VRIJE
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BRUSSEL

DESIGNING OPTOELECTRONIC SENSORS FOR WATER QUALITY MEASUREMENTS

Tim Jäger

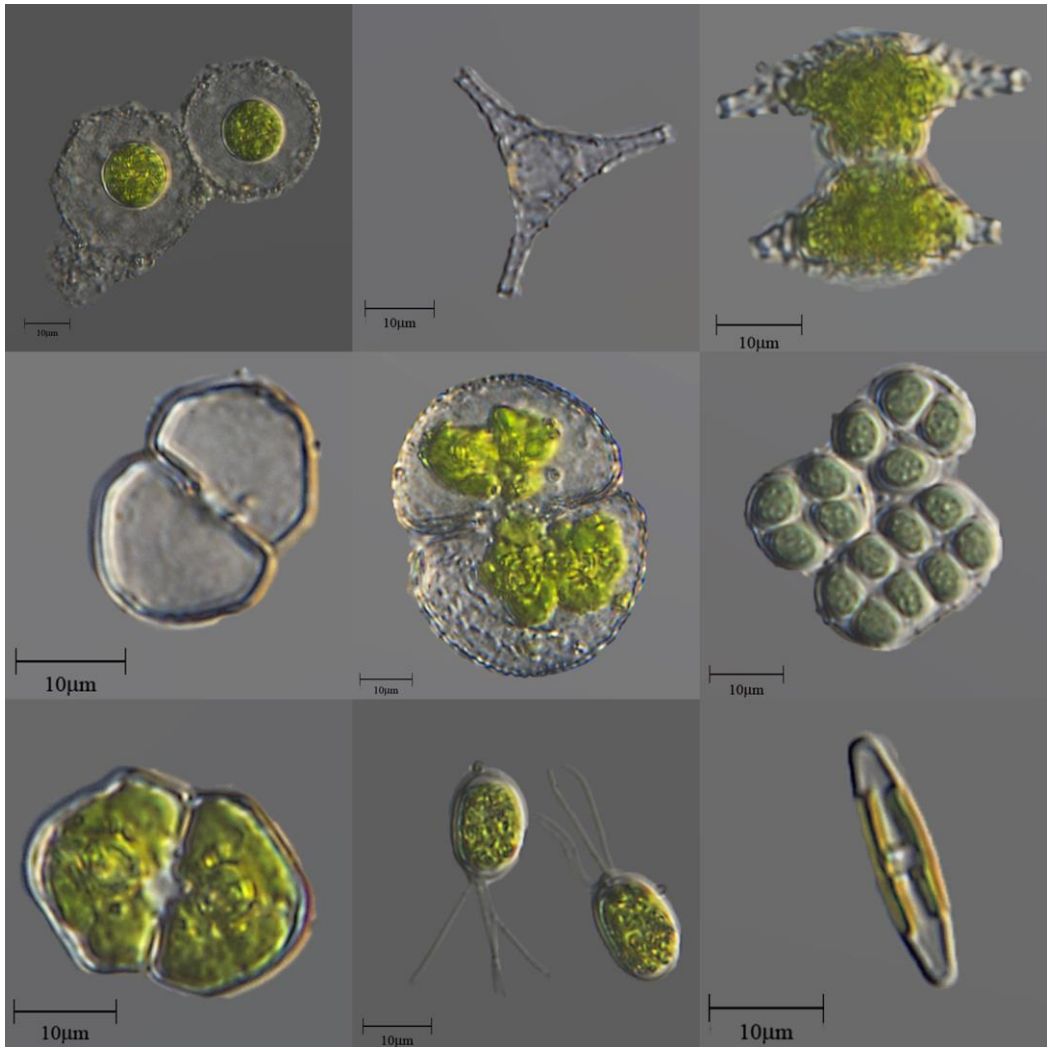
2023-2024

promotor: Prof. dr. ir. Abdellah Touhafi

ENGINEERING SCIENCES

Introduction

- Promotor: Prof. dr. ir Abdellah Touhafi
- Supervisor: Ir. Souhail Fatimi



Author: Alexander Klepnev; Source: https://en.wikipedia.org/wiki/File:Водоросли_пресноводного_водоема_2.jpg

Overarching Project

Detecting and quantifying:

- Algae
- Cyanobacteria

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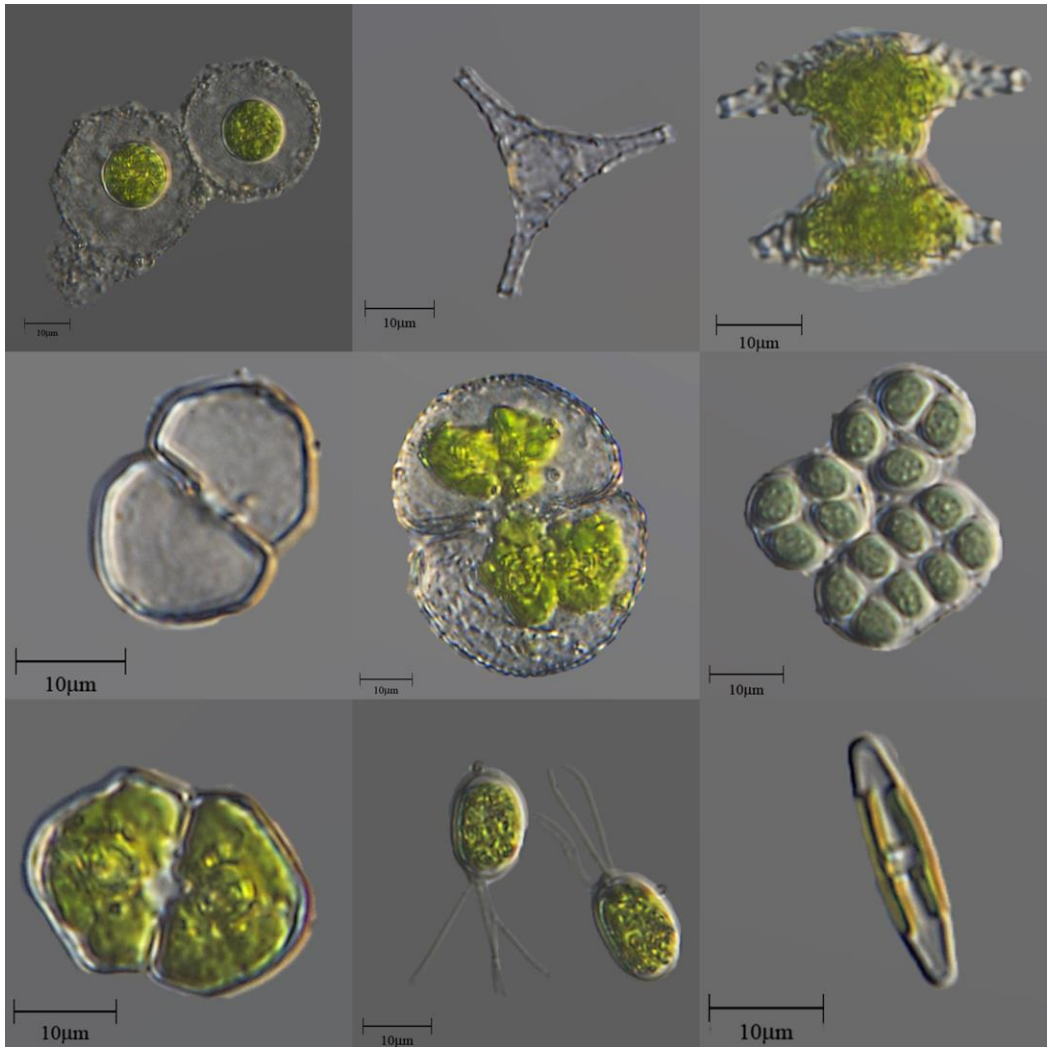

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Byproducts:

- Chlorophyll
- Dissolved oxygen

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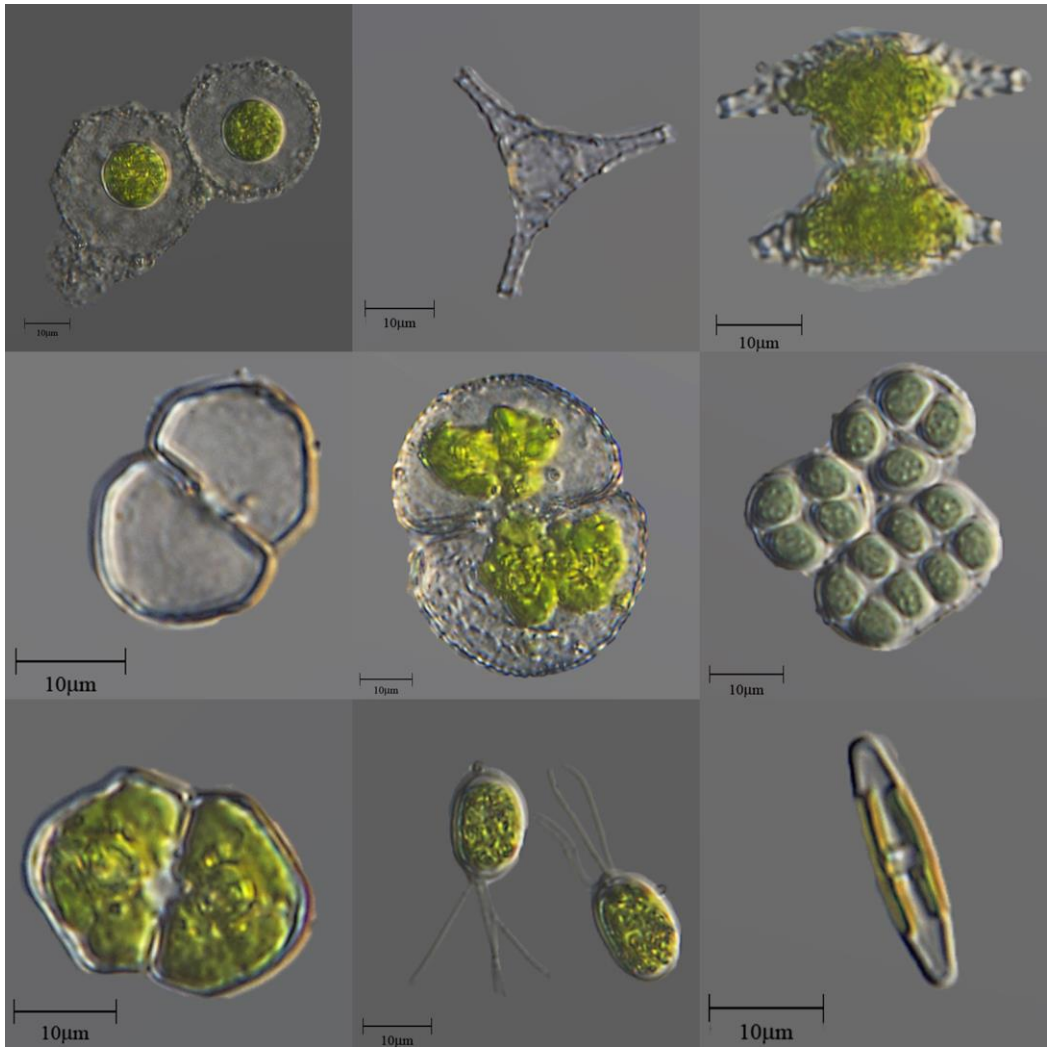

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My goal is to investigate optoelectronic solutions,

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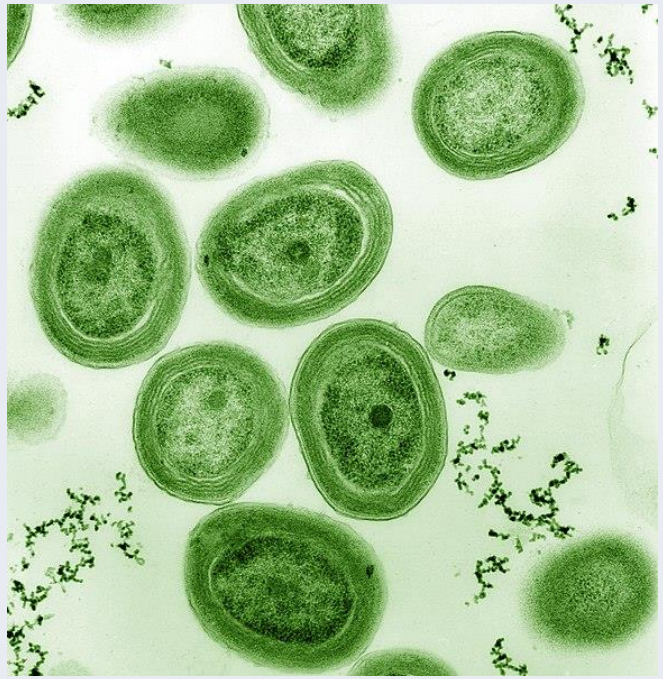
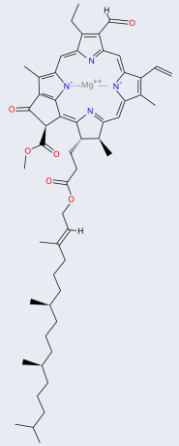
Chlorophyll

- It is everywhere

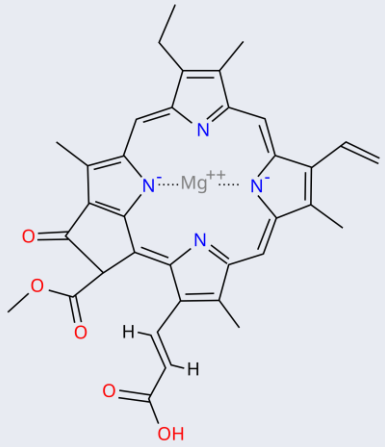
Source: https://en.wikipedia.org/wiki/File:Prochlorococcus_marinus.jpg



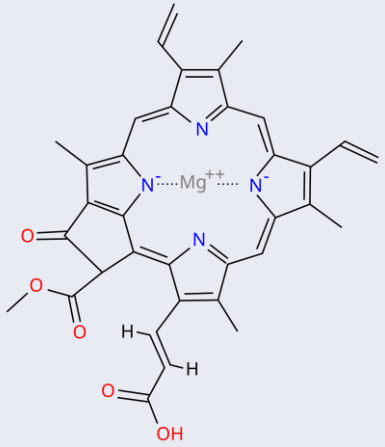
Chlorophyll - Types



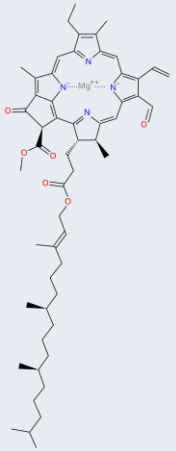
Photosynthesis



Small and large differences molecularly



Large impact on properties



Some are rare

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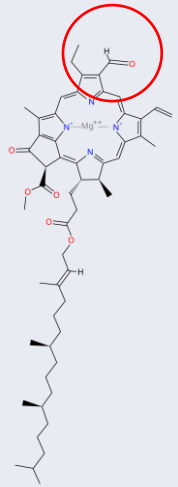
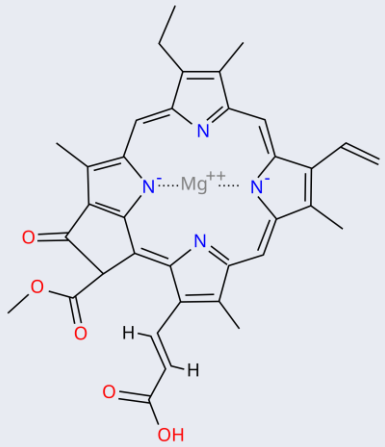
Molecular structure images: Author: David Richeld. Source: Wikimedia Commons

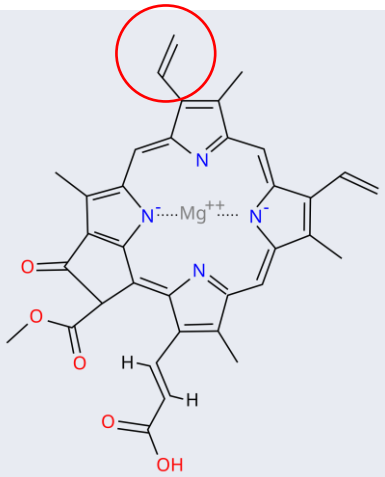
Chlorophyll - Types



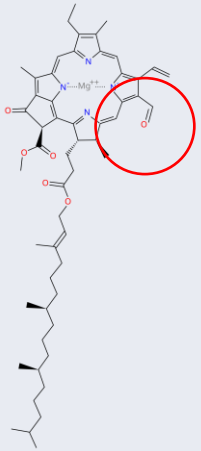
Chlorophyll b



Chlorophyll c_1

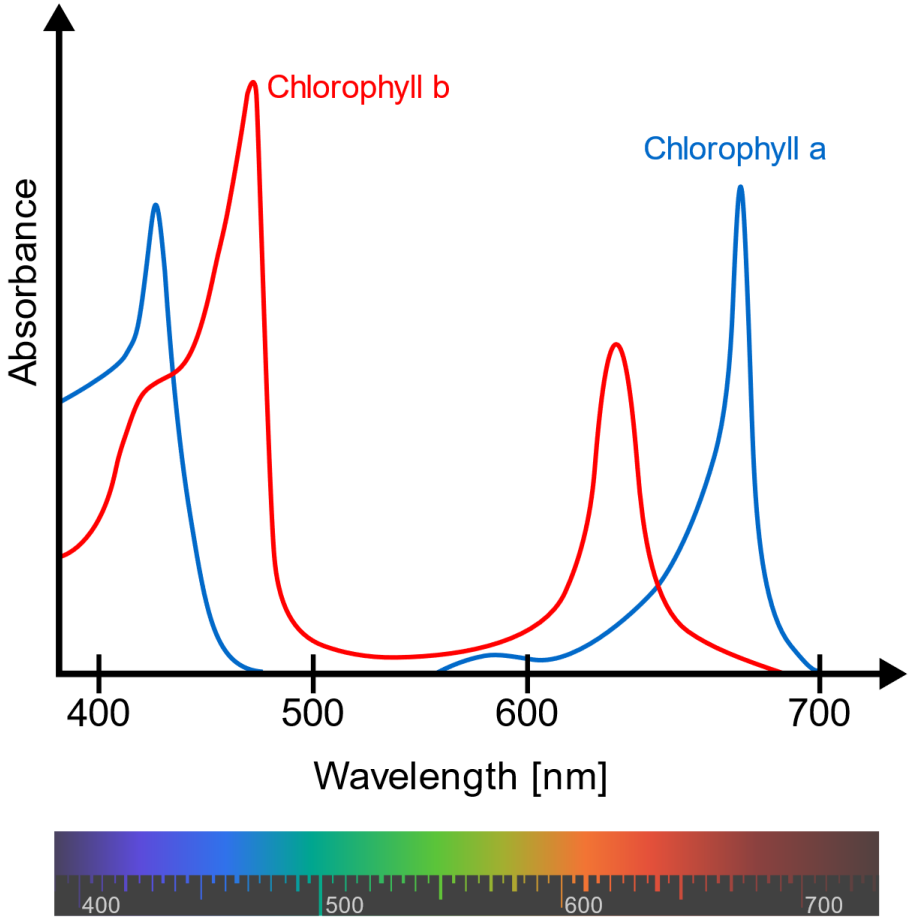


Chlorophyll c_2



Chlorophyll f

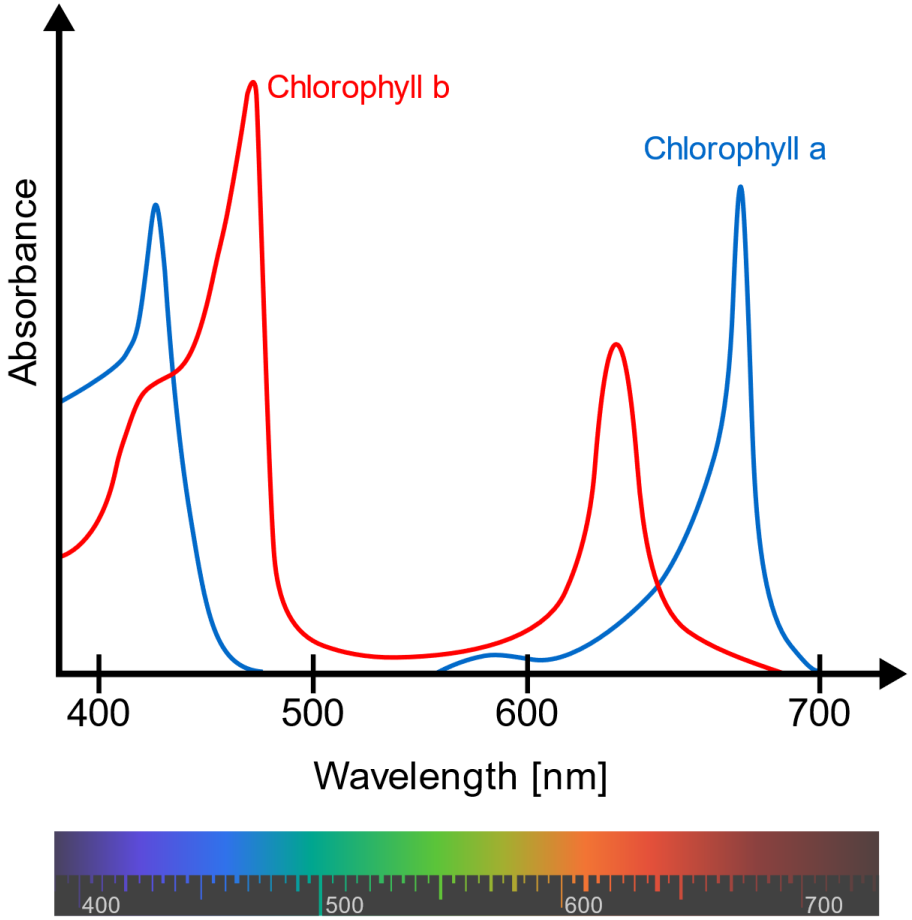
Chlorophyll – Absorption Spectra



Author: Daniele Pugliesi. Source: Wikimedia Commons

- Each type its own spectrum

Chlorophyll – Absorption Spectra



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- Each type its own spectrum
- Organisms have multiple different types
- Larger coverage for photosynthesis

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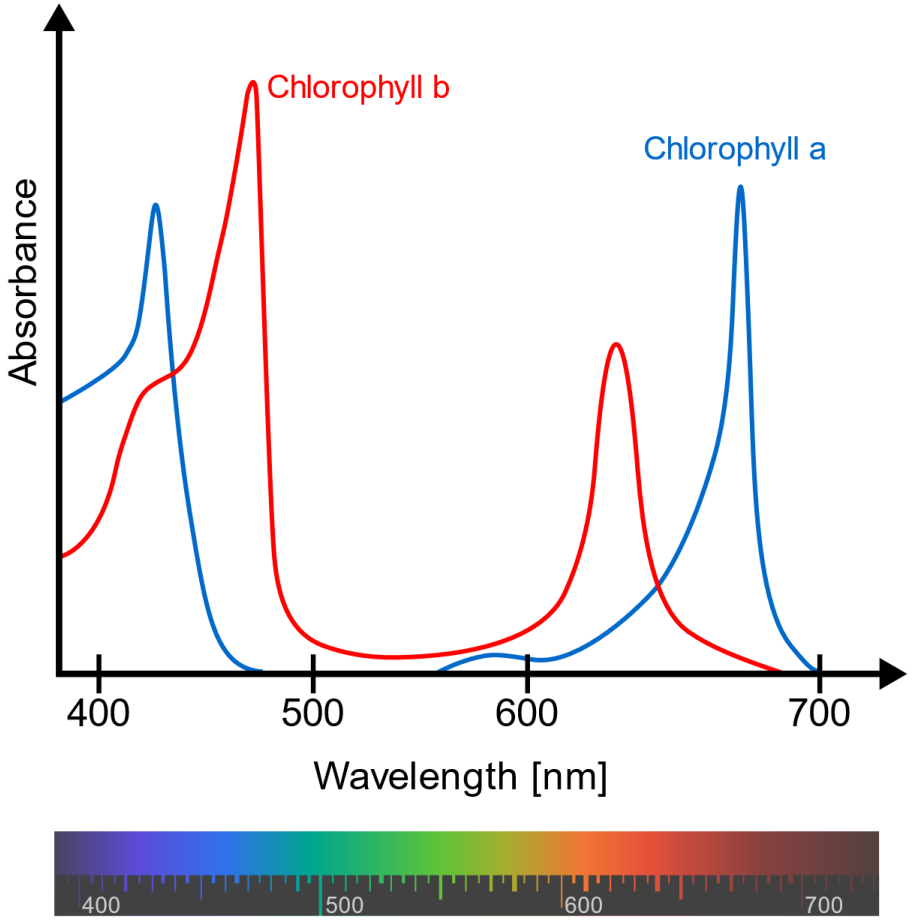

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- Chlorophyll c: Mainly algae
- Chlorophyll d and f: Cyanobacteria (f: 2010)

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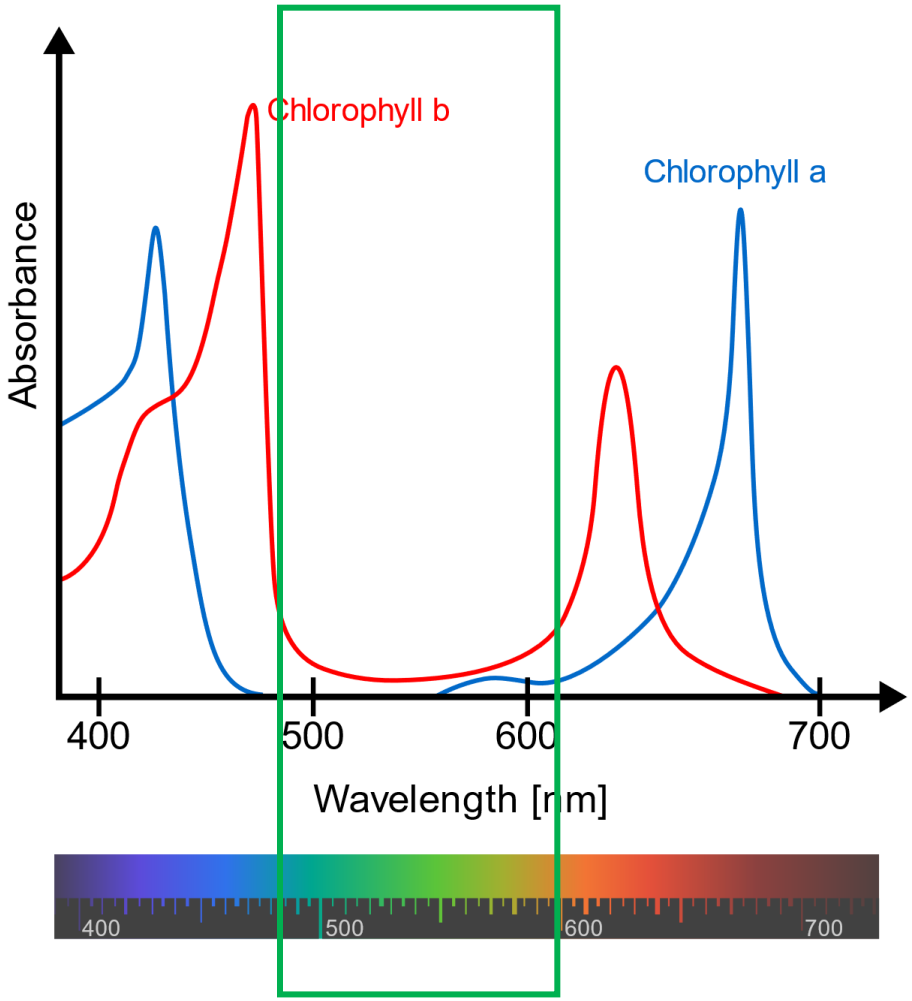

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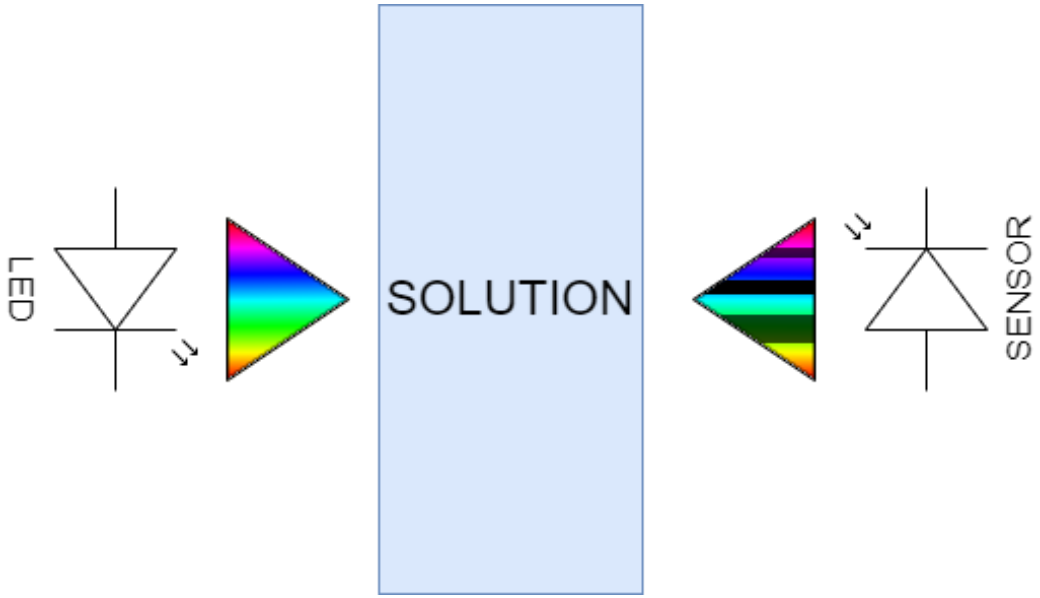

- Broad spectrum light emitted
- Part absorbed by solution
- Sensor sees what is left over

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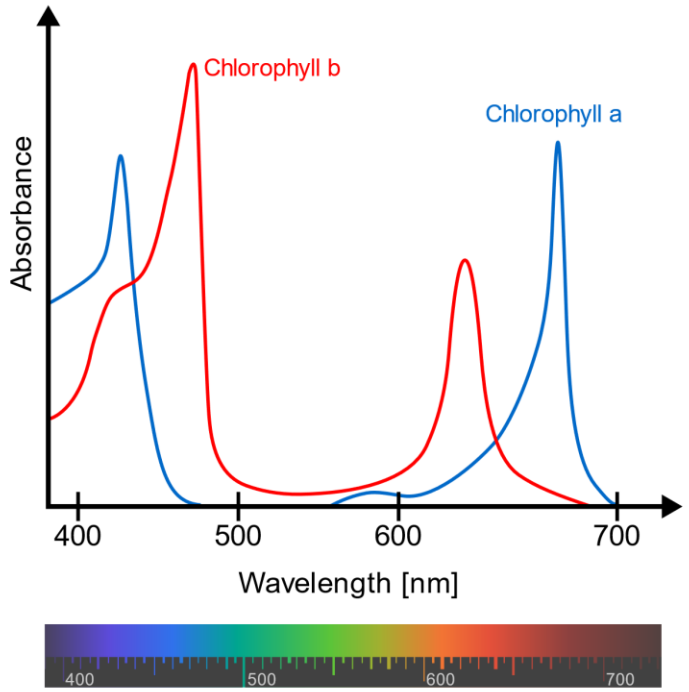

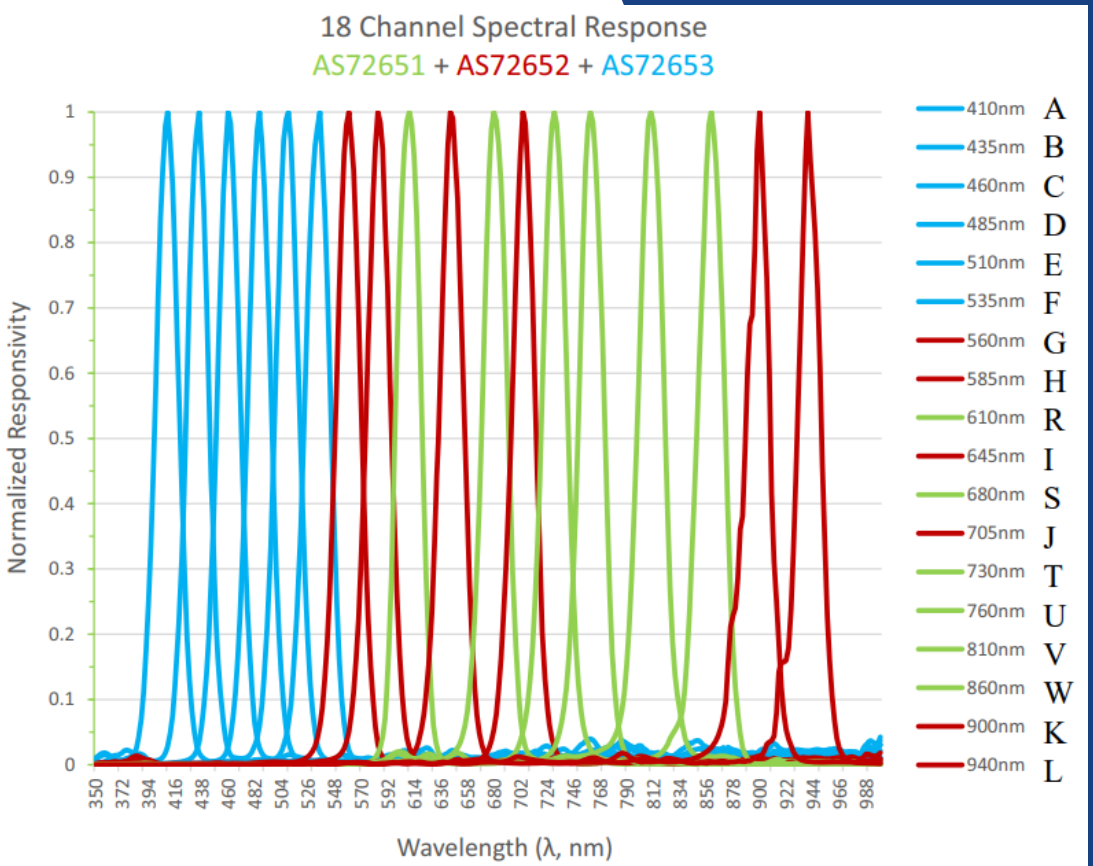

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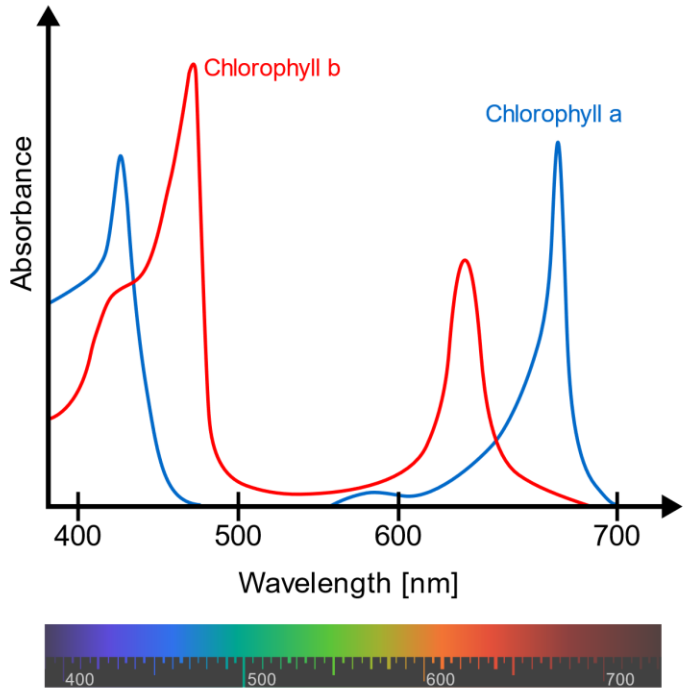

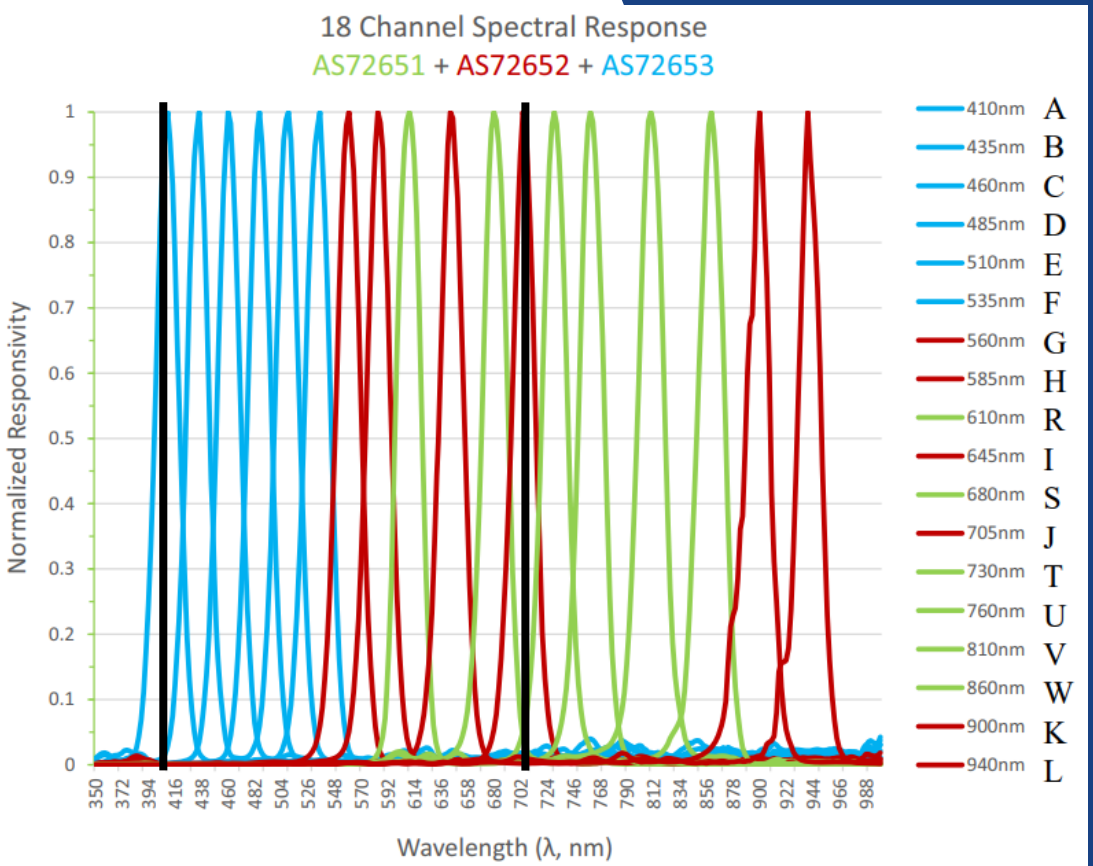

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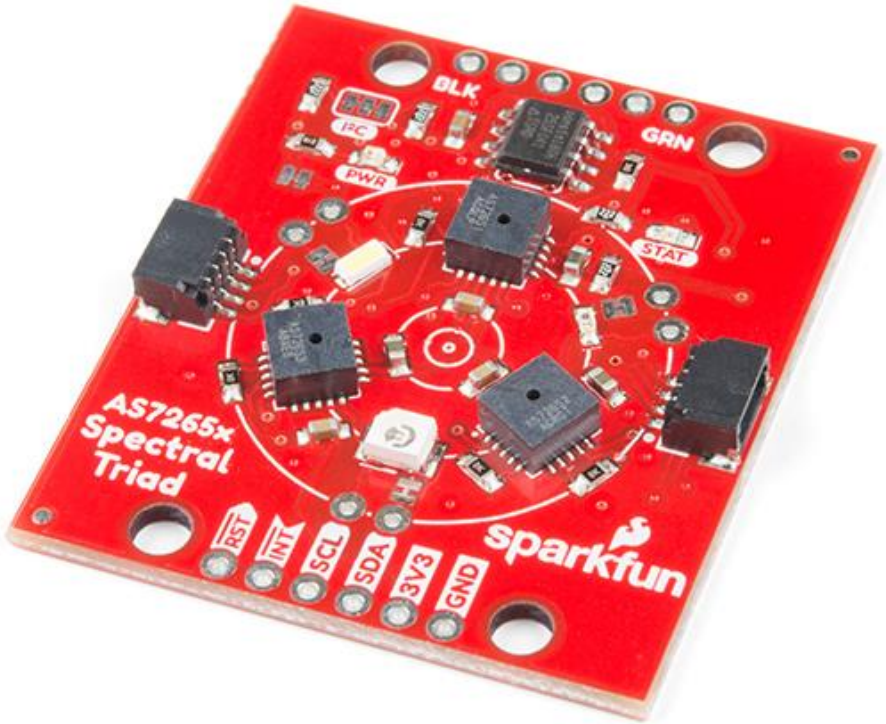
AS7265x

- Triad Spectroscopy Sensor
- 18 wavelengths
- 410 nm (UV) to 940 nm (IR)
- Precision 28,6 nW/cm² at ±12%



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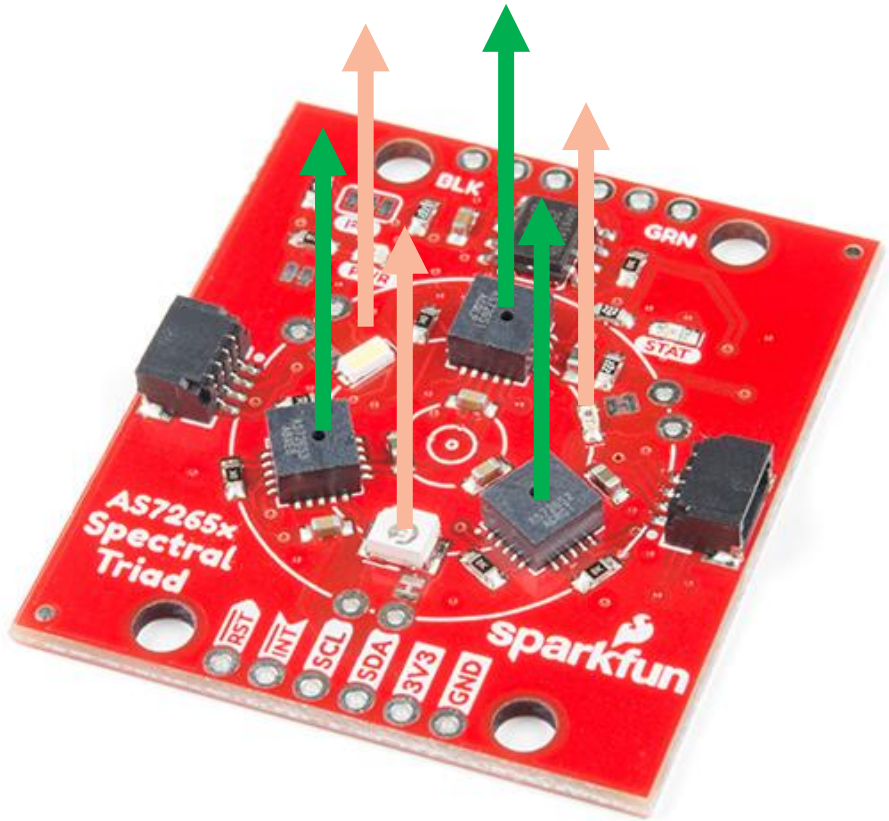

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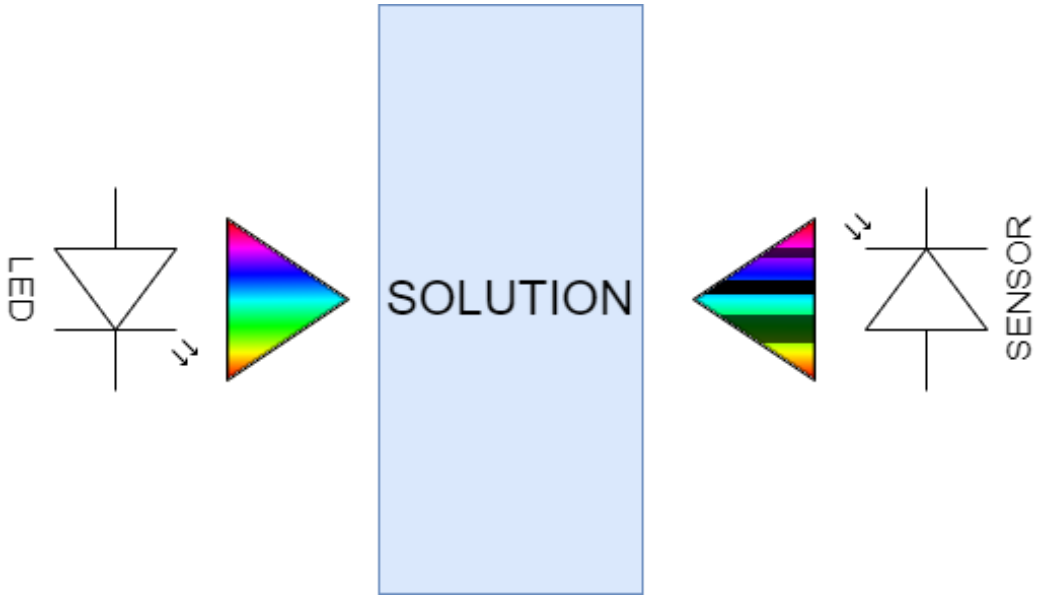

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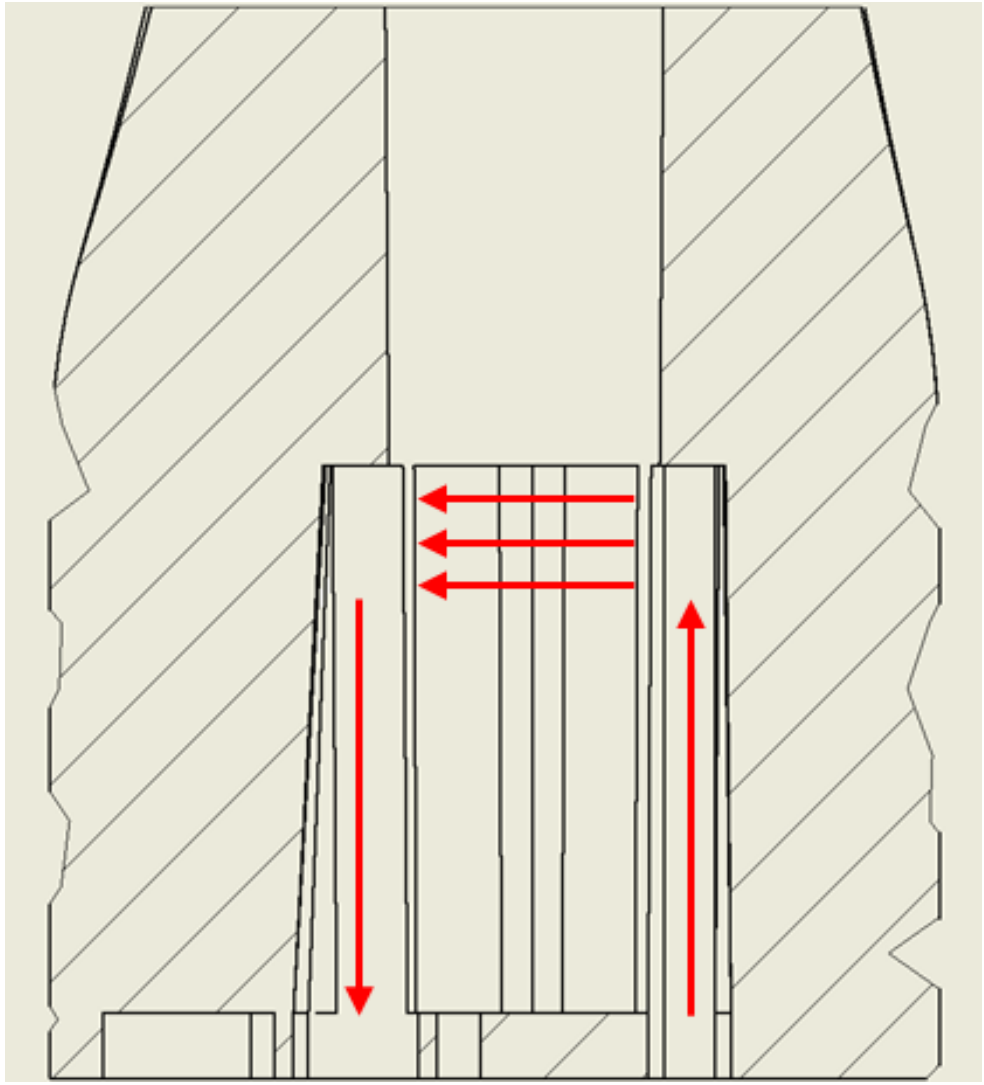

Measuring the spectrum

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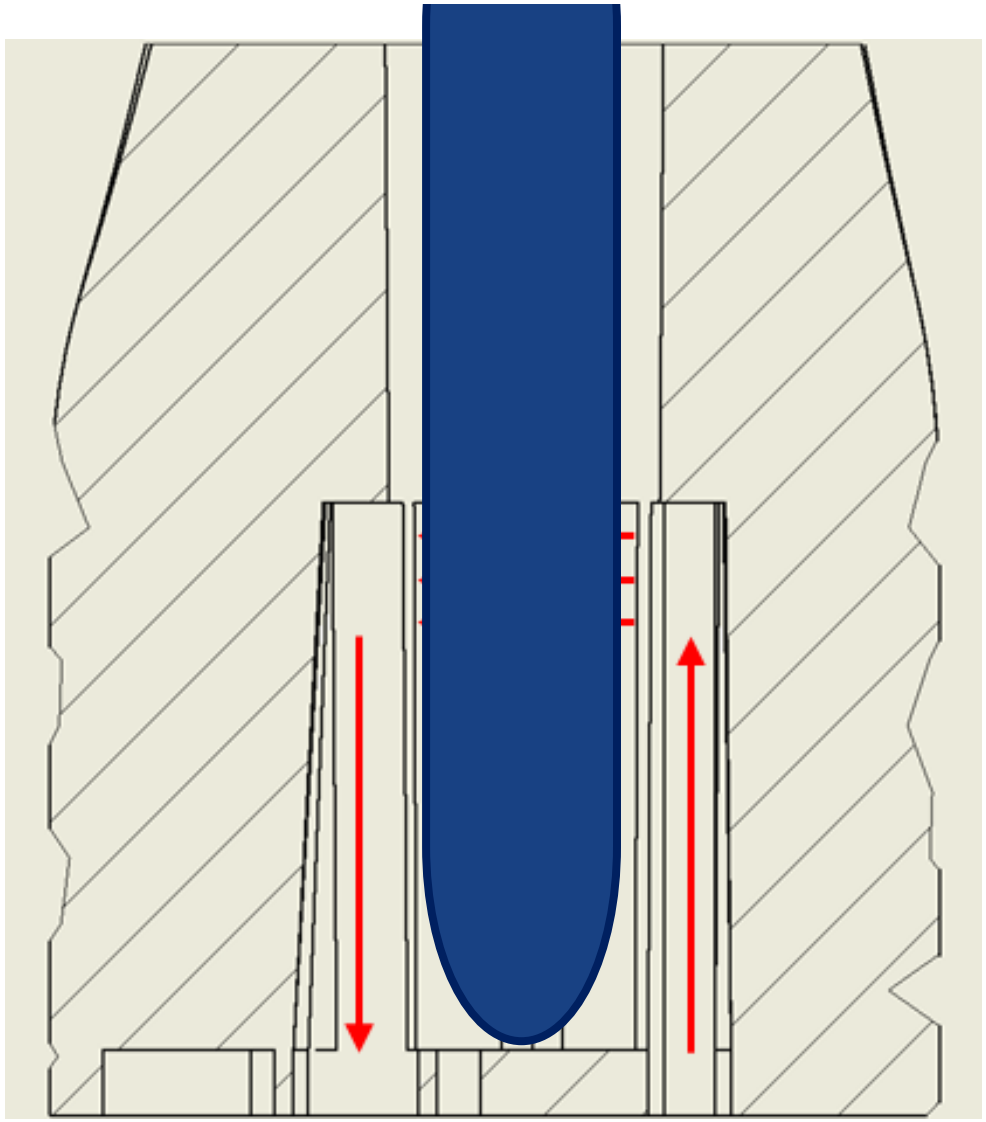

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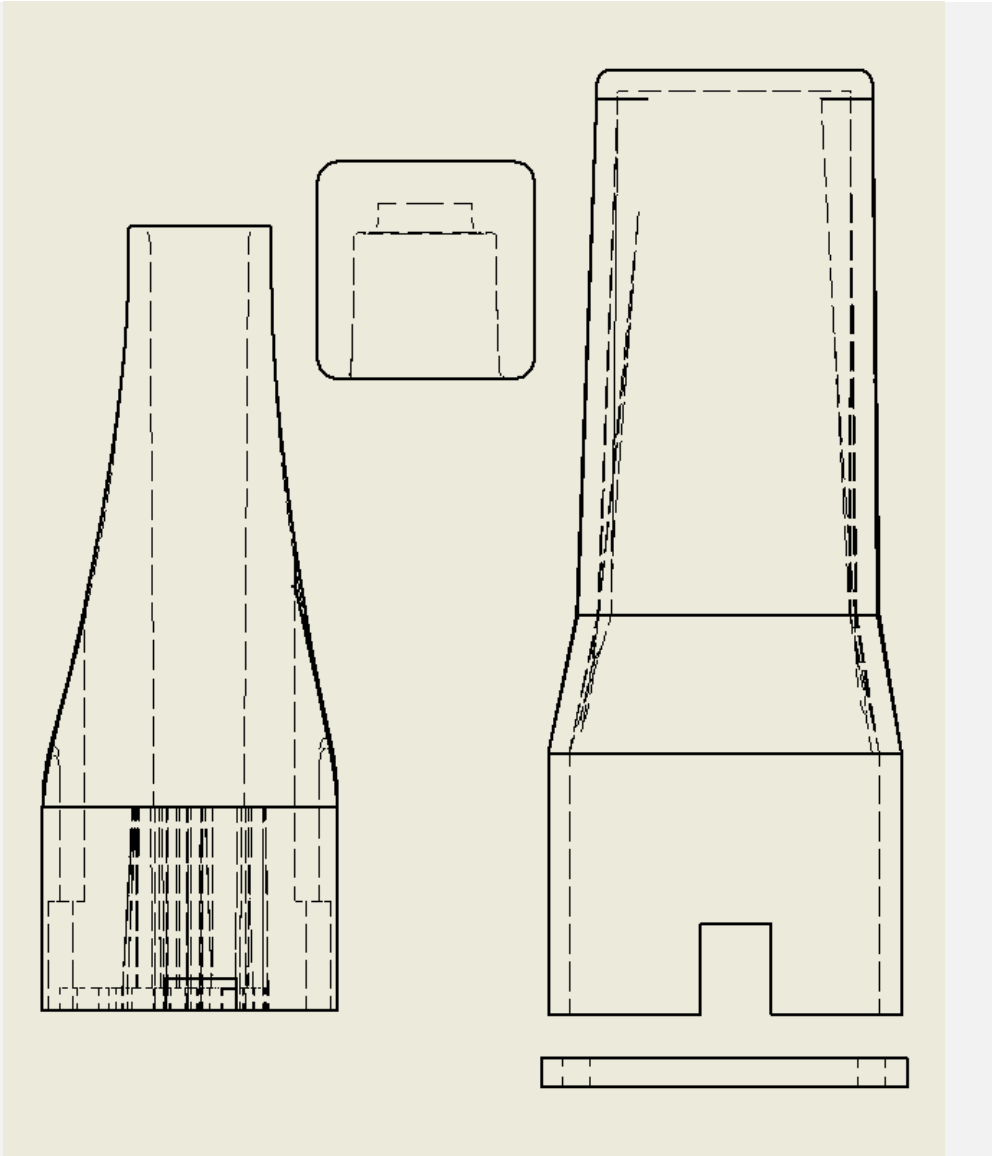

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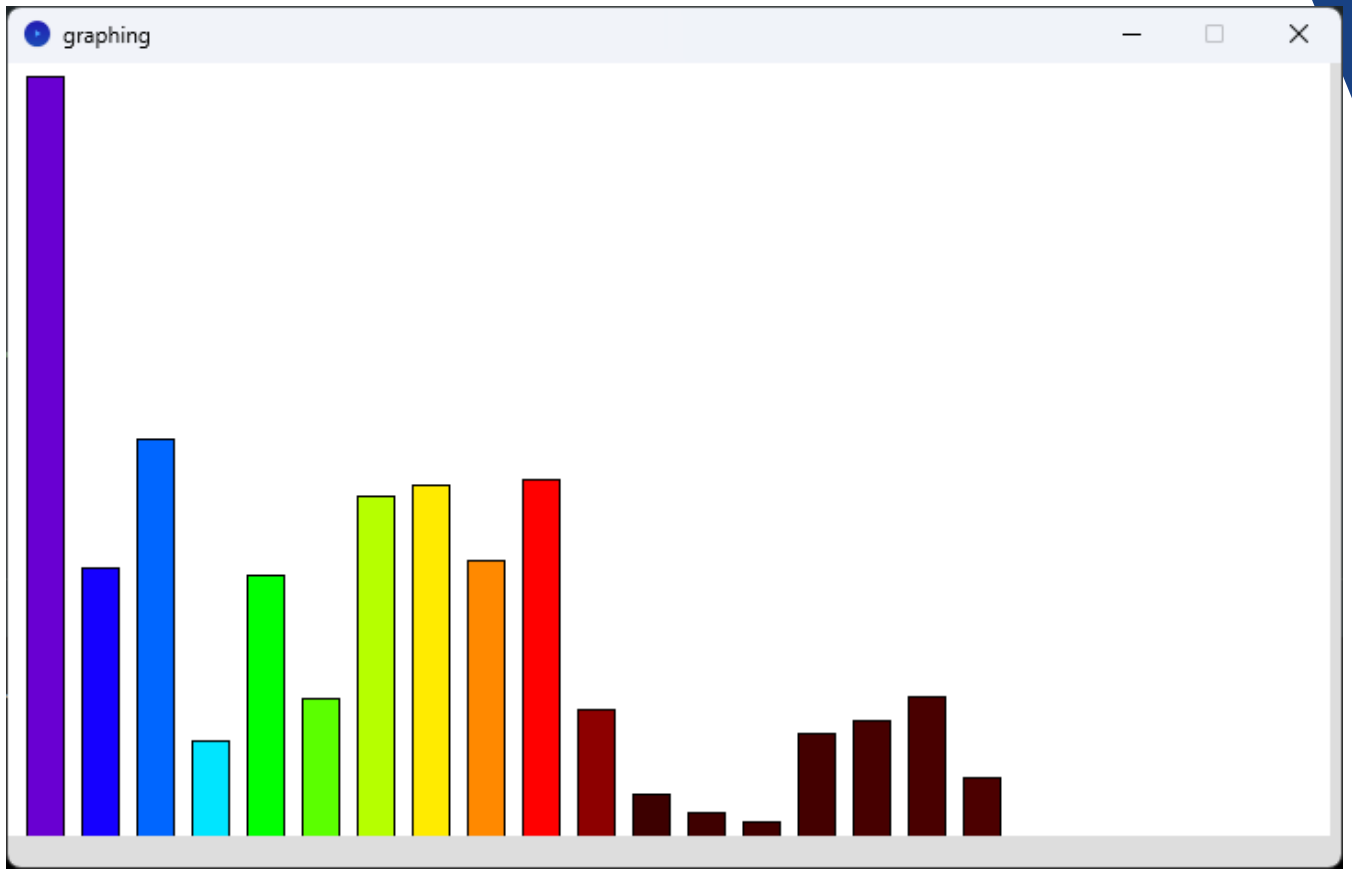
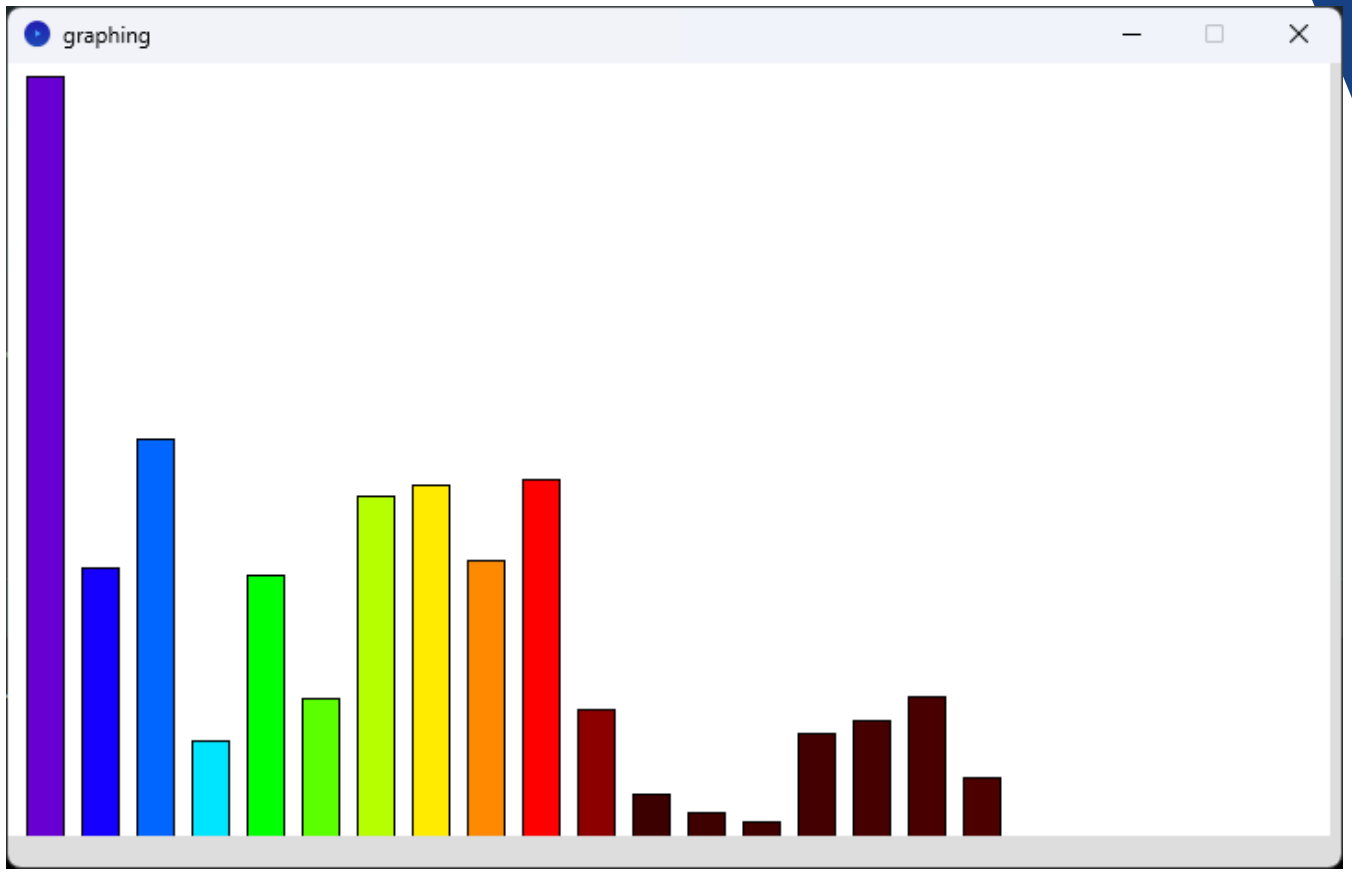


Measuring the spectrum – Tap Water



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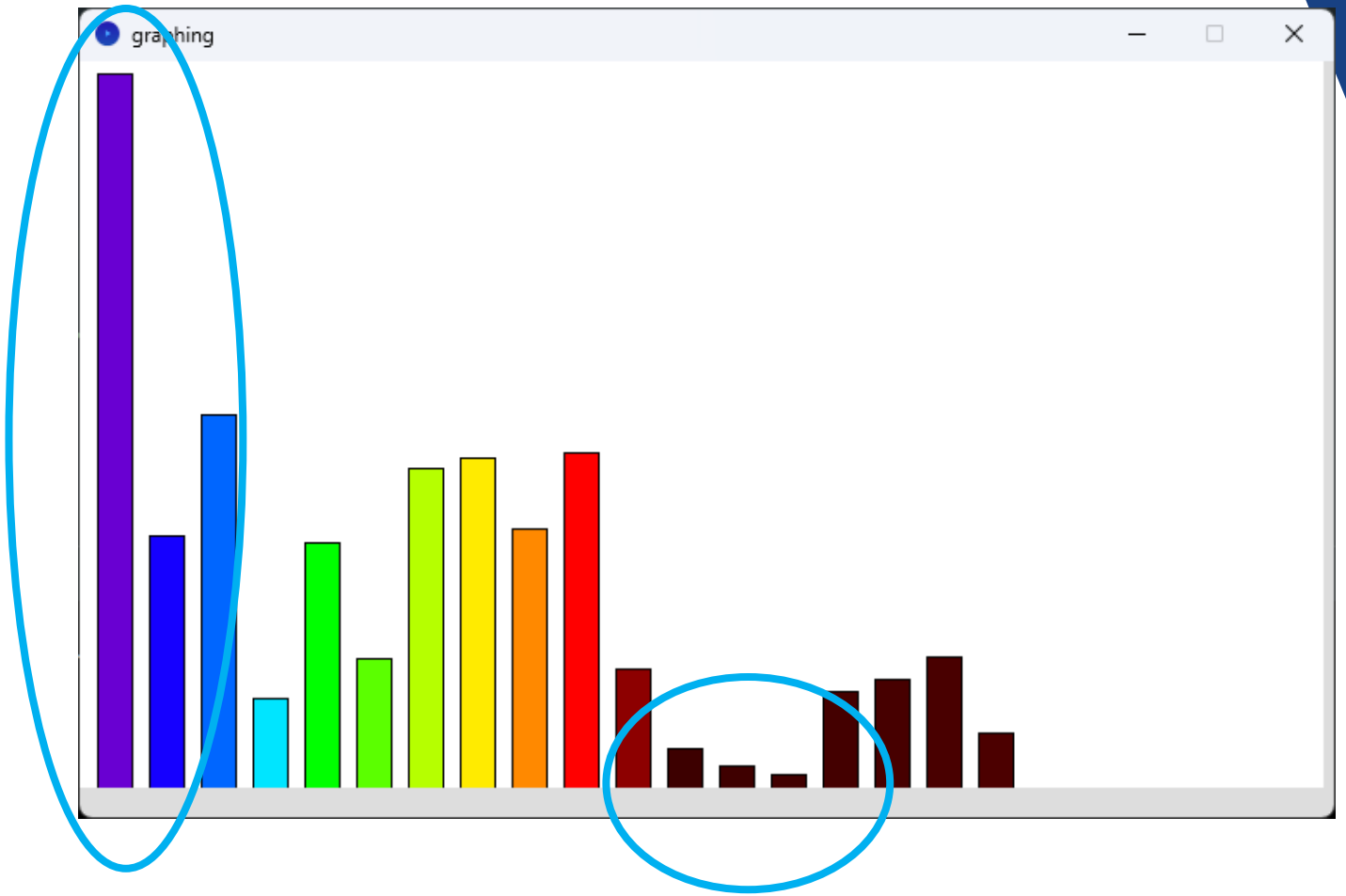

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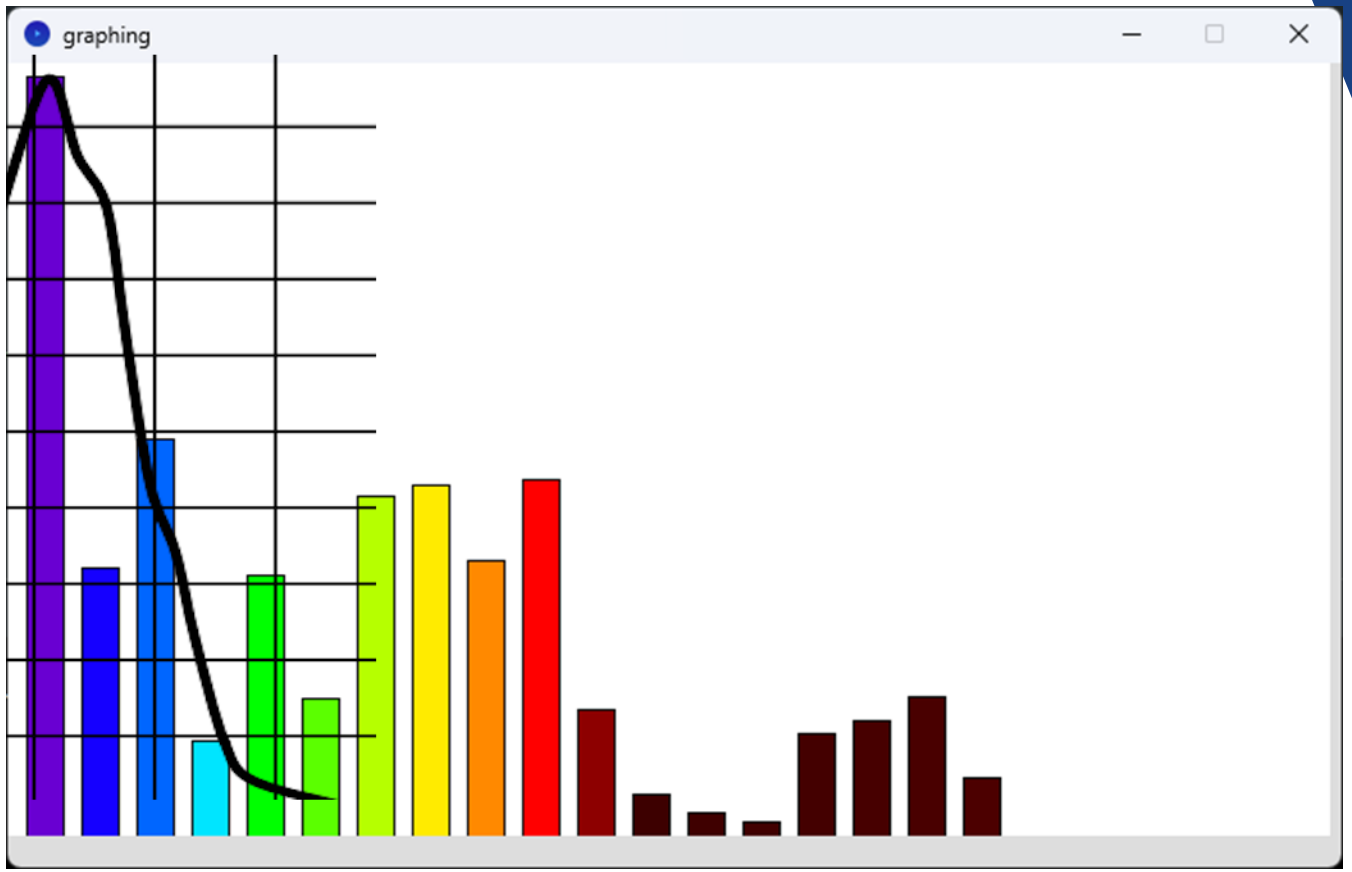

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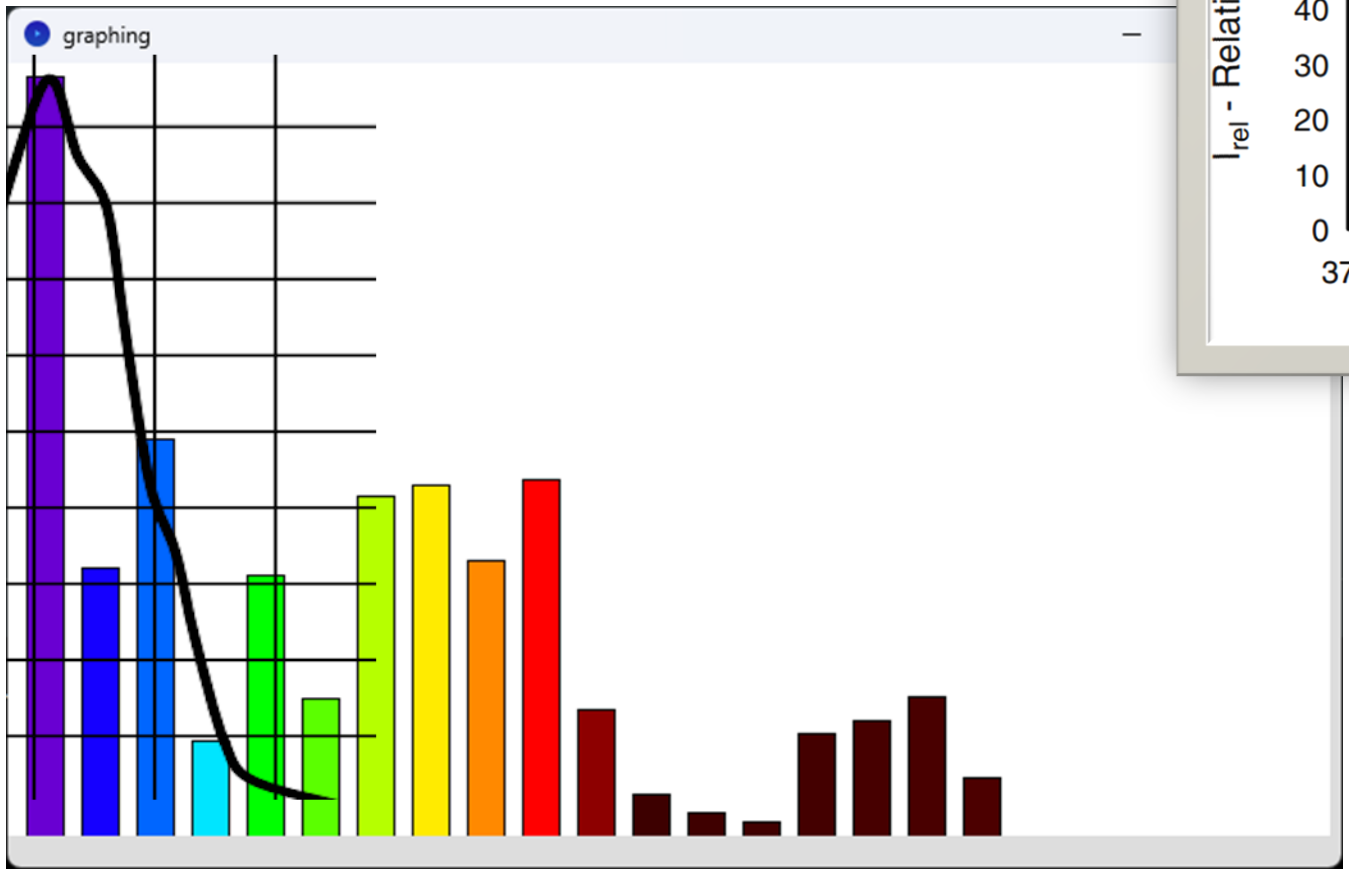

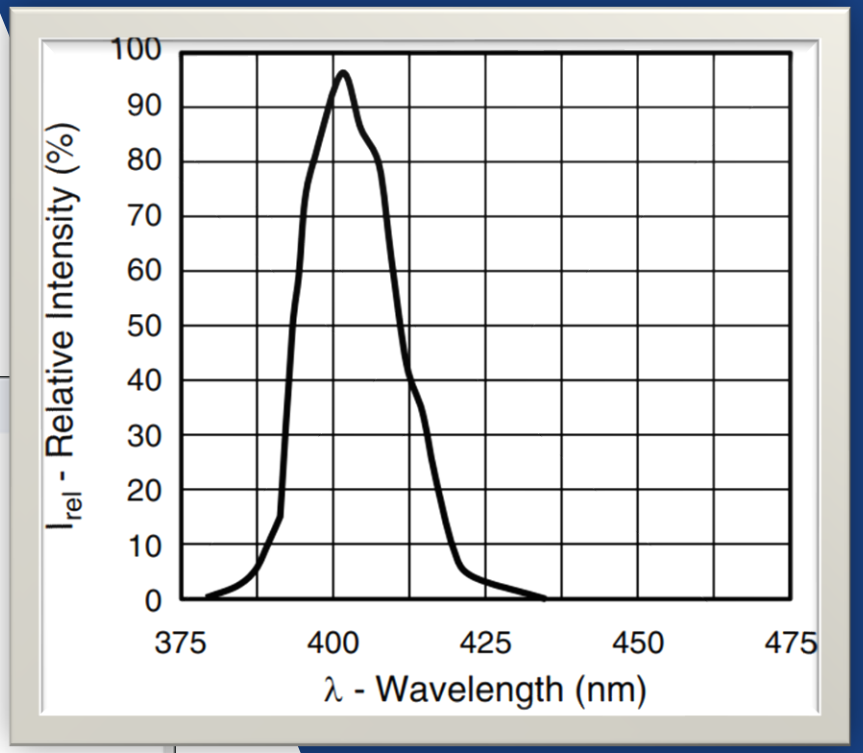

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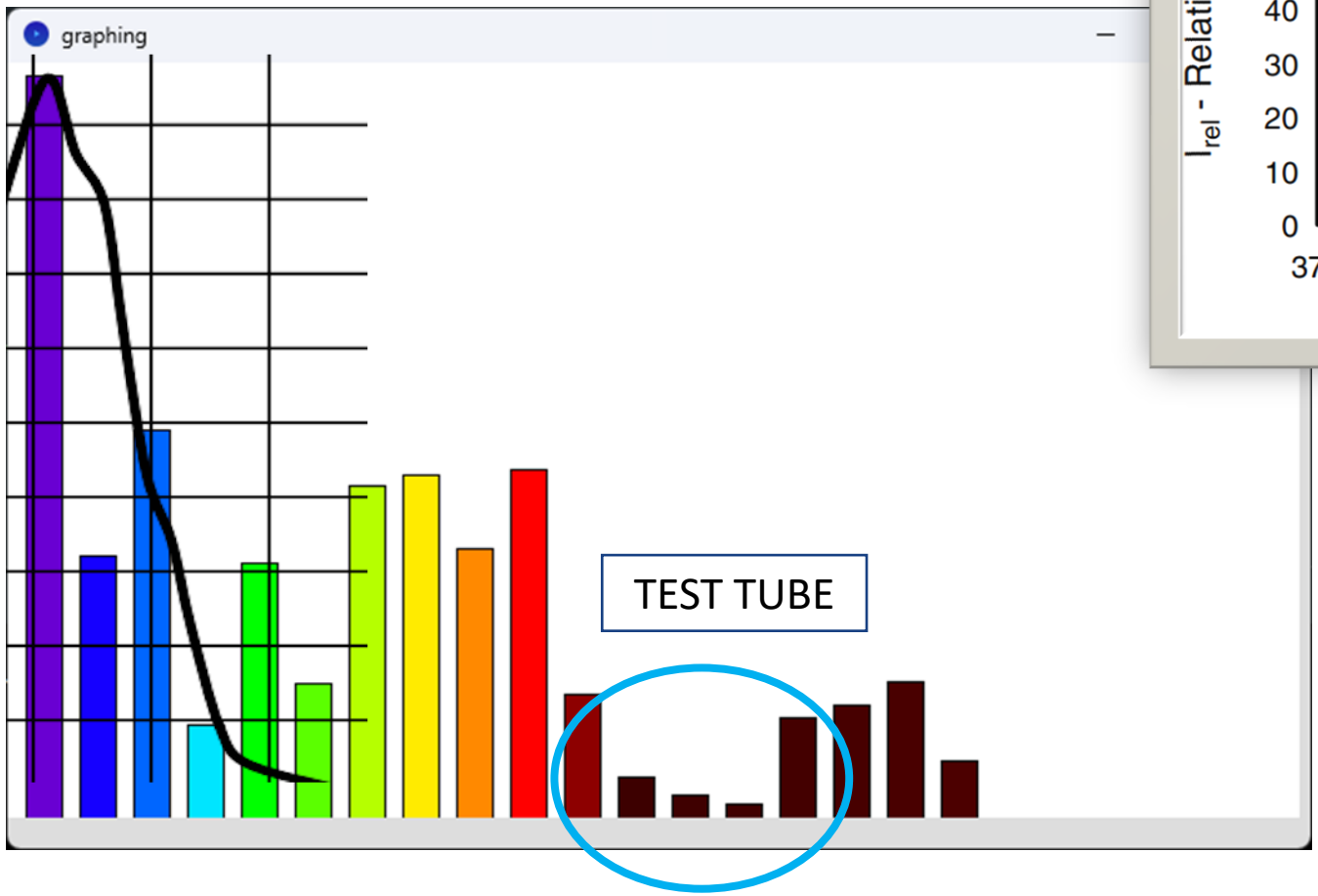
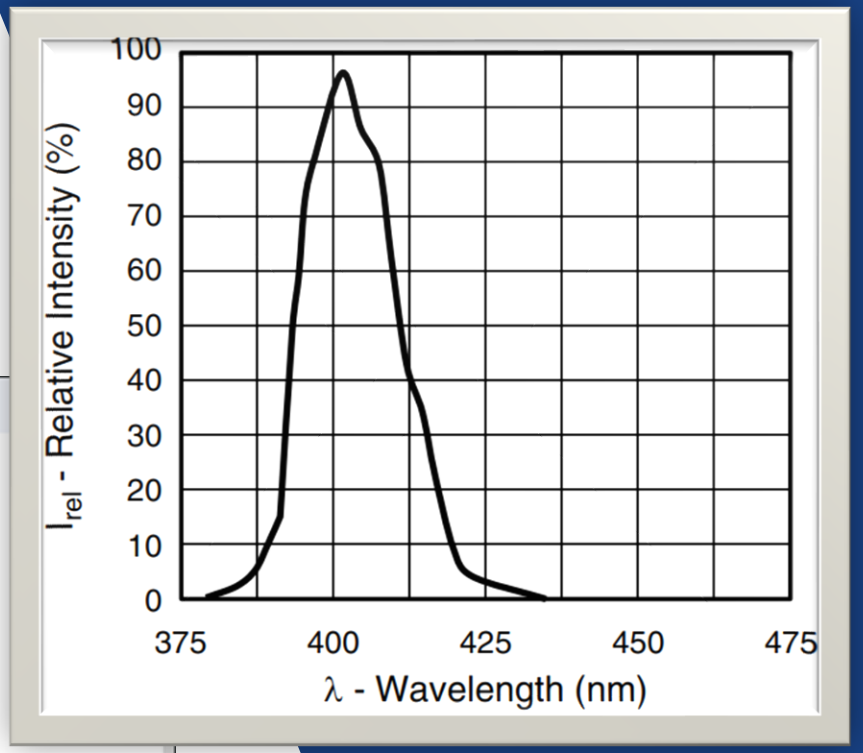
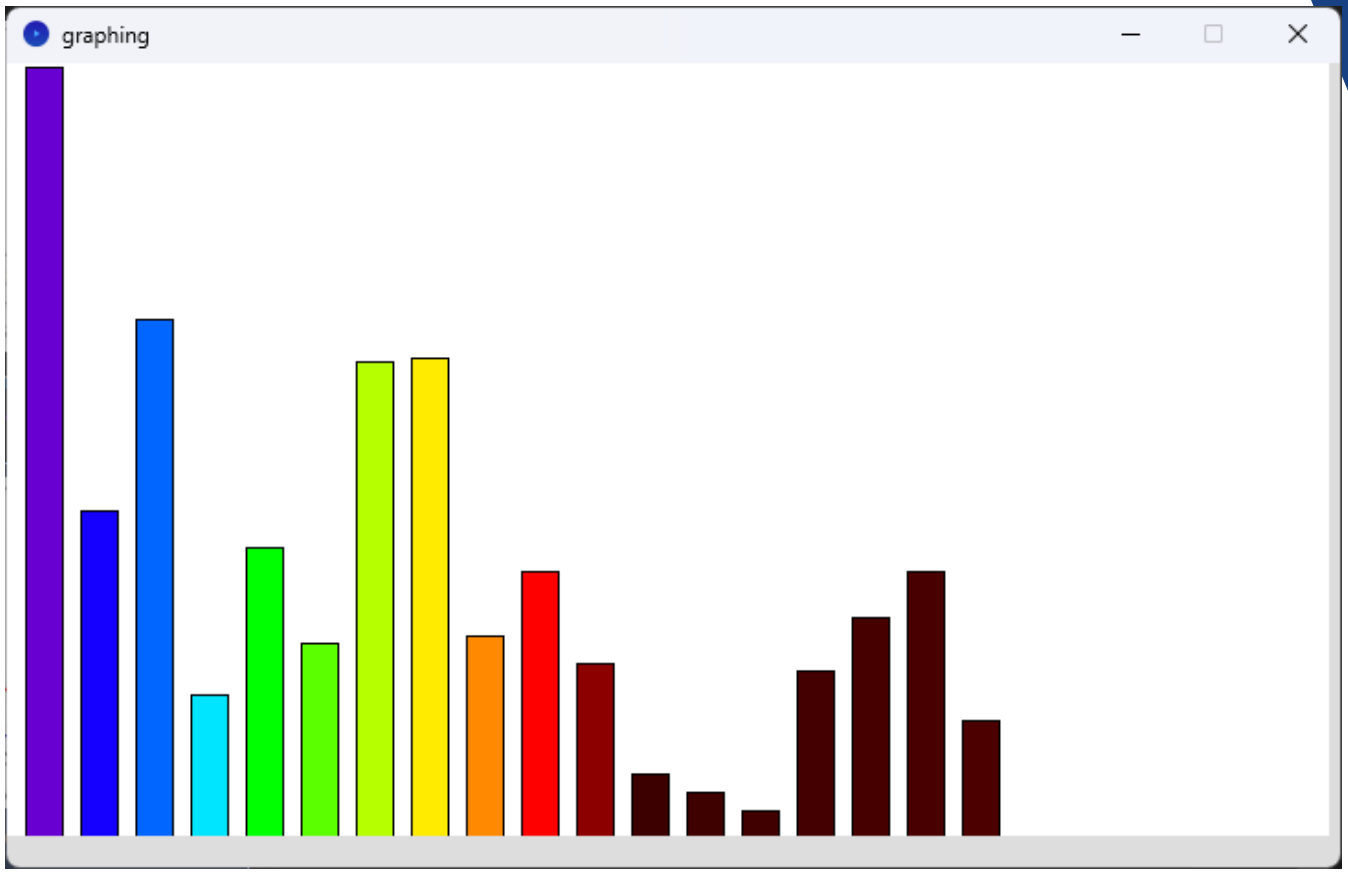




Measuring the spectrum – Chlorophyll



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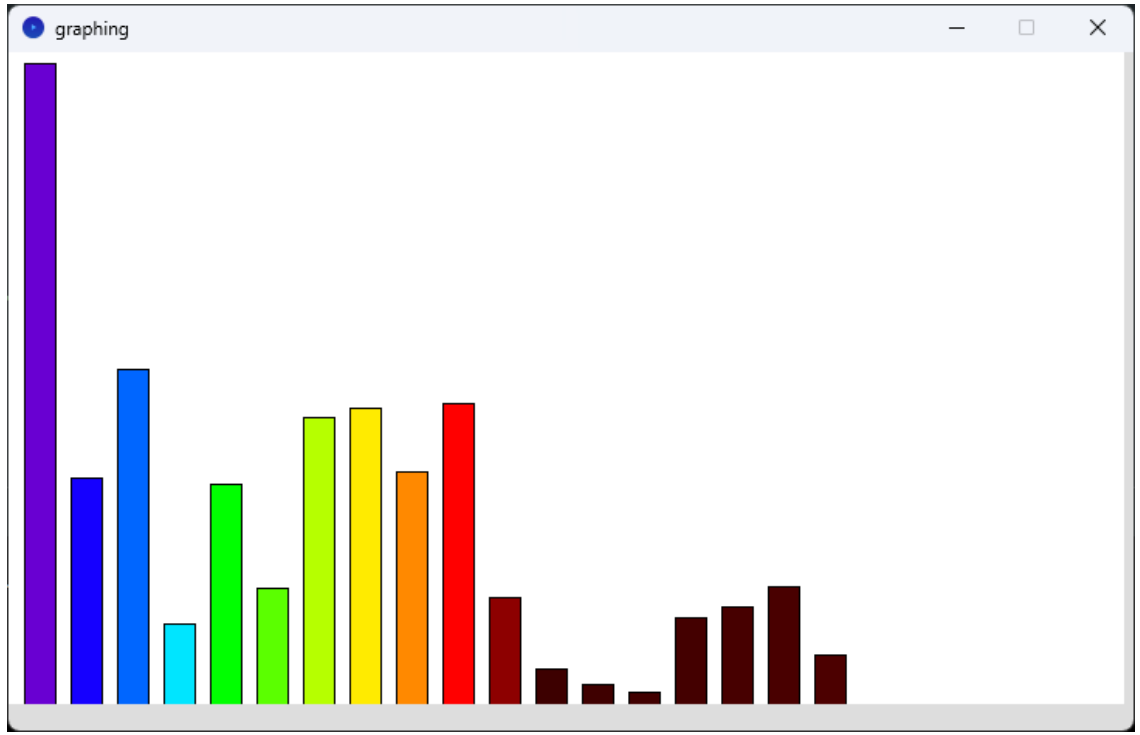

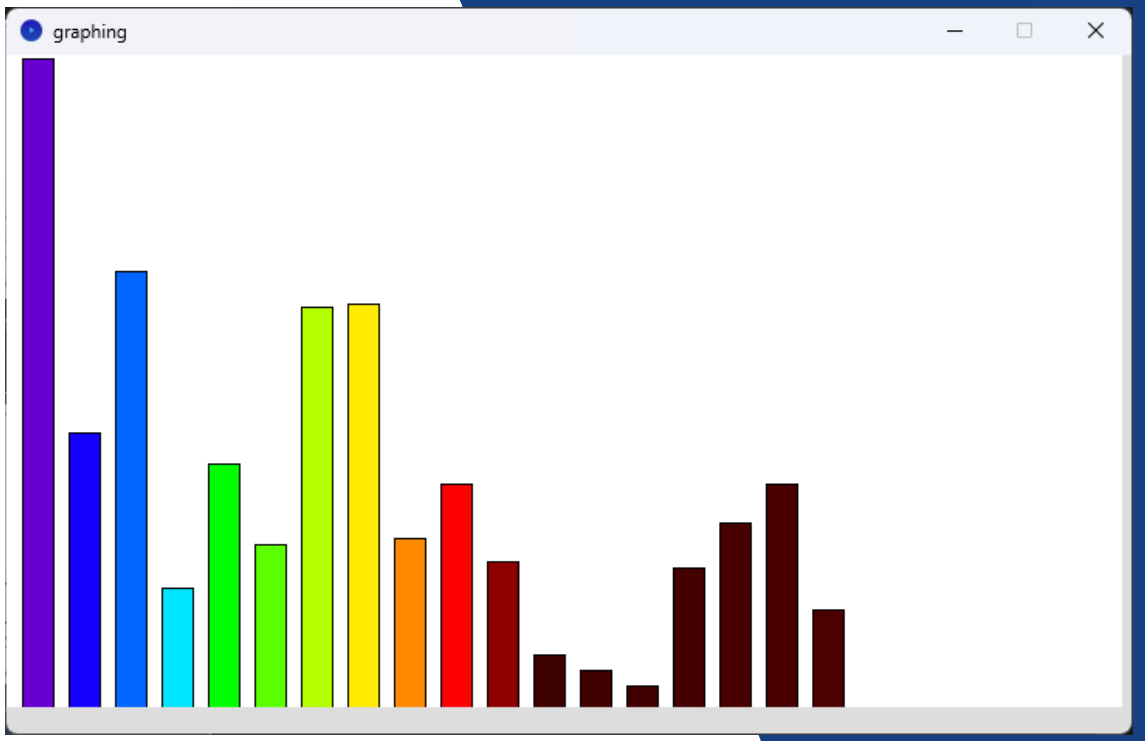

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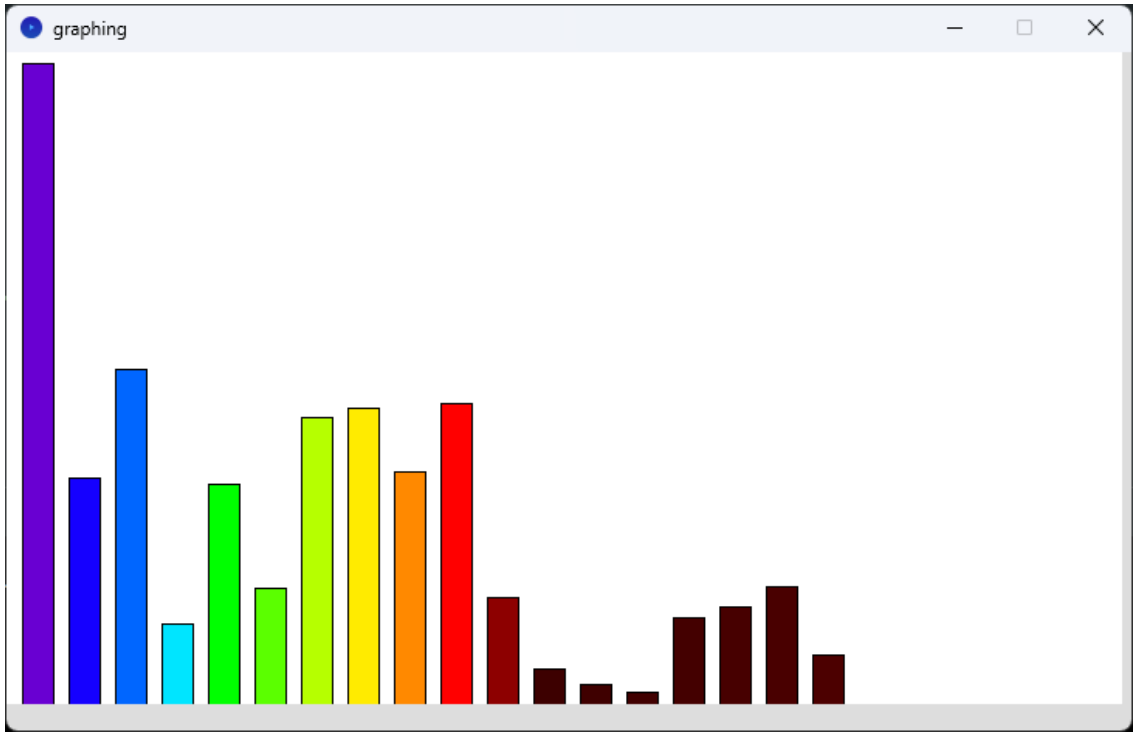
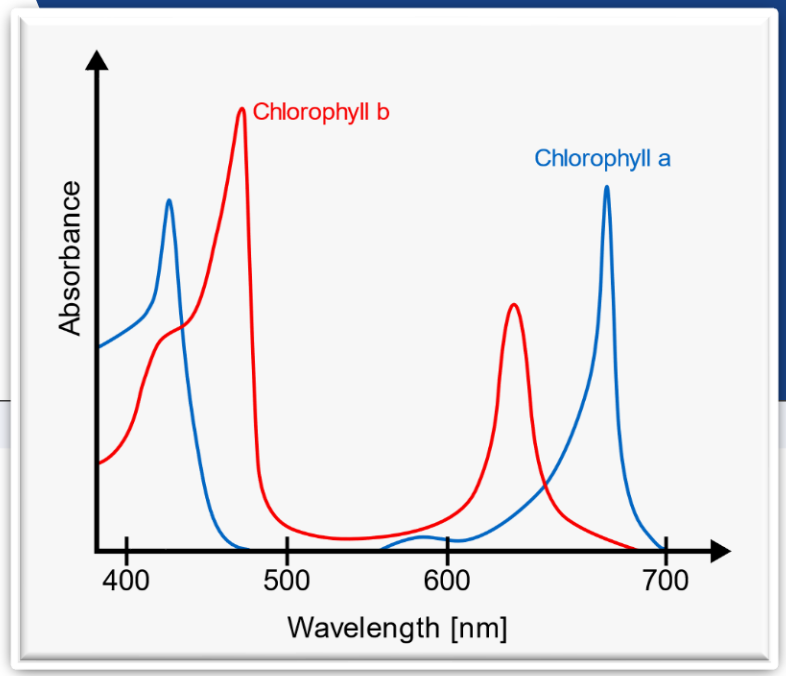
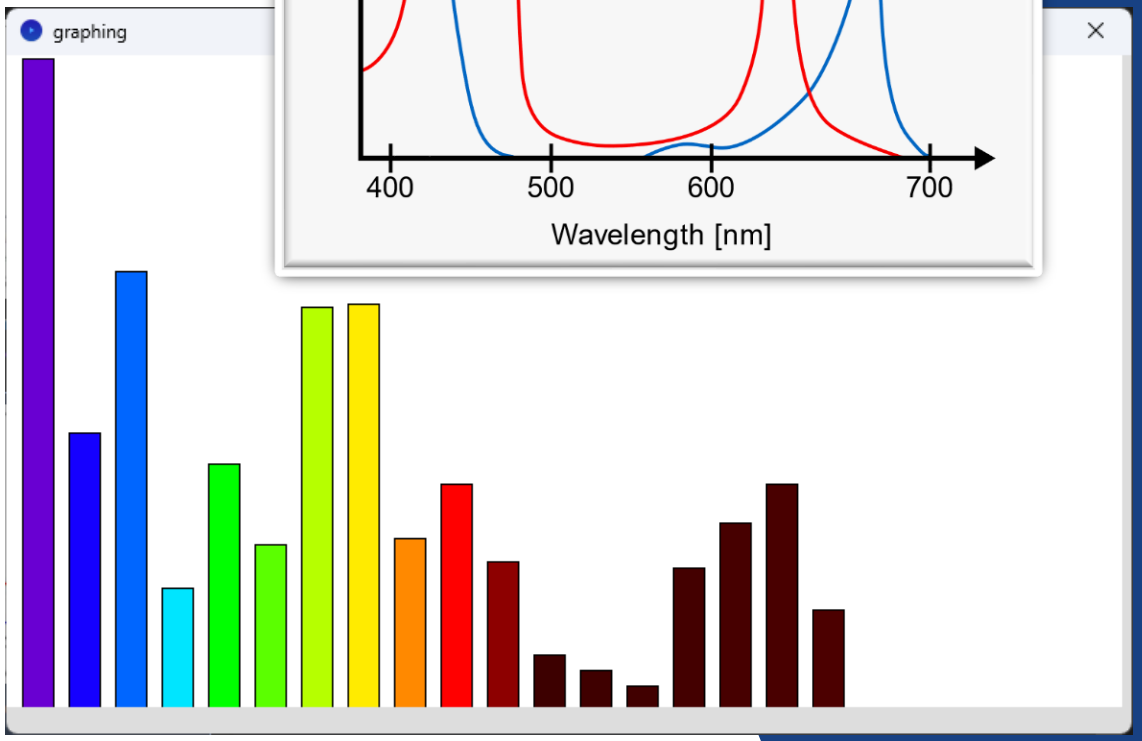
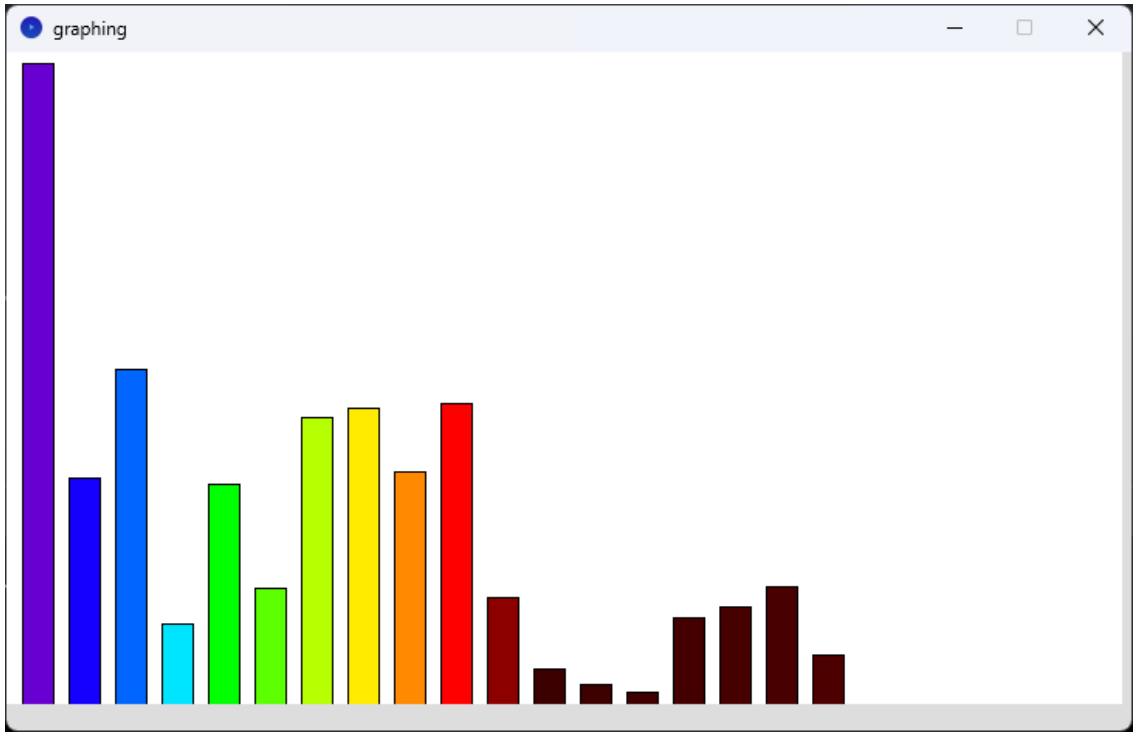
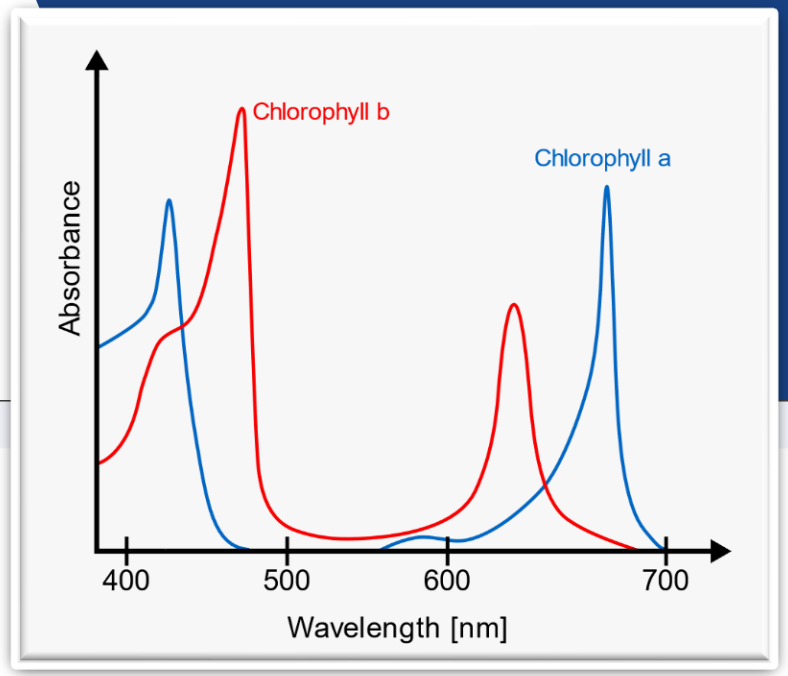


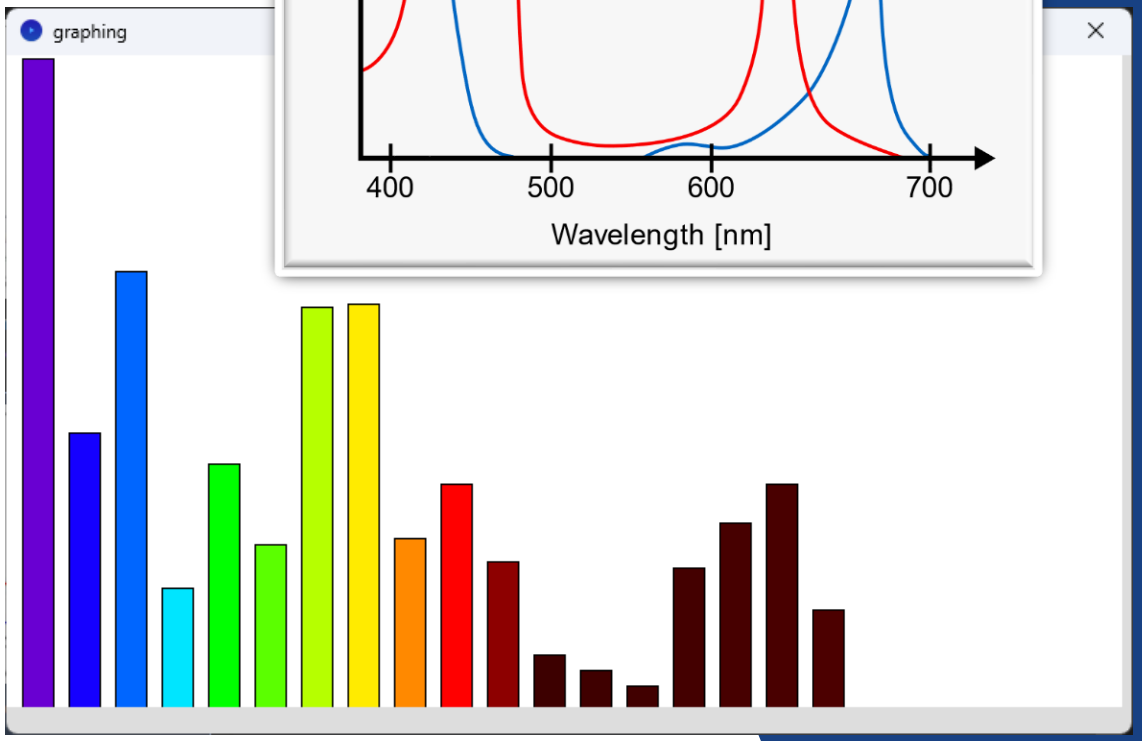




Beer-Lambert Law







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- Pierre Bouguer: Made observations
- Johann Heinrich Lambert: Cited them and laid a foundation with assumption $-dI = \mu I dx$
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I: $Intensity$
A: $Absorbance$
ℓ: $Opticcal\ Length$
$\mathcal{E}$: $Molar\ attenuetion\ coefficient\ (absoptivity)$
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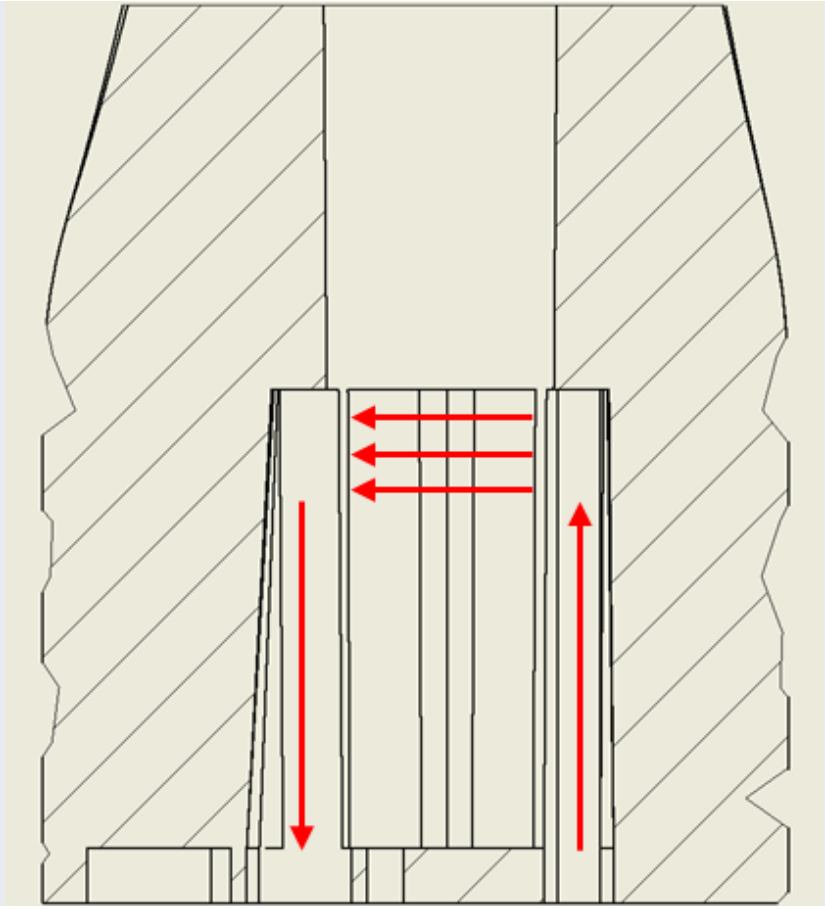

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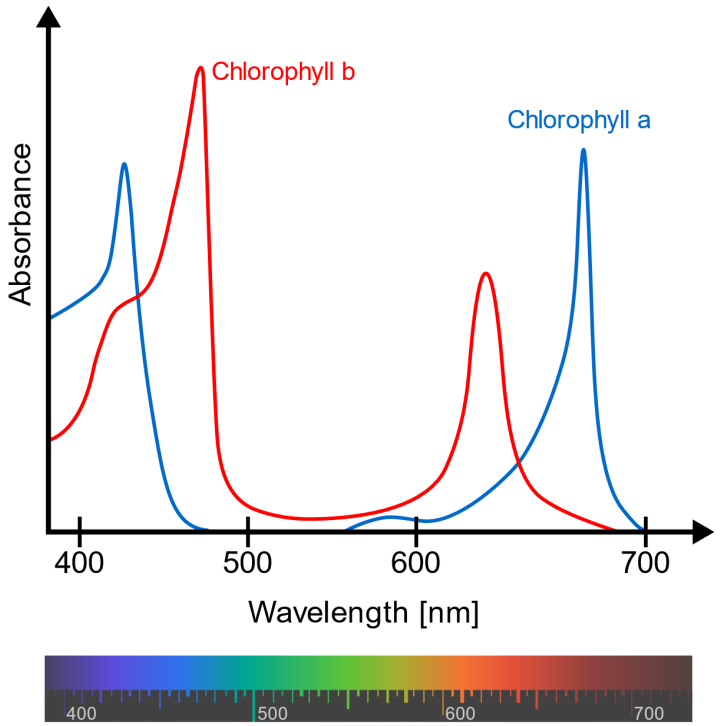

Author: Daniele Pugliesi. Source: Wikimedia Commons

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$$\kappa[\lambda] = \mathcal{E}[\lambda] \cdot \ell$$

Beer-Lambert Law

$$\log_{10}\left(\frac{I_0[\lambda]}{I[\lambda]}\right) = A[\lambda] = \mathcal{E}[\lambda] \cdot \ell \cdot c$$

I: $Intensity$
A: $Absorbance$
ℓ: $Opticcal\ Length$
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$$A[\lambda] = \sum_{i=0}^{n} \mathcal{E}_i[\lambda] \cdot c_i \cdot \ell$$

n: $Number\ of\ different\ substances$

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Beer-Lambert Law

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$$C = (\mathrm{K}^T \cdot \mathrm{K})^{-1} \cdot \mathrm{K}^T \cdot A$$

C: $Matrix\ of\ all\ concentrations$
K: $Matrix\ of\ all\ \kappa$
A: $Matrix\ of\ all\ absobtivities$

* True if more wavelengths are present than species

Implementation

```
#define REF_CONCENTRATION_A 60.0
#define REF_CONCENTRATION_B 60.0

float I_0[N_WAVELENGTHS]; // Intensity
float I_Ref_A[N_WAVELENGTHS];
float I_Ref_B[N_WAVELENGTHS];
float I_S[N_WAVELENGTHS];

float A_Ref_A[N_WAVELENGTHS];
float A_Ref_B[N_WAVELENGTHS];
float A_S[N_WAVELENGTHS];
```

```
float K_A[N_WAVELENGTHS]; // ε[λ]*l
float K_B[N_WAVELENGTHS];

float c_A;
float c_B;
```

Measuring Protocol

- Take clean water test tube.
- Place in sensor.
- Take measurements.
- Rotate test tube.
- Take measurement again and repeat till enough samples.

- Do the same with the reference test tubes, be sure to stir them first.

- Start taking reading from samples to test.

Implementation - Median

```
/**
 * Returns the median of arr[].
 */
float calculateMedian(const float arr[], int size) {
  // Create a copy of the array to avoid altering the original
  float* tmpArr = new float[size];
  for (int i = 0; i < size; i++) {
    tmpArr[i] = arr[i];
  }

  // Sort the copy of the array
  for (int i = 0; i < size - 1; i++) {
    for (int j = i + 1; j < size; j++) {
      if (tmpArr[i] > tmpArr[j]) {
        float temp = tmpArr[i];
        tmpArr[i] = tmpArr[j];
        tmpArr[j] = temp;
      }
    }
  }

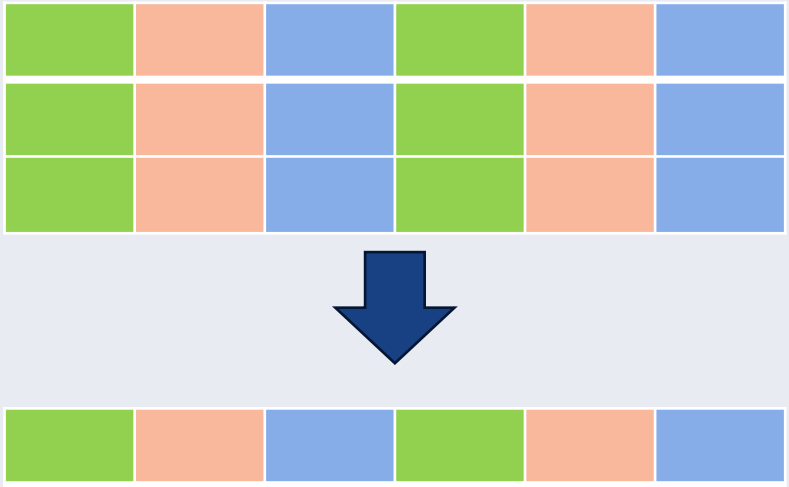
  // Calculate median
  float median;
  if (size % 2 == 0) {
    median = (tmpArr[size / 2 - 1] + tmpArr[size / 2]) / 2.0;
  } else {
    median = tmpArr[size / 2];
  }

  // Free the allocated memory
  delete[] tmpArr;

  return median;
}
```

Implementation – Column Median

```
/**
 * Function to calculate the median of each column in a 2D array.
 * Takes a 2D array and outputs a 1D one with the medians.
 */
template <size_t Rows, size_t Cols> void
calculateColumnMedians(float (&array2D)[Rows][Cols], float*
medians) {
  for (int col = 0; col < Cols; col++) {
    float columnArray[Rows];
    for (int row = 0; row < Rows; row++) {
      columnArray[row] = array2D[row][col];
    }
    medians[col] = calculateMedian(columnArray, Rows);
  }
}
```



Implementation - Concentration

```
// Create the matrix E and vector A
 BLA::Matrix<2, 2> E;
 BLA::Matrix<2> A;
 BLA::Matrix<2> C;
[...]
// Initialize the matrix E and vector A
 for (int i = 2; i < numWavelengths; i++) {
    // Skip invalid values -> Test tube interference
    if (!includeWavelength[i] ||K_A[i] <= 0 || K_B[i] <= 0) {
       continue;
    }
    E(0, 0) += K_A[i] * K_A[i];
    E(0, 1) += K_A[i] * K_B[i];
    E(1, 0) += K_B[i] * K_A[i];
    E(1, 1) += K_B[i] * K_B[i];
    A(0) += K_A[i] * A_S[i];
    A(1) += K_B[i] * A_S[i];
}
```

Implementation - Concentration

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    E(1, 0) += K_B[i] * K_A[i];
    E(1, 1) += K_B[i] * K_B[i];
    A(0) += K_A[i] * A_S[i];
    A(1) += K_B[i] * A_S[i];
}
```

Implementation - Concentration

```
// Check if the matrix E is invertible
 float determinant = E(0, 0) * E(1, 1) - E(0, 1) * E(1, 0);
 if (determinant == 0) {
    serialLogLn("Error: Matrix E is not invertible.", 1);
    c_A = 0;
    c_B = 0;
    return;
 }

// Calculate the pseudo-inverse of E
 BLA::Matrix<2, 2> E_inv = Inverse(E);
```

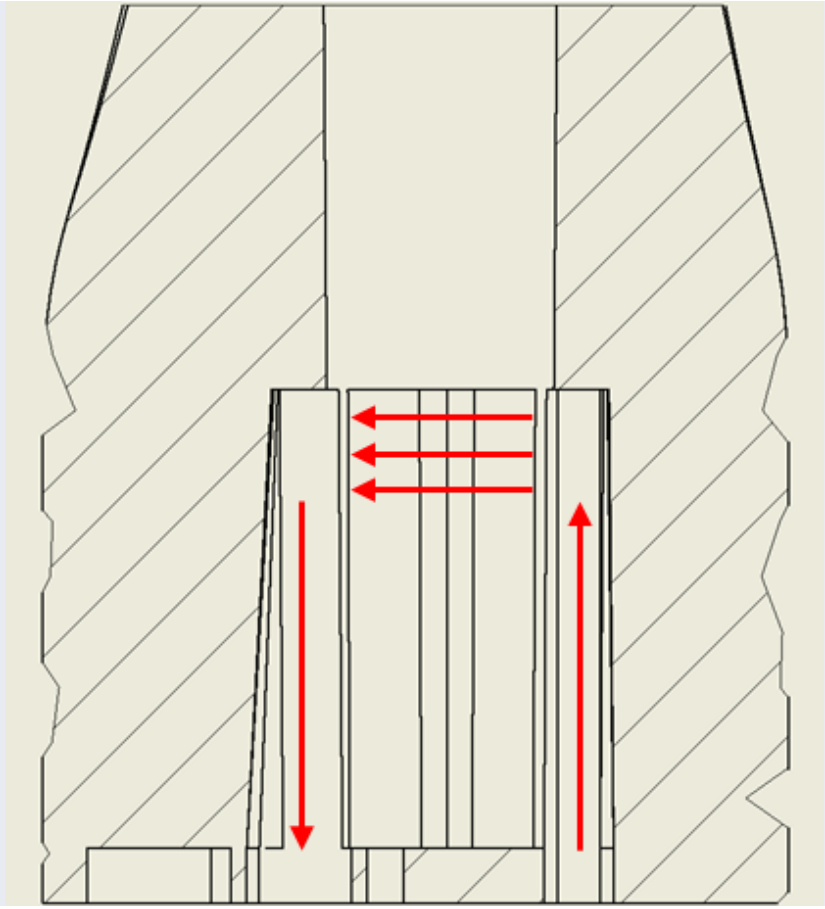
```
// Calculate the concentrations
 C = E_inv * A;

 // Assign the results to the output variables
 c_A = C(0);
 c_B = C(1);
```

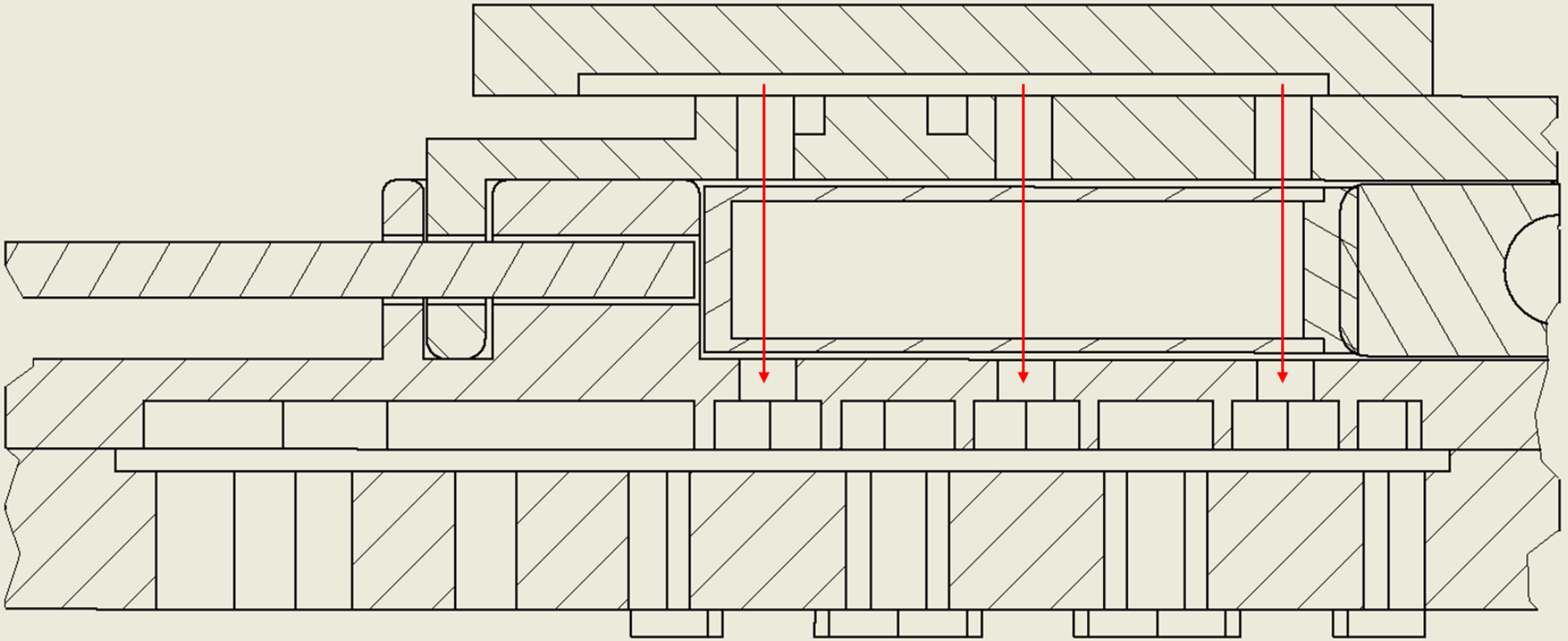
DEMO

Improved design after this

Old Design



Improved Design – AS7265x



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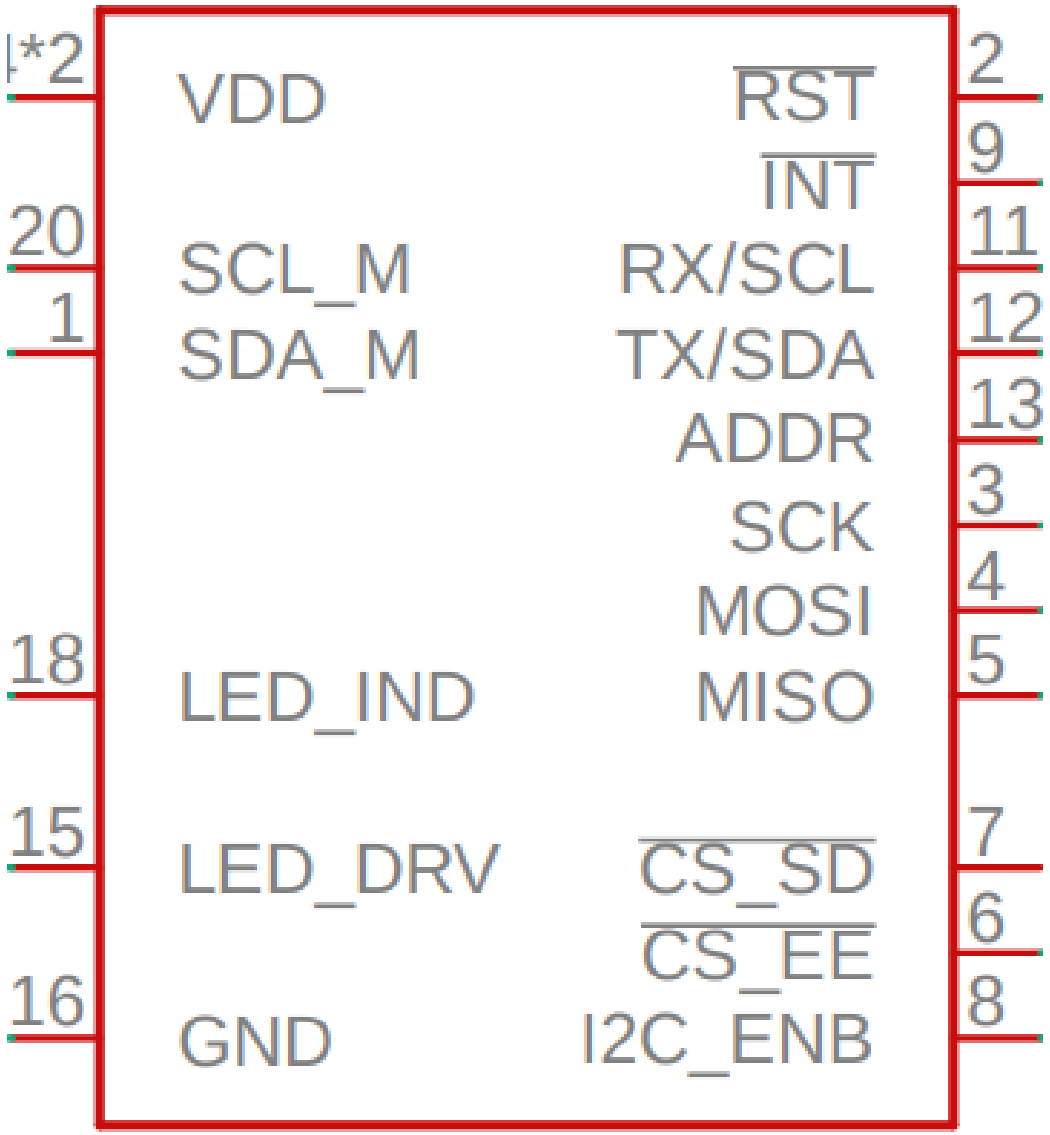

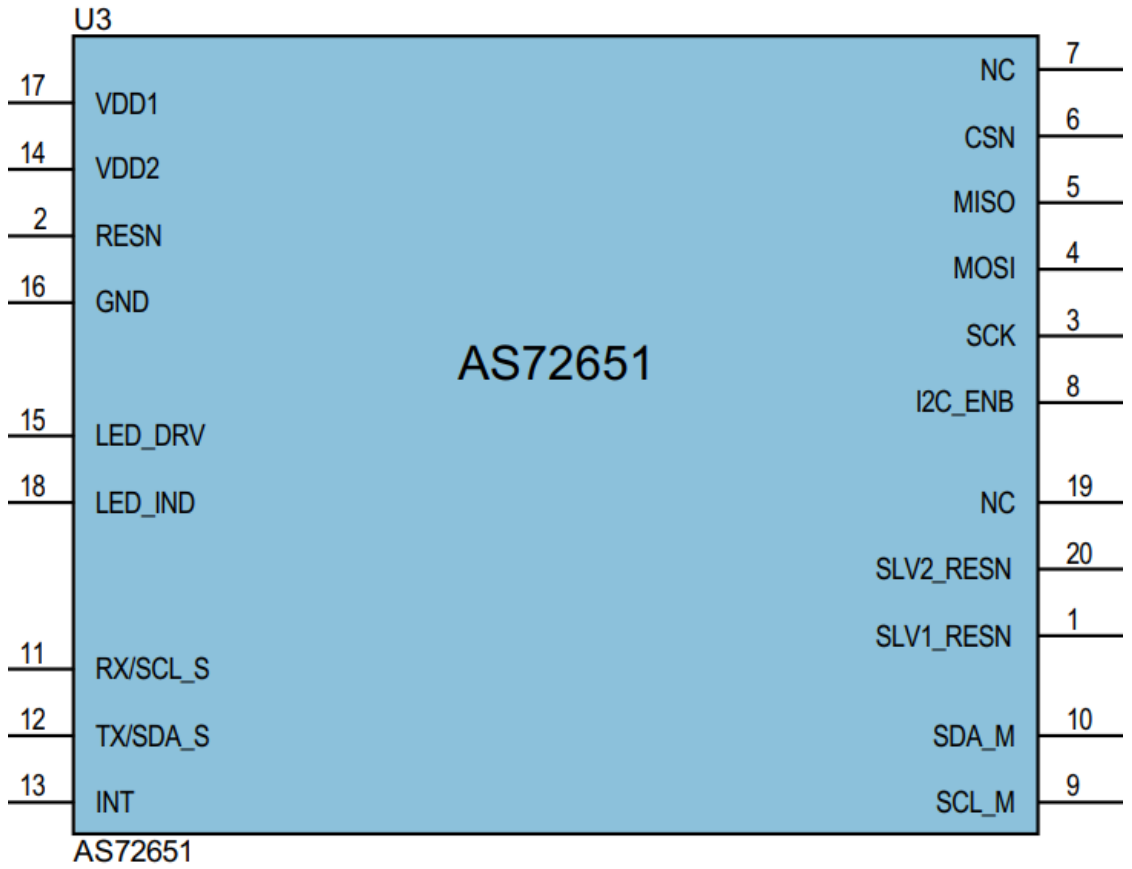

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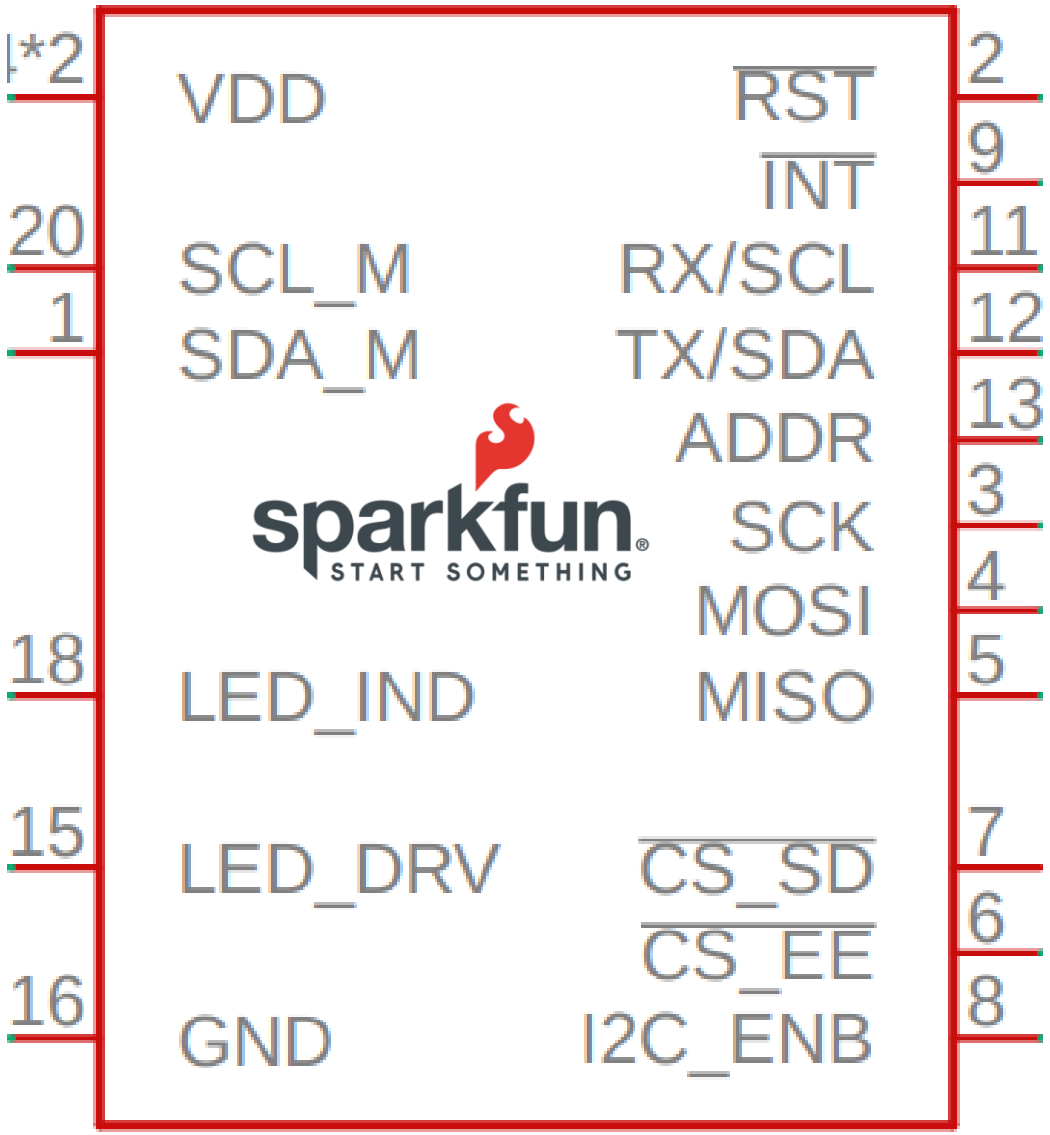
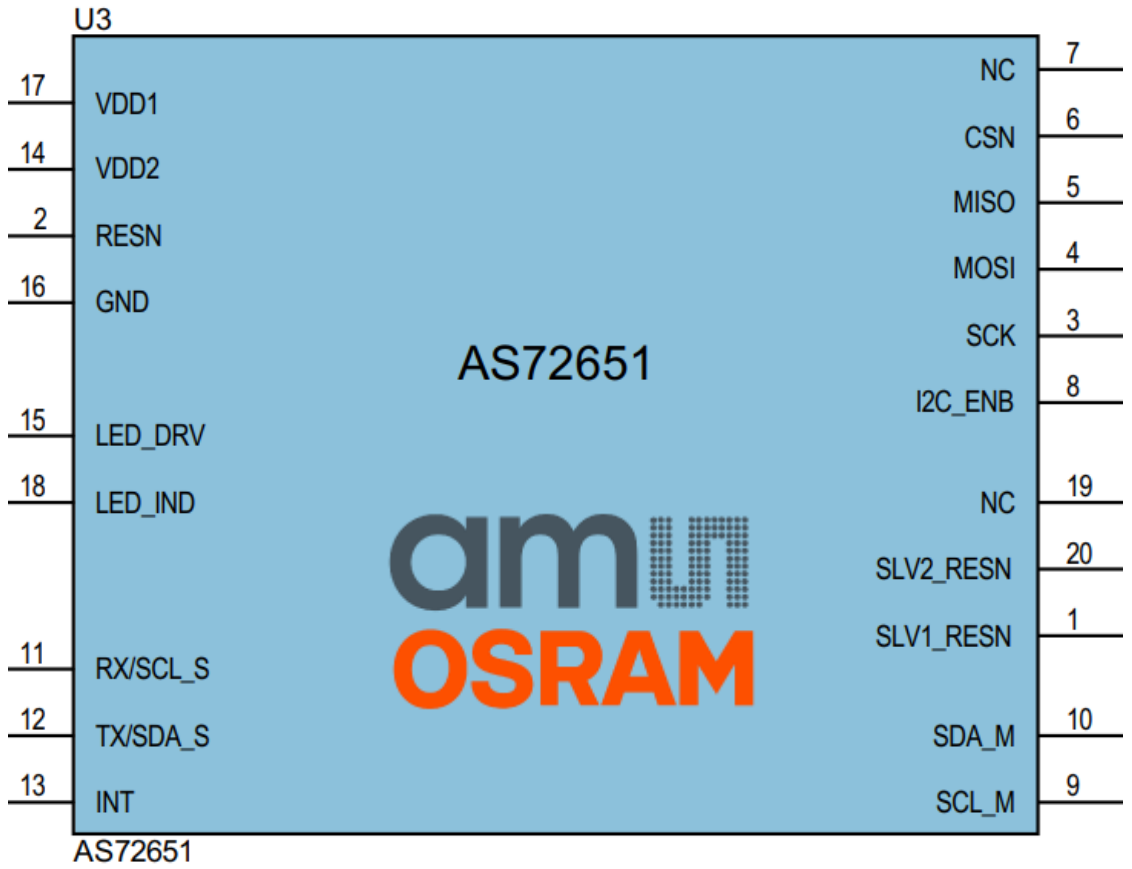
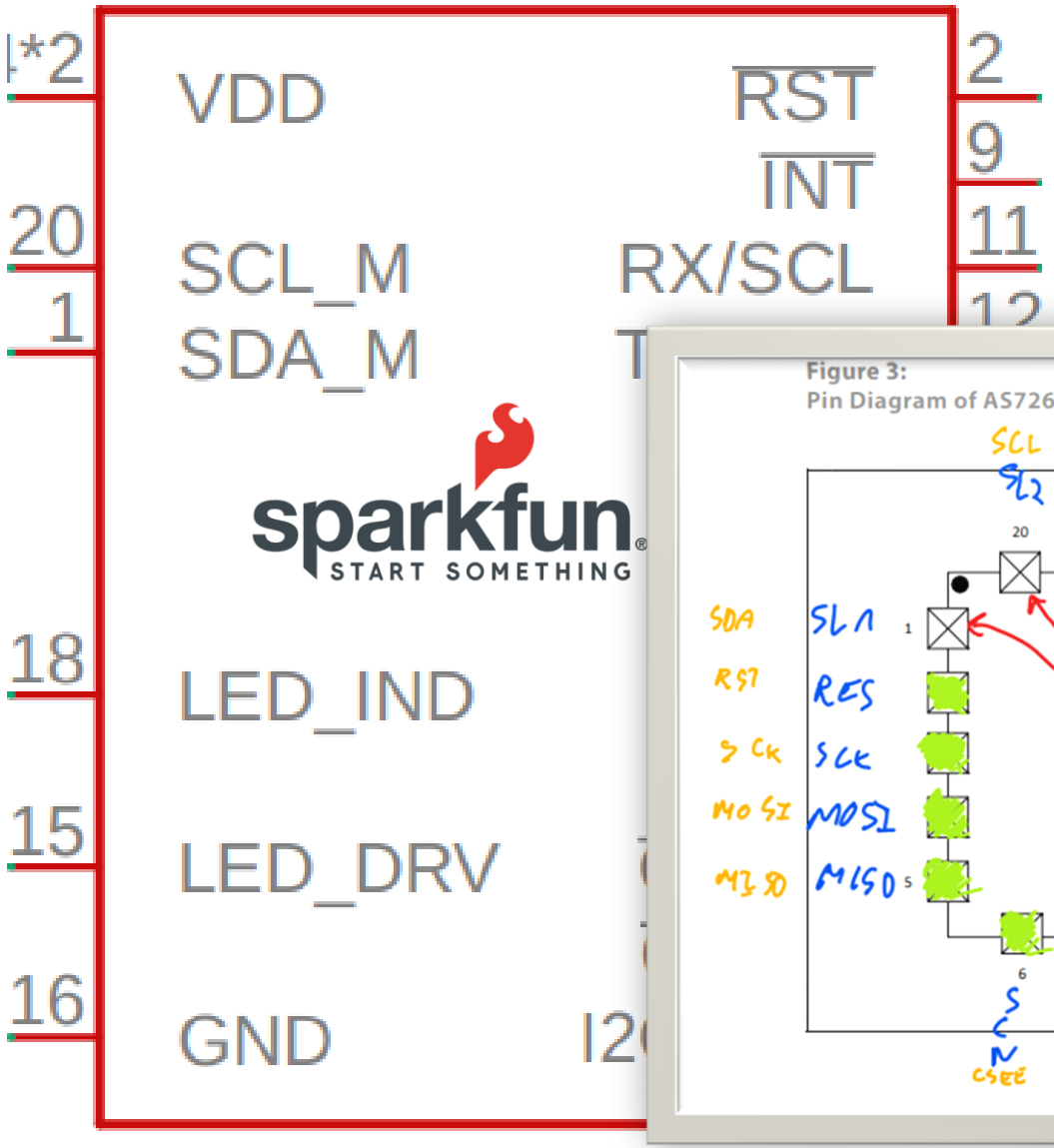
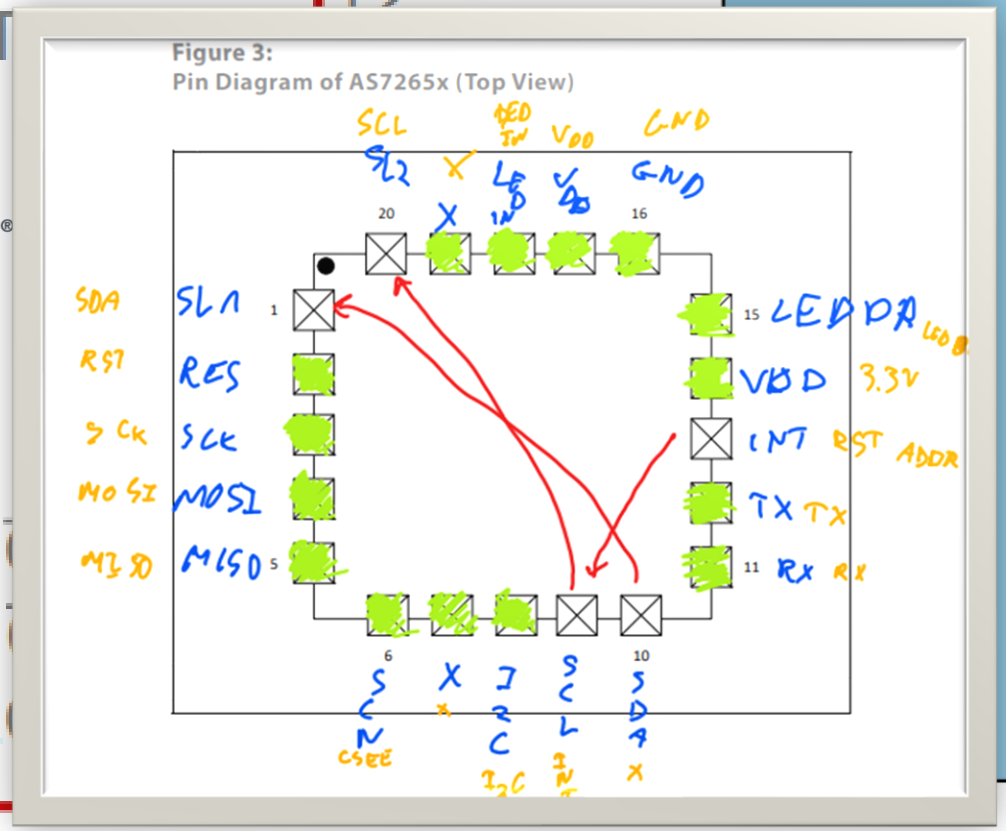
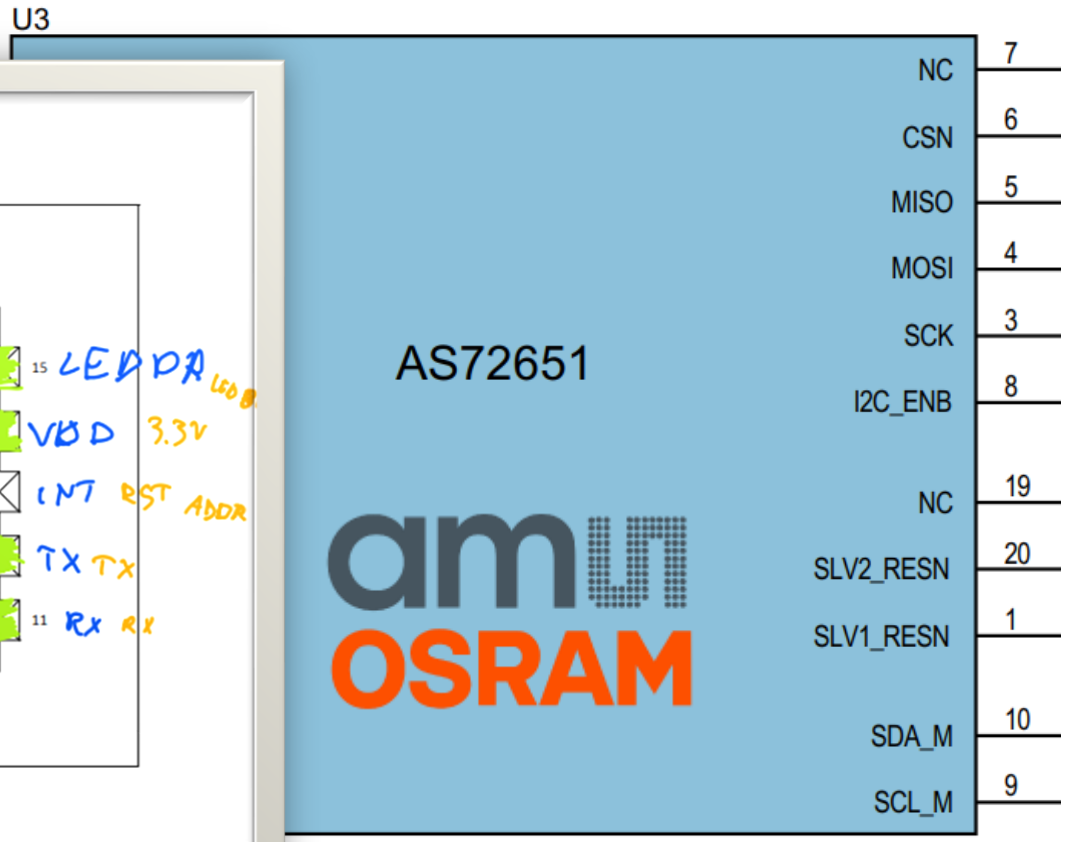




Improved Design – AS7265x







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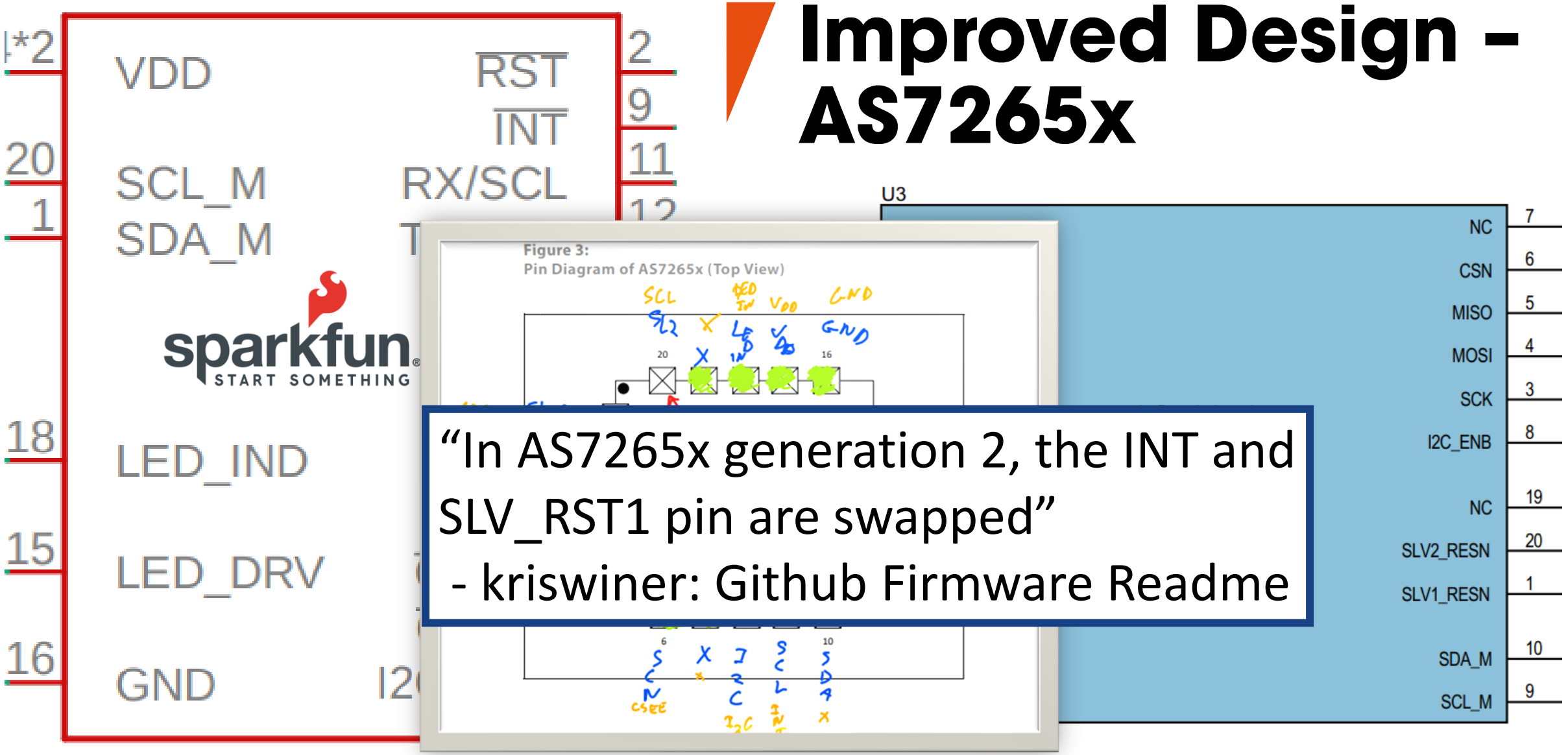
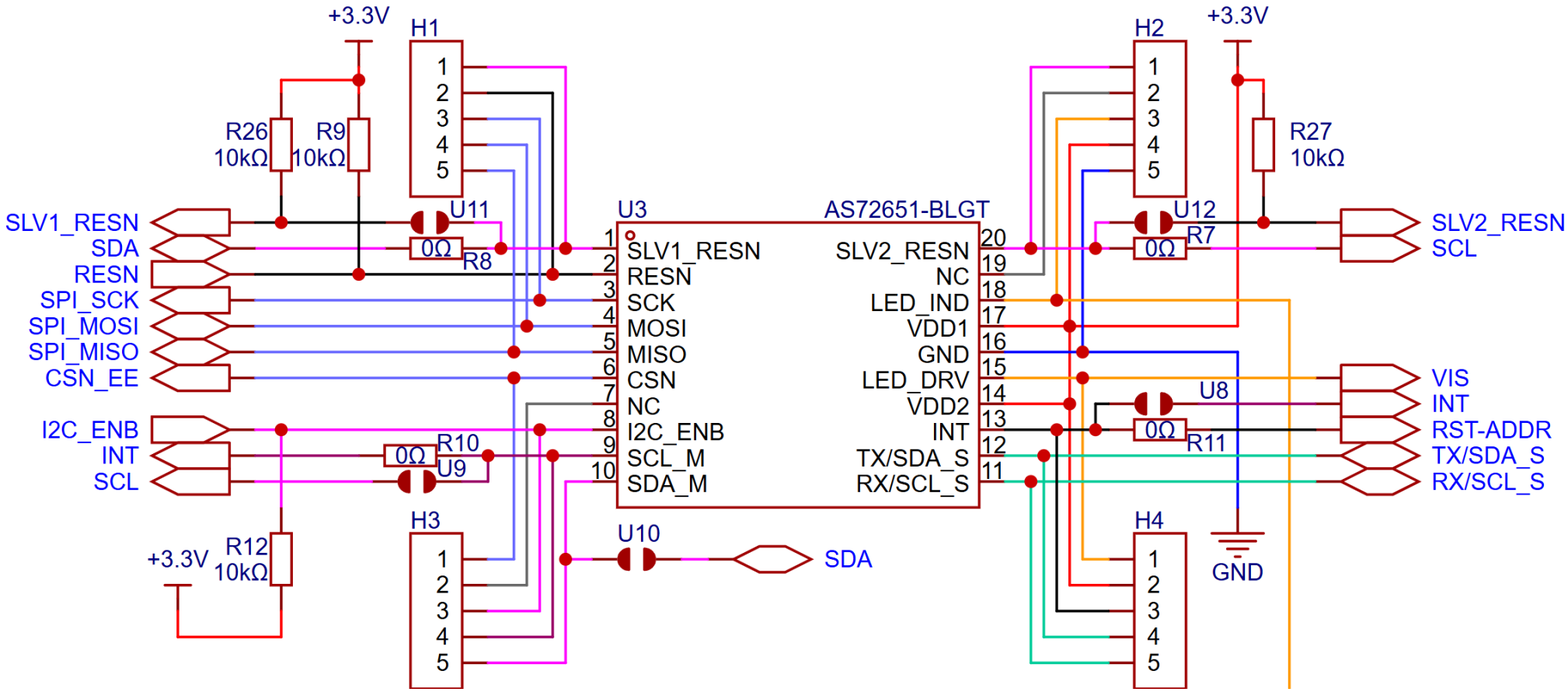


"In AS7265x generation 2, the INT and SLV_RST1 pin are swapped"
- kriswiner: Github Firmware Readme

Improved Design – AS7265x



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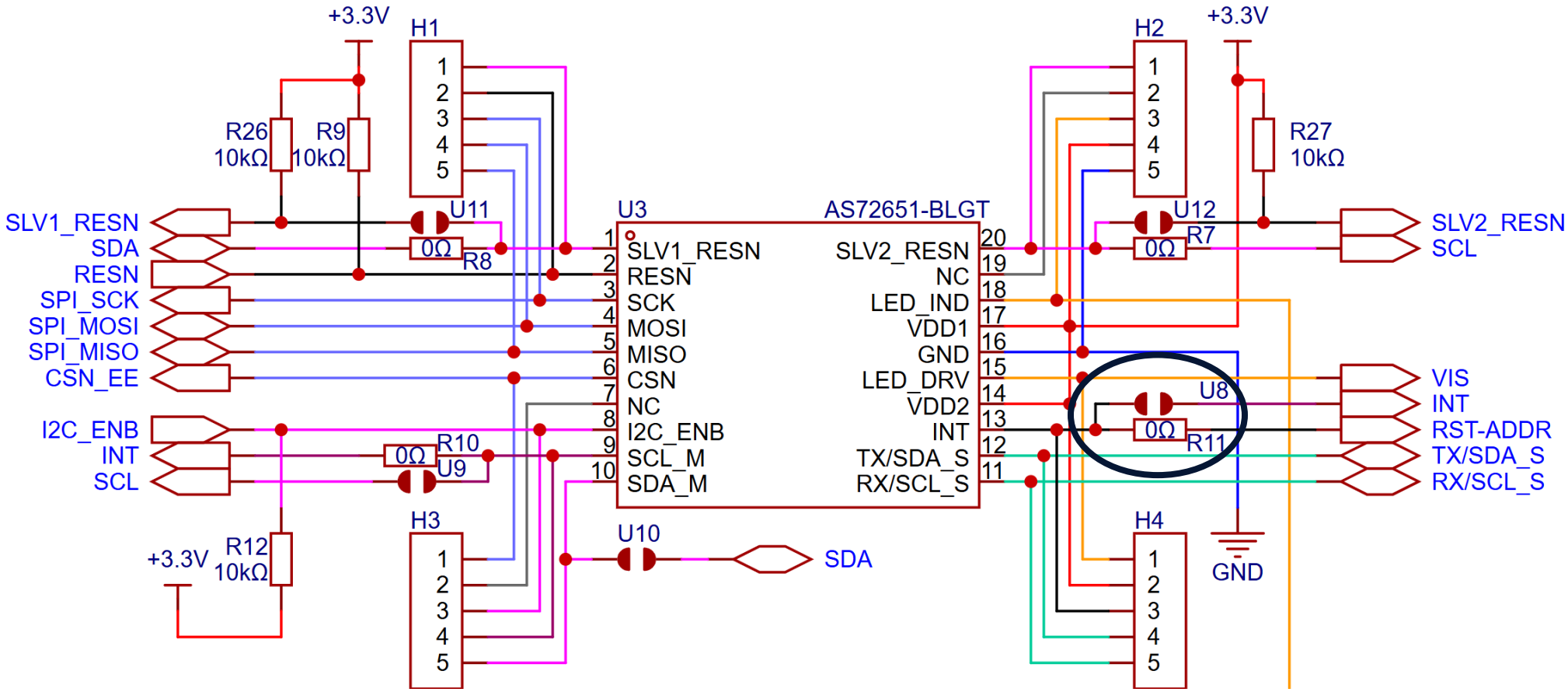

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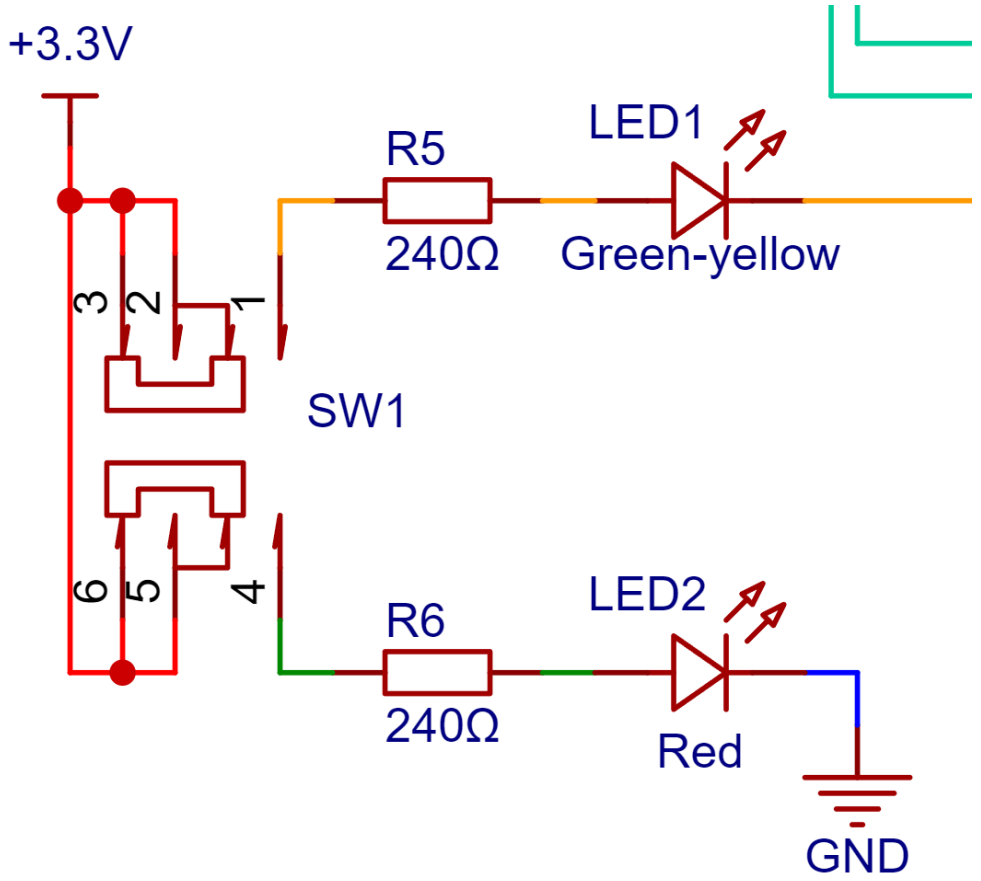

Current state

Questions

(Dissolved Oxygen is next)

Dissolved Oxygen

What is Disolved Oxygen (DO)

- “Dissolved oxygen (DO) is a measure of how much oxygen is dissolved in the water - the amount of oxygen available to living aquatic organisms. The amount of dissolved oxygen in a stream or lake can tell us a lot about its water quality.” – USGS
- Expressed in mg/L

My goal

- “Dissolved oxygen (DO) is a measure of how much oxygen is dissolved in the water - the amount of oxygen available to living aquatic organisms. The amount of dissolved oxygen in a stream or lake can tell us a lot about its water quality.” – USGS
- Expressed in mg/L

- Investigate Tris(2,2'-bipyridyl)dichlororuthenium(II) hexahydrate powder as means of measuring DO
- $Ru(BPY)_3$, Ruthenium-tris(2,2'-bipyridyl) dichloride, $C_{30}H_{24}Cl_2N_6Ru \cdot 6H_2O$

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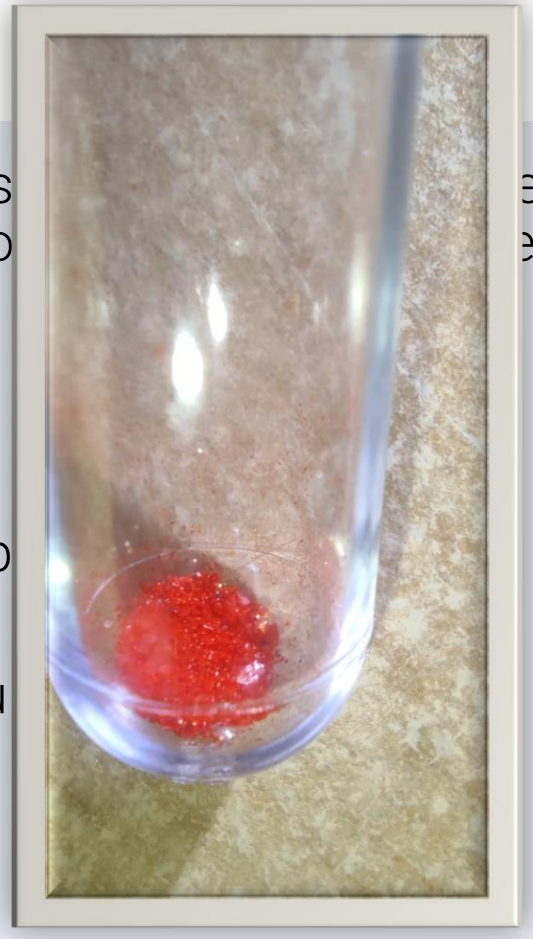

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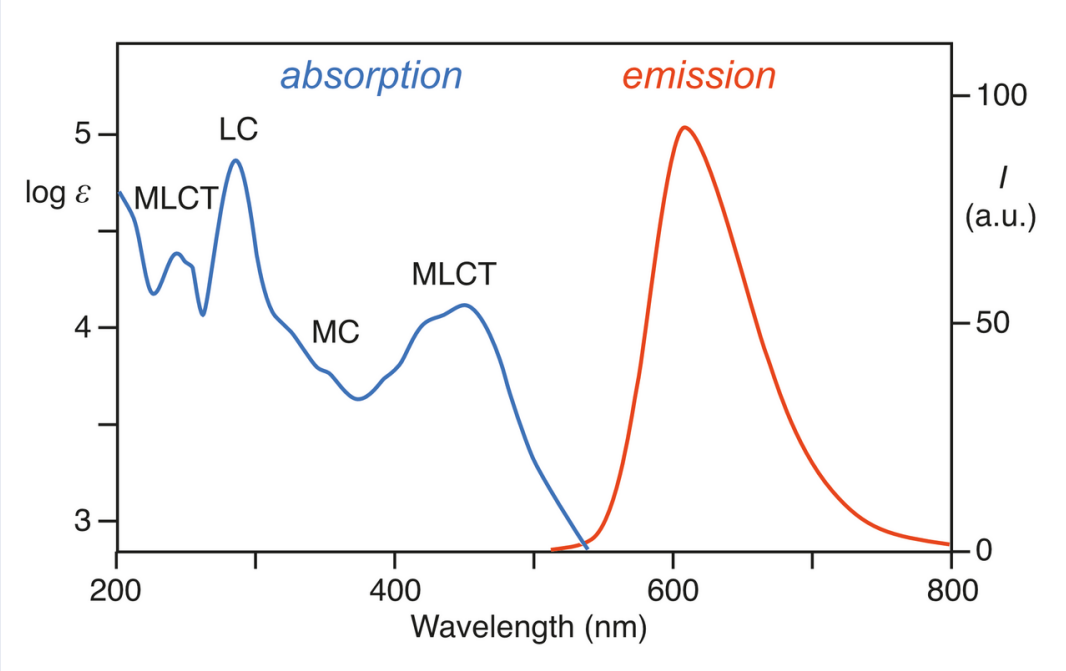
- $Ru(BPY)_3$, Ruthenium-tris(2,2'-bipyridyl) dichloride, $C_{30}H_{24}Cl_2N_6Ru$
- The ruthenium complex

Working principle

- It absorbs UV/Visible light
- Ideally light at 450 nm for MLCT absorption
- Emits at 620 nm
- Quenched by O_2



Author: Albris. Source: Wikimedia Commons

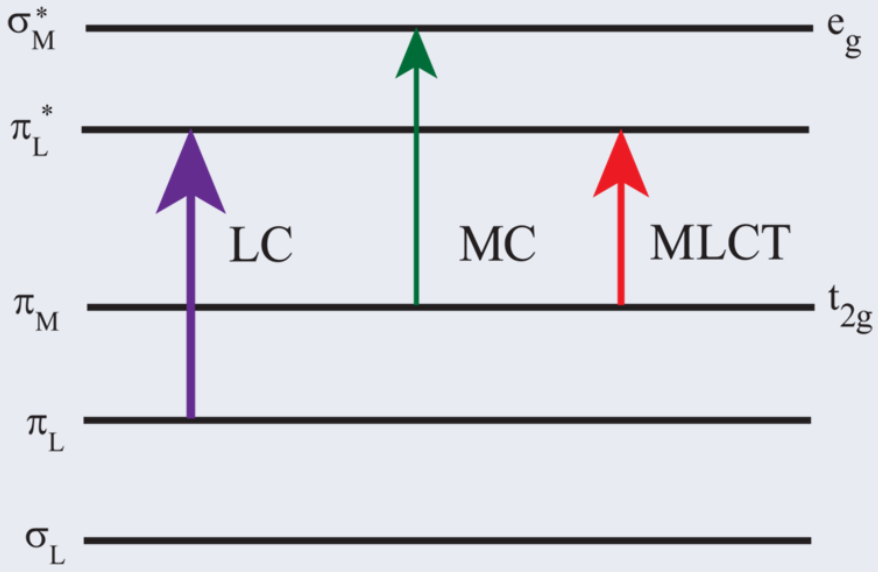
Working principle

- It absorbs UV/Visible light
- Ideally light at 450 nm for MLCT absorption
- Emits at 620 nm
- Quenched by O_2

- Stern-Volmer equation:

$$\frac{I_0}{I} = 1 + K_{SV}\tau_0[O_2]$$

I_0: $Intensity\ without\ quenching\ (without\ O_2)$
I: $Observed\ intensity$
K_{SV}: $Quencher\ rate\ coefficient$
τ_0: $Lifetime\ of\ emissive\ excited\ state$
$[O_2]$: $Oxygen\ concentration$



Author: Sobarwiki. Source: Wikimedia Commons

Powder

- Prevent dispersing
- Turn into sensing foil/disk

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- Silicone

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- Silicone
- Sticks well to glass
  - Even under water

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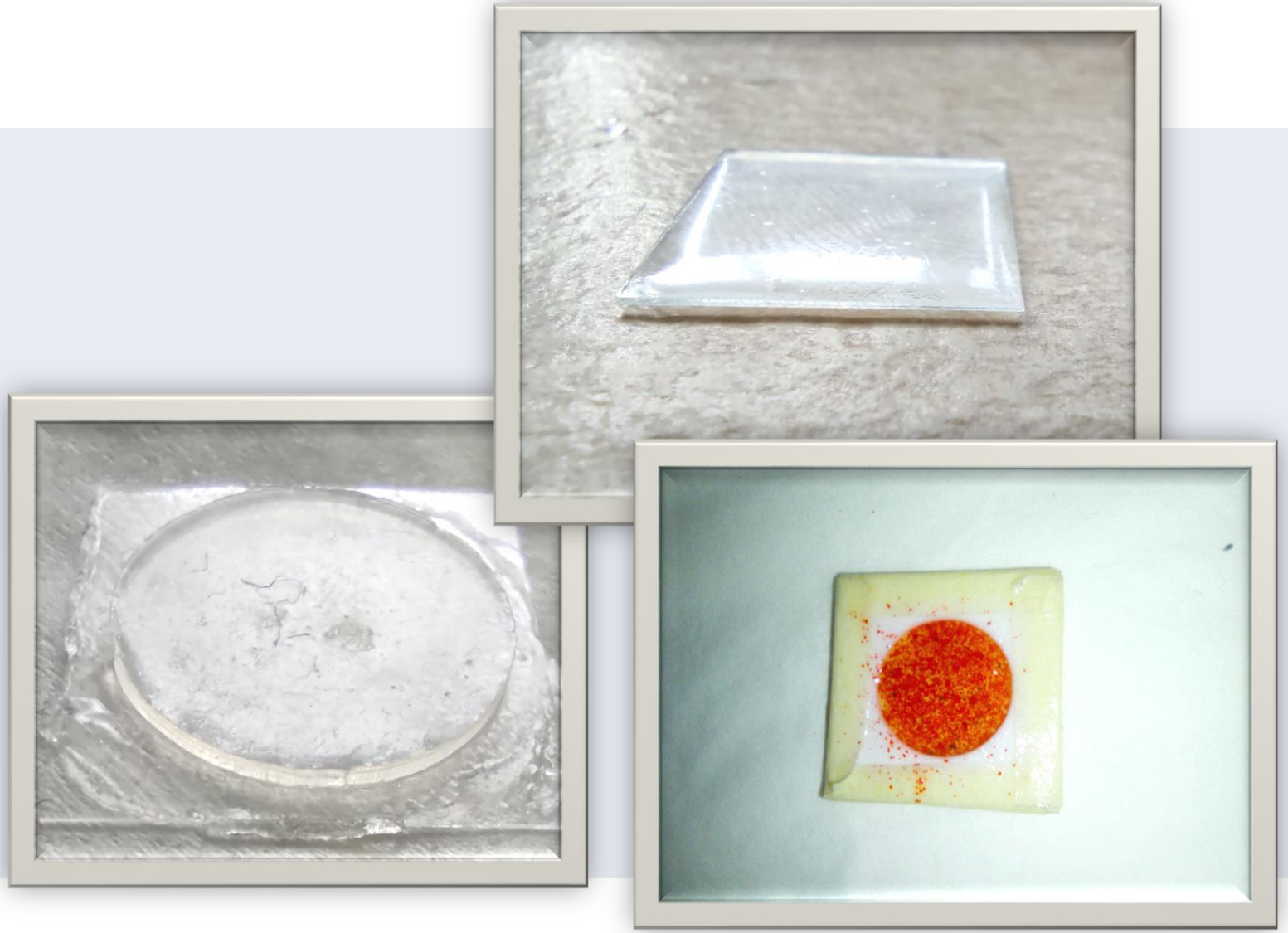


Protection

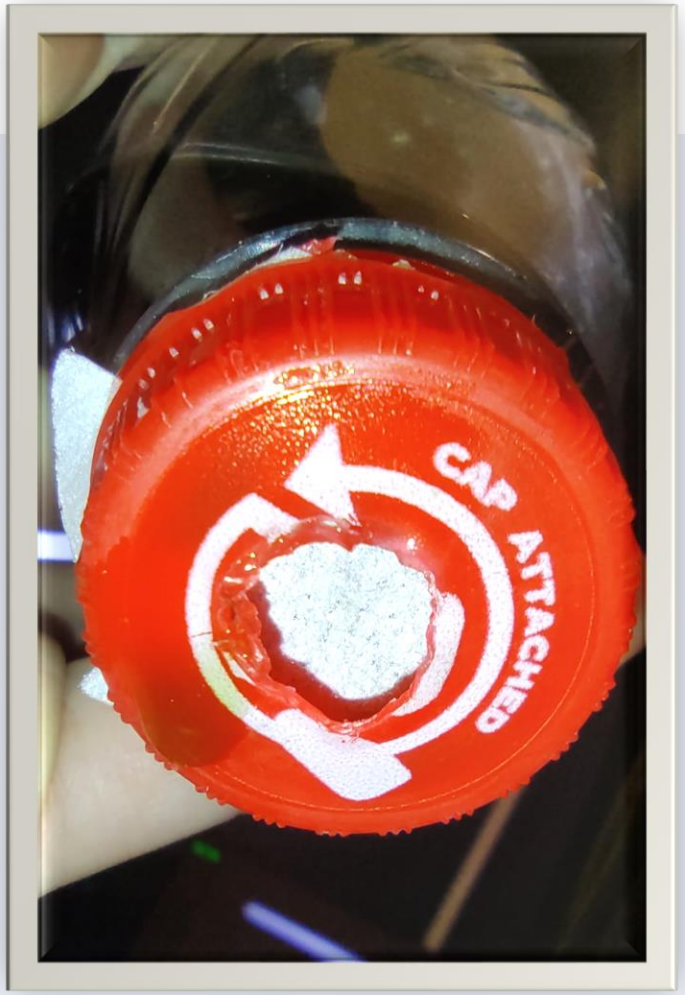
- Harsh environment
- Biofilm

- PTFE
  - Very inert
  - Does not stop oxygen

Protection

- Harsh environment
- Biofilm

- PTFE
  - Very inert
  - Does not stop oxygen
  - Good after over 1 month testing



Enclosure

- Water tight enclosure for electronics
- With PFTE shielding outside
- O-ring for waterproofing

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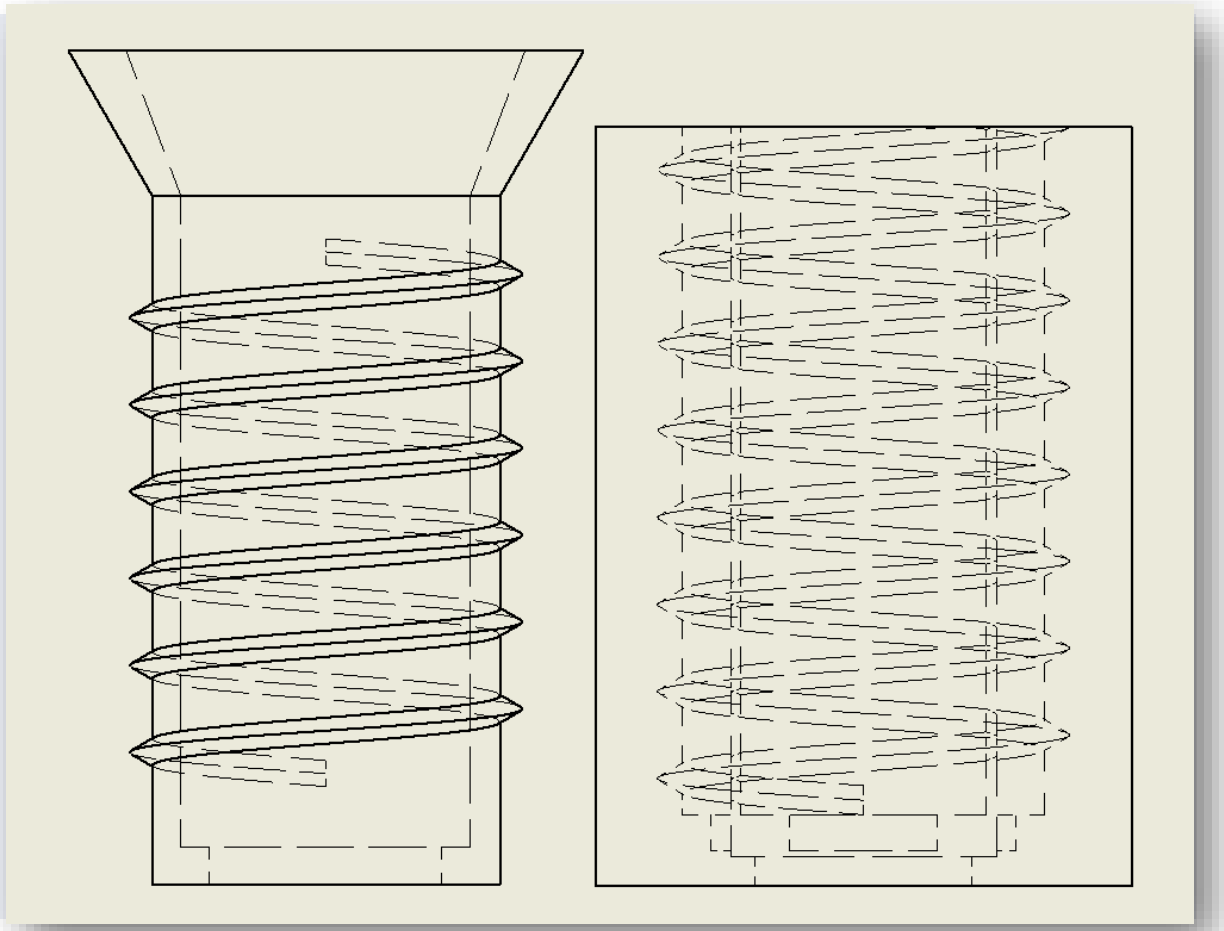
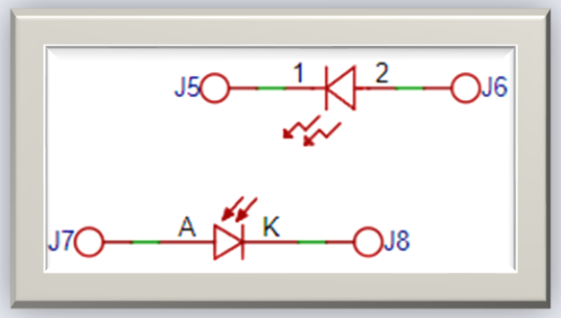
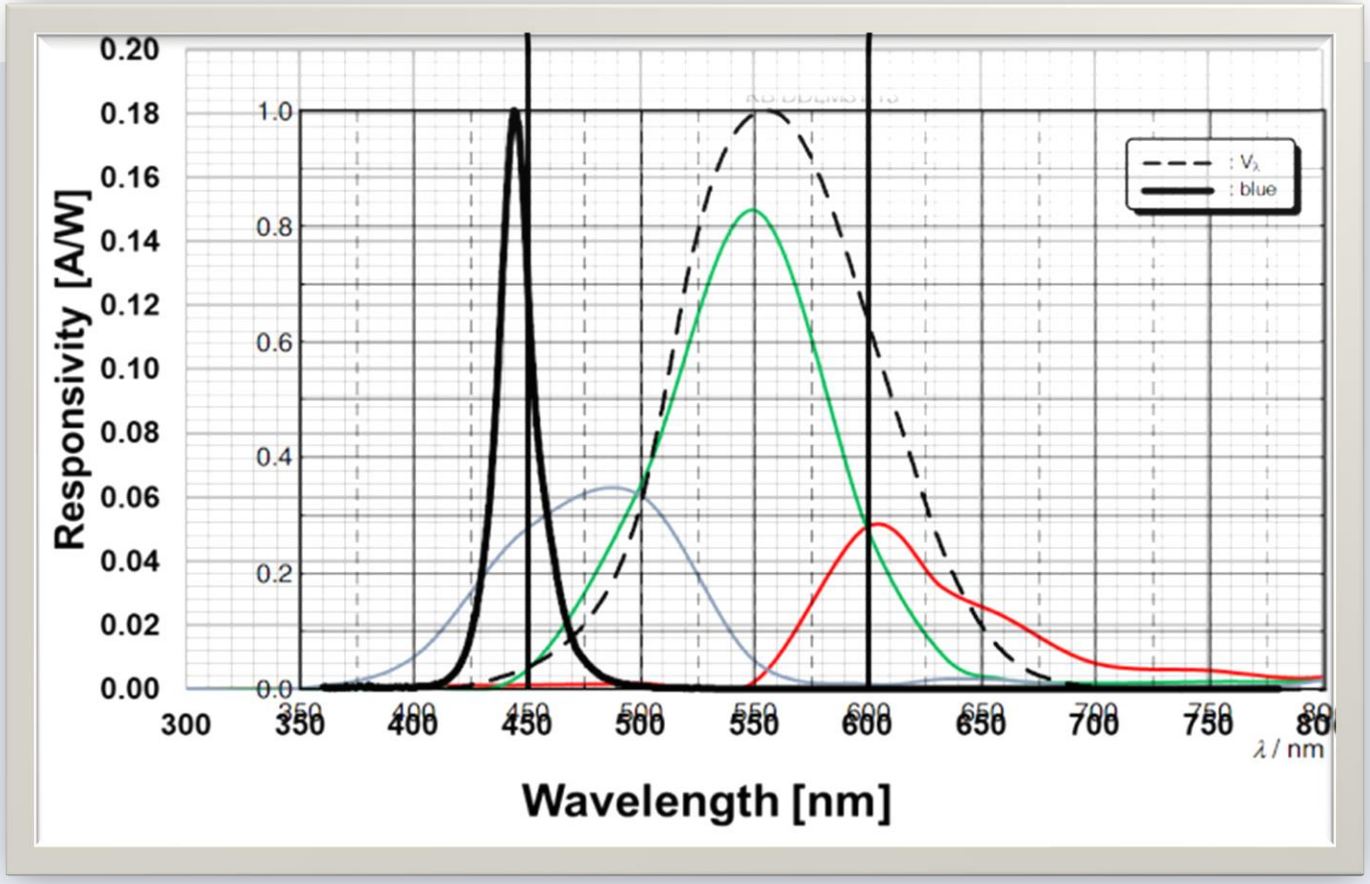


Electronics

- Emit at 450 nm
- Receive at 620 nm





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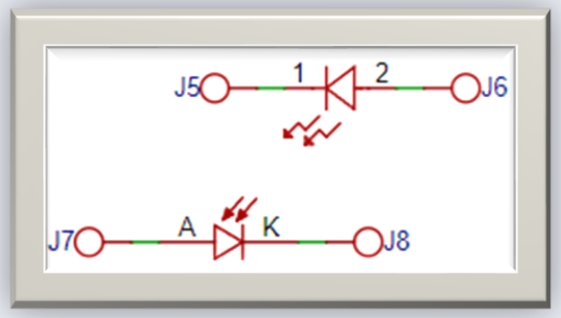
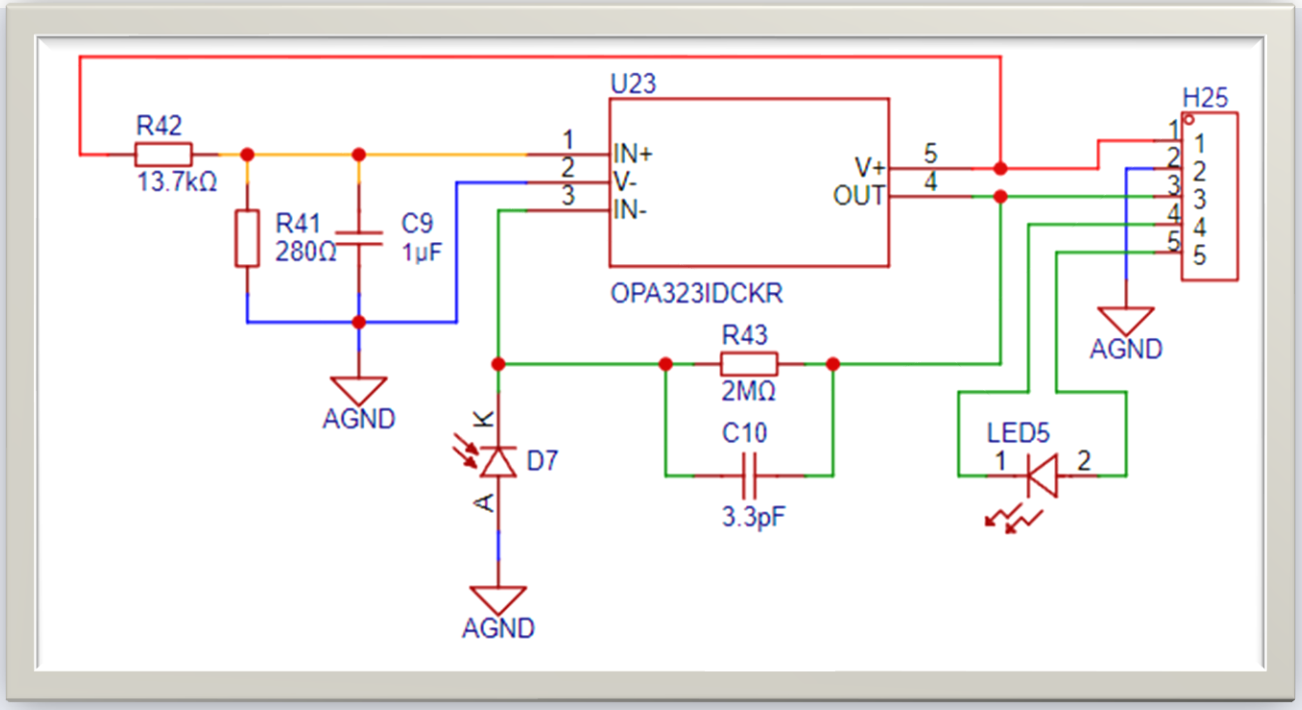
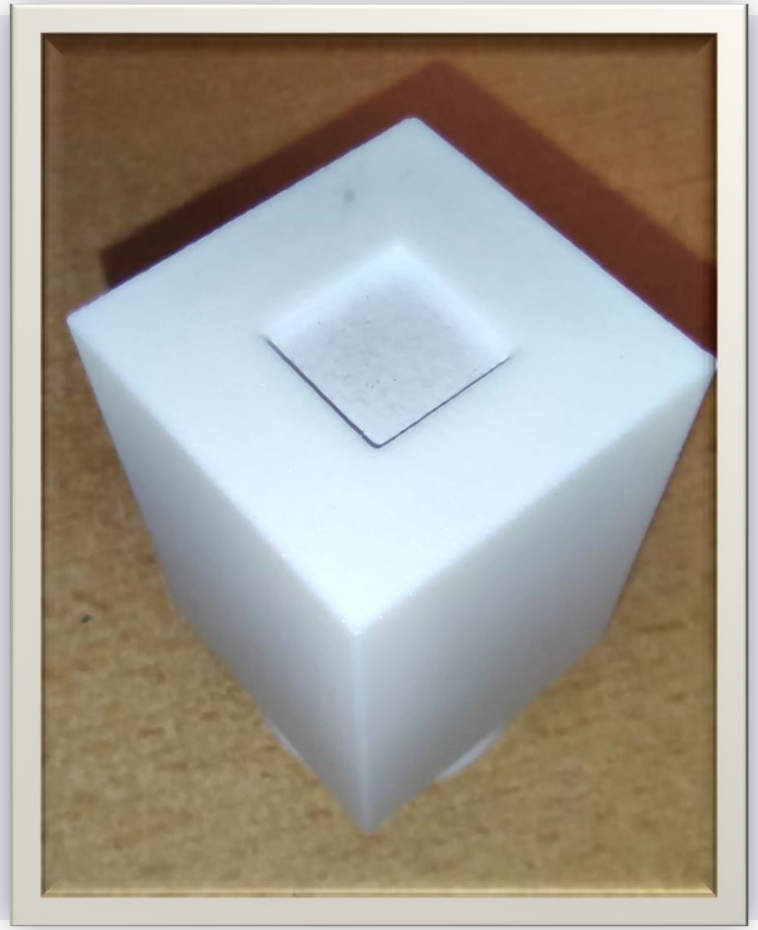
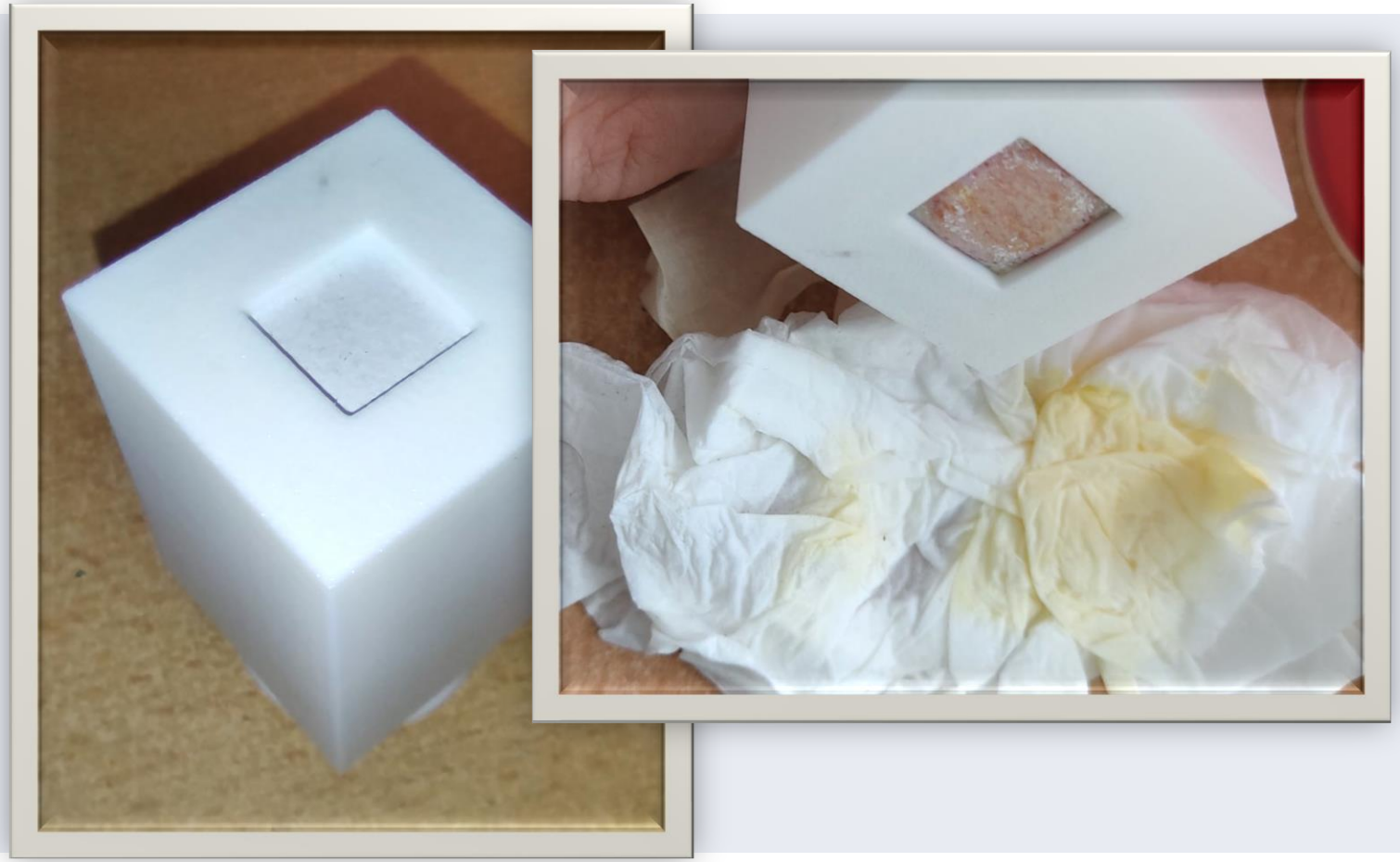




Putting everything together



Observations



Observations

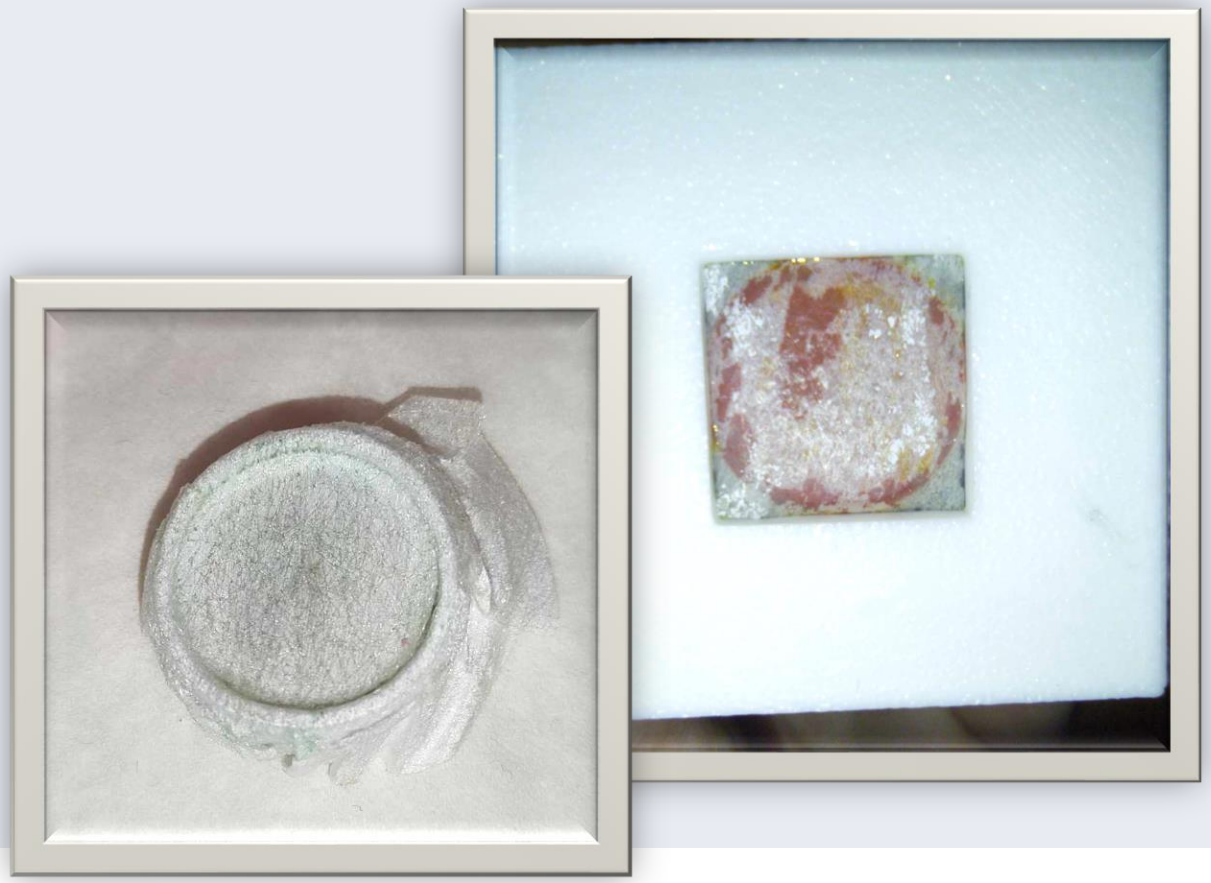
Observations

- It is water soluble

- The ruthenium complex leaches out
- Too fast for proper measurements
- Not sustainable

Observations

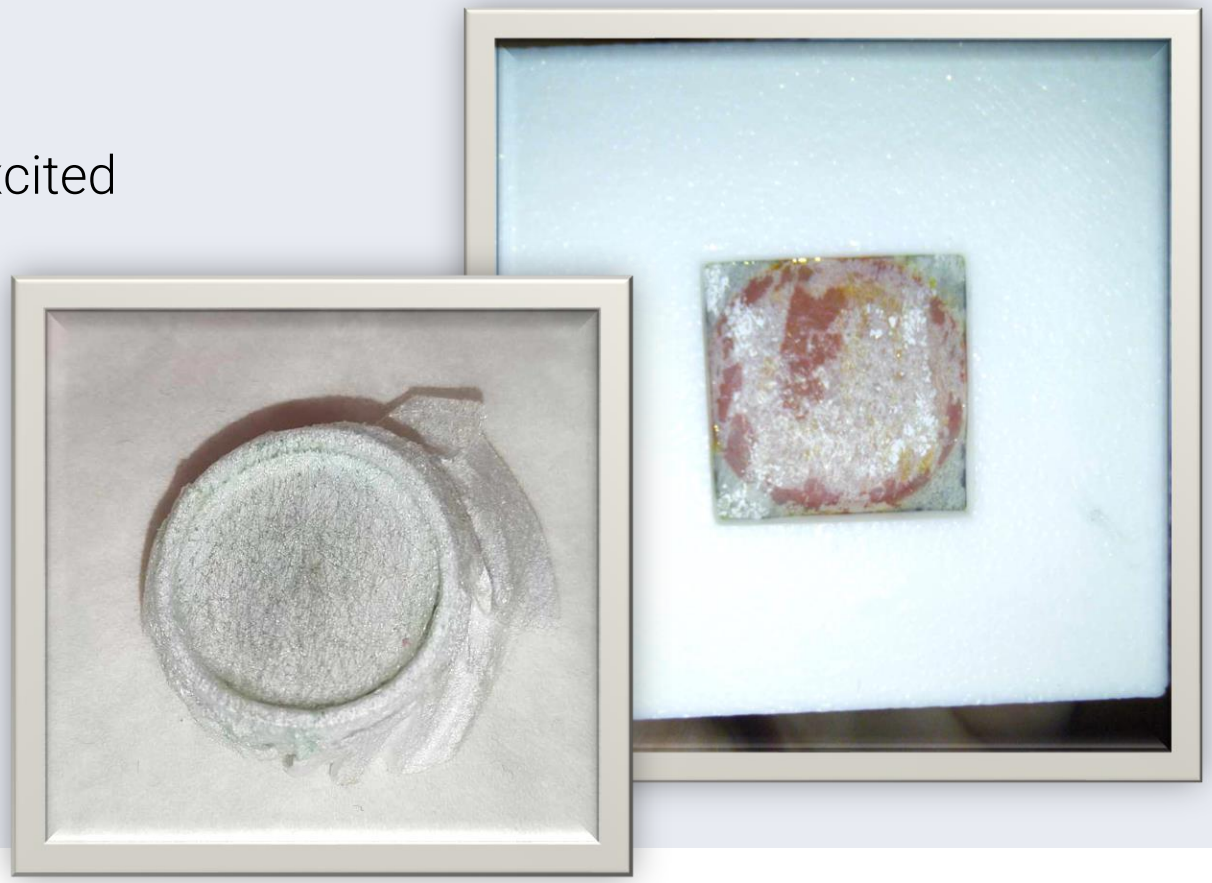
- PTFE is damaged



Observations

- PTFE is damaged

- $[Ru(bpy)_3]^{2+}$ Absorbs light and becomes excited
- => $[Ru(bpy)_3]^{2+*}$
- => Can generate Reactive Oxygen Species
- => Highly reactive
- => Can even interact with PTFE

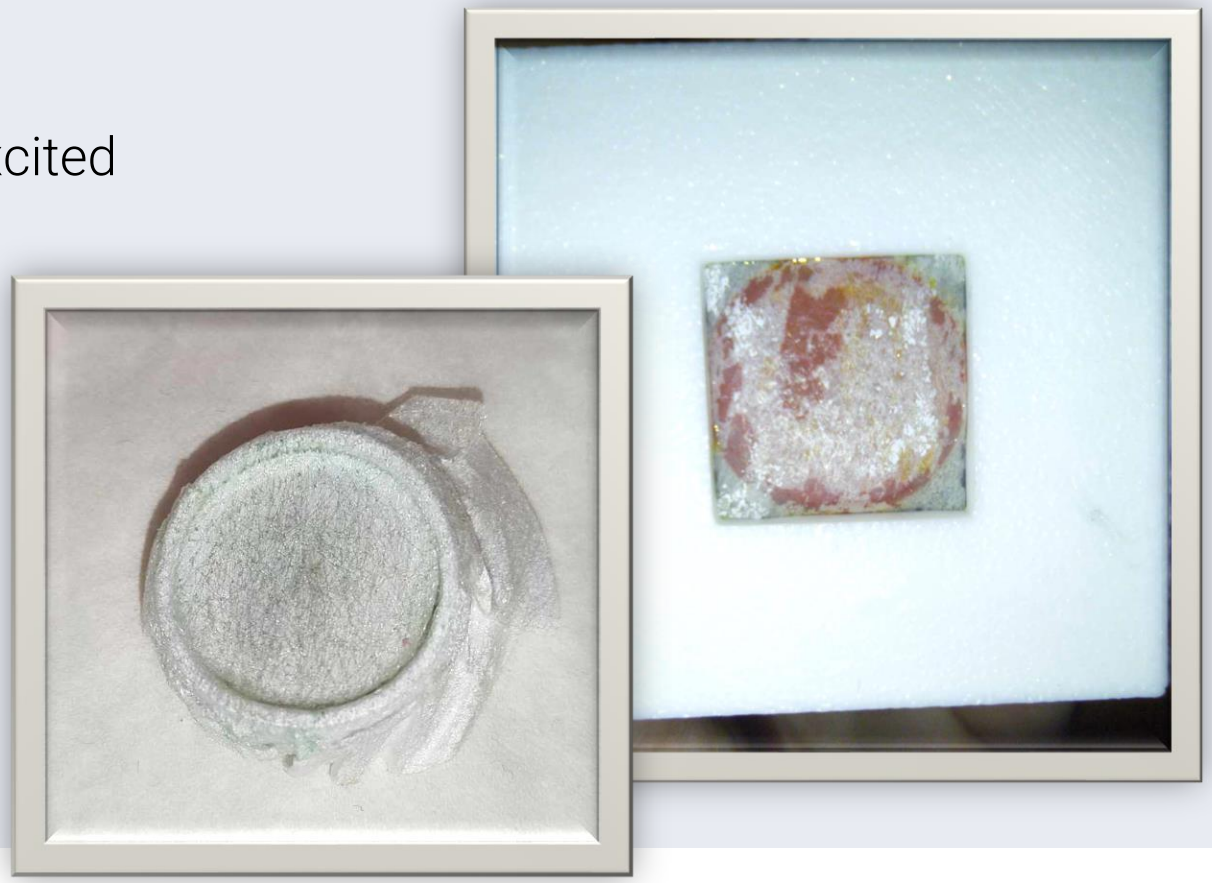


Observations

- PTFE is damaged

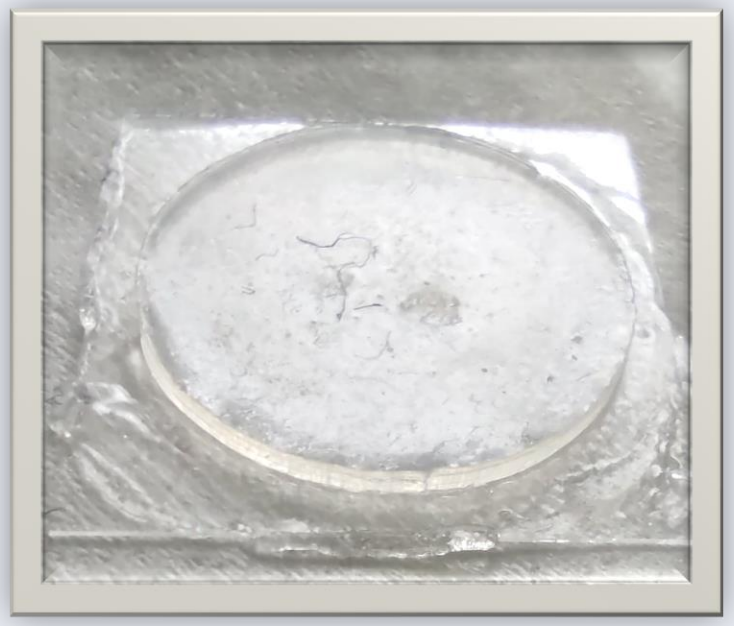
- $[Ru(bpy)_3]^{2+}$ Absorbs light and becomes excited
- => $[Ru(bpy)_3]^{2+*}$
- => ROS

- $[Ru(bpy)_3]^{2+*}$ can transfer electron
- => $[Ru(bpy)_3]^{3+}$
- => Strong oxidant
- => Can split water into O_2 and protons through catalyst.



Observations

- The disks do still stick firmly after prolonged submersion



Conclusion

- While promising on paper
- Not practical
- Also is WGK3 which needs investigation

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- Alternative?

Conclusion

- While promising on paper
- Not practical
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- Alternative?
- Tris(4,7-diphenyl-1,10- phenanthroline) Ruthenium(II) Chloride
  - Not soluble in water
  - Is soluble in alcohol and dimethylformamide

Questions