# Synthesis and Characterization of Gold Nanoparticles

**Collect**

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

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

- Use sodium citrate \((\text{Na}_3\text{C}_6\text{H}_5\text{O}_7)\) 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

\[
\text{HAuCl}_4 + \text{Citrate ion} \xrightarrow{\Delta} \text{Au(s)} + \text{CO}_2 + \text{HCO}_2\text{H} + \text{Cl}^-
\]
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

\[
\text{HAuCl}_4(\text{aq}) + \text{C}_6\text{H}_5\text{O}_7\text{Na}_3(\text{aq}) \rightarrow \text{Au(s)} + \text{CO}_2(\text{g}) + \text{HCOOH}...
\]

Reducing agent nano-gold (< 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:
Outline of Procedure

I. Clean up apparatus

II. Synthesis of gold nanoparticles

III. Vis. absorption Spectrum

IV. Tyndall effect of Colloid
Procedure I. Clean up the Apparatus

- Wear latex gloves
- **Operate the followings 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*
  - *Aqua regia* can be used repeatedly
- Rinse the apparatus with D.I. water once

--- 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(III) 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
- Electric wires and rubber tubes should not contact the hot plate
Procedure II. React with Sodium Citrate

- **Keep stirring on** while Au(III)(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 all at once
- 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 cotton gloves on when removing the sand bath to avoid burns
Expected Gold Nanoparticles

(A) 1.8 mL sodium citrate
15 nm gold nanoparticles

(B) 1.0 mL sodium citrate
33 nm gold nanoparticles
 Obtain two cuvettes  
  - One filled with half volume of D.I. water as Blank  
  - One filled with half volume of diluted gold nanoparticles as Sample soln  
* Dilute 1 mL of gold nanoparticle soln. with 4 mL D.I. water as sample soln. Transfer half of soln to cuvette and the rest to a test tube.

 Notice  
  - Do not brush the cuvettes  
  - Use lens tissue to wipe clean the cuvettes before putting into spectrophotometer  
  - Align cuvettes in fixed direction
Procedure III. Absorption Spectrum of Gold Nanoparticles

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

Absorption spectrum of gold nanoparticles

<table>
<thead>
<tr>
<th>λ, nm</th>
<th>1.8 mL</th>
<th>1.0 mL</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>0.402</td>
<td>0.418</td>
</tr>
<tr>
<td>420</td>
<td>0.402</td>
<td>0.420</td>
</tr>
<tr>
<td>440</td>
<td>0.396</td>
<td>0.412</td>
</tr>
<tr>
<td>460</td>
<td>0.412</td>
<td>0.419</td>
</tr>
<tr>
<td>480</td>
<td>0.458</td>
<td>0.454</td>
</tr>
<tr>
<td>500</td>
<td>0.548</td>
<td>0.533</td>
</tr>
<tr>
<td>510</td>
<td>0.588</td>
<td>0.578</td>
</tr>
<tr>
<td>515</td>
<td>0.606</td>
<td>0.596</td>
</tr>
<tr>
<td>520</td>
<td>0.614</td>
<td>0.608</td>
</tr>
<tr>
<td>525</td>
<td>0.602</td>
<td>0.617</td>
</tr>
<tr>
<td>530</td>
<td>0.573</td>
<td>0.602</td>
</tr>
<tr>
<td>535</td>
<td>0.538</td>
<td>0.573</td>
</tr>
<tr>
<td>540</td>
<td>0.506</td>
<td>0.524</td>
</tr>
<tr>
<td>560</td>
<td>0.348</td>
<td>0.384</td>
</tr>
<tr>
<td>580</td>
<td>0.223</td>
<td>0.260</td>
</tr>
<tr>
<td>600</td>
<td>0.140</td>
<td>0.162</td>
</tr>
<tr>
<td>620</td>
<td>0.090</td>
<td>0.096</td>
</tr>
<tr>
<td>640</td>
<td>0.072</td>
<td>0.075</td>
</tr>
<tr>
<td>660</td>
<td>0.059</td>
<td>0.061</td>
</tr>
<tr>
<td>680</td>
<td>0.047</td>
<td>0.053</td>
</tr>
<tr>
<td>700</td>
<td>0.039</td>
<td>0.043</td>
</tr>
</tbody>
</table>

- Absorbance as y axis and wavelength as x axis
- Excel: insert XY scattering diagram with smooth curve fitting
- Indicate $\lambda_{\text{max}}$
Expected Color, Spectra and Particle Size Analysis (TEM)

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

(A) Dia. = 15 ± 1 nm (50 particles)  
Polydispersity = 7%

(B) Dia. = 33 ± 3 nm (50 particles)  
Polydispersity = 9%
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 **diluted sample soln in test tube**
  - Observe the coagulation of gold nanoparticles and color changes
Notice

- Be cautious while operating aqua regia which is corrosive
- Recycle aqua regia into specific waste bin after lab
- DO NOT waste HAuCl₄ 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
- You may fill some gold nanoparticles solution in a sample vial 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 week