# Exp 1. Calculation of Molar Extinction coefficient for Fe (II) using Spectrophotometer through 1, 10-PHENANTHROLINE

**Structure**



**1.2 PRINCIPLE**

As mentioned in the introduction, UV-visible absorption spectrophotometry provides a convenient method of determination of concentration of any substance which can be treated to form a coloured solution in which the colour intensity is proportional to the concentration of the substance. This experiment is based on the determination involving the formation of a complex species that absorbs in the visible region. The general procedure usually involves the following basic steps.

• Treatment of the properly prepared sample with a reagent to form a coloured solution,

• Controlling factors influencing absorption by the coloured species,

• Measurement of absorbance of the coloured solution at the appropriate wavelength,

• Preparation of an absorbance-concentration plot (calibration plot) by measurements of the absorbance of the standard solutions of known concentrations, and

• Estimation of concentration in the unknown sample corresponding to the absorbance measured by using the calibration plot.

In the determination of iron (II) in aqueous solutions, a tricyclic nitrogen heterocyclic compound,1, 10-phenanthroline ($C_{12}H_8N_2$, ortho-phenanthroline or o-Phen) is used as the ligand that reacts with metals such as iron, nickel, ruthenium, and silver to form strongly coloured complexes. With ferrous ions ($Fe^{2+}$), it reacts in a ratio of 1:3 to form an orange red coloured complex $[(C_{12}H_8N_2)_3Fe]^{2+}$ in aqueous medium as per the following equation

$$Fe\ (II) + 3\ Phen \rightarrow Fe(Phen)_3^{\ 2+}$$

The ligand is a weak base that reacts to form phenanthrolinium ion, $phenH^+$ , in acidic medium. Accordingly, the complex formation may be represented as follows,

$$Fe\ (II) + 3\ PhenH^+ \rightarrow Fe(Phen)_3^{\ 2+} + 3H^+$$

Under these conditions the complex obeys Beer-Lambert's law in the range of the concentrations being determined (~0.5–2.0 ppm). The range for the validity of Beer- 9 Lambert's law can be determined by plotting a calibration curve by measuring the absorbance values for a series of standard solutions of

the complex being determined at a fixed wavelength of 508 nm. The curve so obtained is then used for the determination of concentration of unknown solutions from a measurement of its absorbance at the same wavelength.

**1.3 REQUIREMENTS**

Apparatus: Spectrophotometer/ Filter photometer Matched cuvette Volumetric flasks (1 $dm^3$ ) Volumetric flasks (50 $cm^3$ ) Graduated pipette, 10 $cm^3$ Pipettes (5, 10 cm3 ) Weighing bottle,

Chemicals: Ferrous ammonium sulphate hexahydrate 1, 10-Phenanthroline Hydroxylamine hydrochloride Sulphuric acid Acetic acid Sodium acetate

**1.4 SOLUTIONS PROVIDED**

i) Standard ferrous solution (10 ppm (10 mg/ dm3 )); prepared as follows.

• Weigh 0.0702 g of analytical grade ferrous ammonium sulphate hexahydrate [Fe(NH4)2(SO4)2.6H2O].

• Quantitatively transfer the weighed sample to a volumetric flask of 1 dm3 capacity and add sufficient distilled water to dissolve it.

• Add 2.5 cm3 of concentrated sulphuric acid and make up the solution to the mark.

ii) 1, 10-phenanthroline; prepared by dissolving 100 mg of the reagent in 100 cm3 of distilled water. The reagent can be stored in a bottle

iii) Hydroxylamine hydrochloride; prepared by dissolving 10 g of hydroxylamine hydrochloride in 100 cm3 of distilled water.

iv) Sodium acetate (0.1M); prepared by dissolving 10 g of sodium acetate in 100 cm3 of water.

v) Acetic acid (0.1M); prepared by diluting about 6 cm3 of glacial acetic acid to 100 cm3

vi) Acetic acid-sodium acetate buffer (pH = 4.5); prepared by mixing 65 cm3 of 0.1 M acetic acid and 35 cm3 of 0.1 M sodium acetate in a 100 cm3 flask. (Prepare the buffer whenever required.)

**1.5 PROCEDURE**

1. Pipette out 1, 2, 3, 5, 10, 15 and 20 $cm^3$ of the standard ferrous ion solution into a series of 100 $cm^3$ standard flasks labelled from 1 to 7.

2. In another flask, labelled ‘Sample’, take 10 cm3 of the unknown sample.

3. To another 100 cm3 standard flask, labelled ‘Blank’, add about 20 cm3 of distilled water to prepare the blank solution.

4. To each of the above flasks (standards, sample and blank) add 1 cm3 of hydroxylamine hydrochloride and 5 cm3 of 1, 10-phenanthroline.

5. Buffer each solution by adding 8 cm3 of acetic acid / sodium acetate buffer.

6. Allow at least 15 minutes after the addition of the reagents for full colour development (The colour once developed is stable for hours).

7. Dilute each solution exactly to 100 cm3 mark with distilled water and mix well.

8. The standard solutions so obtained correspond to 0.1, 0.2, 0.3, 0.5, 1.0, 1.5 and 2.0 ppm respectively. You may label the flasks accordingly.

9. Record the absorption spectrum for the 2.0 ppm standard solution against the reagent blank in the range of 400 – 700 nm.

10. If the instrument is of manual type, measure the absorption value after every 10 nm over the spectral range and record the readings in Observation Table 1.1. Draw the spectrum by plotting the absorbance as a function of the wavelength in the graph.

11. Select the wavelength which gives maximum absorbance ( max λ ) and record the same under observations. The reported value is 508 nm.

12. Calculate the molar absorption coefficient (ε ) of the complex from the molar concentration and path length of the cuvette. Use the relation A = εcb.

13. Measure the absorbance for all the standard solutions at the wavelength of maximum absorption and record the readings in the column no. 4 of the Observation Table 1.2.

14. Measure and record the absorbance for the 'Sample' also in the same way.

15. Make a plot of absorbance at Y-axis (column 4) vs. concentration of the standard solutions at X-axis (column 3) to get the calibration curve. (The linear region of the curve obeys Beer- Lambert's law and is used for the estimation of unknown samples.)

16. Determine the concentration of the given sample solution with the help of the calibration curve.
17. Calculate the ferrous ions present in the unknown sample solution by accounting for the dilution factor and report the value

**1.6 OBSERVATIONS AND CALCULATIONS**

A. Recording the visible spectrum of the iron-phen complex Observation Table 1.1: Absorbance of the iron-phen complex obtained from 2ppm standard solution of iron (II) as a function of the wavelength

| Wavelength(nm) | Absorbance | Wavelength(nm) | Absorbance | Wavelength(nm) | Absorbance |
|---|---|---|---|---|---|
| 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 | |
| 500 | | 600 | | 700 | |

Calculation of molar absorption coefficient

The absorbance at the max λ = A = ..... Path length of the sample (cuvette cell length) = b = ..... cm

Concentration of the standard solution = c = 2.0 ppm = 2.0 mg / $dm^3$

= 2 ×$10^{-3}$ g/ 605.85 g mol $dm^{-3}$ = 3.3 × $10^{-6}$ mol $dm^{-3}$

Using the relation, A = ε cb

The value of molar absorption coefficient =……$m^{-1}$ $mol^{-1}$ $dm^{3.}$

**1.7 RESULT**

The wavelength of maximum absorption for the iron-phen complex has been found to be = .....nm. (Ref. step C in the observations and calculations.) ii) The molar absorption coefficient of the complex is found to be = ..... cm–1 mol–1 dm3 .

Reference: https://egyankosh.ac.in