UV-VISIBLE SPECTROSCOPY

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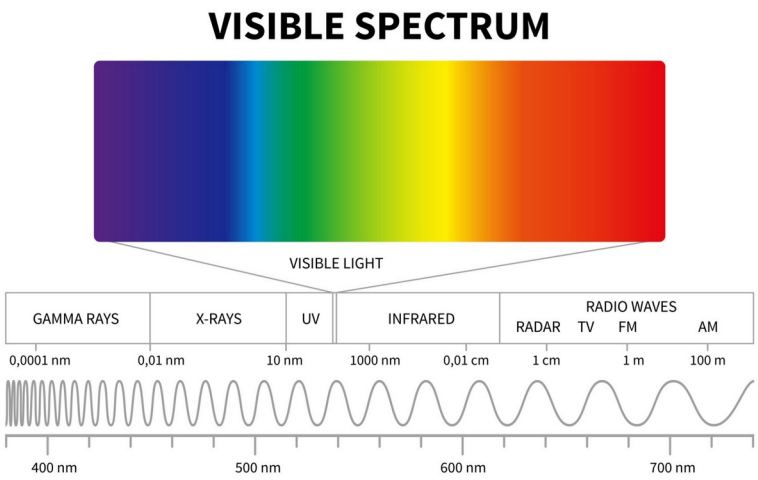
Aim`	**To learn about the UV/visible spectrum, its fundamental concepts and how adsorption follows the law of additivity.**
Theory	

Beer–Lambert's Law: This law establishes a linear relationship between a solution's absorbance and its concentration.

$$A=\varepsilon cl$$

The above formula indicates **absorbance (A)** is directly proportional to the **molar absorptivity (ε)**, **concentration (c)**, and the **path length of the light (l)**. Essentially, the more concentrated a solution is, the more light it absorbs.

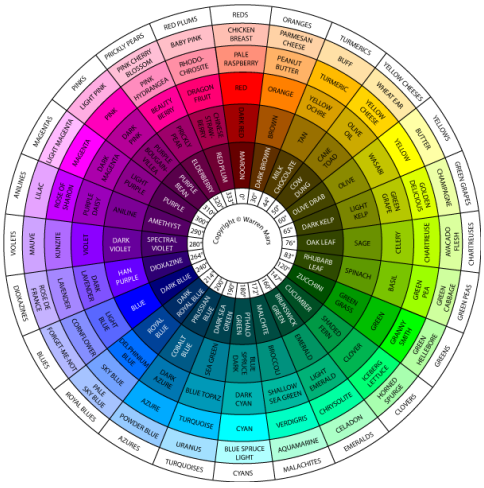
Electronic Transitions: The distinct colors of these compounds, deep purple for permanganate and orange-yellow for dichromate, are not due to typical d-d orbital transitions. Instead, the color arises from a **ligand-to-metal charge transfer (LMCT)**. In this process, an electron is excited and transitions from a molecular orbital predominantly localized on the oxygen atoms (the ligands) to an empty d-orbital on the central metal ion (manganese in $MnO4^{-}$ or

chromium in $Cr_2O_7^{2-}$). This specific transition absorbs photons in the visible region of the electromagnetic spectrum, resulting in the observed color.

Franck–Condon Principle: This principle states that an electronic transition occurs on a timescale significantly faster than the nuclei can move. As a result, the molecular geometry remains essentially constant during the transition. The absorption bands observed in the spectrum are broadened because the electronic transition can occur from various vibrational energy levels within the ground electronic state to different vibrational levels in the excited electronic state, leading to a continuum of closely spaced absorption energies.

Isosbestic Point: This is a specific wavelength at which two or more chemical species have the exact same molar absorptivity. In a solution containing these species, the total absorbance at this wavelength remains constant, regardless of the relative concentrations of the components. Isosbestic points are particularly useful in studying chemical equilibria or reactions where one species is converted into another.

Colour wheel:



Apparatus	Beakers Cuvette Standard volumetric flasks Measuring cylinder Funnel Spectrophotometer
Chemicals required	Potassium permanganate Potassium dichromate Sulfuric acid (0.1 M) Distilled water
Procedure	**Step 1: Preparing a Permanganate Solution** • Accurately weigh out 8 mg of potassium permanganate ($KMnO_4$). Using a volumetric flask, dissolve this in enough distilled water to bring the final volume to exactly 100 mL. This will create a stock solution with a concentration of 5×10-4 M. • **Step 2: Preparing the Acid Solution** • Prepare 100 mL of 0.1 M sulfuric acid (H_2SO_4). This is done using a standard volumetric flask to ensure the correct concentration. This acid will be used to dissolve the next compound and to prepare the final mixtures. • • **Step 3: Preparing a Dichromate Solution** • Now, weigh out 3 mg of potassium dichromate ($K_2Cr_2O_7$). You will dissolve this solid in the 0.1 M H_2SO_4 solution you just prepared, bringing the final volume to 100 mL in a volumetric flask. This will result in a stock solution with a concentration of $1×10^{-4}$ M. • • **Step 4: Creating the Mixtures** • Using the two stock solutions you've made, you will now prepare four different mixtures in separate 10 mL volumetric flasks. The total volume in each flask should be 10 mL. The specific volumes for each mixture are: Mixture 1: 8 mL of $KMnO_4$+ 2 mL of $K_2Cr_2O_7$ Mixture 2: 6 mL of $KMnO_4$+ 4 mL of $K_2Cr_2O_7$

Mixture 3: 4 mL of $KMnO_4$ + 6 mL of $K_2Cr_2O_7$
Mixture 4: 2 mL of $KMnO_4$ + 8 mL of $K_2Cr_2O_7$

Step 5: Measuring the Absorbance

Place each of the four mixtures into a cuvette and use a spectrophotometer to measure their absorption spectrum. The data from these measurements will be recorded and analyzed.

Calculations

We use this formula to calculate no. of moles of H_2SO_4

$$M = \frac{\%\ \text{purity} \times \text{specific gravity} \times 1000}{100 \times \text{Mol. Weight}}$$

% purity = 97
Specific gravity = 1.835
Molecular weight = 98.08
Thus, M = 18.148

Now,

$$M_1V_1 = M_2V_2$$
$$V_1 = 0.1 \times 100/18.148$$
$$= 0.551\ mL$$

Vol of H2SO4 taken = 0.551 mL
[KMnO4]= 5×10^{-4} M
[K2Cr2O7]= 1×10^{-4} M

Observations

At, λ = 539 nm, experimental values

Absorbance of pure $KMnO_4$	1.2389
Absorbance of (8ml $KMnO_4$ + 2ml $K_2Cr_2O_7$)	1.0002
Absorbance of (6ml $KMnO_4$ + 4ml $K_2Cr_2O_7$)	0.6510
Absorbance of (4ml $KMnO_4$ + 6ml $K_2Cr_2O_7$)	0.4459
Absorbance of (2ml $KMnO_4$ + 8ml $K_2Cr_2O_7$)	0.1318
Absorbance of pure $K_2Cr_2O_7$	0.0185

Molar absorptivity calculations, λ = 539nm

For $KMnO_4$,

A = 1.2389, C = 5 x 10^{-4} M

A= εcl

ε = A/cl = 2477.8 M^{-1} cm^{-1}

For $K_2Cr_2O_7$,

A= 0.0185 , C = 1 x 10^{-4} M

ε= A/Cl = 185 M^{-1} cm^{-1}

Theoretical Absorbance calculations at λ = 539 nm

8 ml $KMnO_4$ + 2 ml $K_2Cr_2O_7$	A_{total} = (2477.8 × 4 ×10^{-4}) + (185 × 2 ×10^{-5}) = 0.99112 + 0.00370 = 0.9948 A_{total} = 0.9948
6 ml $KMnO_4$ + 4 ml $K_2Cr_2O_7$	A_{total} = (2477.8×3×10^{-4}) + (185×4×10^{-5}) = 0.74334 + 0.00740 = 0.7507 A_{total} = 0.7507
4 ml $KMnO_4$ + 6 ml $K_2Cr_2O_7$	A_{total} = (2477.8×2×10^{-4}) + (185×6×10^{-5}) = 0.49556 + 0.01110 = 0.5067 A_{total} = 0.5067
2 ml $KMnO_4$ + 8 ml $K_2Cr_2O_7$	A_{total} = (2477.8×1.0×10^{-4}) + (185×8.0×10^{-5}) = 0.24778 + 0.01480 = 0.2626 A_{total} = 0.2626

Experimental values at λ = 315 nm

Absorbance of pure $KMnO_4$	1.0412
Absorbance of (8ml $KMnO_4$ + 2ml $K_2Cr_2O_7$)	1.0396

Absorbance of (6ml $KMnO_4$ + 4ml $K_2Cr_2O_7$)	0.8797
Absorbance of (4ml $KMnO_4$ + 6ml $K_2Cr_2O_7$)	0.5125
Absorbance of (2ml $KMnO_4$ + 8ml $K_2Cr_2O_7$)	0.2815
Absorbance of pure $K_2Cr_2O_7$	0.2114

Molar absorptivity calculation at λ = 315 nm

a) For KMnO4,
A = 1.0412, C = 5 x 10-4 M ε = A / Cl = 1.0412 / (5 x 10-4 M * 1 cm) = 2082.4 M-1cm-1
b) For K2Cr2O7, A= 0.2114, C = 1 x 10-4 M ε = A / Cl = 0.2114 / (1 x 10-4 M * 1 cm) = 2114 M-1cm-1

Theoretical Absorbance calculation for additivity at λ = 315 nm

8 ml $KMnO_4$ + 2 ml $K_2Cr_2O_7$	Atotal = (2082.4 x 4.0×10−4) + (2114 x 2.0×10−5) = 0.83296 + 0.04228 = 0.8752 Atotal = 0.8752
6 ml $KMnO_4$ + 4 ml $K_2Cr_2O_7$	Atotal = (2082.4 * 3.0 * 10-4) + (2114 * 4.0 * 10-5) = 0.62472 + 0.08456 = 0.7093 Atotal = 0.7093
4 ml $KMnO_4$ + 6 ml $K_2Cr_2O_7$	Atotal = (2082.4 * 2.0 * 10-4) + (2114 * 6.0 * 10-5) = 0.41648 + 0.12684 = 0.5433 Atotal = 0.5433

	2 ml $KMnO_4$ + 8 ml $K_2Cr_2O_7$	Atotal = (2082.4 * 1.0 * 10-4) + (2114 * 8.0 * 10-5) = 0.20824 + 0.16912 = 0.3774 Atotal = 0.3774

Observations table

Table1: Observed values from graph

	539 nm	315 nm
Pure KMnO4	1.2389	1.0412
8mL KMnO4 + 2mL K2Cr2O7	1.0002	1.0396
6 mL KMnO4 + 4 mL K2Cr2O7	0.651	0.8797
4 mL KMnO4 + 6 mL K2Cr2O7	0.4459	0.5125
2 mL KMnO4 + 8 mL K2Cr2O7	0.1318	0.2815
Pure K2Cr2O7	0.0185	0.2114

Table 2: Comparision of observed vs theoretical

S.No	Vol of KMnO4	Vol of K2Cr2O7	Observed A	Calculated A	Observed A	Calculated A
			539 nm	539 nm	315 nm	315 nm
1	0	10	0.0185	0.0185	0.2114	0.2114
2	2	8	0.1318	0.2626	0.2815	0.3774
3	4	6	0.4459	0.5607	0.5125	0.5433
4	6	4	0.651	0.7507	0.8797	0.7093
5	8	2	1.0002	0.9948	1.0396	0.8752
5	10	0	1.2389	1.2389	1.0412	1.0412

Table 3: Molar Absorptivity at 315 nm ($KMnO_4$)

Sr. No	Concentration	Absorbance	Molar absorptivity 315nm
1	0.0005	1.0412	
2	0.0004	0.83296	
3	0.0003	0.62472	2082.4
4	0.0002	0.41648	
5	0.0001	0.20824	

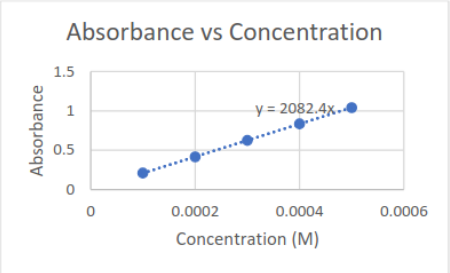
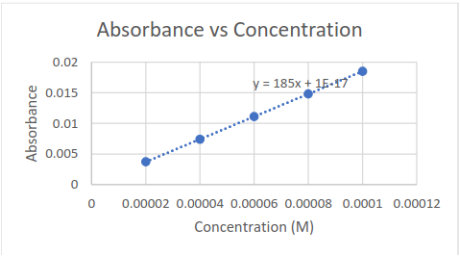


Table 4: Molar Absorptivity at 539 nm (KCr_2O_7)

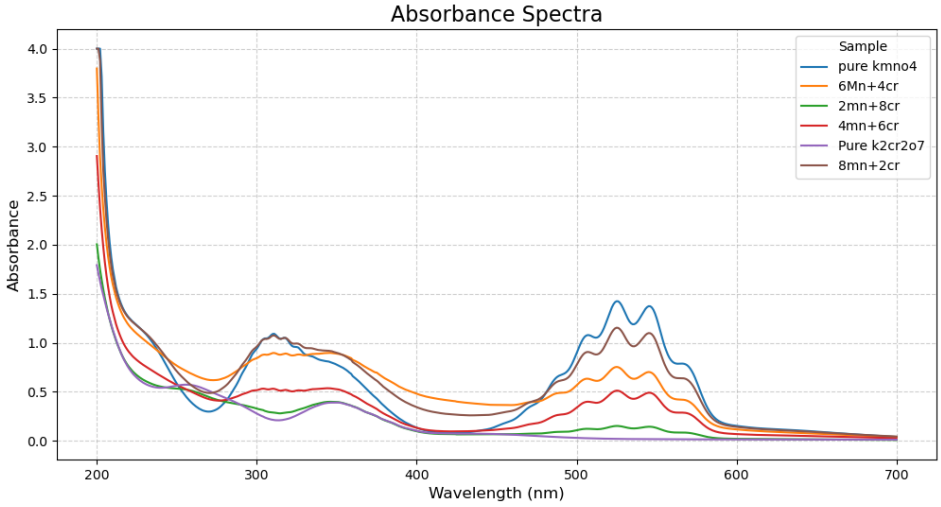
Sr. No	Concentration	Absorbance	Molar Absorptivity 539 nm
1	0.00002	0.0037	
2	0.00004	0.0074	
3	0.00006	0.0111	185
4	0.00008	0.0148	
5	0.0001	0.0185	



Results

1. ϵ Values for $KMnO_4$ for λ = 315 nm and λ = 539 nm were found to be
   a. $\epsilon_{315} = 2082.4\ M^{-1}\ cm^{-1}$
   b. $\epsilon_{539} = 2477.8\ M^{-1}\ cm^{-1}$

2. ϵ Values for $K_2Cr_2O_7$ for λ = 311 nm and λ = 536 nm were found to be
   a. $\epsilon_{315} = 2114\ M^{-1}\ cm^{-1}$
   b. $\epsilon_{539} = 185\ M^{-1}\ cm^{-1}$



Isobestic points:
X = 250.519, 281.979, 419.792

Precautions	1. Be careful while handling $KMnO_4$ and $K_2Cr_2O_7$ since they are strong chemicals – avoid spilling or touching them directly. 2. Make sure the cuvettes and glassware are clean, because even small smudges or dust can mess up the readings. 3. Don't leave the solutions in direct sunlight, as they can break down and give wrong results.
References	1. Atkins, P. & de Paula, J. (2018). Atkins' Physical Chemistry (11th ed.). Oxford University Press. 2. Willard, H.H., Merritt, L.L., Dean, J.A., & Settle, F.A. (1988). Instrumental Methods of Analysis (7th ed.). Wadsworth Publishing.