UNIT 4

SPECTROPHOTOMETRIC TITRATION

Structure

4.1 INTRODUCTION

In the previous experiment, you estimated magnesium (or zinc) and determined total hardness of water using by complexometric titrations method. In this experiment, you will perform spectrophotometric titration and determine the concentration of the $KMnO_4$ in the given coloured solution of $KMnO_4$.

Expected Learning Outcomes

After performing the given experiment you should be able to:

- state Beer-Lambert law,
- describe the spectrophotometer and its calibration, and
- use the spectrophotometric titration method to determine the concentration of the $KMnO_4$ in the given coloured solution of $KMnO_4$

4.2 Beer-Lambert Law

When light of an appropriate wavelength is passed through a coloured solution contained in a cell, a fraction of the light is absorbed depending on the concentration of the absorbing species and the thickness of the absorbing medium, and the rest of the light is transmitted. Though some light is reflected back from the solution, its amount is negligibly small and is eliminated by using a control. For all practical purposes we may say,

$$I_0 = I_a + I_t$$

Where,

I_0 = Intensity of incident light

I_a = Intensity of light absorbed

I_t = Intensity of transmitted light.

The relationship between the intensity of incident radiation and that of the transmitted one is best given be **Lambert's** and **Beer's** laws which correlate I_a with the thickness and concentration of the medium, respectively. Let us understand these two laws first.

Lambert's Law

According to this law, when a light beam passes through a medium/solution, equal fractions of the incident light are absorbed by layers of equal thickness or we may say that the differential decrease in intensity with thickness of the absorbing medium is proportional to the intensity of the incident light. Mathematically,

$$\frac{-dI}{db} = kI$$

where,

k = proportionality constant

b = thickness

Rearranging, we get,

$$\frac{-dI}{I} = kdb$$

Integrating and taking the condition that when b = 0, $I = I_o$, we get,

$$\log_e \frac{I}{I_o} = -kb$$

or $$\log_{10} \frac{I_o}{I} = \frac{kb}{2.303}$$

$$\frac{k}{2.303} = K$$

$\log 10 \frac{I_0}{I}$ is called **'absorbance'** while K *(k/2.303)* is referred to as the **absorption coefficient.**

Beer's law

This law states that the intensity of a beam of light decreases exponentially as the concentration of the medium decreases arithmetically. We may say that the differential decrease in the intensity of light as a function of concentration (c) is directly proportional to the intensity of incident light.

$$\frac{-dI}{dc} = k'I$$

Rearranging, we get,

$$\frac{-dI}{I} = k'dc$$

Integrating and putting the condition that when $c = 0$, $I = I_o$, we get,

$$\log_e \frac{I}{I_o} = -k'c$$

or $\log_{10} \frac{I_o}{I} = \frac{k'c}{2.303} = K'c$

$\log I_o/I$ = A, i.e., absorbance

K' = absorption coefficient

As you can see $K = K'$

Beer-Lambert Law

The two laws explained above are combined to give the commonly known Beer-Lambert law which states that the fraction of light absorbed by a given absorbing medium is directly proportional to the thickness of the medium of the concentration of the absorbing species. Solving the mathematical expression similar to the one in Lambert's law and Beer's law, we get,

$$A = \varepsilon cl \quad \text{… (4.1)}$$

where,

l = thickness of the medium

c = concentration in mol dm^{-3}

ε = molar absorption coefficient

ε the **molar absorption coefficient** is the absorbance of a solution having unit concentration, 1 *M*, placed in a cell of unit thickness, 1 cm. absorbance is also called **optical density (OD).**

According to Eq. 4.1 the absorbance or OD of a solution in a container of fixed path length is directly proportional to the concentration. A plot between absorbance and concentration is expected to be linear and a solution showing such a behaviour is said to said to obey Beer-Lambert law. Dilute solutions obey the law over a considerable concentration range, the upper limit varies from system to system. At higher concentrations discrepancies are found which are attributed to the changes occurring in the coloured solute, which may undergo association at higher concentration. It is, therefore, advisable to prepare a calibration curve using a series of standards of known concentration.

Spectrophotometric determination can be done with the help of a spectrophotometer. The details of the instrument and the instructions for its use are discussed in the instruction manual. Further, the use of the instrument would also be explained by your counsellor. The basic principle on which the instrument is based in briefly given here before going over to that try the following SAQ.

SAQ 1

Tick √ in front of the right statements and put × in front of the wrong statements given below:

i) Transmittance of sample increases with a decrease in absorbance.

ii) Absorbance of a sample decrease with an increase in its concentration.

iii) Absorbance of a sample is independent of its length.

iv) An air bubble in the sample will not affect the value of absorbance.

4.3 EXPERIMENT 4: DETERMINATION OF THE CONCENTRATION OF THE $KMnO_4$ IN THE GIVEN COLOURED SOLUTION USING SPECTROPHOTOMETRIC TITRATION

In the previous experiment, you estimated magnesium (or zinc) and determined total hardness of water using by complexometric titrations method. In this experiment, you will use the spectrophotometer for determining the concentration of the $KMnO_4$ in the given coloured solution of $KMnO_4$.

4.3.1 Principle

The spectrophotometric determination of the concentration of $KMnO_4$ in the given coloured solution is based on a simple principle. The intensity of the colour of the solution can be used as a measure of concentration of $KMnO_4$ in the given coloured solution. Here you will prepare a number of solutions containing known but variable amounts of $KMnO_4$. First you you have to determine the wavelength of maximum absorption (λ_{max}) of the coloured compound ($KMnO_4$). Then, at this maximum wavelength, measure the absorbance of different concentrations of $KMnO_4$ in the spectrophotometer to make a concentration-absorbance calibration curve. The concentration of the unknown solution is determined by the help of this calibration curve.

4.3.2 Requirements

In this experiment the following apparatus, chemicals and solutions are required.

Apparatus	No.	Chemicals
Spectrophotometer with cuvettes	1	$KMnO_4$
Burette(50 cm^3)	1	
Burette stand	1	
Test Tubes	15	
Test tube stand	1	
Volumetric flask (100 cm^3)	1	
Beaker	2	
Measuring cylinder	1	

Solutions Provided

Stock solution of $KMnO_4$ (0.001 *M*) prepared by dissolving appropriate amount of $KMnO_4$ in water and making the volume upto 100 cm^3.

4.3.3 Procedure

- Turn the spectrophotometer 'on' and allow warming up for about ten minutes.
- Take a clear dry cuvette and fill it with distilled water (blank) solution.
- Open the sample compartment cover and insert the cuvette in the sample holder.
- Always insert the cuvette the same way.
- Close the sample compartment.
- Set the spectrophotometer at zero absorbance or 100% transmittance.
- Remove the the cuvette, pour off the reference solution, rinse and dry it.

Selection of the wavelength of maximum absorption (λ_{max})

- First, you have to determine the wavelength of maximum absorption (λ_{max}) of the coloured compound ($KMnO_4$).
- Prepare 100 cm^3 of $KMnO_4$ (0.001 *M*) stock solution. Fill the cuvette with the stock solution. Insert the cuvette in the sample holder in the same orientation as in Step 1.
- Take the appropriate reading of the corresponding absorbance.
- For this, take solution of $KMnO_4$ (0.001 *M*) in cuvette.
- Record the absorption spectrum of the Stock solution of $KMnO_4$ (0.001 *M*) in the range of 400-700 nm. If the instrument is of manual type, measure

the absorption value after every 10 nm over the spectral range (or at all wavelengths) and record the readings in Observation Table I.
- Draw the spectrum by plotting the absorbance as a function of the wavelength in the graph. Then, select the wavelength which gives maximum absorbance, i.e. λ_{max}.

Next, at this maximum wavelength, you have to do the **calibration of the spectrophotometer** for spectrophotometric titration.

Linearity Check

- Select the wavelength with the wavelength selector knob (for $KMnO_4$ the wavelength for which it shows maximum absorbance is……)
- Take ten clean, dry test tubes and add 10.0 cm^3, 9.0 cm^3, 8.0 cm^3, 7.0 cm^3, 6.0 cm^3, 5.0 cm^3, 4.0 cm^3, 3.0 cm^3, 2.0 cm^3 and 1.0 cm^3 of the $KMnO_4$ (0.001 *M*) stock solution in them respectively. Dilute each with distilled water to make 10.0 cm^3 of total volume.

- Take the same cuvette as used for calibration. Record the absorption for each of the solutions as in Observation Table II making sure that the cuvette is rinsed propertly before pouring the solution.

- Plot the absorbance against the volume of stock solution taken in each of the test tubes. A linear graph is expected as $KMnO_4$ solution is known to obey the Beer-Lambert law in this concentration range.

You will be using the spectrophotometer for detecting the absorbance of the sample. A **spectrophotometer** is a device which detects the percentage transmittance (%T) of light radiation when light of certain intensity and frequency range is passed through the sample. The instrument compares the intensity of the transmitted light with that of the incident. The source of radiation in such as instrument is usually hydrogen or deuterium lamp.

Cuvette

Fig. 4.1 UV-visible spectrophotometer

- Lastly, at this maximum wavelength, note the absorbance value of solution of unknown concentration and determine its concentration with the help of the calibration curve. Now plot the observations recorded in Observation Table II in a graph.
- From the graph, note the absorbance value of solution of unknown concentration and determine its corresponding concentration. Keep in mind the dilution factor and report the value.

- Calculate the concentration of $KMnO_4$ in the unknown sample solution by accounting for the dilution factor and report the value.

4.3.4 Observations and Calculations

Observation Table I: Determination of the wavelength of maximum absorption (λ_{max})

Wavelength (nm)	Absorbance	Wavelength (nm)	Absorbance	Wavelength (nm)	Absorbance
400		500		600	
410		510		610	
420		520		620	
430		530		630	
440		540		640	
450		550		650	
460		560		660	
470		570		670	
480		580		680	
490		590		690	
				700	

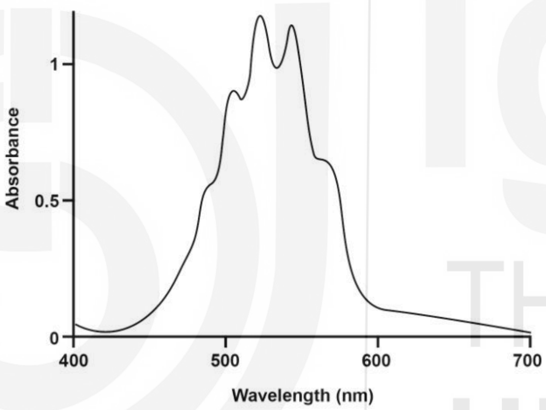

Fig. 4.2: Graph between wavelength and absorbance for the standard solution

From the spectrum, the wavelength of maximum absorption, λ_{max} is found to be: ....nm.

Observation Table II

Absorbance as a function of concentration of potassium permanganate

S.No.	Strength of $KMnO_4$ in % m / v	Absorbance at λ_{max}
1	0	
2	2	
3	4	
4	6	
5	8	
6	10	
Unknown	……………	

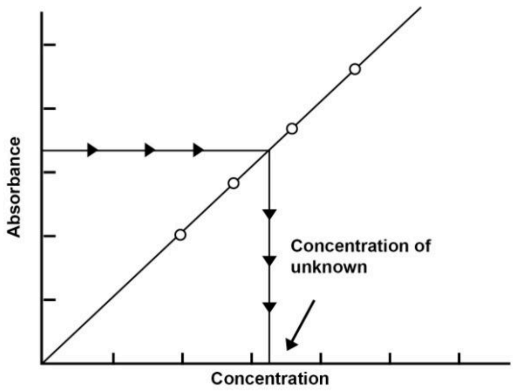

Fig. 4.3: Graph between concentration of $KMnO_4$ and absorbance

4.3.6 Result

The strength of the given $KMnO_4$ is …………..

4.4 ANSWERS

Self Assessment Questions

1) i) √ ii) × iii) × ii) √