Chapter 1 – NO₂ Measurement

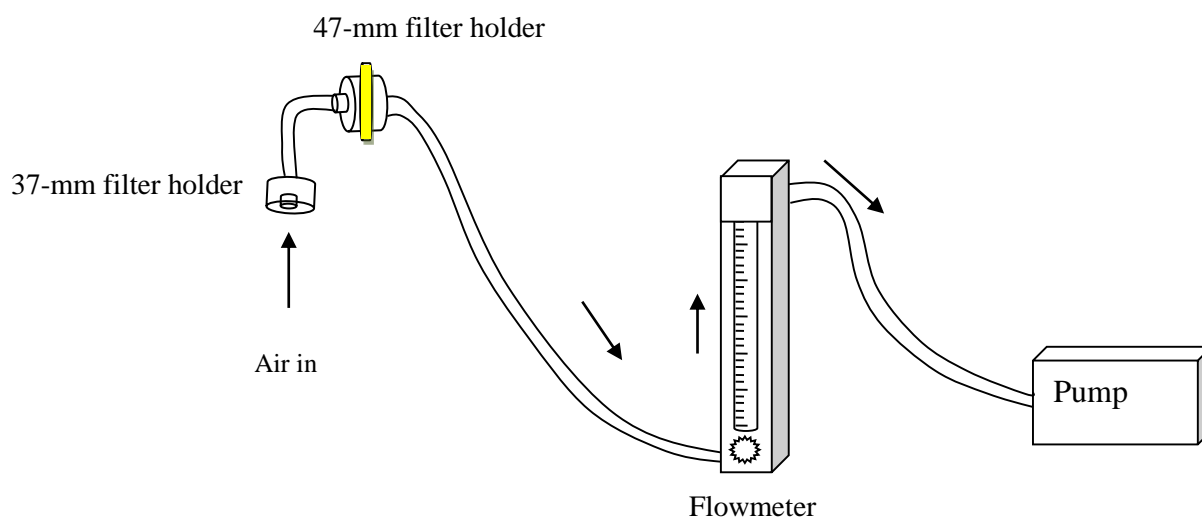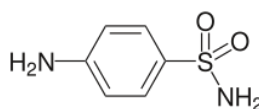## *1.1 Basic principle of the experiment*

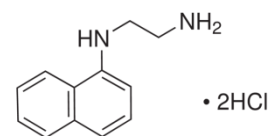*Figure 1-1. Schematic of the experimental setup for NO₂ measurement*

When the pump is turned on as shown in Figure 1-1, air sample will first go through an upstream pre-filtration (37-mm filter) which can remove particles that may interfere with the sampling. After that, NO_2 in the air sample stream is captured by a 47-mm glass fiber filter coated with triethanolamine (*TEA*), which is a good absorption medium for NO_2.

The captured NO_2 on the TEA-coated filter will become NO_2^- ions during sampling and we can carry out the extraction step by submerging the filter in deionized water.

Next, a mix of sulfanilamide (*Solution A*) and acidified N-(1-naphthyl)ethylenediamine dihydrochloride (*Solution B*) are added to react with NO_2^- in the extract to form a purple-red color azo-compound (R-N=N-R'). In this way, NO_2^- concentration in the solution can be determined by measuring how much azo-compound is formed (or in other words, measuring how intense the purple color) using the techniques of photo-spectrometry at 540 nm.

(Reference: Hsu, P.P., Hui, L.C., Ye, Y., and Yuan, M.Y., Design and development of an analytical protocol for measuring atmospheric NO_2 in high school, Final Year Project, Department of Chemical Engineering, the HKUST, 16 May 2008.)

1.2 Apparatus or equipment required

HKUST photometer
Photometer color comparison tube, 10 ml
Electronic balance
Multimeter/ohmmeter
Pump (rotary vane)
Flowmeter (rotameter with needle valve, 1-5 L min^{-1})
Tubing
47-mm filter holder
47-mm glass fiber filter
37-mm filter holder
37-mm glass fiber filter
Timer/stop-watch
Laboratory stand
Clamps
Forceps
Pipette, 1-ml
100-ml beaker x 2
Glass stirring rod
Volumetric flask, 50-ml
Volumetric flask, 1-L
Amber bottle, 100-ml, x 3
Amber bottle, 50-ml
Amber bottle, 1-L
Test-tube
Glass Petri dish
Measuring cylinder, 100-ml
Measuring cylinder, 10-ml
Zip-lock plastic bags
Cling wrap

HKUST photometer

Photometer cylinder

Flowmeter

47-mm filter holder

37-mm filter holder

1.3 Chemicals required

Sodium nitrite, 0.25 g
Sulfanilamide, 8 g (for 50 tests)
Phosphoric acid, 85%, 25 ml (for 50 tests)
N-(1-naphthyl)ethylenediamine dihydrochloride, 0.12 g (for 100 tests)
Triethanolamine, 10 ml (for 50 tests)
Acetone, 100 ml (for 50 tests)
Deionized water, about 2 L

(Note: All chemicals should be reagent grade.)

1.4 Experimental procedures explained

As mentioned in the previous section, the amount of purple-red azo compounds formed is proportional to the amount of NO_2^- ions present in the extract, which is equivalent to the amount of NO_2 in the 20-mins air sample. If we have several samples collected from different locations, we can figure out which sample has a higher NO_2 concentration by comparing how intense their purple colors are
(i.e. more purple => more azo compound formed => more NO_2 in air). But when it comes to very pale color or when their colors are very similar, a more scientific and quantitative comparison method is preferred to comparing the colors with our eyes.

Here we apply a quantitative spectroscopic technique to determine the purple color intensity by measuring how much green LED light can pass through the purple-red azo compound solution (also known as transmittance). We will use a photo-resistor for light detection and use its resistance to measure and quantify the amount of transmitted green light. (Be careful that the resistance of the photo-resistor will decrease with an increase in light illumination. Try to guess how will resistance change if we measure a more purple solution?)

Incident green light

Transmitted green light

Photo-resistor connected to a multi-meter
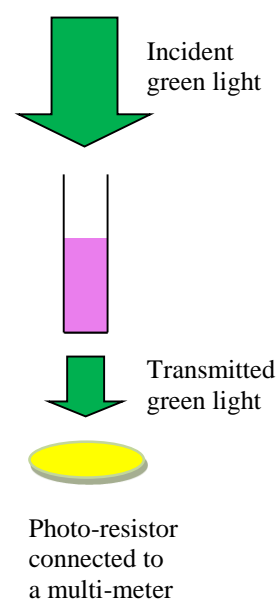
Once we know how to quantitatively compare different purple color intensity using resistance readings, the next thing we want to understand is how resistance corresponds to the actual NO_2 concentration. To do so, we can prepare a calibration curve which is a general method for determining the concentration of a substance in an unknown sample by comparing the unknown to a set of standard samples of known concentration. So in our case, we need to measure the resistances from a set of standard solutions containing different known concentration of purple azo compounds (prepared by adding solution A and B to a set of solutions of different known concentration of NO_2^-). By expressing this relation as a graph of converted resistances against known NO_2^- concentration, we can simply find the resistance of an unknown sample and use this graph to trace back the actual NO_2 concentration value.
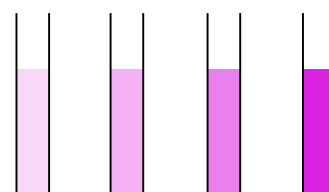
NO$_2$ sampling Procedures

1.4.1 Preparation of the dye indicator
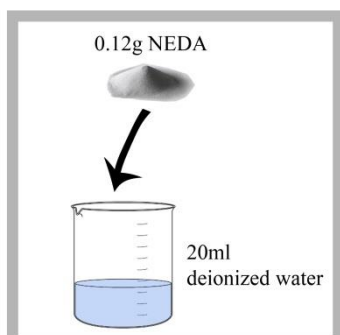
Solution A Preparation
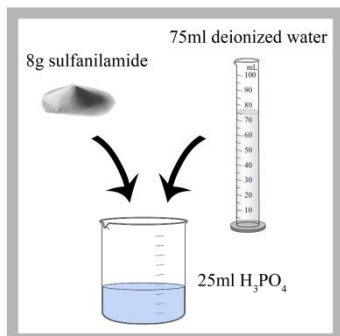
1. Dissolve 8 g of sulfanilamide in 25 ml of phosphoric acid (H$_3$PO$_4$) and then add 75 ml of deionized water. Mix them well afterwards.

2. Store the solution in a clean amber bottle and mark it as Solution A with the preparation date and your name. Store at 4 °C (or in a common refrigerator in your laboratory).
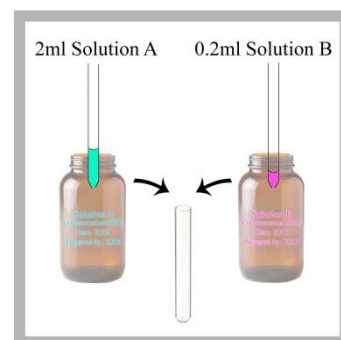
Solution B Preparation

1. Dissolve 0.12 g of N-(1-naphthyl)ethylenediamine dihydrochloride (NEDA) in 20 ml of deionized water. Mix them well afterwards.

2. Store the solution in a clean amber bottle and mark it as Solution B with the preparation date and your name. Store at 4 °C (or in a common refrigerator in your laboratory).

Just before use, pipette 2 ml of Solution A and 0.2 ml of Solution B in a small test-tube and mix them well to act as our dye indicator (or any amount with volume ratio 10$_A$:1$_B$)

1.4.2 Preparation of the pre-filters

Put a 37-mm filter into the 37-mm filter holder (or use a new sealed and prepared one) and then attach it to the setup for pre-filtration as shown in figure 1-1.

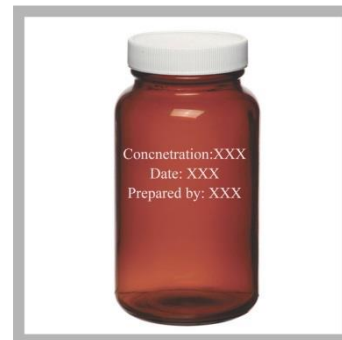! This filter can be used many times until it becomes grey (known as loaded).

1.4.3 Preparation of the diluted triethanolamine absorption solution
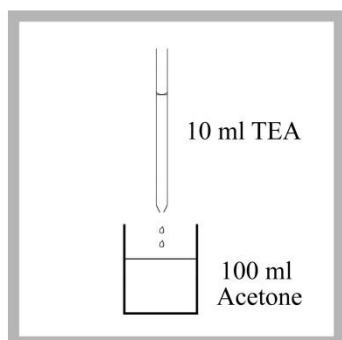
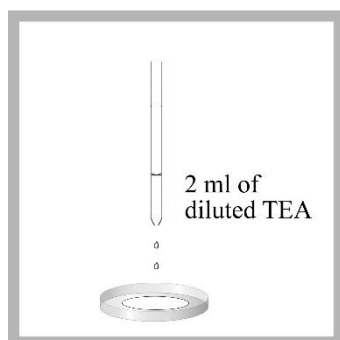1. Dissolve 10 ml of triethanolamine (TEA) in 100 ml of acetone and mix it well
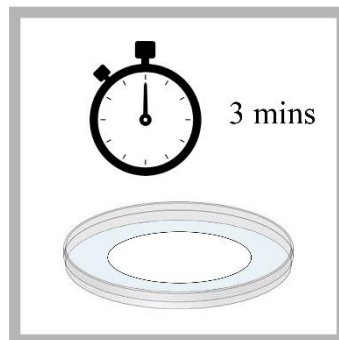
2. Store it in a clean amber bottle

3. Label it as 'Dilute TEA solution' with the concentration, preparation date and your name on the bottle

1.4.4 Coating of the filters

1. Put a 47-mm filter in a Petri dish and use a pipette to drop 2 ml of the diluted TEA absorption solution onto the filter inside a fume cupboard

2. Cover the Petri dish and allow the filter to absorb the solution for about 3 mins

3. Carefully take out the filter with forceps and wave the filter in the fume cupboard until the filter is dried.

4. Load the prepared filter into the 47-mm filter holder (sampler)
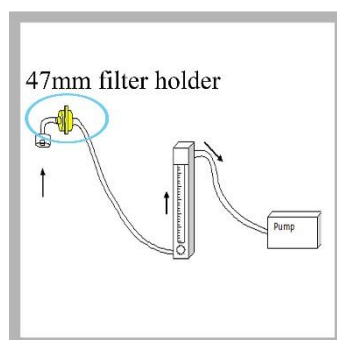
5. Attach the filter holder to the setup as shown in Figure 1-1.

(For best results, coat your filter just before sampling. If necessary, you can seal the sampler in a clean zip-lock plastic bag for later on sampling)

## 1.4.5 Measurement of atmospheric NO$_2$ concentration
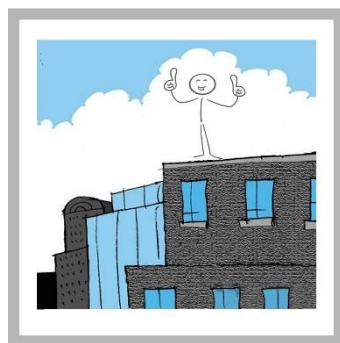
1. Find a location that is free from any obstacles such as short walls, fences, trees, etc. within 3m and far away from any pollution sources to setup your sampling equipment. The rooftop or high floors of the school building are good choices.
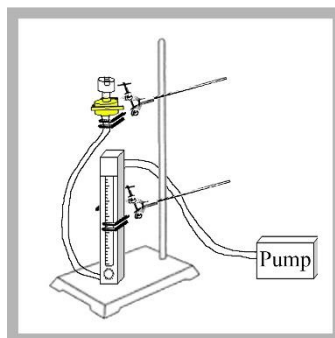

2. Connect the filter holders with coated filter, flowmeter and pump as shown in Figure 1-1. Use a laboratory stand and a clamp to hold the flowmeter.
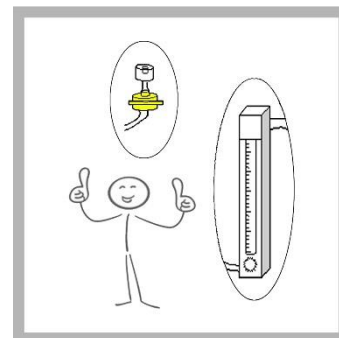

3. Secure the prepared sampler so that it will not topple over by outside disturbances such as wind during sampling. Also make sure that all tubings, wires, cables, and electrical lines are secured to ensure safety and no air leakage.
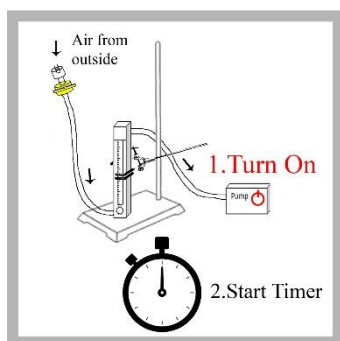
4. Switch on the pump to draw air through the filter. Start the timer.
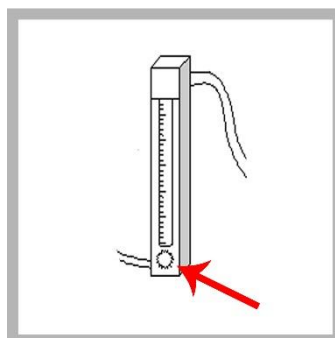
5. Adjust the flowrate (range: 2 - 3 L min^{-1}) to the marked level if needed and record its value in the notebook.
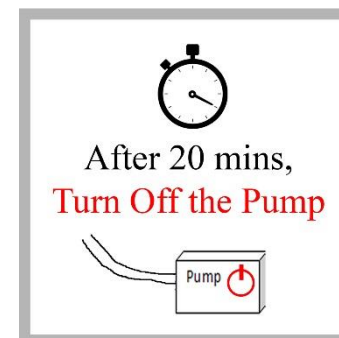
6. Switch off the pump after about 20 minutes. Jot down the sampling time from the stopwatch (you need it to compute your NO$_2$ concentration).


7. Disconnect the 47mm filter holder. Seal the sampler in a zip-lock plastic bag and take it back to the laboratory as soon as possible.
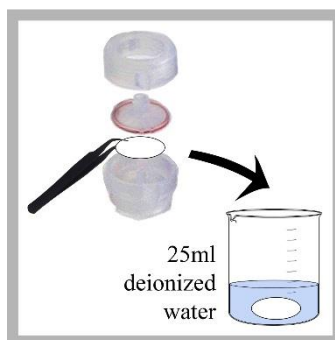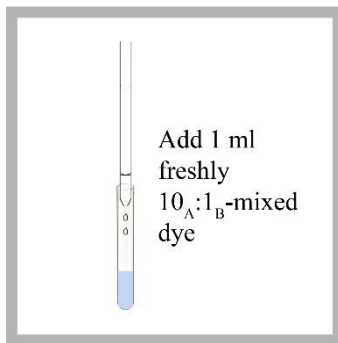

8. In the laboratory, take the filter out with forceps and put it in a clean beaker containing 25 ml of deionized water.
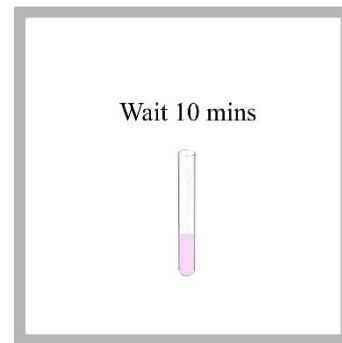

9. Cover the beaker with plastic wrap. Let the filter soak for 30 mins to extract the NO$_2^-$ ions into deionized water. Shake the beaker gently to enhance the extraction.
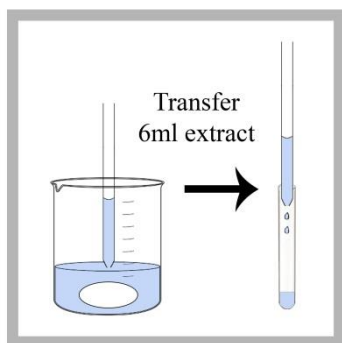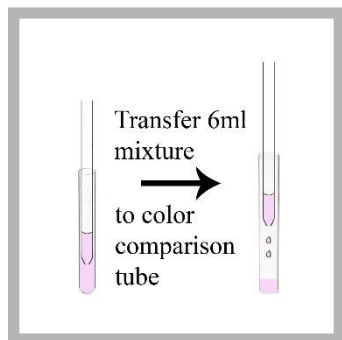
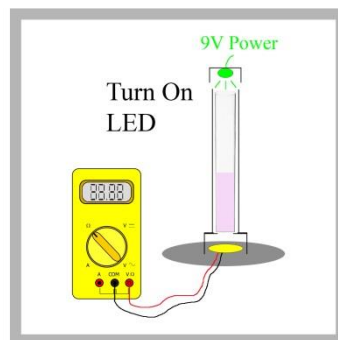10. After 30 minutes, pipette 6 ml of the extract into a clean test-tube.

11. Add 1 ml of freshly 10_A:1_B mixed dye to the test-tube and shake the test-tube to mix the solution.
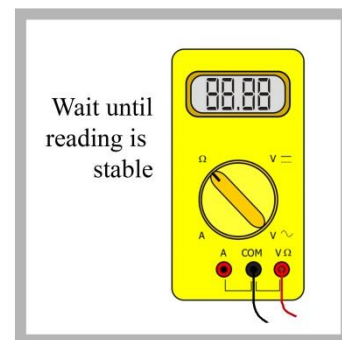

12. Wait 10 minutes for the color to develop.

13. Transfer 6 ml of the developed mixture into a 10-ml color comparison tube for light measurement.
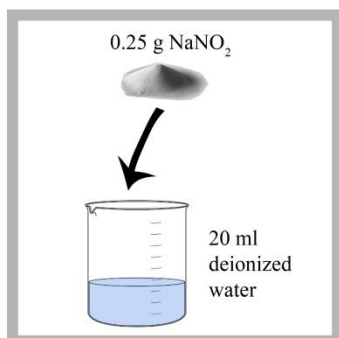

14. Put the color comparison tube into the photometer and switch on the LED light source.


15. Wait until the reading is stable and record the resistance in the notebook. Then calculate the NO_2 concentration using the calibration curve.

# Making NO$_2$ Calibration Curve with standard solution

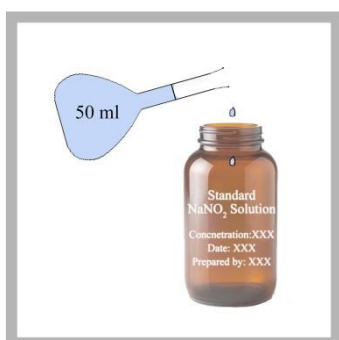## 1.4.6 Preparation of the NO$_2^-$ standard solution

1. Weigh 0.25 g of Sodium Nitrite (NaNO$_2$) and then dissolve it in 20ml of deionized water in a 100ml beaker. Mix it well afterwards.
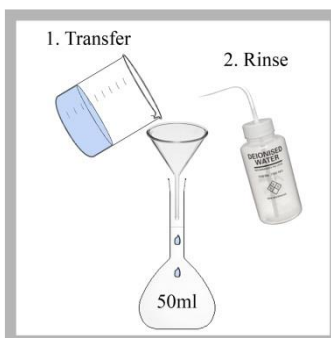

2. Transfer it to a 50-ml volumetric flask. Rinse the beaker and glass stirring rod with deionized water to ensure all NaNO$_2$ is transferred to the volumetric flask.
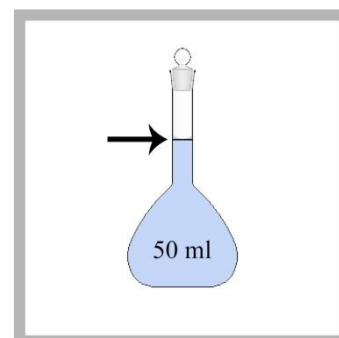
3. Add deionized water to the flask until the water level reaches the mark. Mix it well afterwards.

4. Store the solution in a clean amber bottle and mark it as "Standard NaNO$_2$ solution" with the preparation date, concentration and your name.
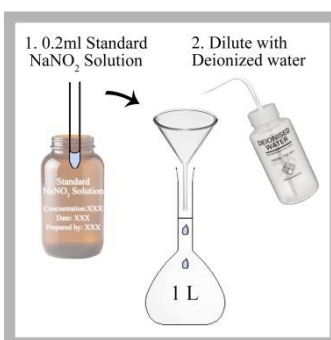
5. Transfer 0.2 ml of the standard NaNO$_2$ solution into a clean, 1-L volumetric flask. Dilute it by adding deionized water until the water level reaches the mark of the flask. Mix it well afterwards.


6. Transfer the resultant solution to a clean amber bottle for storage. Then label the bottle as "Dilute NaNO$_2$ solution" with the concentration, preparation date and your name. (You can calculate the concentration of the solution and record it in the notebook.)
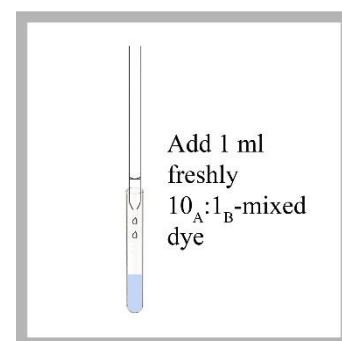
1.4.7 Calibration of the HKUST photometer using dilute standard NO_2^- solutions
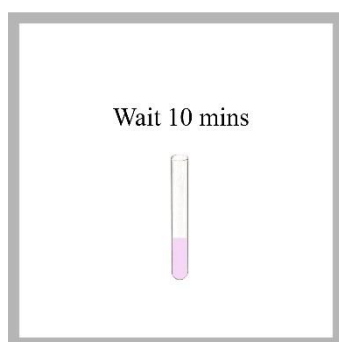

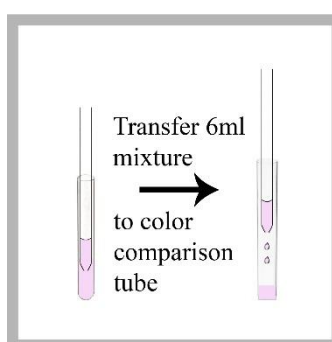1. Pipette 0.2 ml of diluted $NaNO_2$ solution into a clean test-tube.
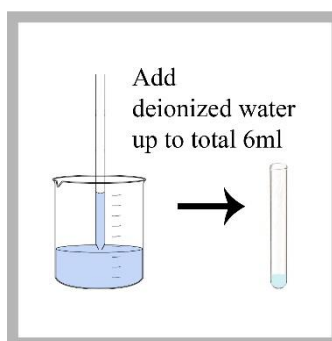
2. Pipette deionized water into the test-tube to make the total volume of the mixture to be 6 ml. (e.g. here $0.2_{NaNO2} + 5.8_{water}$)
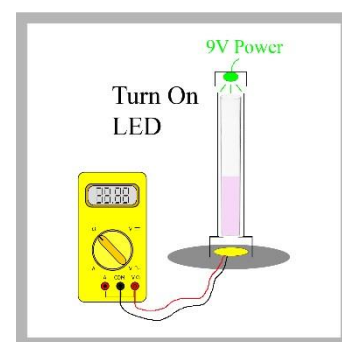

3. Add 1 ml of freshly $10_A:1_B$ mixed dye to the test-tube and shake the test-tube to mix the solution.

4. Wait 10 minutes for the color to develop.

5. Transfer 6 ml of the developed mixture into a 10-ml color comparison tube for light measurement

6. Put the color comparison tube into the photometer and switch on the LED light. Connect the photometer to a multimeter and record the resistance reading when it is stable.

7. Repeat above resistance measurement steps (1) to (6) with 0 ml, 0.5 ml, 0.8 ml, 1 ml, 1.5 ml, 2.0 ml, 2.5 ml and 3.0 ml of dilute $NaNO_2$ solution. (Add corresponding amount of deionized water to make the total volume to be 6 ml in step 2)
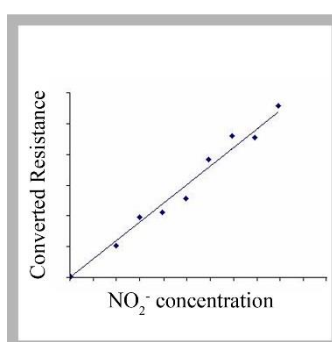
8. Determine the relationship between converted resistances and different NO_2^- concentrations using linear regression analysis which is available in Microsoft Excel or similar software packages.

1.5 Calculation of NO₂ concentration

1.5.1 Calibration curve

$$\text{concentration of standard NaNO}_2 \text{ solution (g/L)} = \frac{\text{mass of NaNO}_2 \text{ (g)}}{\text{volume of water (L)}}$$

$$\text{concentration of diluted NaNO}_2 \text{ solution (mg L}^{-1}) = \text{concentration of standard NaNO}_2 \text{ solution (g L}^{-1}) \times \frac{1}{5000} \times \frac{1000 \text{ mg}}{1 \text{ g}}$$

$$\text{NO}_2^- \text{ concentration in the diluted solution (mg L}^{-1}) = \frac{\text{concentration of diluted NaNO}_2 \text{ solution (mg L}^{-1}) \times (14 + 2 \times 16)}{23 + 14 + 2 \times 16}$$

$\text{NO}_2^- \text{ concentration of each data point of calibration (mg L}^{-1})$

$$= \frac{\text{NO}_2^- \text{concentration in diluted NaNO}_2 \text{ solution (mg L}^{-1}) \times \text{volume of diluted NaNO}_2 \text{ added (ml)}}{\text{volume of diluted NaNO}_2 \text{ added (ml)} + \text{volume of deionized water added (ml)}}$$

Plot the converted resistance readings against known NO_2^- concentrations and get a regression line in the form of y = ax + b.

1.5.2 Calculation of unknown NO₂ concentration in the air

$$\text{concentration of NO}_2^- \text{ in extraction (mg L}^{-1}) = \frac{\text{reading of ohmmeter } (\Omega) \text{ - b}}{a}$$

$$\text{total mass of NO}_2^- \text{ in the extract (mg)} = \text{concentration of NO}_2^- \text{ in extraction (mg L}^{-1}) \times \text{volume of water added for extraction (L)}$$

$$\text{NO}_2 \text{ concentration in the air (mg L}^{-1}) = \frac{\text{total mass of NO}_2^- \text{ in the extract (mg)}}{\text{sampling flowrate (L min}^{-1}) \times \text{sampling time (min)}}$$

1.5.3 Unit conversion, from mg L⁻¹ to ppb:

$\text{NO}_2 \text{ concentration in the air (ppb)}$

$$= \frac{\text{NO}_2 \text{ concentration in the air (mg L}^{-1}) \times \frac{1000 \, \mu g}{1 \, mg} \times \frac{1000 L}{1 \, m^3} \times V_m \text{ (L mol}^{-1}) \times T \text{(K)} \times 1013 \text{ (hPa)}}{\text{molecular mass of NO}_2 \text{ (g mol}^{-1}) \times 298 \text{(K)} \times P \text{ (hPa)}}$$

where V_m = molar volume of gas = 24.45 L mol⁻¹
$\quad$ T = temperature during sampling (K)
$\quad$ P = atmospheric pressure during sampling (hPa)