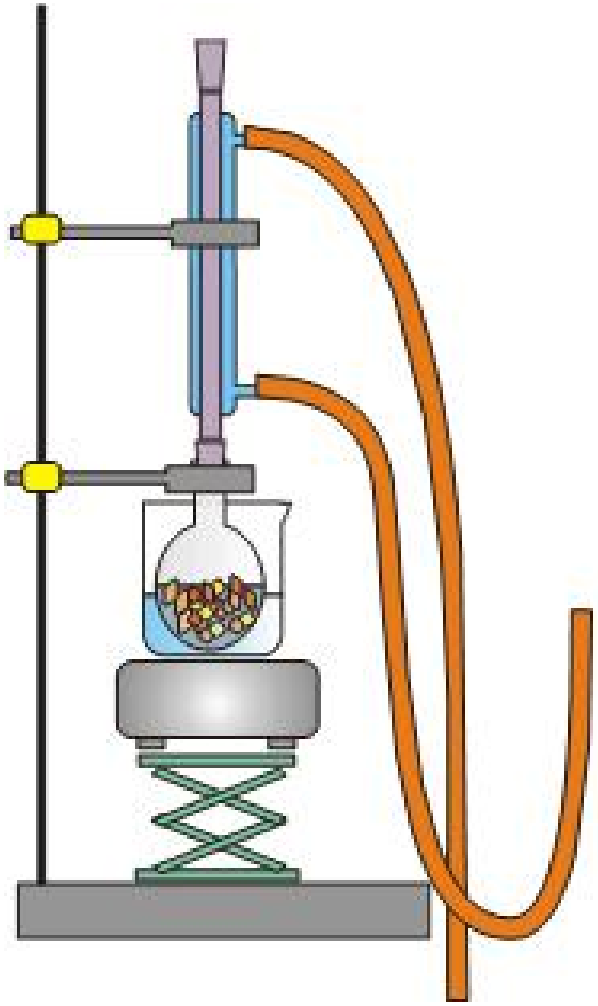
- Use sodium citrate ($Na_3C_6H_5O_7$) as reducing agent to reduce tetrachloroaurate(III) ion to gold nanoparticles
- Synthesize gold nanoparticles with various sizes
- Measure and compare the surface plasmon resonance (SPR) spectra
- Observe Tyndall effect of gold nanoparticles



Citrate ion

Techniques

- Prepare aqua regia to clean up the surface of reacting apparatus
- Manipulate graduated pipette and pipette filler
- Set up reflux system
- Use magnetic stirrer / hot plate
- Operate spectrophotometer

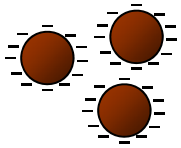


Preparation of Gold Nanoparticles

- Reduction of tetrachloroaurate(III) ions by sodium citrate

$$\mathbf{HAuCl_{4(aq)}} + C_6H_5O_7Na_{3(aq)} \rightarrow \mathbf{Au_{(s)}} + CO_2 + HCOOH\ldots$$

Reducing agent nanogold (< 100 nm)



- **Control the amount of citrate** (1.8 or 1.0 mL) used to prepare gold nanoparticles of different diameters (15 or 33 nm)

Reference:

- K. C. Grabar; R. G. Freeman; M. B. Hommer; M. J. Natan; *Anal. Chem.* **1995**, *67*, 735-743.

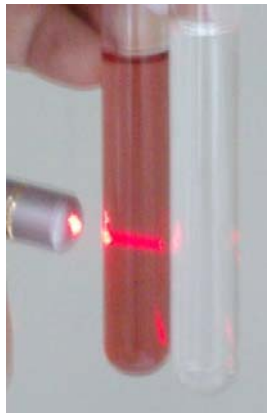
Outline of Procedure

I. Clean up apparatus

II. Synthesis

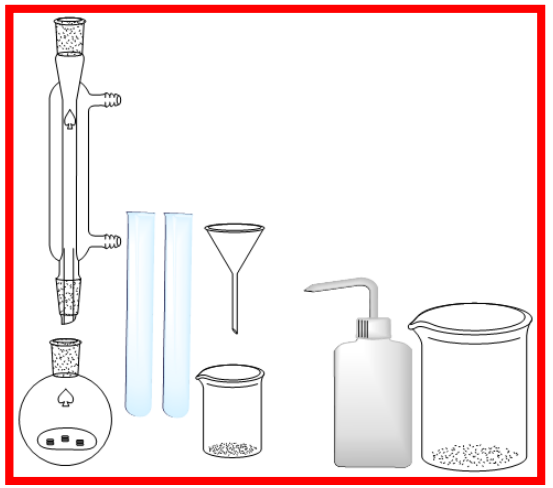
III. Spectrum

IV. Colloid



Procedure I. Clean up the Apparatus

- **Wear latex gloves**
- Operate the following in fume hood
  - Mix 5 mL conc. HNO_3 and 15 mL conc. HCl in a beaker to prepare aqua regia
  - Clean magnetic stir bar, round-bottomed flask, condenser, and 2 cuvette with aqua regia
  - Rinse the apparatus with D.I. water once
  - Aqua regia can be used repeatedly



===Back to bench==========

- **Wash off the acids with large amounts of D.I. water**
- Drip-dry the washed apparatus

Procedure II. Set up Reflux System

- Measure 15 mL of Au^{3+} with transfer pipet to round-bottomed flask
- Fix the round-bottomed flask with small-sized extension clamp
- **Set round-bottomed flask in the sand bath container and place on the top center of hot plate**
- Test the stirring to make sure the stir-bar can stir smoothly
- Fix the condenser with large-sized extension clamp
- **Cooling water:**
  - Connect the rubber tubes firmly
  - **Run the cooling water from the bottom to the top**
  - Adjust the water flow properly
- **Lastly, add sea-sand in sand bath container**
- **Heat the soln. after checking by TA**

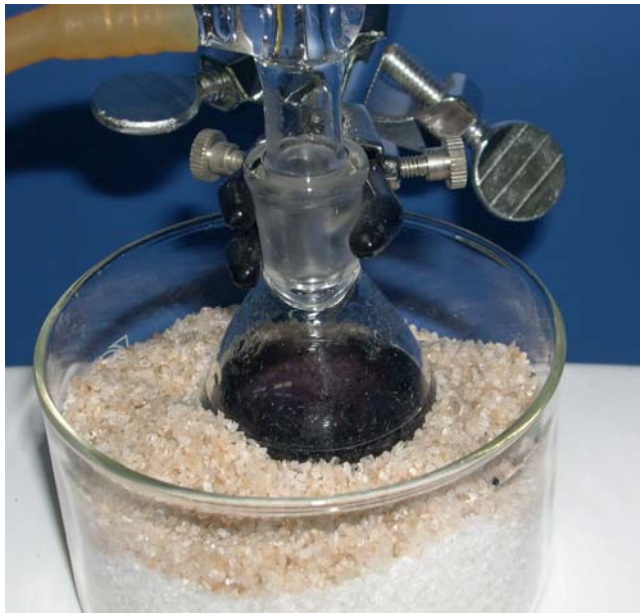
Note:
- **Wipe the top of hot plate with wet cloth before setting up**
- **Power wires and rubber tubes should not contact the hot plate**

Procedure II. React with Sodium Citrate

- **Keep stirring on** when Au^{3+}(aq) boils vigorously
- Obtain 1.8 mL (odd groups) or 1.0 mL (even groups) of sodium citrate with 2 mL graduated pipet
- Add through condenser immediately
- **Observe color change with reaction time**

Procedure II. Synthesis of Gold Nanoparticles

- **Keep on heating and stirring** until solution boils for 10 min.
- Turn off heating
- Remove sand bath, continue stirring while cooling for 10 min.



Note: Put on linen gloves when removing the hot sand bath to avoid burn

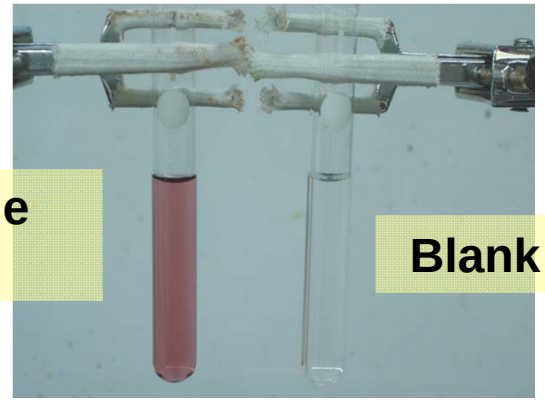
Expected Gold Nanoparticles

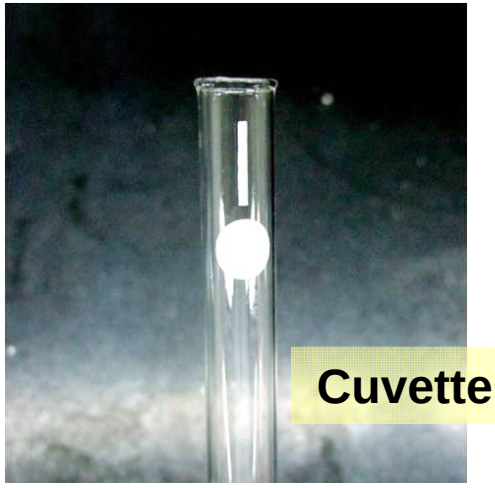
(A) 1.8 mL sodium citrate
15 nm gold nanoparticles

(B) 1.0 mL sodium citrate
33 nm gold nanoparticles

Procedure III. Take the Absorbance of Gold Nanoparticles Soln.

- Prepare sample: add 1 mL of gold nanoparticle soln. and 4 mL deionized water, then **mix thoroughly**
- Obtain two cuvettes
  - One with blank soln.: ½ volume of deionized water
  - One with sample soln.: ½ volume of dilute sample soln
- Manipulation with cuvette
  - Do not use brush to clean the cuvettes
  - Use lens cloth to wipe clean the cuvettes before putting into spectrophotometer
  - Align cuvettes in fixed direction





Procedure III. Take the Absorbance of Gold Nanoparticles Soln.

Calibration and Measurement

(1) Turn on power to warm up

(2) Empty the cuvette holder

(3) Set the mode to A

(4) Set wavelength to 400 nm

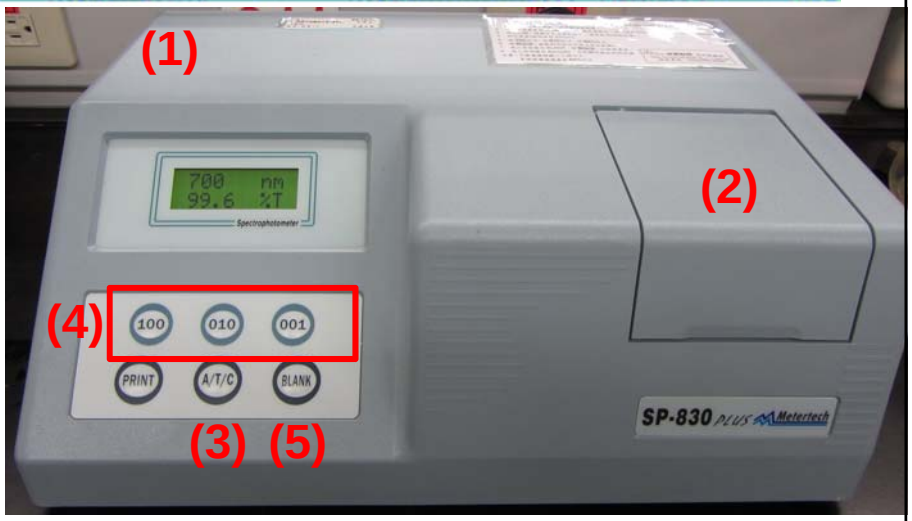
(5) Press [BLANK] to adjust zero

(6) Place blank soln to cuvette holder

(7) Press [BLANK] to calibrate

(8) Place sample soln into cuvette holder and record the Abs

(9) Change wavelength (420 nm), repeat (6)~(8) to calibrate and measure the absorbance

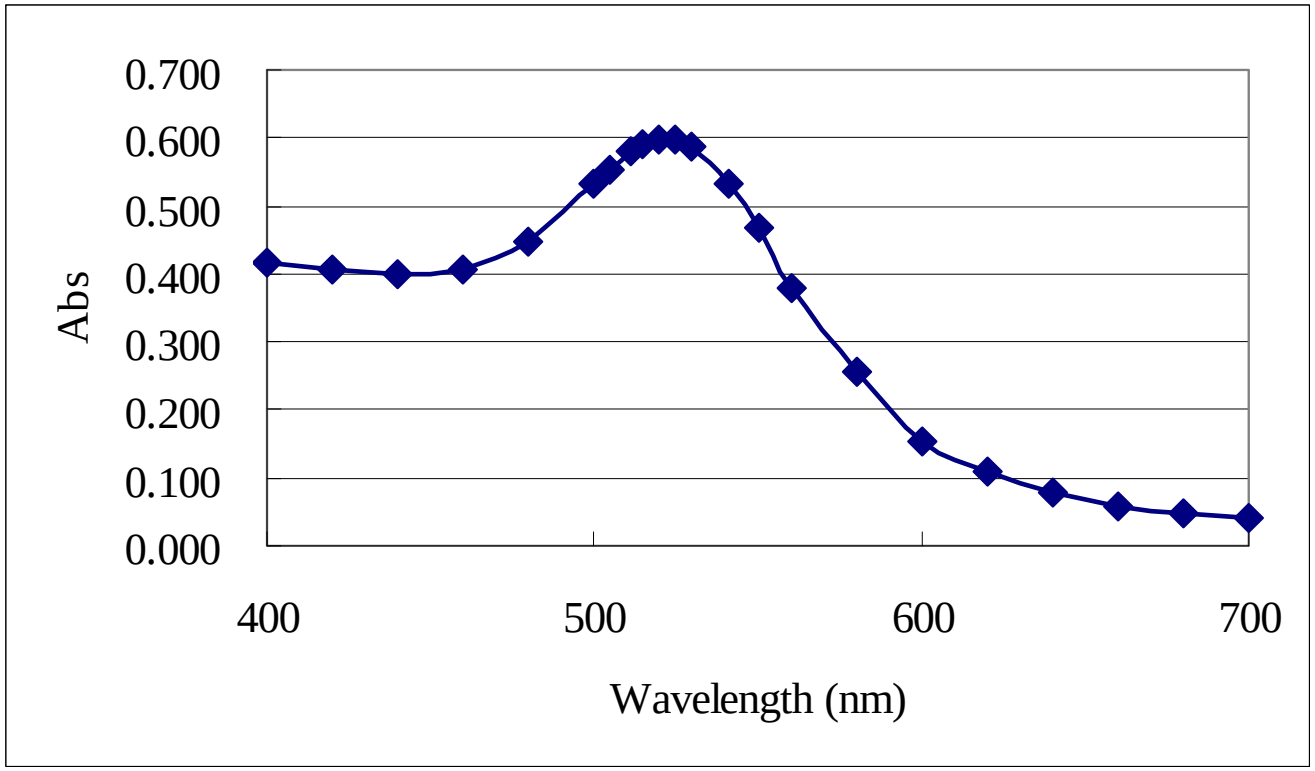


Note:

Repeat calibration while changing the wavelength

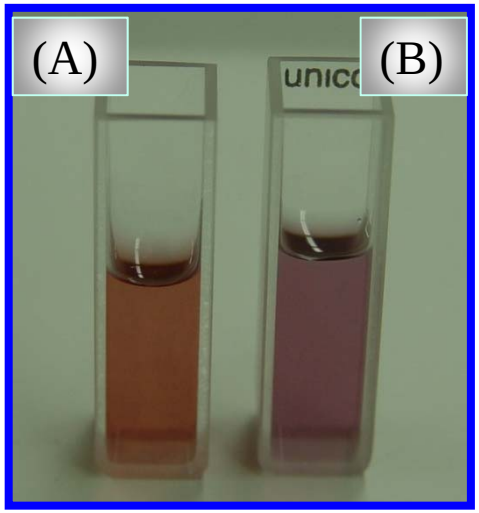
400 ~ 700 nm: measured in **20 nm** intervals
510 ~ 540 nm: measured in 5 nm intervals

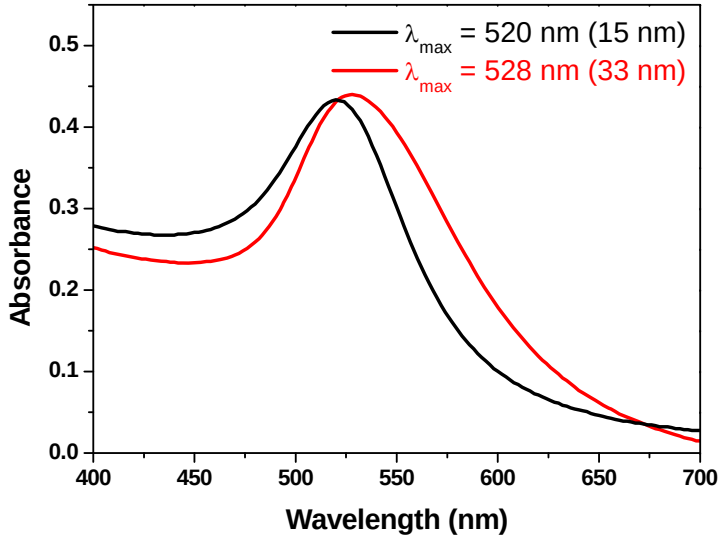
Plot Absorption Spectrum



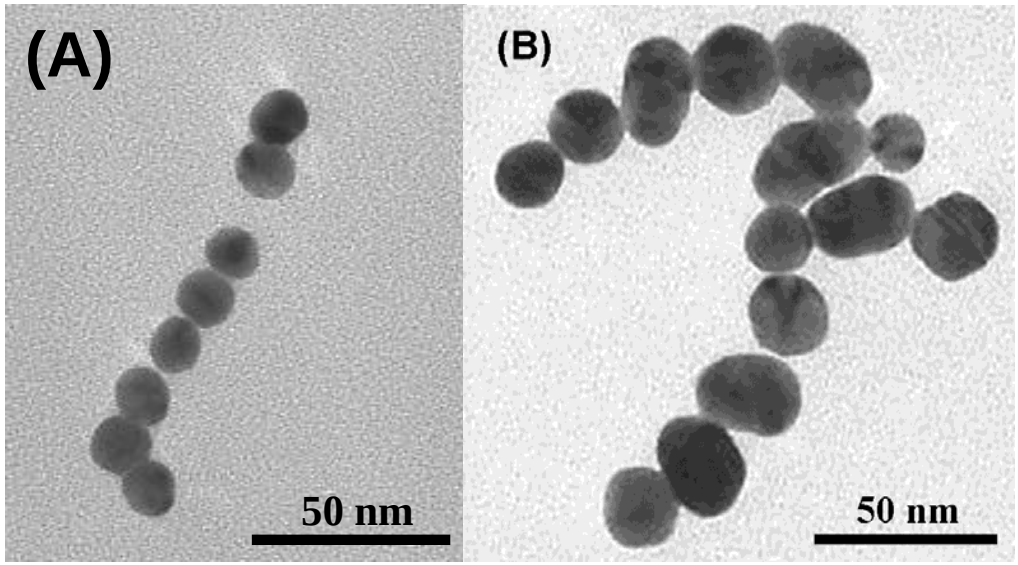
- **Absorbance vs. analytical wavelength**
- **XY scattering diagram with smooth curve fitting**
- Find the λ_{max}

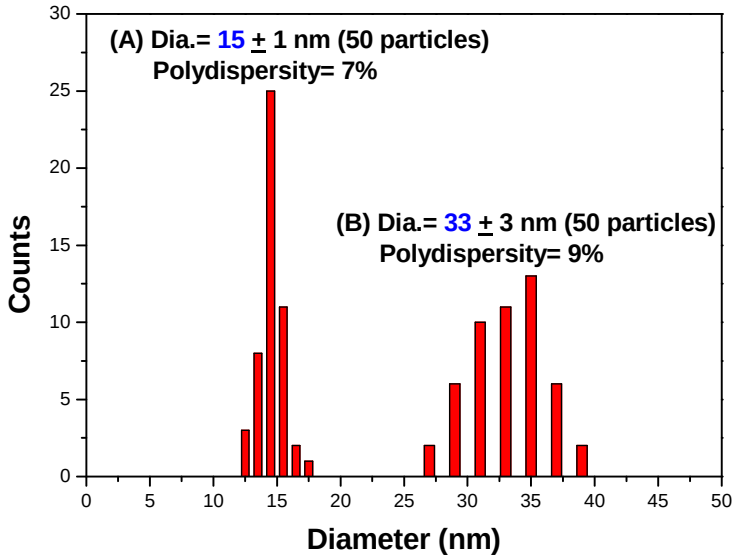
Expected Color, Spectrum and Particle Size Analysis





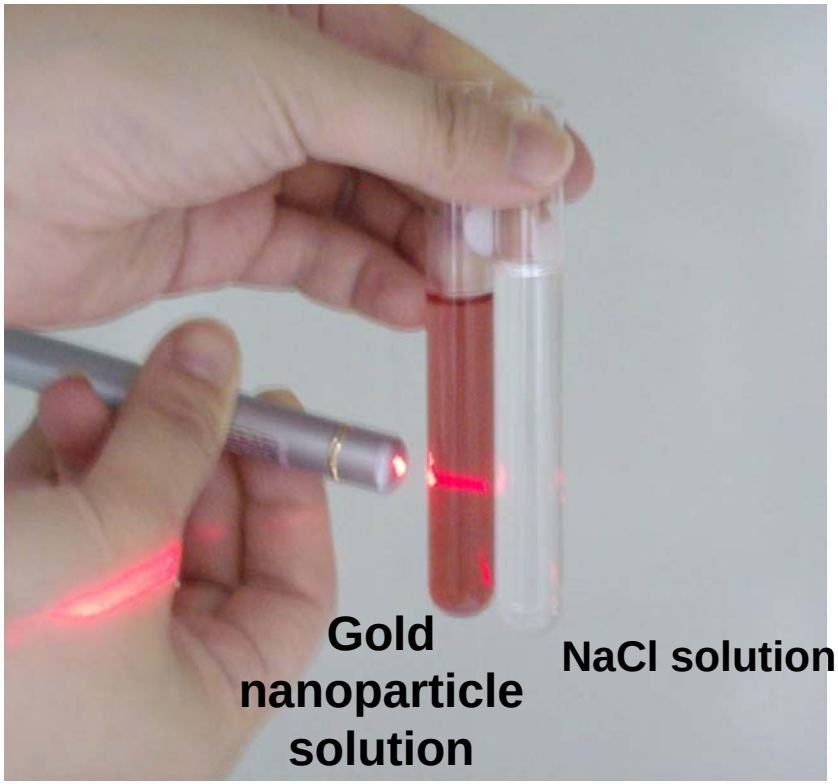
(A) 1.8 mL Citrate **(B) 1.0 mL Citrate**



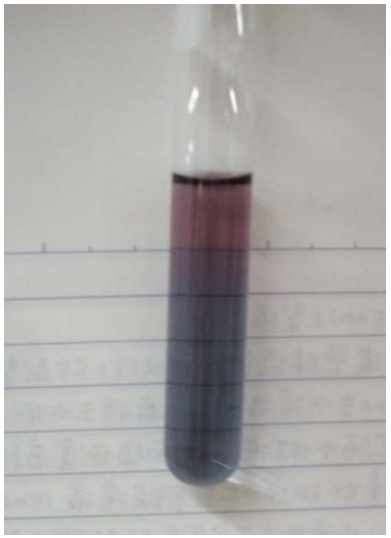


Colloid Property of Gold-nanoparticles

- Colloids: solute with diameter in 1-1000 nm
- Tyndall effect: light scattering by colloids



- Effect of electrolyte on colloids
  - Add 1 M NaCl(aq) drop by drop to gold nanoparticles
  - Observe the coagulation of gold nanoparticles and color changes



Notice

- Be careful while operating aqua regia which is corrosive
- Recycle aqua regia into specific waste bin after lab
- DO NOT waste $HAuCl_4$ which is expensive
- Wash apparatus thoroughly with plenty of D.I. water before synthesis
- Be careful with hot plate and sand bath to avoid burning
- Gold nanoparticles solution can be filled into sample vials and taken home as a souvenir or discard into gold nanoparticles recycling bin
- Wash specific equipment with water and put back in place
- Clean up hot plate, benchtop, and apparatus
- Hand in lab report next weak