Synthesis and Characterization of Gold Nanoparticles

Last revised: 2024/03/31

Preparation

Collect the following items

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

✓ Clean the top of hot plate with wet cloth first

Objective and Principles

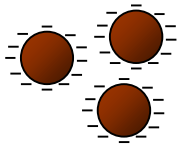
- **Objective:**
  - Use sodium citrate ($Na_3C_6H_5O_7$) as reducing agent to reduce tetrachloroaurate(III) ion to gold nanoparticles
  - Synthesize gold nanoparticles with various sizes
  - Measure and compare the surface plasmon resonance (SPR) spectra
  - Observe Tyndall effect of gold nanoparticles
- **Lab techniques:**
  - Prepare aqua regia
  - Manipulate graduated pipette
  - Set up reflux system
  - Use magnetic stirrer / hot plate
  - Operate spectrophotometer

Gold Nanoparticles

- Synthesis of gold nanoparticles (Au-NP)
  - Reduction of tetrachloroaurate(III) ions by sodium citrate:

$$\mathbf{HAuCl_4(aq)} + C_6H_5O_7Na_3(aq) \rightarrow \mathbf{Au(s)} + CO_2(g) + HCOOH + ...$$

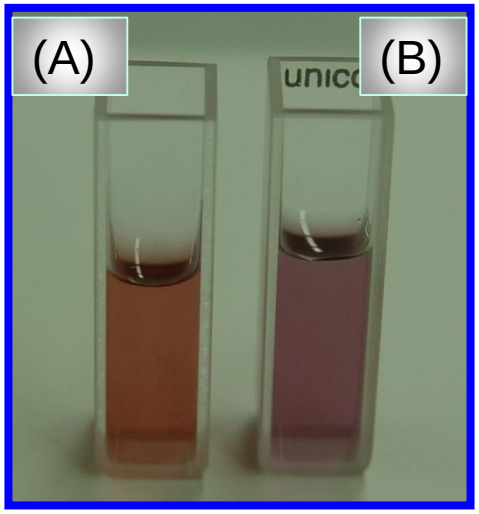
Reducing agent Nano-gold (< 100 nm)

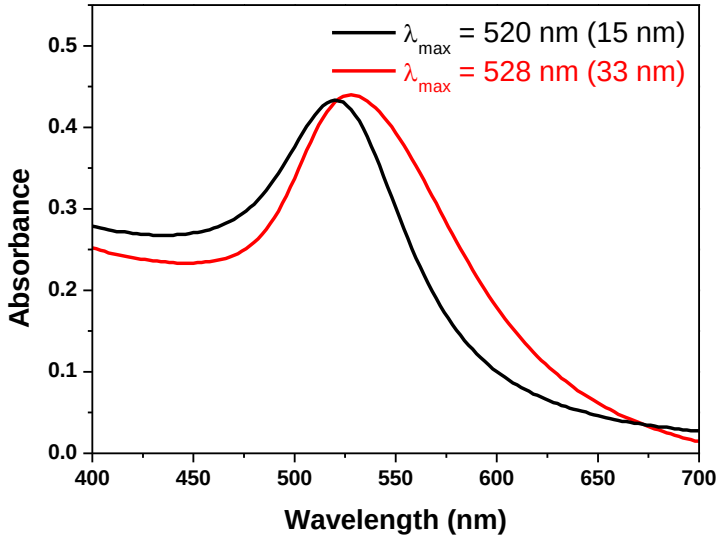


  - Control the amount of citrate (1.8 or 1.0 mL) used to prepare gold nanoparticles, with different diameters (15 or 33 nm)

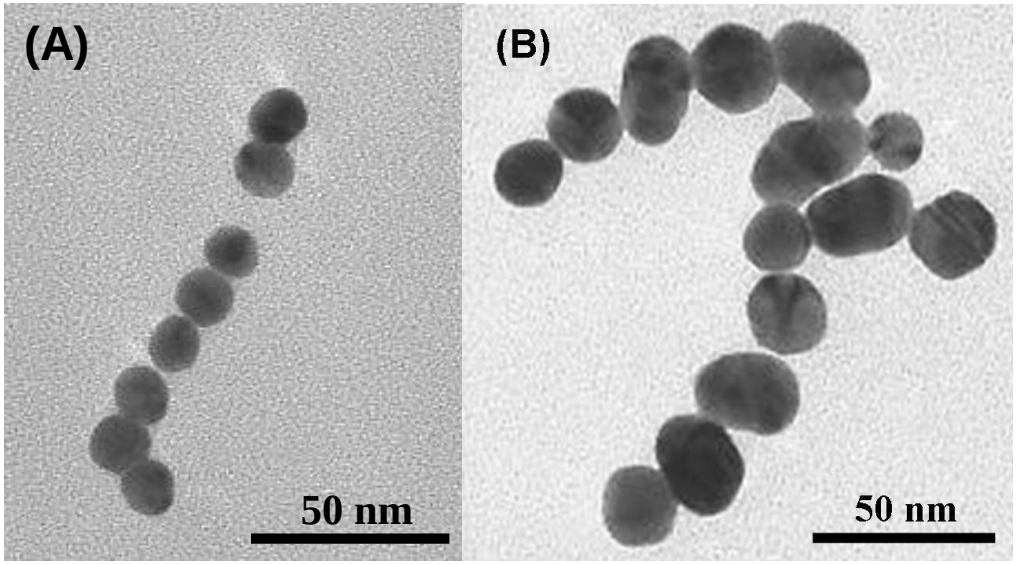
- Property of gold nanoparticles
  - Surface plasmon resonance (SPR) spectra
  - Colloids: solute with diameter in 1-1000 nm
  - Tyndall effect: light scattering by colloids

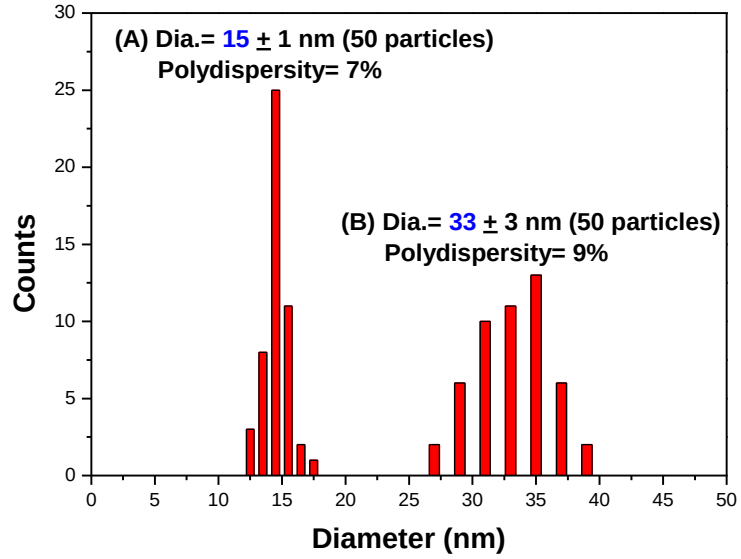
Expected Color, Spectra and Particle Size Analysis (TEM)



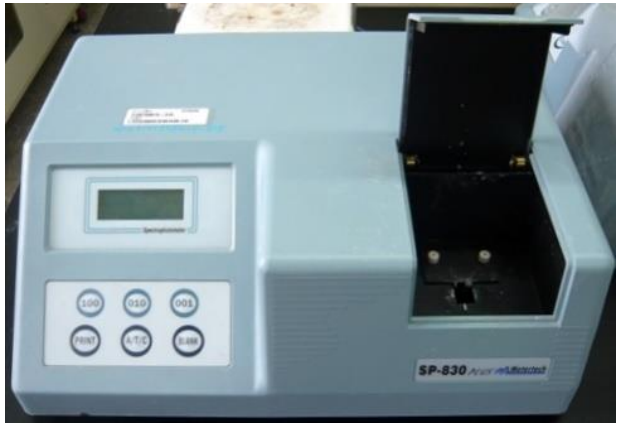


(A) 1.8 mL Citrate **(B) 1.0 mL Citrate**





Experiment Tasks



I. Clean up apparatus with aqua regia
II. Synthesis of gold nanoparticles
III. Visible absorption spectrum
IV. Tyndall effect of gold nanoparticles

Step 1: Clean up Apparatus

- **Wear NBR 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 DI water once**

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

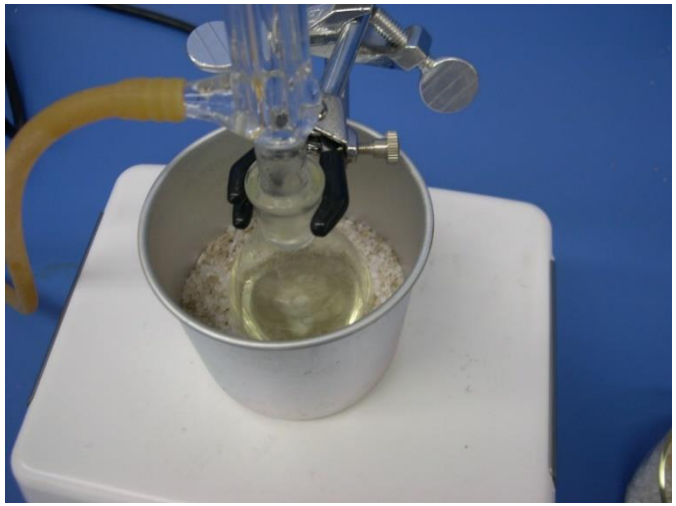
- **Wash off the acids with large amounts of DI water**
- Drip-dry the washed apparatus

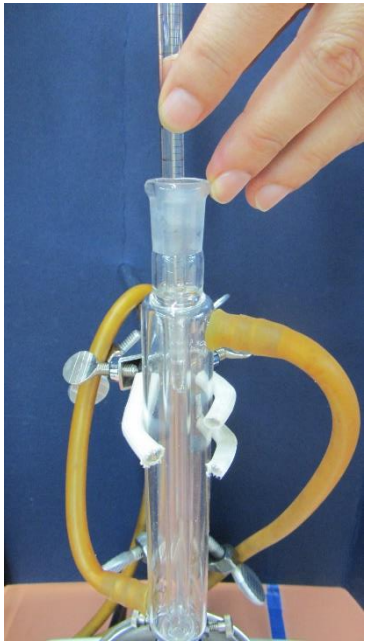
Step 2: Set up Reflux System

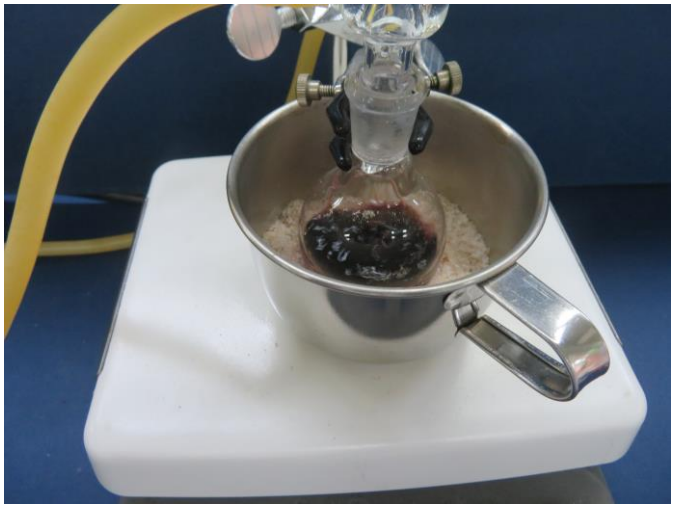
- Measure 15 mL of Au(III) with transfer pipet to round-bottomed flask
- Fix the round-bottomed flask with small-sized extension clamp
- **Set round-bottomed flask in the sand bath container and place on the top center of hot plate**
- Test the stirring to make sure the stir-bar can stir smoothly
- Fix 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**

✓ Wipe the top of hot plate with wet cloth before setting up
✓ Electric wires and rubber tubes should not contact the hot plate

Step 3: React with Sodium Citrate



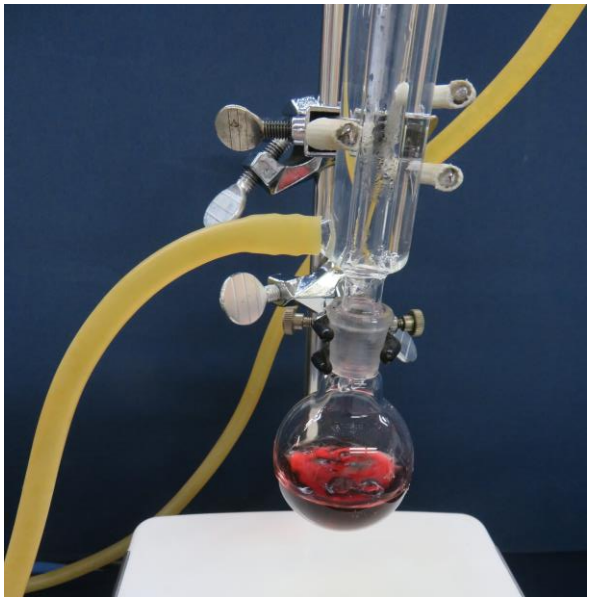




- Keep stirring on while Au(III)(aq) boils vigorously
- Obtain 1.8 mL (odd groups) or 1.0 mL (even groups) of sodium citrate with 2 mL graduated pipet
- Add sodium citrate through condenser all at once
- **Observe color change with reaction time**

Step 4: 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 15 min



✓ Stirring may keep the homogeneity of the size of Au-NP

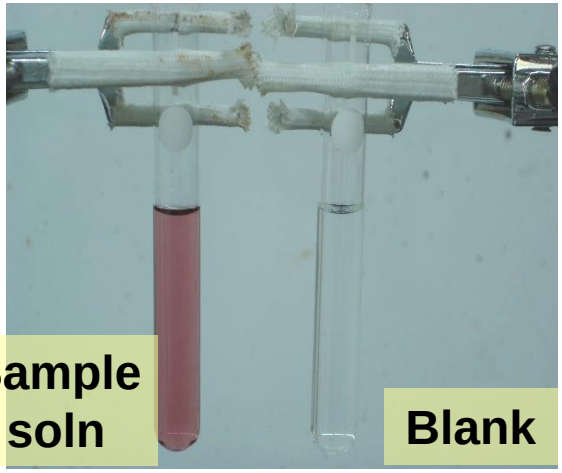
✓ Put cotton gloves on when removing the sand bath to prevent burns

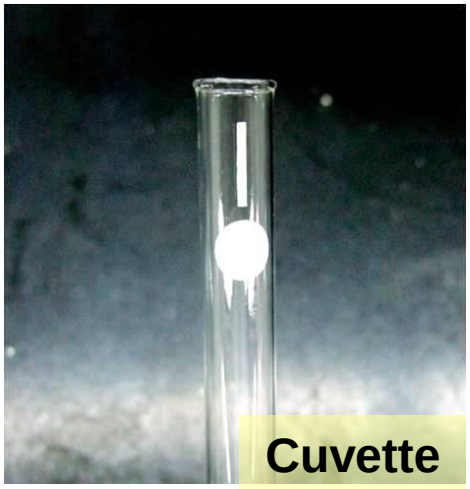
Expected Gold Nanoparticles

(A) 1.8 mL sodium citrate
15 nm gold nanoparticles

(B) 1.0 mL sodium citrate
33 nm gold nanoparticles

Step 5: Prepare Au-NP Sample Solution





- Dilute **2** mL of gold nanoparticle soln with **8** mL DI water as **sample soln**
- Obtain two cuvettes:
  - One filled with half volume of DI water as **Blank**
  - One filled with half volume of diluted gold nanoparticles as **Sample soln**

  ***** Keep the rest sample soln in a test tube

- ✓ Do not brush the cuvettes
- ✓ Use lens tissue to wipe clean the cuvettes before putting into spectrophotometer
- ✓ Align cuvettes in fixed direction

Step 6: Absorption Spectrum of Au-NP

Calibration and Measurement

(1) Turn on power to warm up 15 min

(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 absorbance

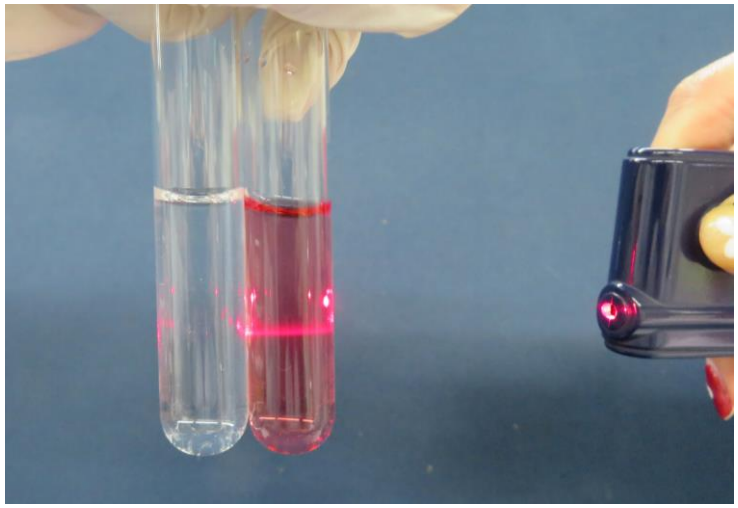
(9) Change wavelength (420 nm), repeat (6)~(8) to calibrate and measure the absorbance

✓ Repeat calibration while changing the wavelength

✓ 400 ~ 700 nm: measured in 20 nm intervals

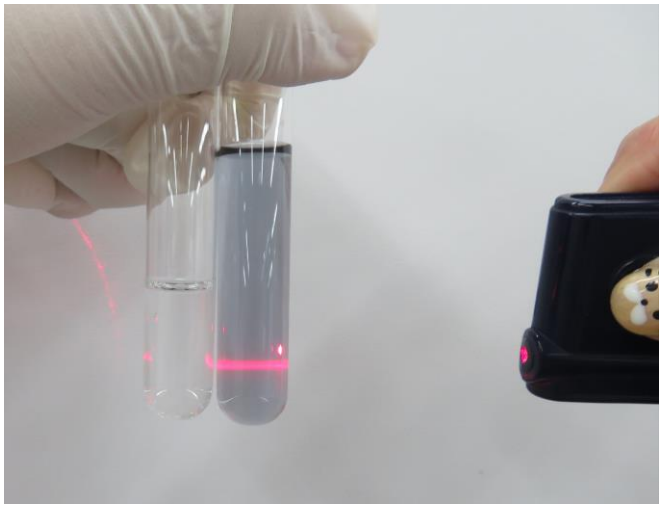
✓ **500** ~ 540 nm: measured in 5 nm intervals

Step 7: Colloid Property of Au-NP



Left:
NaCl(aq)

Right:
Au-NP soln



After adding NaCl(aq) to Au-NP

- Exam light scattering by diluted Au-NP sample soln in test tube and compare with NaCl(aq)
- Add 1 M NaCl(aq) drop by drop to **diluted sample soln**
- Observe and record the effect of electrolyte on coagulation of gold nanoparticles and color changes

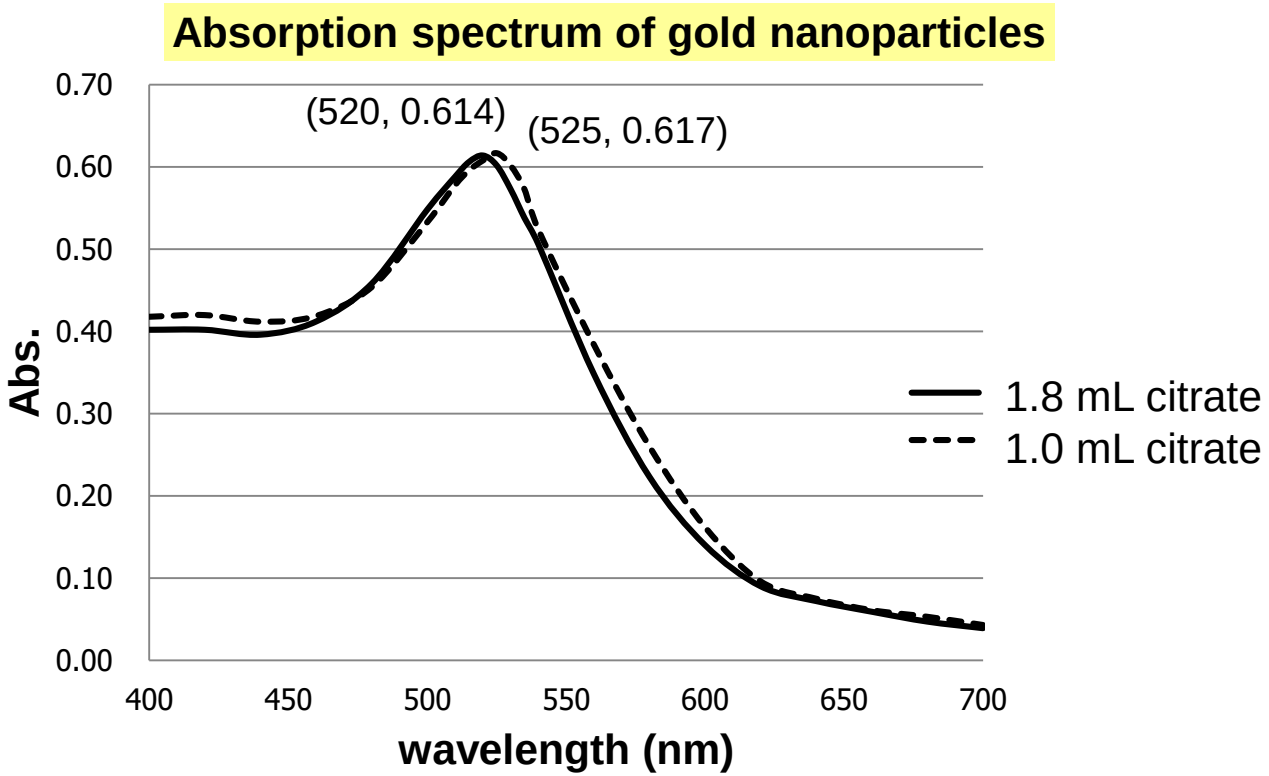
Clean-up and Check-out

- You may fill some gold nanoparticle solution in a sample vial as souvenir or discard into Au-NP recycling bin
- Recycle aqua regia into specific waste bin after lab
- Wash specific equipment with water and put back in place
- Clean up hot plate, benchtop, and apparatus
- Return the magnetic stir bar, timer, and cuvettes to TA
- Clean up the lab bench and check personal equipment inventory (have an associate TA sign the check list)

- This is a **Full Report** experiment:
  - Member A/B: **Have the lab notes and results checked by the TA, and hand in the report next week.**
  - Member B/A: **Hand in prelab to the TA**
- Groups on duty shall stay and help clean up the lab

Data Sheet & Absorption Spectrum

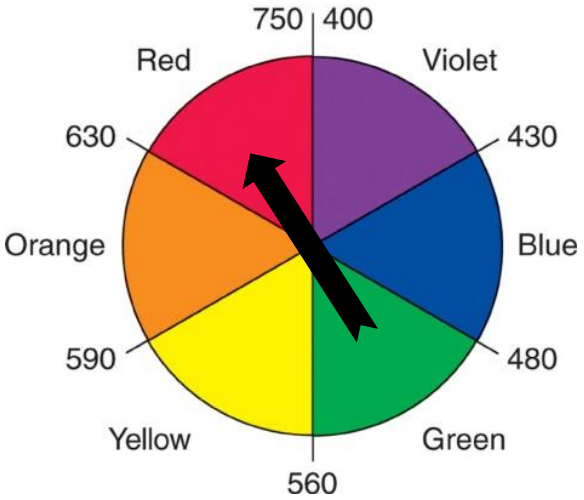
λ (nm)	1.8 mL	1.0 mL
400	0.402	0.418
420	0.402	0.420
440	0.396	0.412
460	0.412	0.419
480	0.458	0.454
500	0.548	0.533
510	0.588	0.578
515	0.606	0.596
520	0.614	0.608
525	0.602	0.617
530	0.573	0.602
535	0.538	0.573
540	0.506	0.524
560	0.348	0.384
580	0.223	0.260
600	0.140	0.162
620	0.090	0.096
640	0.072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

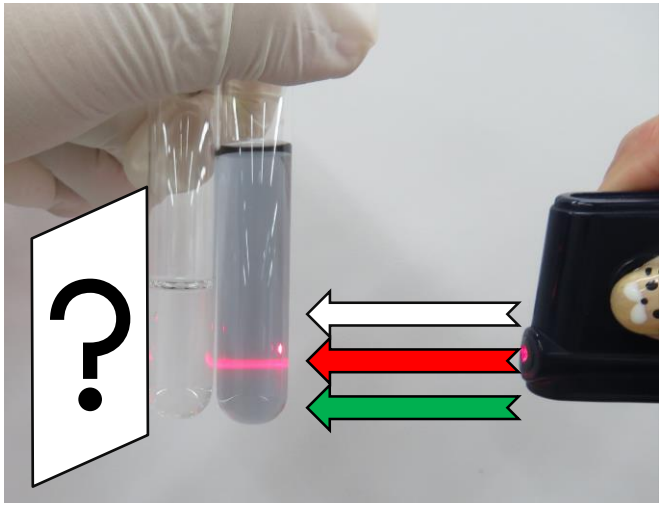


Plot using Excel:

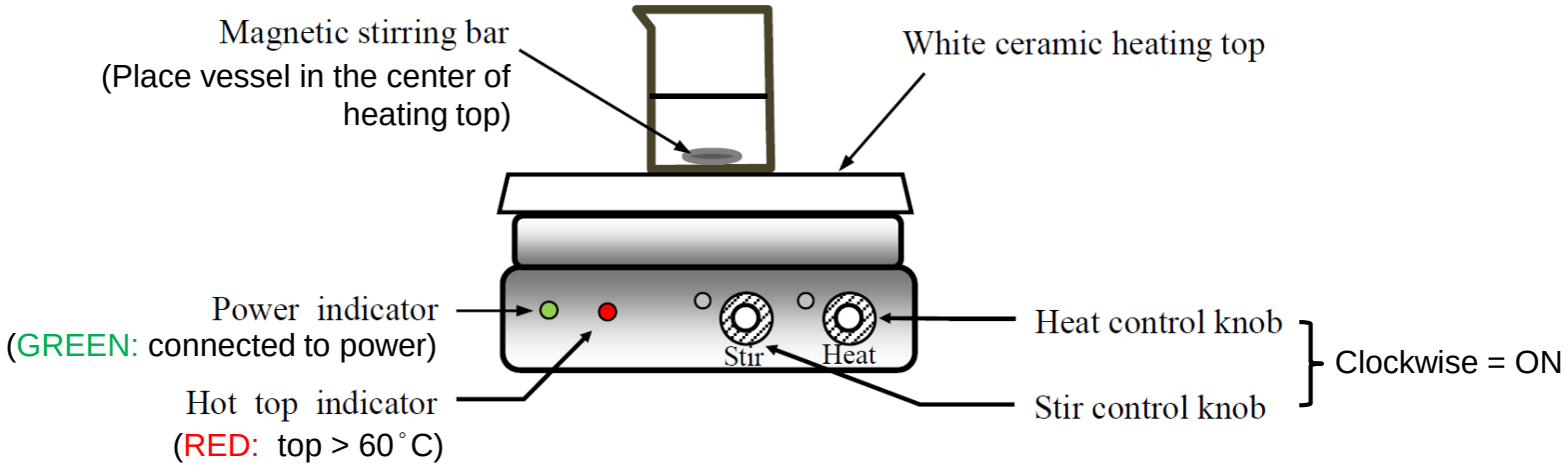
- Select columns of wavelength and absorbance
- Insert xy scatter diagram with smooth curve fitting
- Set wavelength as *x* axis, absorbance as *y* axis
- Indicate λ_{max}

Exploration





T2 – Stirrer/Hot Plate

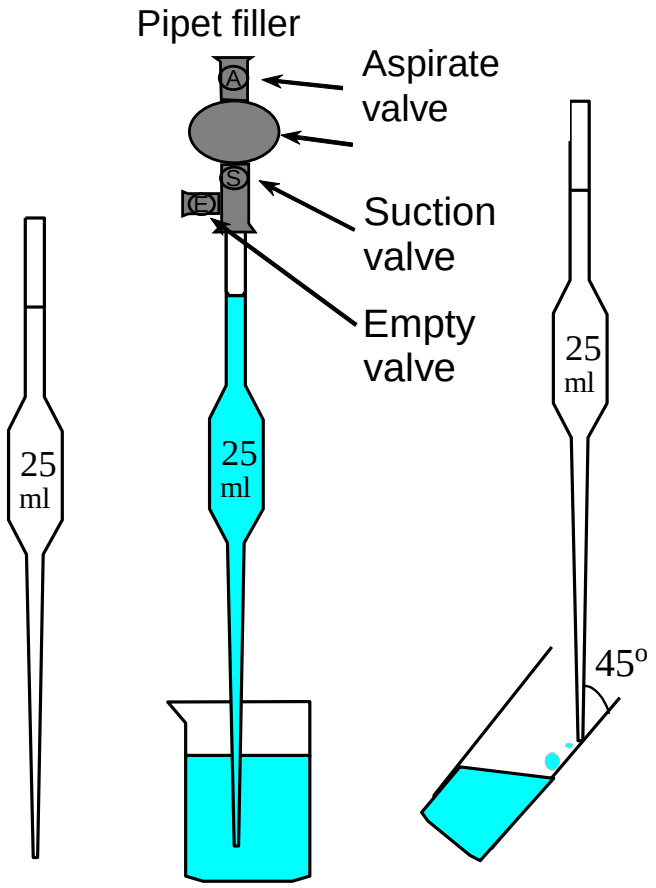


- Connect the stirre/hot plate to a grounded 110 V power outlet (replace damaged power cord and plug immediately)
- Keep power cord away from the ceramic heating top
- Clean the heating top with non-corrosive detergent after use or when liquid spills
- NEVER heat a large amount of volatile and flammable liquid (e.g. ether, acetone) directly on the hot plate
- If the stirring bar jumps erratically, turn the stirring function off and adjust the vessel position, then restart the stirring
- Do not remove the stirring bar from solution with hand – instead use a Teflon-coated magnetic rod (“fishing pole”)

T2 Video (YouTube link)

T12.1 – Transfer (Volumetric) Pipet

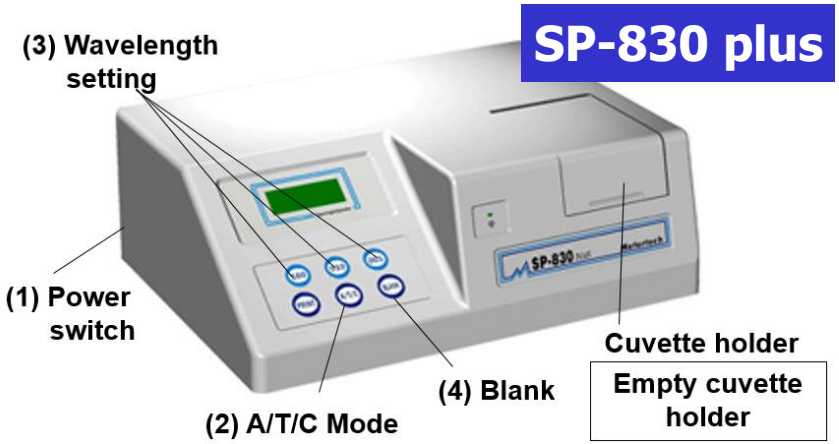
- Clean the pipet and rinse it twice with small amount of the liquid to be transferred
- Press valve **A** of the pipet filler and simultaneously squeeze the bulb to expel air from it, then insert the top of pipet gently into the pipet filler
- Bring the pipet tip below the liquid surface, press valve **S** to draw liquid until it rises above the inscribed line
- Remove the pipet filler and quicky use an index finger to close the top of pipet
- Use finger to adjust the liquid level to the inscribed line. Wipe off any excess liquid near the pipet tip
- Use the other hand to hold the new container. Maintain the pipet in a vertical position and let its tip touch the inner wall of the container. Release the index finger so that liquid is transferred
- Do not force out any liquid remaining at the tip
- Wash the pipet thoroughly after use



T12 Video (YouTube link)

T17 – Spectrophotometer

- Turn on the power switch and let the instrument warm up for at least 20 minutes
- Ensure the *cuvette holder* is empty
- Press the "Mode" button several times until "A" (absorbance) appears on the screen
- Set the wavelength to the desired value (e.g. 620 nm)
- Press the "Blank" button to zero the reading
- Place a *cuvette* with blank solution into the cuvette holder. Align the white line on the cuvette toward you (do NOT use regular test tubes in the spectrophotometer)
- Press the "Blank" button to calibrate
- Place a sample solution into cuvette holder
- Close the lid of the sampel compartment, record the absorbance reading



Note – the T17 video shows the older Spectronic 20 model instead of the currently used SP-830

T17 Video (YouTube link)