UNIT 4 ESTIMATION OF IRON

Structure

4.1 INTRODUCTION

You have learnt about the theory and applications of acid-base titrations in Units 2 and 3. A large number of analytical determinations make use of another important kind of titration, namely, redox titration. As the name suggests these titrations are based on oxidation-reduction reactions. In contrast to acid-base titrations in which the titration reaction involves the formation of undissociated molecules of a weak electrolyte (water or a weak acid), a redox titration reaction is associated with the transfer of electrons. The electrons are transferred from a reducing agent to an oxidising agent. In this unit we will discuss such titrations. An attempt is made here to make you understand some fundamental concepts related to redox titrations and the theory behind the reactions involved. Analytical redox titrations involve the use of a variety of oxidising and reducing agents. Different types of redox titrations are named on the basis of oxidising/reducing agents involved. Of these, two types of titrations, namely, **permanganatometry** using potassium permanganate, $KMnO_4$ and **chromatometry** using potassium dichromate, $K_2Cr_2O_7$ would be the basis of the two experiments which you are going to do in this unit. In the next unit you will perform another type of redox titration, namely, **iodometry** using iodine.

Objectives

After reading this unit and performing the experiments you will be able to:

- define oxidation, reduction and redox titrations,
- explain the significance of redox potential in redox titrations,
- interpret redox titration curves,
- explain the use of various types of redox indicators,
- apply the redox titration methods, viz., permanganatometry and chromatometry, for estimating iron in the given solution,
- state and explain the principle involved in permanganatometry and chromatometry, and
- calculate the percentage of iron in the given solution by permanganatometric and chromatometric methods.

4.2 OXIDATION-REDUCTION: REDOX POTENTIAL

In this section we will briefly review the theory of oxidation and reduction reactions.

Oxidation is the process which results in the loss of one or more electrons by an atom or an ion, e.g.,

$$Fe^{++} \longrightarrow Fe^{+++} + e \qquad ...(4.1)$$

Reduction, on the other hand, is the process which results in the gain of one or more electrons by an atom or an ion, e.g.,

$$Cl_2 + 2e \longrightarrow 2Cl^- \qquad ...(4.2)$$

An oxidising agent is the one which gains electrons and gets reduced, e.g., Cl_2 in Eq. 4.2 and a reducing agent is the one which loses electrons and gets oxidised, e.g., Fe^{++} in Eq. 4.1.

Different oxidising/reducing agents differ from one another in their strength. An oxidising agent can behave as a reducing agent in the presence of a stronger oxidising agent. For a reaction of the type:

$$\underset{\text{agent}}{\text{Oxidising (I)}} + \underset{\text{agent}}{\text{Reducing (II)}} \longrightarrow \underset{\text{agent}}{\text{Reducing (I)}} + \underset{\text{agent}}{\text{Oxidising (II)}}$$

where we have a pair of oxidising-reducing agents such that either of the species can act as an oxidising or a reducing agent, the direction of the reaction is determined by comparing the **redox potential** of the oxidising/reducing agents. The redox potential is a quantitative characteristic of the oxidising/reducing power of a reagent. Let us try to understand the significance of redox potential.

In a system containing both an oxidising agent and its reduction product, there will be an equilibrium between them and the electrons. If an inert electrode, such as platinum, is placed in such a redox system, e.g., one containing Fe^{3+} and Fe^{2+} ions, it will assume a definite potential indicative of the position of equilibrium. If the system tends to act as an oxidising agent, then $Fe^{3+} \longrightarrow Fe^{2+}$ and it will take electrons from the platinum electrode leaving the latter positively charged, if, on the other hand, the system has reducing properties ($Fe^{2+} \longrightarrow Fe^{3+}$), electrons will be given up to the metal which will then acquire a negative charge. The magnitude of the potential will thus be a measure of the oxidising or reducing properties of the system. It is quite difficult to measure this potential between the metal and the solution or between different oxidation states of a metal. For this purpose, such a system is coupled with a standard hydrogen electrode (SHE), i.e., we make a galvanic cell and measure electromotive force (e.m.f.) of the cell. The e.m.f. of such a cell is the difference of potential of the given system and SHE, the potential of which is taken to be 0.01 *V*. This e.m.f. is referred to as the **redox potential.**

The potential of the standard hydrogen electrode is conventionally taken as zero, just as the temperature of melting ice is taken as zero in celsius scale.

It should be noted that a solution of a pure oxidising agent or a pure reducing agent always contains the products of their reduction or oxidation, respectively. For example, reductant Fe^{2+} always contains some Fe^{3+} and the oxidant MnO_4^- always contains Mn^{2+} ions. That is why it is more correct to speak of the redox potentials of oxidation-reduction couples such as Fe^{3+}/Fe^{2+}, MnO_4^-/Mn^{2+}, etc., rather than of the individual oxidant or reductant potentials.

For a simple reduction reaction,

$$\text{Ox. form} + ne \longrightarrow \text{Red. form}$$

Here, Ox. form = Oxidised form
Red. form = Reduced form

the reduction potential, E, is given by **Nernst Equation:**

$$E = E^\circ + \frac{RT}{nF} \log \frac{[Ox]}{[Red]} \qquad ... (4.3)$$

where R = Gas constant (= 8.314 J $mol^{-1}K^{-1}$)
T = Absolute temperature (K)
F = Faraday's constant (= 96,500 C)
E° = Standard redox potential
n = number of electrons gained or lost

When [Ox] = [Red], the log term in Eq. 4.3 becomes zero, then the potential of the system is called **standard potential.** It is a characteristic of a given system.

At 300 K, substituting the values of R, T and F in Eq. 4.3,

$$E = E^{\circ} + \frac{0.059}{n} \log \frac{[Ox]}{[Red]} \quad \ldots (4.4)$$

Knowing the chemical reaction involved and the potential of the solution, we can use the Nernst equation to evaluate the relative concentrations of oxidised and reduced forms. The solution potential can also be calculated if we know the concentrations of the two forms.

SAQ 1
Write equations for the following half reactions:

i) Oxidation of hydrogen molecule to form hydrogen ions:

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ii) Oxidation of sulphide ions to form sulphur:

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iii) Reduction of chlorine molecule to form chloride ions:

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iv) Oxidation of cuprous ions to form cupric ions:

.....

v) Reduction of oxygen molecule to form oxide ions:

.....

4.3 REDOX TITRATIONS

You know, a redox titration is based upon the oxidation-reduction reaction between a titrand and a titrant. Here the end point can be detected either by the colour change of a redox indicator or by plotting data taken by using a potentiometer. In this section we first discuss the redox titration curves and then the redox indicators. These concepts will tell you how redox indicator and potentiometric detection procedures work.

4.3.1 Redox Titration Curves

We can see from Eq. 4.4 that the potential of a given reaction depends upon the relative concentrations of oxidised/reduced forms. In the course of a redox titration, the solution potential also changes, since the concentration of oxidised and reduced forms goes on changing. At one stage, when either of the forms gets exhausted, i.e., at the end point, there is a sharp change in otherwise gradually varying potential. You may recall here what you studied in acid-base titrations, where either the pH or the conductance shows a sharp change at the end point. We shall theoretically try to see the variation of potential during the course of titration which is called redox titration curve. Let us illustrate this by taking an example of the titration between ferrous iron and potassium permanganate solution which incidentally is also the first experiment in this unit.

Redox titration curve for ferrous sulphate-potassium permanganate titration
In the titration of $FeSO_4$ with $KMnO_4$ in the acidic medium, the permanganate ions oxidise ferrous ions to ferric ions and get reduced to divalent manganese ions. The ionic reactions involved are as follows:

$$[Fe^{2+} \rightleftharpoons Fe^{3+} + e] \times 5 \quad \ldots.(4.5)$$

$$MnO_4^- + 8H^+ + 5e \rightleftharpoons Mn^{2+} + 4H_2O \quad \ldots.(4.6)$$

Adding Eq. 4.5 and Eq. 4.6,

$$MnO_4^- + 5Fe^{2+} + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O \quad \text{... (4.7)}$$

The system contains two redox couples, viz., Fe^{2+}/Fe^{3+} and MnO_4^-/Mn^{2+}. Since both the reactions are in equilibrium, at any stage of titration, the solution contains all the species. To calculate the potential of the solution theoretically at any instance of titration, we can make use of Nernst equation using the standard redox potentials for the two couples; and substituting the values of R, T and n in Eq. 4.3. The values of n can be obtained from Eq. 4.5 and Eq. 4.6.

Thus:

$$E = 0.77 + \frac{0.059}{1} \log \frac{[Fe^{3+}]}{[Fe^{2+}]} \quad \text{... (4.8)}$$

$$E = 1.51 + \frac{0.059}{5} \log \frac{[MnO_4^-]\,[H^+]^8}{[Mn^{2+}]} \quad \text{... (4.9)}$$

However, it is simpler to use Fe^{2+}/Fe^{3+} couple in the region before the equivalence point and MnO_4^-/Mn^{2+} couple after it. This is because it is easier to calculate the amounts of the corresponding ions under such conditions.

Before we start the titration we have only ferrous ions in solution. When we add $KMnO_4$, MnO_4^- ions oxidise some of the ferrous ions to ferric ions and a potential is developed, point A in Fig. 4.1, between Fe^{2+} and Fe^{3+} ions. As we go on adding more and more of permanganate, the amount of Fe^{3+} ions goes on increasing and that of Fe^{2+} goes on decreasing whereby the potential (cf. Eq. 4.8) also goes on increasing gradually. At a stage just before the equivalence point, say about 0.1 cm^3 less than that required for the end point, almost all the ferrous ions are oxidised and the potential is approximately equal to the maximum for Fe^{2+}/Fe^{3+} system under given conditions, point B in Fig. 4.1.

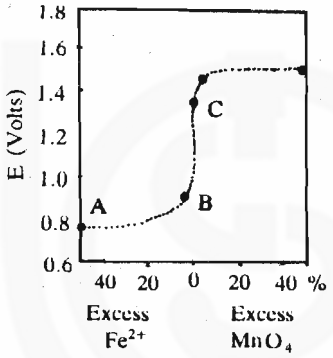

Fig. 4.1: Redox titration curve for ferrous sulphate-potassium permanganate titration.

At equivalence point, point C in Fig. 4.1, the potential is given by the following general equation:

$$E = \frac{bE^{\circ} + aE^{\circ}}{a + b} \quad \text{... (4.10)}$$

where E° and E° are the standard potentials of the oxidising and the reducing agent, respectively and a and b are the corresponding stoichiometric coefficients. In the present case $E^{\circ} = 0.77$, $E^{\circ} = 1.51$, $b = 1$, $a = 5$ and $E = 1.387$ V.

Immediately after the equivalence point the amount of Fe^{2+} is negligibly small and is difficult to calculate. The potential can be calculated by making use of MnO_4^-/Mn^{2+} couple as, at this stage it becomes easier to evaluate the amount of MnO_4^- and Mn^{2+} ions. The potential now corresponds to the minimum for the MnO_4^-/Mn^{2+} couple, point D in Fig. 4.1. Beyond this, further addition of MnO_4^- merely alters the relative amounts of MnO_4^- and Mn^{2+} and there is a gradual variation in the potential of the solution. The calculated redox potential during the titration of 100 cm^3 of $FeSO_4$ solution at $[H^+] = 1M$ with permanganate solution of the same molarity is given in Table 4.1. You would notice that Eq. 4.9 for determining the potential of MnO_4^-/Mn^{2+} couple contains $[H^+]$ term. The concentration of $[H^+]$ is kept $1M$ so that in the effective equation we need only the amounts of MnO_4^- and Mn^{2+}. However, it may be mentioned here that the hydrogen ion concentration has an enormous effect upon the oxidation potential of the oxidising agent, MnO_4^- in this case. At a pH of 6, e.g., it is found that the oxidation potential of permanganate is about 0.6 volt lower than with $1M$ acid solution, where pH = 0. Use is made of this fact, e.g., in the fractional oxidation of halides to the corresponding halogen. At a pH of 5 or 6, iodide is oxidised to I_2 by permanganate, whereas bromide and chloride are not affected. At a pH of about 3 (acetic acid), bromide is oxidised, but chloride is still unaffected. The latter is oxidised only at a much higher hydrogen ion concentration.

Table 4.1: Variations of the redox potential during titration of 100 cm³ of 0.1*M* $FeSO_4$ solution with 0.02*M* $KMnO_4$ solution at $[H^+] = 1M$

$KMnO_4$ added, cm³	Excess cm³		$[Fe^{+++}]$	$[MnO_4^-]$	Calculation	Oxidation potential *E*, V
	$FeSO_4$	$KMnO_4$	$[Fe^{++}]$	$[Mn^{++}]$		
50	50	—	50:50=1	—	$E=0.77+0.059 \log 1$	0.770
91	9	—	91:9≃10	—	$E=0.77+0.059 \log 10$	0.829
99	1	—	99:1≃100	—	$E=0.77+0.059 \log 100$	0.888
99.9	0.1	—	99.9:0.1 ≃1,000	—	$E=0.77+0.059 \log 1{,}000$	0.947
100 (equiv. pt.)	—	—	—	— =	$E=\frac{0.77+5\times1.51}{5+1}$	1.387*
100.1	—	0.1	—	0.1:100=0.001	$E=1.51+\frac{0.059}{5} \log 0.001$	1.475
101.0	—	1.0	—	1:100=0.01	$E=1.51+\frac{0.059}{5} \log 0.01$	1.487
110.0	—	10	—	10:100=0.1	$E=1.51+\frac{0.059}{5} \log 0.1$	1.498
150	—	50	—	50:100=0.5	$E=1.51+\frac{0.059}{5} \log 0.5$	1.507

* These figures show that the equivalence point is not in the middle of the break, as was the case in titration curves by the neutralisation method.

Redox potential of a redox system remains unaffected by dilution, this is because dilution affects both the oxidised and the reduced species equally. This is justified because in the Nernst equation also, the relative concentrations and not the absolute concentrations of the two forms are required. On the other hand, in the region beyond the equivalence point, the actual potential would be slightly different from the calculated one, since $[H^+]$ ions are involved in the calculations and their concentration does depend upon dilution. This error, however, does not affect the general conclusions and can, therefore, be neglected.

The above description of redox titration curves is given to make you aware of the changes in potential taking place during the reaction. Since you are going to use only the indicator method to detect the end point, you would not be required to draw such curves. However, these titrations can also be followed by actually measuring the potential of the solution with the help of a potentiometer (pH meter). In such cases, one has to plot these curves and determine the equivalence point by using derivative curves as was done in case of acid-base titrations.

4.3.2 Redox Indicators

You have seen how the potential varies during the titration and also that at the equivalence point there is a sharp change in the potential. As said before, this change is similar to the sharp change observed in the pH during acid-base titrations. As you used an acid-base indicator which changes colour in the pH range corresponding to the sharp change in pH at the end point, here we need a chemical species which can change colour in the potential range corresponding to the sharp change at the end point. A chemical substance which changes colour when the potential of the solution reaches a definite value is termed an **oxidation-reduction or redox indicator.**

Redox indicators are substances which can be reversibly oxidised or reduced and have different colours in oxidised and reduced forms.

In redox titrations, indicators are used in three different ways. These have already been discussed briefly in Unit 1. Let us recall it here. In certain titrations, e.g., those involving $KMnO_4$, one of the reacting species itself changes colour at the equivalence point and is called a **self indicator**. In some cases the indicator needs to be added to the solution, as phenolphthalein or methyl orange in the case of acid-base titrations, or, diphenylamine in case of chromatometry. Such indicators are called **internal indicators**. In yet some other cases, redox indicator may be replaced by a reagent which is used as a spot test reagent for the ion being determined. Such indicators are not added into the solution but are used externally. At various stages of the titration, a drop of the reaction mixture is taken out and tested for the ion by mixing with the indicator on a porcelain plate. Potassium ferricyanide, $K_3[Fe(CN)_6]$, is an example of

an **external indicator** which is used in the titration of Fe^{2+} ions with dichromate. Having learnt about oxidation/reduction reactions, redox potential and redox indicators, let us now actually do a redox titration.

4.4 EXPERIMENT 5: DETERMINATION OF PERCENTAGE OF IRON IN THE GIVEN IRON FILINGS SOLUTION BY PERMANGANATOMETRY

As said before, potassium permanganate is a good oxidising agent. It is used in a number of titrimetric determinations where the method is known as permanganatometry. One of the most important determinations by this method is titrimetric determination of ferrous iron. A ferrous salt when titrated with $KMnO_4$ is oxidised to a ferric salt. The amount of iron in the unknown solution is easily calculated from the volume of the $KMnO_4$ solution needed for the titration and its molarity. In the next experiment you will use $K_2Cr_2O_7$ for the same purpose.

4.4.1 Principle

Potassium permanganate is an oxidising agent and gets reduced in the presence of a suitable reducing agent as, for example, Fe^{++} in the present case. Its reduction can be brought about in acidic, neutral or alkaline medium. The permanganate ion, MnO_4^-, gets reduced to Mn^{2+} ion in acidic medium as shown in Eq. 4.6, and to MnO_2 in neutral and alkaline media, as shown in Eq. 4.11.

$$\underset{+7\text{ state}}{MnO_4^-} + 8H^+ + 5e \rightleftharpoons \underset{+2\text{ state}}{Mn^{2+}} + 4H_2O, E^\circ = 1.51\text{ V} \quad \text{... (4.6)}$$

$$\underset{+7\text{ state}}{MnO_4^-} + 2H_2O + 3e \rightleftharpoons \underset{+4\text{ state}}{MnO_2} + 4OH^-, E^\circ = 0.57\text{ V} \quad \text{... (4.11)}$$

The oxidising power of permanganate ion is medium dependent; it is related to the change in the oxidation state of manganese in a particular medium.

Usually titrations involving potassium permanganate are carried out in acidic medium. This is due to the higher oxidising power of permanganate ion in acidic medium than in neutral or alkaline medium; secondly, the formation of brown coloured MnO_2 in alkaline medium interferes with the detection of the end point.

While permanganate ion gets reduced, ferrous ion, Fe^{2+} gets oxidised to the ferric ion, Fe^{3+}

$$Fe^{2+} \rightleftharpoons Fe^{3+} + e \quad \text{... (4.5)}$$

The overall ionic equation for the titration in acidic medium can be obtained by adding Eq. 4.5 and Eq 4.6 after balancing the number of electrons between them as follows:

$$[Fe^{2+} \rightleftharpoons Fe^{3+} + e] \times 5 \quad \text{... (4.5)}$$

$$MnO_4^- + 8H^+ + 5e \rightleftharpoons Mn^{2+} + 4H_2O \quad \text{... (4.6)}$$

$$MnO_4^- + 5Fe^{2+}\ 8H \rightleftharpoons 5Fe^{3+} + Mn^{2+} + 4H_2O \quad \text{... (4.7)}$$

We see from Eq. 4.7, that one mole of potassium permanganate reacts with 5 moles of ferrous ions. Therefore, substituting the values of p and q in Eq. 1.8, the molarities are related as per the following equation:

$$\frac{M_{KMnO4}\ V_{KMnO4}}{M_{FeSO4}\ V_{FeSO4}} = \frac{1}{5} \text{ , i.e., } 5\ M_{KMnO4}\ V_{KMnO4} = V_{FeSO4}\ M_{FeSO4} \quad \text{... (4.12)}$$

A slight excess of $KMnO_4$ at the end point imparts a distinct pink colour to the solution and, therefore, acts as a self indicator. The solution of $KMnO_4$ is not stable,

its strength changes on storage. It is, therefore, a secondary standard. You have to standardise it by titrating against a suitable primary standard. A number of primary standards can be used for this purpose. Here you would be using a standard solution of ferrous ammonium sulphate, $FeSO_4(NH_4)_2SO_4.6H_2O$ or Mohr's salt. Mohr's salt is preferred to ferrous sulphate because it has better shelf-life. However, the ionic equations are the same as given for ferrous iron solution, viz., Eq. 4.7. You can use Eq. 4.12 as the molarity equation to find out the molarity of the given $KMnO_4$ solution.

Permanganatometry finds its use also in the estimation of hydrogen peroxide, nitrites and persulphates, etc.

SAQ 2

Write the chemical reaction involving a titration of $KMnO_4$ and $FeSO_4$ solution in presence of dilute H_2SO_4.

[Hint: Two steps are involved in the reaction]

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SAQ 3

Why $KMnO_4$ cannot be taken as a primary standard?

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4.4.2 Requirements

Apparatus	
Burette (50 cm^3)	– 1
Pipette (20 cm^3)	– 1
Conical flasks (250 cm^3)	– 2
Test tube	– 1
Volumetric flask (250 cm^3)	– 1
Beaker (250 cm^3)	– 1
Weighing bottle	– 1
Funnel (small)	– 1
Wash bottle for distilled water	–1
Burette stand	– 1

Chemicals

Ferrous ammonium sulphate $FeSO_4.(NH_4)_2SO_4.6H_2O$, FAS also known as **Mohr's salt.**

Sulphuric acid (1 *M*)

Solutions Provided

Iron filings solution: It is prepared by dissolving 1.2 g of iron filings in about 20 cm^3 of dilute sulphuric acid. A piece of zinc is added to this solution to prevent aerial oxidation of Fe^{2+} to Fe^{3+}. The solution is then transferred to a 1000 cm^3 volumetric flask and made up to the mark by adding distilled water carefully.

Approximately *M*/250 solution of potassium permanganate, prepared by dissolving 0.79 g of potassium permanganate in distilled water and making up the solution to 250 cm^3. It is then stored in a dark place preferably in an amber coloured bottle for a few days. Potassium permanganate solution is stored in dark because light accelerates decomposition of $KMnO_4$ by the reaction given below:

$$4KMnO_4 + 2H_2O \longrightarrow 4MnO_2\downarrow + 4KOH + 3O_2\uparrow$$

Indicator

$KMnO_4$ acts as a self indicator, so no other indicator is required.

4.4.3 Procedure

As indicated above, you are provided with approximately *M*/250 potassium permanganate solution and a solution of ferrous sulphate (prepared from iron filings) which is to be estimated.

You can start your experiment with the standardisation of $KMnO_4$ solution with standard ferrous ammonium sulphate solution.

Preparation of standard ferrous ammonium sulphate solution (concentration = *M*/50).

Take approximate mass of a glass weighing bottle. Then weigh it accurately with about 1.956 g of Mohr's salt. Transfer the salt to a clean and dry volumetric flask of 250 cm^3 capacity through a glass funnel. Find out the accurate mass of the bottle after transferring Mohr's salt. The difference between the two masses gives the actual amount of Mohr's salt transferred. Record these values in your observation note book. To the contents of the volumetric flask add about 10 cm^3 of dilute H_2SO_4 (1*M*) and about 50 cm^3 of distilled water, dissolve the salt completely; add more water, if necessary. Finally, make the volume upto the mark by adding distilled water carefully.

Caution: If the solution turns brownish, then the amount of acid added is not sufficient. Discard this solution. Do the whole exercise again using more H_2SO_4.

Titrations

In case of potassium permanganate it is convenient to use the upper meniscus.

Standardisation of potassium permanganate solution: Fill up the burette with the given $KMnO_4$ solution and mount the burette on a stand; also insert a parallex card. Note the reading in the burette and record it in the observation Table I. Pipette out 20 cm^3 of standard ferrous ammonium sulphate solution into a 250 cm^3 conical flask. Add approximately 10-15 cm^3 of dilute H_2SO_4(1*M*) to the solution. **For this purpose take a test tube and fill it a little more than half with H_2SO_4 and mark its level so that you add the same amount of H_2SO_4 in every titration.**

Titrate ferrous ammonium sulphate solution by slowly adding small amounts of potassium permanganate solution and continuously shaking the conial flask. The pink colour, obtained on addition of $KMnO_4$ solution, disappears on shaking. Continue the titration until a permanent pale pink colour appears. This indicates the end point of the titration. Note the burette reading and record it in observation Table I. The difference of two readings gives a rough estimate of the volume of $KMnO_4$ required.

Repeat the titration to get at least two concordant readings to ensure a correct and exact measurement.

Do not throw the FAS solution left. You will use this for Experiment 6.

Titration of given iron filing's solution against standardised $KMnO_4$ solution: Perform this titration in exactly the same manner as given above by taking the solution prepared from iron filings in place of Mohr's salt solution. Record the readings in observation Table II.

SAQ 4

Can HCl or HNO_3 be used in place of H_2SO_4 for making the medium acidic in a redox titration where $KMnO_4$ is used as an oxidant? Justify your answer.

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4.4.4 Observations

Approximate mass of the weighing bottle = m_1 = ... g
Mass of bottle + ferrous ammonium sulphate (before transferring the salt) = m_2 = ...g
Mass of bottle (after transferring the salt) = m_3 = ... g
Mass of ferrous ammonium sulphate transferred = $m_2 - m_3 = m$ = ... g
Molar mass of ferrous ammonium sulphate = 392.15 g mol^{-1}
Volume of ferrous ammonium sulphate solution prepared (V) = 250 cm^3.

Molarity of ferrous ammonium sulphate solution (M_1)

$$= \frac{m \times 1000}{\text{Molar mass} \times 250} \text{ mol dm}^{-3}$$

$$= \frac{m \times 4}{392.15} \text{ mol dm}^{-3}$$

..... mol dm^{-3}

Observation Table I
Ferrous ammonium sulphate solution vs. potassium permanganate solution

Sl. No.	Volume of FAS solution in cm^3	Burette reading		Volume of $KMnO_4$ in cm^3 (Final − Initial)
		Initial	Final	
1	20			
2	20			
3	20			

Observation Table II
Ferrous iron solution prepared from iron filings vs. potassium permanganate solution

Sl. No.	Volume of Ferrous iron solution in cm^3	Burette reading		Volume of $KMnO_4$ in cm^3 (Final − Initial)
		Initial	Final	
1	20			
2	20			
3	20			

4.4.5 Calculations

Estimation of the strength of potassium permanganate

Molarity of FAS solution = M_1 = ...mol dm^{-3}
Vol. of FAS solution used = V_1 = 20 cm^3
Vol. of $KMnO_4$ solution used (from Table I) = V_2 = ... cm^3
Molarity of $KMnO_4$ solution = M_2 = ?
Using the molarity equation (Eq. 4.12),
$M_1 V_1 = 5M_2 V_2$

Molarity of $KMnO_4$ solution (M_2)

$$= \frac{M_1 V_1}{5 V_2},$$

= ..... mol dm^{-3}

Estimation of strength of ferrous iron solution prepared from iron filings
Molarity of $KMnO_4$ = M_3 = M_2 = ... mol dm^{-3}
Vol. of $KMnO_4$ solution used = V_3 = ... cm^3
Vol. of Fe^{++} solution taken = V_4 = 20 cm^3
Molarity of ferrous iron solution = M_4 = ?

Using the molarity equation,
$M_4 V_4 = 5M_3 V_3$

Molarity of ferrous iron solution

$$M_4 = \frac{5M_3 V_3}{V_4}$$

= ..... mol dm^{-3}

Determination of percentage of iron in iron filings
Mass of iron in 1000 cm^3 = Molarity of the solution × Molar mass of iron of the solution prepared from the iron filings
= M_4 × 55.85 g
= m_4 = ... g

Percentage of Fe in iron filings = $\frac{\text{Estimated mass of iron in iron filings}}{\text{Mass of iron filings}} \times 100$

$$\frac{m_4}{1.2} \times 100$$

= ..... %

4.4.6 Result

The percentage of iron in the sample of iron filings used for preparing the solution = ... %.

The above value can be compared with the actual one which you can get from your counsellor.

4.5 EXPERIMENT 6: DETERMINATION OF THE PERCENTAGE OF IRON IN THE GIVEN IRON FILINGS SOLUTION BY CHROMATOMETRY

In permanganatometry you used potassium permanganate as the oxidising agent to estimate Fe^{2+} ions in the given solution. In chromatometry, potassium dichromate is used for the same purpose. Dichromate acts as an oxidising agent only in the acidic medium. The general theory behind chromatometry is the same as for permanganatometry. The only difference being that while $KMnO_4$ acts as a self indicator, an indicator has to be used in chromatometry. The relevant equations along with the potentials are given below as well as the chemistry involved in the colour changes that the indicator undergoes.

4.5.1 Principle

Potassium dichromate is an oxidising agent and in acidic medium reacts according to the following half-reaction to give chromium (III) as the reduction product.

$$\underset{\text{(Cr in +6 state)}}{Cr_2O_7^{2-}} + 14H^+ + 6e \rightleftharpoons \underset{\text{(Cr in +3 state)}}{2Cr^{3+}} + 7H_2O \ (E^\circ = 1.33 \text{ V}) \quad \text{... (4.13)}$$

Fe^{2+} when titrated with dichromate gets oxidised to Fe^{3+} as per the following equation:

$$Fe^{2+} \rightleftharpoons Fe^{3+} + e \ (E^\circ = 0.77 \text{ V}) \quad \text{... (4.5)}$$

The overall ionic equation of the titration can be obtained by adding Eq. 4.12 and Eq. 4.5 after balancing the number of electrons between them as follows:

$$[Fe^{2+} \rightleftharpoons Fe^{3+} + e] \times 6 \quad \text{... (4.5)}$$

$$Cr_2O_7^{2-} + 14H^+ + 6e \rightleftharpoons 2Cr^{3+} + 7H_2O \quad \text{... (4.13)}$$

$$\boxed{Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \longrightarrow 6Fe^{3+}\ 2Cr^{3+} + 7H_2O} \quad \text{... (4.14)}$$

We see from Eq. 4.14, that one mole of potassium dichromate reacts with 6 moles of iron (II) in solution. Therefore, substituting the values of p and q in Eq. 1.8, the molarities are related by the following equation:

$$\frac{M_1 V_1}{M_2 V_2} = \frac{6}{1}$$

or $M_1 V_1 = 6 M_2 V_2$ ...(4.15)

Where M_1 and M_2 represent the molarities of iron (II) and potassium dichromate solutions, then V_1 and V_2 represent their volumes, respectively.

As you know, the factor 6 signifies that each mole of potassium dichromate reacts quantitatively with 6 moles of iron (II).
1 mole $K_2Cr_2O_7$ = 6 moles Fe(II)

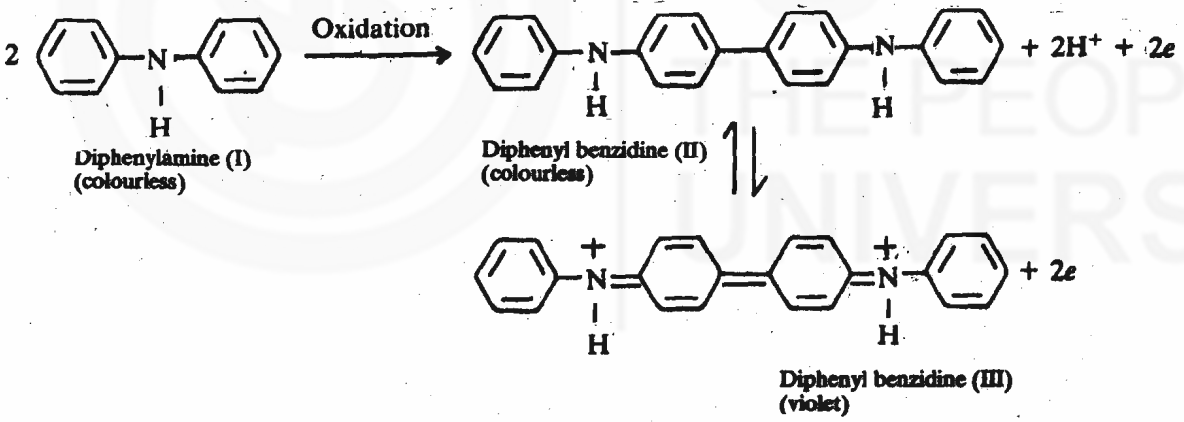
Potassium dichromate does not oxidise HCl, whereas $KMnO_4$ oxidises it to Cl_2. Hence, $KMnO_4$ cannot be used as an oxidising agent in estimating metal ions where the solution is made using HCl, whereas $K_2Cr_2O_7$ can be used in such cases too. Since metals are leached out from their minerals with HCl in many cases, chromatometry is the preferred technique of estimation in such cases.

Indicator

A dilute solution of $K_2Cr_2O_7$ has a faint orange colour and chromium (III) obtained as the reduction product is green in colour. So, a drop of $K_2Cr_2O_7$ in excess at the end point, unlike $KMnO_4$, is not sufficient to give a distinct colour to the solution. Further, the green colour of chromium (III) ions produced also interferes, therefore, $K_2Cr_2O_7$ cannot be used as a self indicator.

A redox indicator must, therefore, be used. Diphenylamine was one of the first internal redox-indicators used in this titration. However, as it is sparingly soluble in water, sodium salt of diphenylamine sulphonic acid can be used instead, as it is water soluble. These indicators are colourless in the reduced form and become intensely coloured on oxidation (deep blue-violet with diphenylamine; red-violet with sodium diphenylamine sulphonate).

At potentials lower than 0.73 V, iron is in +2 state and the indicator is present in form I which is colourless. In the course of the titration, when Fe^{2+} gets converted to Fe^{3+}, the potential increases gradually (cf. Eq. 4.8). At equivalence point all the ferrous ions are oxidised and as discussed earlier, at this stage there is a jump in the potential. This increase in the redox potential of the solution is sufficient to cause the oxidation of the indicator to form II. Form II gets readily converted into form III, which has a distinct colour and marks the end point. The above description about the indicator can be represented as shown below:



SAQ 5

a) Write the chemical reaction involving a titration of $K_2Cr_2O_7$ and $FeSO_4$ solution in presence of dilute H_2SO_4.
[Hint: The reaction involves two steps]

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b) Explain why $K_2Cr_2O_7$ reacts as an oxidising agent only in the acidic medium.

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SAQ 6

In the following tick √ on the correct and × on the wrong statements.
$K_2Cr_2O_7$ is superior to $KMnO_4$ because:

i) $K_2Cr_2O_7$ is more stable than $KMnO_4$ both in the dry state as well as in solution.

ii) A solution of $K_2Cr_2O_7$ is not intensely coloured.

iii) $K_2Cr_2O_7$ is not reduced by cold HCl if acid concentration does not exceed 1 or 2 *M*.

iv) $K_2Cr_2O_7$ can be easily weighed.

4.5.2 Requirements

Apparatus

Burette (50 cm^3) – 1
Pipette (20 cm^3) – 1
Conical flask (250 cm^3) – 1
Beaker (250 cm^3) – 1
Weighing bottle – 1
Funnel (small) – 1
Volumetric flask (250 cm^3) – 1
Wash bottle for distilled water – 1
Burette stand – 1

Chemicals

Ferrous ammonium sulphate, FAS (Mohr's salt)
Sulphuric acid, dilute (1*M*)
Phosphoric acid (85%)

Solutions Provided

Iron filings solution: As for the previous experiment, it is prepared by dissolving 1.2 g of iron filings in about 20 cm^3 of dilute H_2SO_4. A piece of zinc is added to this solution to prevent aerial oxidation of Fe^{2+} to Fe^{3+}. The solution is then transferred to a 1000 cm^3 volumetric flask and made up to the mark by adding distilled water carefully.

Approximately ***M*/300 solution of potassium dichromate,** prepared by dissolving 0.245 g of potassium dichromate in distilled water and making up the volume to 250 cm^3.

Diphenylamine (1%) solution in concentrated sulphuric acid or sodium diphenylamine sulphonate (0.2% aqueous solution).

4.5.3 Procedure

Potassium dichromate, as mentioned earlier, can be used as a primary standard which means that a standard solution of dichromate can be made by weighing an exact amount of the substance, dissolving it in water and making up to the known volume with distilled water. However, in this particular experiment, we are provided with solution of $K_2Cr_2O_7$, the molarity of which has to be found by titrating with a standard ferrous ammonium sulphate salt solution.

Standard ferrous ammonium sulphate solution (concentration = *M*/50) prepared in the previous experiment can be used here.

Titrations

Standardisation of potassium dichromate solution: Pipette out 20 cm^3 aliquot of standard ferrous ammonium sulphate solution into a 250 cm^3 conical flask. Add approximately 20 cm^3 of dilute sulphuric acid (1*M*), 5 cm^3 of phosphoric acid and 5 to 10 drops of the indicator solution. Titrate this with the dichromate solution. As the titration proceeds, the colour changes to a pale green, then to a greyish blue-green and with one drop to a persistent deep blue-violet colour of the indicator in the oxidised form. Record the volume of the titrant accurately.

Phosphoric acid combines with yellow Fe^{3+} ions to form $[Fe(HPO_4)]^+$ rendering the end point more visible.

Repeat the titration to get at least two concordant readings to ensure a correct and exact measurement. Record the observations in observation Table I.

Titration of the given iron (II) solution against standardised $K_2Cr_2O_7$ solution: Perform this titration exactly in the same manner as in the above experiment by taking the given iron (II) solution instead of ferrous ammonium sulphate solution. Record the observations in observation Table II.

4.5.4 Observations

Molarity of ferrous ammonium sulphate solution (M_1) as calculated in Exp. 5 = ... mol dm^{-3}

Observation Table I
Ferrous ammonium sulphate solution vs potassium dichromate solution

Sl. No.	Volume of FAS in cm^3	Burette reading		Volume of $K_2Cr_2Cr_2O_7$ in cm^3 (Final − Initial)
		Initial	Final	
1	20			
2	20			
3	20			

Observation Table II
Given Iron (II) solution prepared from iron filings vs potassium dichromate solution

Sl. No.	Volume of Ferrous iron solution in cm^3	Burette reading		Volume of $K_2Cr_2O_7$ in cm^3 (Final − Initial)
		Initial	Final	
1	20			
2	20			
3	20			

4.5.5 Calculations

Estimation of strength of $K_2Cr_2O_7$

Molarity of FAS solution = M_1 = ... mol dm^{-3}
Volume of FAS solution used = V_1 = 20 cm^3
Volume of $K_2Cr_2O_7$ solution used (from Table I) = V_2 = ... cm^3
Molarity of $K_2Cr_2O_7$ solution = M_2 = ?
Using the molarity equation,

$$M_1 V_1 = 6M_2 V_2$$

Molarity of $K_2Cr_2O_7$

$$M_2 = \frac{M_1 V_1}{6 V_2}$$

= ..... mol dm^{-3}

Estimation of strength of Iron (II) solution prepared from iron filings

Molarity of $K_2Cr_2O_7$ solution = M_3 = M_2 = ... mol dm^{-3}
Volume of $K_2Cr_2O_7$ solution used = V_3 = ... cm^3
Volume of iron (II) solution taken = V_4 = 20 cm^3
Molarity of iron (II) solution = M_4 = ?

Using the molarity equation

$$M_4 = \frac{6M_3 V_3}{V_4}$$

Molarity of Fe(II)

M_4 = ... mol dm^{-3}

Determination of percentage of iron in iron filings

Mass of iron in 1000 cm^3 (1 dm^3) = Molarity of the solution × Molar mass of iron of the solution prepared from iron filings

= $M_4 \times 55.85 = m_4$
= ..... g

$$\text{Percentage of iron in iron filings} = \frac{\text{Estimated mass of iron filings}}{\text{Mass of iron filings}} \times 100$$

$$= \frac{m_4}{1.2} \times 100$$

= ..... %.

4.5.6 Result

The percentage of iron in the sample of iron filings used for preparing the solution = ... %.

The above value can be compared with the actual one which you can get from your counsellor. Since in both permanganatometry and chromatometry experiments, you have used the same iron solution, compare the difference in two results obtained. The two results should be almost the same if the weighing is accurate and the titration error is not much. If the difference is more, then discuss the reasons for the difference with your counsellor.

4.6 ANSWERS TO SAQs

1) i) $H_2 \longrightarrow 2H^+ + 2e$
   ii) $S^{2-} \longrightarrow S + 2e$
   iii) $Cl_2 + 2e \longrightarrow 2Cl^-$
   iv) $Cu^+ \longrightarrow Cu^{2+} + e$
   v) $O_2 + 2e \longrightarrow 2O^{2-}$

2) $2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$

$[2FeSO_4 + H_2SO_4 + (O) \longrightarrow Fe_2(SO_4)_3 + H_2O] \times 5$

$2KMnO_4 + 10FeSO_4 + 8H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O$

3) $KMnO_4$ is not pure and always contains some of its reduction products such as MnO_2; also it is easily decomposed by reducing agents present in H_2O.

4) HCl acts as a reducing agent, itself getting oxidised to Cl_2; and HNO_3 acts as an oxidising agent again competing with the action of $KMnO_4$. Therefore, neither of these can replace H_2SO_4.

5) a) $K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3[O]$

$[2FeSO_4 + H_2SO_4 + (O) \longrightarrow Fe_2(SO_4)_3 + H_2O] \times 3$

$K_2Cr_2O_7 + 6FeSO_4 + 7H_2SO_4 \longrightarrow 3Fe_2(SO_4)_3 + Cr_2(SO_4)_3 + K_2SO_4 + 7H_2O$

   b) In presence of an alkali, potassium dichromate reacts to give chromate salt and cannot act as an oxidising agent.

6) i) ✓
   ii) ×
   iii) ✓
   iv) ×

UNIT 5 ESTIMATION OF COPPER

Structure

5.1 INTRODUCTION

In the previous unit, you have estimated the amount of ferrous iron, Fe^{2+}, in a sample of iron filings by using two redox titrations, namely, permanganatometry and chromatometry. In this unit, we would estimate the amount of copper in a given sample. Here too, you would perform two experiments, one of which is based on a redox reaction, iodometry, while the other is based on colorimetric determination. Iodometric titrations make use of I_2/I^- redox reaction and the end point is detected by using starch as an indicator. Colorimetry, on the other hand, is a method of analysis based on comparing the colour intensity of an unknown with that of a standard solution, i.e., the solution of a definite known concentration. The theory behind iodometric and colorimetric determination of cupric ions, Cu^{2+} is given along with the procedural details of the experiments.

Objectives

After studying this unit and performing the experiments, you will be able to:

- define and differentiate between iodometry and iodimetry,
- explain the redox reactions involved in iodometry,
- explain the use of indicator in iodometry and standardise the given sodium thiosulphate solution,
- use the iodometric method in estimating Cu^{2+} ions,
- state Beer-Lambert law,
- explain the principle of colorimetry,
- describe the colorimeter and its calibration, and
- use the colorimetric method in estimating Cu^{2+} ions.

5.2 IODIMETRY AND IODOMETRY

Iodine is a mild oxidising agent and in the presence of a suitable reducing agent, gets reduced to iodide ions, I^-, according to the following equation:

$$I_2 + 2e \rightleftharpoons 2I^-, \quad E^0 = 0.54V \qquad \ldots(5.1)$$

Iodimetric titrations are used for estimating reducing agents while iodometric titrations are used for oxidising agents.

Iodimetry: Titration with iodine
Iodometry: Titration of iodine produced by a chemical reaction

On the other hand, a variety of oxidising agents can oxidise I^- ions into I_2. In fact, both these reactions are made use of in analytical chemistry. Titrations involving the use of I_2 as a titrant to estimate the reducing agents are termed as **iodimetric titrations**. Iodine, being a much weaker oxidising agent than potassium permanganate and potassium dichromate, has limited applicability. Moreover, it is very volatile in nature and also has poor solubility.

In certain cases, the oxidising agent to be determined is mixed with an excess of potassium iodide, KI, and kept for some time. The iodine, liberated during the reaction, is titrated against a standard solution of a reducing agent, e.g., sodium thiosulphate, $Na_2S_2O_3$. These titrations are referred to as **iodometric titrations**. Since Cu^{2+} ions, can behave as an oxidising agent by getting reduced to Cu^+ ions, we can use iodometric method for their determination.

Ideally an iodometric titration should be a titration using KI as a titrant to titrate the oxidising agent. In such a reaction, more and more of iodine is liberated from iodide ions as the titration proceeds. The end point of such a titration would be a stage where the liberation of iodine ceases. It is impossible to detect this end point with the help of an indicator. Starch can be used to detect the 'just appearance' or the 'just disappearance' of iodine but not the cessation of I_2 formation.

An indirect method of end point determination becomes essential in such cases. A known amount of the solution of the oxidising agent (to be determined) is measured and mixed with an excess of a solution of KI and acid. The solution is then left for about five minutes in the dark for the reaction to complete and the liberated iodine is titrated with a standardised solution of sodium thiosulphate using starch as the indicator. The following reaction takes place:

$$I_2 + 2Na_2S_2O_3 \rightleftharpoons 2NaI + Na_2S_4O_6 \qquad ...(5.2)$$

An excess of KI is used because iodine has got very poor solubility in water. Iodine forms an unstable complex, KI_3, with KI which is readily soluble in H_2O.

$$KI + I_2 \rightleftharpoons K[I_3]$$

In fact, iodine in an aqueous solution containing KI exists mainly as the triiodide ion, I_3^- and there is an equilibrium between I_3^- ion and I_2. In the course of the titration, as I_2 is consumed, more and more of I_3^- ions dissociate to give I_2 which reacts with thiosulphate. Further, such a titration should be carried out in cold, as I_2 is volatile and also the indicator, starch, loses its sensitivity at high temperatures.

SAQ 1

Give two limitations of I_2 as a titrant.

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5.2.1 Indicator

In principle, iodine can be used as a self indicator like $KMnO_4$, as a drop of iodine can impart a pale yellow colour to a solution. Since the colour imparted by iodine is quite faint, in practice, it becomes difficult to use this as an indication of the end point. Iodine is known to form a blue coloured adsorption complex with starch. This property of starch is exploited in using it as an indicator for titrations involving iodine.

The use of starch enhances the sensitivity of the determination of the end point.

In an iodometric determination, we titrate I_2 with $S_2O_3^{2-}$ ions and at the end point, addition of one drop of $S_2O_3^{2-}$ ions should just decolourise the blue colour of starch-iodine complex. In such titrations, starch should be added just before the end point, when a very little amount of I_2 remains and the solution being titrated has a faint straw yellow colour. If starch is added earlier, i.e., when a large amount of iodine is present, a large amount of starch-iodine complex is formed. This complex reacts quite slowly with $S_2O_3^{2-}$ and it is likely that the solution is over titrated.

5.2.2 Standardisation of Thiosulphate

As said above, in iodometry we titrate the liberated iodine with a standardised solution of sodium thiosulphate. Though sodium thiosulphate, $Na_2S_2O_3.5H_2O$, can be obtained chemically pure, a standard solution of thiosulphate cannot be made by exact weighing. This is because thiosulphate reacts with atmospheric O_2 and also the CO_2 dissolved in water. More so, even some microorganisms decompose thiosulphate.

A number of oxidising agents are available for the standardisation of $Na_2S_2O_3$. Potassium dichromate is normally used for the purpose.

In acidic medium $Cr_2O_7^{2-}$ ion gets reduced to Cr (III) as shown in the following equation :

$$Cr_2O_7^{2-} + 14H^+ + 6e \rightleftharpoons 2Cr^{3+} + 7H_2O \quad ...(5.3)$$

and iodide ions from KI get oxidised to I_2:

$$2I^- \rightleftharpoons I_2 + 2e$$

To maintain electron balance, multiplying the above equation by 3, we get,

$$6I^- \rightleftharpoons 3I_2 + 6e \quad ...(5.4)$$

The overall ionic equation for the titration can be obtained by adding Eq.5.3 and Eq. 5.4,

$$Cr_2O_7^{2-} + 14H^+ + 6I^- \longrightarrow 2Cr^{3+} + 3I_2 + 7H_2O \quad ...(5.5)$$

We see from Eq. 5.5 that one mole of potassium dichromate reacts with 6 moles of potassium iodide liberating 3 moles of iodine.

The liberated iodine, in turn, reacts with sodium thiosulphate solution as,

$$2S_2O_3^{2-} \rightleftharpoons S_4O_6^{2-} + 2e \quad ...(5.6)$$

$$I_2 + 2e \rightleftharpoons 2I^- \quad ...(5.1)$$

Since three moles of I_2 are liberated by $Cr_2O_7^{2-}$,

$$3I_2 + 6e \rightleftharpoons 6I^- \quad ...(5.7)$$

The overall ionic equation for the titration of liberated I_2 with sodium thiosulphate can be obtained by adding Eq. 5.6 and Eq. 5.7,

$$[2S_2O_3^{2-} \rightleftharpoons S_4O_6^{2-} + 2e] \times 3 \quad ...(5.6)$$

$$3I_2 + 6e \rightleftharpoons 6I^- \quad ...(5.7)$$

$$3I_2 + 6S_2O_3^{2-} \longrightarrow 6I^- + 3S_4O_6^{2-} \quad ...(5.8)$$

The net chemical reaction involving a titration of potassium dichromate and sodium thiosulphate in the presence of excess potassium iodide can be written by combining Eq. 5.5 and Eq. 5.8,

$$Cr_2O_7^{2-} + 14H^+ + 6I^- \longrightarrow 2Cr^{3+} + 3I_2 + 7H_2O \quad ...(5.5)$$

$$3I_2 + 6S_2O_3^{2-} \longrightarrow 6I^- + 3S_4O_6^{2-} \quad ...(5.8)$$

$$Cr_2O_7^{2-} + 14H^+ + 6S_2O_3^{2-} \longrightarrow 2Cr^{3+} + 3S_4O_6^{2-} + 7H_2O \quad ...(5.9)$$

We see from Eq. 5.9 that one mole of potassium dichromate is equivalent to 6 moles of sodium thiosulphate. Therefore, substituting the values of p and q in Eq.1.8, the molarities are related by the following relationship.

$$\frac{M_1 V_1}{M_2 V_2} = \frac{6}{1}$$

or $M_1 V_1 = 6M_2V_2$

where M_1 and M_2 represent the molarities of sodium thiosulphate and potassium dichromate solutions and V_1 and V_2 represent the volumes of sodium thiosulphate and potassium dichromate solutions respectively.

Factor '6' here signifies that one mole of $K_2Cr_2O_7$ liberates 3 moles of I_2 which is equivalent to 6 moles of sodium thiosulphate.

5.3 EXPERIMENT 7 : DETERMINATION OF PERCENTAGE OF COPPER IN THE GIVEN SOLUTION BY IODOMETRIC METHOD

Many a time, an analytical chemist is confronted with the problem of finding out the amounts of some metals, e.g., Fe, Cu, etc. in a given sample. The sample may be of an ore or an alloy. Let us see how we carry out such an estimation for Cu in a given sample. We can do this by iodometric titrations. As said before, like permanganatometry and chromatometry, this titration is also based on a redox reaction.

To determine the amount of Cu in a given sample, a known mass of it is dissolved by suitable chemical treatment giving a solution of Cu^{2+} ions. This solution is titrated against a standard solution of sodium thiosulphate in the presence of an excess of KI. The Cu^{2+} ions on reacting with KI get reduced to Cu^{+} ions and liberate an equivalent amount of I_2 by oxidising I^- ions. This liberated iodine then reacts quantitatively with $S_2O_3^{2-}$ ions, and in turn, gets reduced to I^- ions. The principle and the equations involved are given in the next sub-section.

5.3.1 Principle

The reaction between Cu^{2+} and $Na_2S_2O_3$ in acidic medium, in the presence of excess of KI, involves oxidation of $S_2O_3^{2-}$ to $S_4O_6^{2-}$, tetrathionate ion, and reduction of Cu^{2+} to Cu^{+}. The reaction between Cu^{2+} and KI is given as,

$$2I^- \rightleftharpoons I_2 + 2e \quad \text{...(5.10)}$$
$$Cu^{2+} + e \rightleftharpoons Cu^{+} \quad \text{...(5.11)}$$

Balancing the reaction between Cu^{2+} and potassium iodide by combining Eq. 5.10 and Eq. 5.11, we get,

$$2I^- \rightleftharpoons I_2 + 2e \quad \text{...(5.10)}$$
$$[Cu^{2+} + e \rightleftharpoons Cu^{+}] \times 2 \quad \text{...(5.11)}$$
$$2Cu^{2+} + 2I^- \longrightarrow 2Cu^{+} + I_2 \quad \text{...(5.12)}$$

We see that two moles of Cu^{2+} react with two moles of potassium iodide and the liberated iodine reacts with sodium thiosulphate, shown earlier also, in the following manner:

$$2S_2O_3^{2-} \rightleftharpoons S_4O_6^{2-} + 2e \quad \text{...(5.6)}$$
$$I_2 + 2e \rightleftharpoons 2I^- \quad \text{...(5.7)}$$
$$I_2 + 2S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-} \quad \text{...(5.8)}$$

The net chemical reaction involving a titration of copper (II) and sodium thiosulphate in the presence of excess potassium iodide can be written by combining Eq. 5.12 and Eq. 5.8.

$$2Cu^{2+} + 2I^- \longrightarrow 2Cu^{+} + I_2 \quad \text{...(5.12)}$$
$$I_2 + 2S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-} \quad \text{...(5.8)}$$
$$2Cu^{2+} + 2S_2O_3^{2-} \longrightarrow 2Cu^{+} + S_4O_6^{2-} \quad \text{...(5.13)}$$

We see from Eq. 5.13, that two moles of copper (II) are equivalent to two moles of sodium thiosulphate. In other words one mole of copper (II) is equivalent to one mole of sodium thiosulphate.

Therefore, substituting the values of p and q in Eq. 1.8, the molarities are related by the following relationship :

$$\frac{M_3\ V_3}{M_4\ V_4} = \frac{1}{1}$$

or $M_3 V_3 = M_4 V_4$

where M_3 and M_4 represent the molarities of sodium thiosulphate and copper (II) solutions, and V_3 and V_4, the volumes of sodium thiosulphate and copper (II) solutions, respectively.

According to the above discussion, the iodometric determination of Cu^{2+} ions is based on the following reaction :

$$2Cu^{2+} + KI \longrightarrow 2CuI + 4K^+ + I_2 \quad \text{...(5.14)}$$
(excess)

where cupric ions are reduced to cuprous ions and iodide ions are oxidised to iodine. A look at the standard reduction potentials of Cu^{2+}/Cu^+ and I_2/I^- couples :

$$Cu^{2+} + e \rightleftharpoons Cu^+ \qquad E^0 = 0.17\ V \quad \text{...(5.15)}$$

$$I_2 + 2e \rightleftharpoons 2I^- \qquad E^0 = 0.54\ V \quad \text{...(5.1)}$$

suggests that the reaction represented by Eq. 5.14 should proceed in the reverse direction, i.e. iodine should oxidise Cu^+ to Cu^{2+}, but actually the reaction occurs as given in Eq. 5.14. The CuI formed during the reaction has a very low solubility in water, therefore, the concentration of the reduced form, Cu^+, is greatly reduced and the potential of Cu^{2+}/Cu^+ couple becomes greater than that of $I_2/2I^-$. This explains the actual course of reaction.

SAQ 2

Write the chemical equations involving a titration of copper (II) with thiosulphate in presence of excess KI.

[Hint : It involves two steps]

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5.3.2 Requirements

Apparatus

Burette (50 cm^3) – 1
Pipette (20 cm^3) – 1
Conical flasks (250 cm^3) – 1
Beaker (250 cm^3) – 2
Funnel (small) – 1
Volumetric flask (250 cm^3) – 1
Measuring cylinder (10 cm^3) – 1
Test Tube – 1
Wash bottle for distilled water – 1
Weighing bottle – 1
Volumetric flask (1000 cm^3) – 1
Burette stand – 1

Chemicals

Potassium dichromate
Dilute sulphuric acid
Potassium iodide
Glacial acetic acid
Potassium thiocyanate
Distilled water

Solutions Provided

Procedures for the preparation of these solutions are given for the sake of information. These solutions would be prepared for you by the counsellor.

Preparation of solution of Cu^{2+} ions from Cu wire

Some clean copper wire is taken. If tarnished, it is cleaned first with fine emery cloth, or rinsed with dilute sulphuric acid, washed well with water, and dried before weighing. An amount of 1.5 g of the wire is weighed and placed in a 250 cm^3 conical flask. Then 5-10 cm^3 of 6*M* nitric acid is added. If the reaction is slow to start, a few drops of concentrated nitric acid are added. If the reaction goes too fast, a small watch glass is put over the top of the flask to catch the spray. The copper wire is dissolved by warming the solution on a water bath over a low flame. When all the copper has dissolved, the solution is diluted with about 50 cm^3 water and boiled gently for 10 minutes to remove oxides of nitrogen. Then 1 g of urea is added and the solution boiled for five minutes. The solution is cooled to room temperature and neutralised with 1:3 ammonia solution adding ammonia carefully, mixing well, until a faint permanent light blue precipitate of $Cu(OH)_2$ appears. In case the solution becomes deep blue on addition of ammonia, the latter is boiled off. Then glacial acetic acid is added a drop at a time, until the precipitate is dissolved and the solution is clear. The solution is transferred to a 1000 cm^3 volumetric flask, made up to the mark with distilled water, and shaken well to get a homogeneous solution.

Sodium thiosulphate solution (approx. *M*/50)

About 5g of sodium thiosulphate crystals are dissolved in 1dm^3 of water that has

been recently boiled and cooled. An amount of 0.2 g of sodium bicarbonate is added as a preservative and the solution stored in a clean bottle. Sodium thiosulphate solutions are somewhat unstable. Apart from oxygen and dissolved CO_2 they are easily attacked by air-borne bacteria with the liberation of sulphur. In case any turbidity is observed, the solution should be discarded.

Starch Solution: About 150 cm^3 distilled water is heated to boiling in a beaker. While this is being heated, 0.5 g to 1 g of soluble starch is stirred with about 10 cm^3 of distilled water to give a paste. The paste is stirred into the boiling water and boiled gently for a few minutes and cooled. The solution should be almost clear. It is kept in a stoppered bottle. (Starch solution should be freshly prepared before use).

Potassium Iodide Solution: Prepared by dissolving 5.0 g KI in 100 cm^3 of distilled water.

5.3.3 Procedure

Preparation of standard potassium dichromate solution: Prepare this solution using the same procedure as given in Experiment 6.

Standardisation of sodium thiosulphate solution

Pipette 20 cm^3 of potassium dichromate solution in a 250 cm^3 conical flask, add 10 cm^3 of dilute sulphuric acid and 1 g sodium hydrogen carbonate with gentle swirling to liberate carbon dioxide. Sodium hydrogen carbonate maintains an atmosphere of CO_2 in the solution which displaces the air and prevents the oxidation of iodide from air. The reaction $4I^- + O_2 + 4H^+ \rightleftharpoons 2I_2 + 2H_2O$ is catalysed by light, heat and acids. Then add 0.5 g potassium iodide or 10 cm^3 of 5% KI solution, swirl, cover the flask with a watch glass and allow the solution to stand for 5 minutes in a dark place. Titrate against sodium thiosulphate solution from the burette until a light pale yellow colour of iodine appears. Then add 2 cm^3 starch solution and continue to titrate until the blue colour of starch-iodine complex disappears on addition of a drop of the titrant. The final solution will be green coloured because of the presence of chromium (III) ions. Record the burette readings before and after the titration in observation Table I. Repeat the same exercise to get at least two concordant readings.

Titration of Copper (II) Solution

After standardising sodium thiosulphate solution, you can titrate the solution containing Cu^{2+} ions. For this, pipette out 20 cm^3 aliquot into a 250 cm^3 conical flask, and add 0.5 g solid potassium iodide or 10 cm^3 of 5% KI solution, swirl it to dissolve; then titrate with the standardised sodium thiosulphate which is taken in a burette. When the brown colour of iodine becomes pale yellow, add 2 cm^3 of fresh starch solution. The colour of the solution at this stage is deep blue. Swirl the flask for about 15 seconds and complete the titration adding sodium thiosulphate solution dropwise. During the titration, as CuI is formed, it absorbs I_3^- on the surface, as a result the reaction of I_2 with $Na_2S_2O_3$ titrant is very slow. Therefore, very close to the end point, when the colour is very light blue, add 1 g potassium thiocyanate, KSCN. Thiocyanate added at this stage reacts with CuI and forms CuSCN displacing iodine from the surface, making it available for the reaction.

$$CuI + SCN^- \rightleftharpoons CuSCN + I^-$$

However, if thiocyanate is added earlier during the titration, it will be slowly oxidised to sulphate by iodine. At the end point, the blue colour of the solution disappears and the precipitate appears white, or slightly grey, when allowed to settle. After standing for a couple of minutes at the end point, the precipitate should become pure white. Record the burette readings in observation Table II. Repeat the same exercise to get at least two concordant readings.

SAQ 3

During iodometric titrations, starch is added only towards the end of the titration. Why?

.....

.....

.....

SAQ 4

Why is sodium hydrogen carbonate or sodium bicarbonate added in the standardisation of sodium thiosulphate using potassium dichromate as titrand?

.....

.....

.....

5.3.4 Observations

Mass of the weighing bottle	=	m_1 = ... g
Mass of bottle + potassium dichromate crystals	=	m_2 = ... g
Mass of the bottle (after transferring $K_2Cr_2O_7$)	=	m_3 = ... g
Mass of potassium dichromate transferred	=	$m_2 - m_3 = m$ = ... g
Molar mass of potassium dichromate	=	294.19 g mol^{-1}
Volume of $K_2Cr_2O_7$ prepared (V)	=	250 cm^3
Molarity of $K_2Cr_2O_7$ solution	=	M_1
	=	$\frac{m \times 4}{\text{Molar mass}}$ mol dm^{-3}
	=	$\frac{m \times 4}{294.19}$
	=	..... mol dm^{-3}

Observation Table I
Potassium dichromate solution vs. sodium thiosulphate solution

Sl. No.	Volume of $K_2Cr_2O_7$ solution in cm^3	Burette reading		Volume of $Na_2S_2O_3$ solution in cm^3 (Final − Initial)
		Initial	Final	
1	20			
2	20			
3	20			

Observation Table II
Sodium thiosulphate solution vs. copper (II) solution prepared from copper wire

Sl. No.	Volume of Copper (II) solution in cm^3	Burette reading		Volume of $Na_2S_2O_3$ solution in cm^3 (Final − Initial)
		Initial	Final	
1	20			
2	20			
3	20			

5.3.5 Calculations

Estimation of the strength of sodium thiosulphate solution

Molarity of $K_2Cr_2O_7$ solution = M_1 = ... mol dm^{-3}
Volume of $K_2Cr_2O_7$ solution = V_1 = 20 cm^3
Volume of $Na_2S_2O_3$ solution used = V_2 = ... cm^3
(From Table I)
Molarity of $Na_2S_2O_3$ solution = M_2 = ?
Using the molarity equation,

$$6M_1V_1 = 6M_2V_2$$

Molarity of $Na_2S_2O_3$ solution = $M_2 = \frac{6M_1V_1}{6V_2}$

= ..... mol dm^{-3}

Estimation of the strength of Copper (II) solution prepared from copper wire

Molarity of $Na_2S_2O_3$ solution = $M_3 = M_2$ = ... mol dm^{-3}
Volume of $Na_2S_2O_3$ solution used = V_3 = ... cm^3
Volume of copper (II) solution taken = V_4 = 20 cm^3

Molarity of copper (II) solution = M_4 = ?
Using molarity equation $M_4V_4 = M_3V_3$,

$$\text{Molarity of copper (II) solution} = M_4 = \frac{M_3V_3}{V_4}$$

$$= \text{.....} \text{ mol dm}^{-3}$$

Determination of the amount of copper present in copper wire

Mass of copper present in 1 dm^3 of the solution prepared from copper wire = Molarity of the solution × atomic mass of copper

$$= M_4 \times 63.5 = m_4 = \text{.....} \text{ gdm}^{-3}$$

$$\% \text{ of Cu} = \frac{m_4}{1.5} \times 100$$

$$= \text{.....} \%$$

5.3.6 Result

The percentage of copper in the given copper wire = ...%. You can compare the above value with the actual one which you can get from your counsellor.

5.4 COLORIMETRY

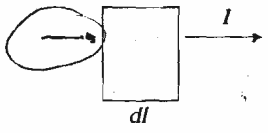
Colorimetry is based on the measurement of the intensity of colour to find the concentration of a given solution. Intensity of the colour depends on the concentration of the species which may be ions, molecules or a complex causing it. The species to be determined may possess an intrinsic capacity to impart colour to the solution or it may give a distinct colour on being complexed with a suitable reagent.

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,

$I_o = I_a + I_t$

where,

I_o = 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 by **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,

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

where,

k = proportionality constant
l = thickness

Rearranging, we get,

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

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

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

or

$$\log_{10} \frac{I_o}{I} = \frac{kl}{2.303}$$

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

$\log_{10} \frac{I_o}{I}$ 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 is directly proportional to the intensity of the incident light.

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

Rearranging, we get,

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

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

$\log_e I/I_o = -kc$

or $\log_{10} I_o/I = \frac{kc}{2.303} = Kc$

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

K = **absorption coefficient**

As you can see $K = k$

5.4.1 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 and the concentration of the absorbing species. Solving the mathematical expression similar to the one in Lambert's law and Beer's law, we get,

$$A = \varepsilon cl \qquad \text{...(5.16)}$$

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, 1M, placed in a cell of unit thickness, 1 cm. Absorbance is also called **optical density (OD).**

According to Eq. 5.16, 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 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.

There are a number of instruments in which a colorimetric determination can be made. We will make use of a simple instrument called colorimeter. 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 is briefly given here. Before going over to that try the following SAQ.

SAQ 5

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

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

5.4.2 Principle of Colorimeter

Generally one determines the intensity of a given colour by the use of one's eyes, i.e. we have a visual estimate of the colour. We can compare two colours and within the limits of human error we may differentiate between the deeper and the lighter colour. But it is difficult to quantify colour **VISUALLY**. For this we need the help of a measuring device. A photoelectric colorimeter is such a device. This, too, gives an indirect estimate. It does not measure the colour, rather it measures the amount of light which comes out after passing through the solution. Knowing the initial intensity of light, we can work out the amount of light absorbed.

A colorimeter consists essentially of a light source, a cell/cuvette for holding the solution, a photoelectric cell to capture the radiation transmitted by the solution and a measuring device to detect the response of a photocell.

A schematic diagram is given in Fig. 5.1. There are three light emitting diodes (LEDs) in the colorimeter which you are going to use. These emit light of different colours. You would be using one of them depending on the colour of absorbing medium. The light from the source is made to pass through a slit so that we get a thin ray, which falls on the cell containing the solution. Some of the light is absorbed and the rest is transmitted. The transmitted light falls on the photocell where a current is generated, whose magnitude is proportional to the intensity of the light falling on it. This current signal is suitably amplified and then measured by the help of an ammeter. The deflection on the meter is proportional to the light intensity. The intensity of incident light is measured by putting only distilled water in the cuvette, when no light is absorbed and the whole of it falls on the photocell. In case the solution is made in a solvent other than water, the reference sample taken as the pure solvent. The difference of the two readings gives the amount of light absorbed.

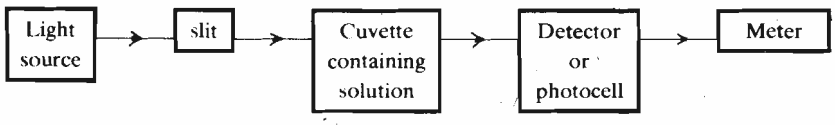


Fig.5.1 : Schematic diagram of a colorimeter

5.5 EXPERIMENT 8: DETERMINATION OF PERCENTAGE OF COPPER IN THE GIVEN SOLUTION USING COLORIMETRIC METHOD

In the previous experiment, you estimated copper using an indicator titrimetric method. In this experiment, you will use the instrument, colorimeter for the same.

Colorimetric determinations are possible only when the colours of the solutions are not too intense. Extremely dilute solutions can be used for such determinations when volumetric methods do not work. These methods are also used widely because of their high speed. You will know the advantages of colorimetry when you do this experiment. You have already read the Beer-Lambert law on which colorimetric determinations are based. Now you will read and learn the principle on which this experiment is based, and about the instrument and its calibration, procedural details and plotting a calibration curve in the following subsections.

5.5.1 Principle

The colorimetric determination of copper in a given solution is based on a simple principle. As you know, the blue colour of copper salts is due to hydrated Cu^{2+} ions. The intensity of the colour can be used as a measure of concentration of Cu^{2+} ions in the solution. Here you will prepare a number of solutions containing known but variable amounts of Cu^{2+} ions and measure their absorbance in the colorimeter to make a concentration-absorbance calibration curve. The concentration of the unknown solution is determined by the help of this calibration curve.

5.5.2 Colorimeter

The colorimeter on which you will perform your experiment is shown in Fig. 5.2.

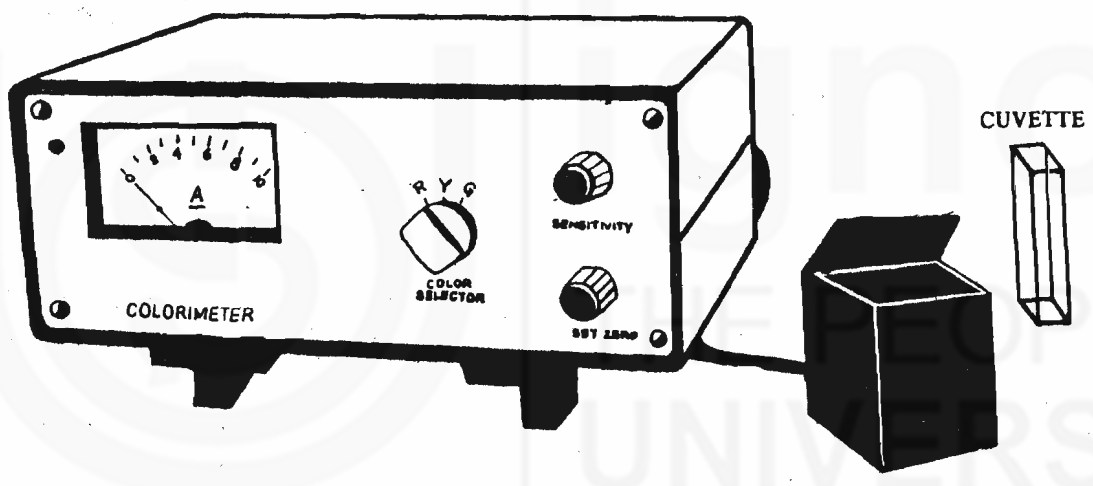


Fig. 5.2 : Colorimeter

Description of Controls

Power Switch: This is a SPST toggle switch, located on the back panel of the instrument, which turns the instrument OFF/ON. When ON, the LED on the front panel will glow if the instrument is plugged to a 220 V supply.

Colour Selector: This is a 2 pole 3 way rotary selector switch used to switch on a particular LED in the cell holder and also to bring into the amplifier circuit a particular parallel resistor. It has three positions R, Y, and G signifying red, yellow and green colours.

Set Zero: This knob is used to set the meter reading to zero when the reference solution is introduced in the cell holder.

Sensitivity: This knob is used to adjust the meter sensitivity.

Six pin plug: This is located at the right hand side of the back panel. The six pin socket from the cell holder is inserted in this plug. (Wires from the LEDs and the LDR are connected to the socket).

Before using the colorimeter, you will have to calibrate it by the procedure given below and plotting a graph to check the linearity.

5.5.3 Calibration of Colorimeter for Colorimetric Measurement

Requirements

Apparatus		**Chemicals**
Colorimeter with cuvettes		$CuSO_4 \cdot 5H_2O$
Burette	– 1	
Test tubes	– 10	
Test tube stand	– 1	

Caution: Do not use a plastic cuvette for organic solvents like chloroform, acetone, etc.

- Take a clear dry cuvette and fill it with distilled water or the reference solution. Note that the cuvette has two plane sides and two striated sides. Mark one of the plane sides with a pen and insert the cuvette in the cell holder with the marked side facing the LEDs inside the holder.
- **Always insert the cuvette the same way**. Close the lid of the cell holder.
- Use the **Set Zero** knob to adjust the meter reading to zero.
- Remove the cuvette, pour off the reference solution, rinse and dry it.
- Prepare 100 cm^3 of 8% copper sulphate stock solution. Fill the cuvette with the stock solution. Insert the cuvette in the cell holder in the **same orientation** as in Step 1. Close the lid of the cell holder.
- Set the **Selector** on **R**. (A copper sulphate solution has an absorption maximum in the red region. For an unknown solution, choose the LED which gives the highest meter reading, i.e. the largest absorbance.) Use the **Sensitivity** knob to adjust the meter reading near to the end of the scale (say 0.9).
- Repeat Steps 1 and 2 for setting the zero with distilled water (or the reference solution.)

Linearity Check

- 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 $CuSO_4 \cdot 5H_2O$ 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. Measure the meter reading, which is proportional to absorbance, for each of the solutions making sure that the cuvette is rinsed properly before pouring the solution. Also make sure that the **set zero** and **sensitivity** knobs are not disturbed throughout this set of measurements.
- Plot the meter readings against the volume of stock solution taken in each of the test tubes. A linear graph is expected as $CuSO_4$ solution is known to obey the Beer-Lambert law in this concentration range. (A linear graph also shows that the vlaue of parallel resistor for red LED is correct.)

5.5.4 Requirements

Apparatus

Colorimeter – 1
Volumetric flask (100 cm^3) – 1
Test tubes – 15
Test tube stand – 1
Measuring cylinder – 1
Beaker – 2
Burette (50 cm^3) – 1
Burette stand – 1

Solutions Provided

Cu^{2+} ion solution, prepared from copper wire using the same procedure as in the iodometry experiment. However, here the mass of Cu wire taken is 1.7 g, and the volume of solution prepared is 100 cm^3.

Stock solution of copper nitrate (10% *m/v*), prepared by dissolving 10 g of $Cu(NO_3)_2 \cdot 3H_2O$ in water and making the volume upto 100 cm^3.

5.5.5 Procedure

Before starting the experiment you will have to prepare copper nitrate solution of varying concentrations as you did for the linearity check of the instrument.

For this purpose take six test tubes and label them 1 to 6. Put $Cu(NO_3)_2 \cdot 3H_2O$ stock solution and water in the marked test tubes with the help of a burette as given in the following table :

S. No.	Volume of $Cu(NO_3)_2 \cdot 3H_2O$ stock solution	Volume of distilled water	% $Cu(NO_3)_2 \cdot 3H_2O$
1	0	10	0
2	2	8	2
3	4	6	4
4	6	4	6
5	8	2	8
6	10	0	10

Thus, you will get six solutions where the concentration of $Cu(NO_3)_2 \cdot 3H_2O$ varies from 0 – 10% as given in the table.

Before estimating Cu^{2+} ions in an unknown solution, a calibration curve will have to be plotted between the concentration and the meter response in the instrument. For this, clean the cuvette thoroughly and fill it with solution no. 1, after rinsing it with the same solution. Place the cuvette in the cuvette holder in the instrument and record the response in the meter in observation Table I. Then remove the solution and rinse the cuvette with solution no.2, fill it with the solution and once again note and record the meter response in the table. Repeat the same procedure with the rest of the solutions too. Plot the calibration curve in the graph sheet.

Wash the cuvette again and fill it with the solution whose concentration has to be determined. Place the cuvette in the cuvette holder and note the meter response. Using the calibration curve, measure the concentration corresponding to this reading.

5.5.6 Observations

Observation Table I
Meter response as a function of concentration of copper nitrate

Sl.No.	Strength of $Cu(NO_3)_2 \cdot 3H_2O$ in % *m/v*	Meter Response
1	0	
2	2	
3	4	
4	6	
5	8	
6	10	
Unknown	.....	

5.5.7 Calibration Curve

A sample reading, Table II, and a calibration curve, reproduced from the readings is shown in the graph given in Fig. 5.3 for your guidance. See it carefully, it will help you to plot the one with the readings you have noted.

Table II
Meter response as a function of concentration of copper sulphate

Sl. No.	Strength of $CuSO_4$ $5H_2O$ in % *m/v*	Meter response
1	2	1.8
2	4	3.9
3	6	6.10
4	8	8.05

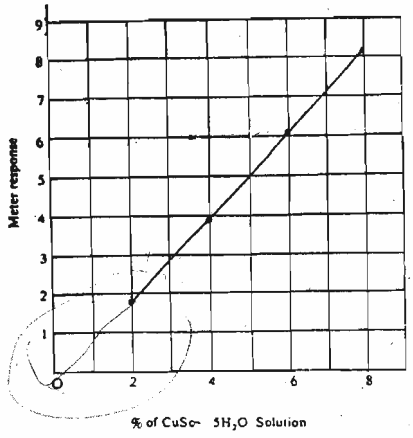


Fig. 5.3: Sample calibration curve drawn from the readings given in Table II

Now plot the observations recorded in Table I in a graph.

5.5.8 Calculations

From the graph, the % of copper nitrate solution is x% = ... %

$$\Rightarrow \frac{x \times 63.5}{187.5} \Rightarrow z \text{ g of Cu/100 cm}^3$$

mass of copper wire taken = 1.7 g/100 cm^3

$$\% \text{ of Cu} = \frac{z}{1.7} \times 100 = p\%$$

= ..... %

5.5.9 Result

The percentage of copper in the given copper solution = ...%. You can compare the above value with the correct value which you can get from your counsellor.

In this unit you have used two methods for the determination of percentage of copper in a given solution. As you know, one of these methods is titrimetric indicator method, the other colorimetric which is an instrumental method. You can very well compare the two methods after having used them. The comparison can be made in terms of:

a) accuracy : Which method is more accurate? Generally the instrumental methods are more accurate because of the very obvious errors which we can make in titrimetric methods, e.g., errors of distinguishing a colour change and thus the end point, etc.

b) facility : Instrumental method is more facile.

c) time : This you can judge yourself and we are sure that you will find that the instrumental method has taken lesser time.

d) cost : For this particular experiment, KI is so expensive that one will like to avoid its use. Instead of this, you are using a low cost instrument so in terms of cost, again, instrumental method is supposed to be better.

You can discuss these experiments in the light of above points with your counsellor.

5.6 ANSWERS TO SAQs

1) i) I_2 is almost insoluble in water.
ii) I_2 is volatile in nature and is lost from an open container in a short period. It requires standardisation every few days.

2) $2CuSO_4 + 4KI \longrightarrow 2CuI + 2K_2SO_4 + I_2$
$I_2 + 2Na_2S_2O_3 \longrightarrow 2NaI + Na_2S_4O_6$

$2CuSO_4 + 4KI + 2Na_2S_2O_3 \longrightarrow 2CuI + 2K_2SO_4 + 2NaI + Na_2S_4O_6$

3) The iodine-starch complex is only slightly dissociated and a diffuse end point will result if large amount of iodine were absorbed on starch.

4) Sodium bicarbonate produces CO_2 in a solution containing KI, $K_2Cr_2O_7$ and acid and displaces the air present in it. Air present in the solution, otherwise, would oxidise iodide to iodine and cause an error in the titration.

5) i) √ ii) × iii) × iv) √

UNIT 6 ANALYSIS OF WATER

Structure

6.1 INTRODUCTION

In the previous unit you were introduced to the iodometric and colorimetric methods for determining copper. In this unit you will first analyse a sample of water for hardness and alkalinity, and then for dissolved oxygen (DO).

As you know water is one of the most important substances used for life. It is indispensable to every form of life. Apart from being essential for agriculture, water has numerous industrial uses. The rapidly expanding needs for pure and clean water for drinking and recreation purposes, in the face of dwindling sources of fresh water, have raised concern among the environmentalists.

Municipal water supplies are derived from two main sources—surface water from rivers, lakes, etc. and ground water from wells, boreholes, etc., or a combination of both. Ground water is a better source of drinking water than surface waters, because most of the bacteria originally present in water are gradually filtered out as it percolates downwards through the soil.

Water, as it occurs in nature, contains organic and inorganic dissolved impurities as well as suspended solids and gases. The chemical and physical behaviour of the impurities present in water forms the basis for the procedures used in the analysis of water.

The dissolved inorganic impurities are mainly chlorides, sulphates, carbonates, and bicarbonates of sodium, potassium, calcium and magnesium. Besides these, natural water also contains dissolved oxygen and carbon dioxide.

Water containing salts of heavy metals, mainly calcium and magnesium is called **'hard water'**. Hard water is not desirable for use at home or in industry. Hardness of water precipitates soap, thus reducing its cleansing action. Dissolved solids precipitate on heating and thus clog boiler pipes and deposit on boiler plate when hard water is used for steam making. You may have noticed a similar hard white deposit called "scale" in the kettle used for boiling water for making tea.

It is important to find out the nature of the dissolved impurities present in water and also their concentration to judge whether a given sample of water is suitable for municipal or industrial use. For example, waters with high magnesium content are not suitable for drinking; similarly, waters with high iron content should not be used in paper or textile industry. High concentrations of carbon dioxide, dissolved oxygen and high salinity, if present in water, speed up corrosion.

In various water systems, the concentration of dissolved oxygen depends on various factors, such as, temperature, salinity and biological activity. Pollution by domestic sewage and industrial wastes can decrease the dissolved oxygen concentration in surface waters. Sewage contains large amounts of organic matter and also of nitrates and phosphates, which accelerate algal growth. Such growth has also been traced to excess amounts of carbon dioxide (CO_2) and carbonates (CO_3^{2-}). Bacterias decompose organic material in the sewage, and consequently use large amounts of oxygen, especially near the bottom. As a result, the large bottom fish which requires more oxygen for survival dies because of the lack of oxygen. The decrease in the amount of dissolved oxygen in water due to increased bacterial activity is called **eutrophication**. So, determination of dissolved oxygen in water is of prime importance in the study of natural waters.

There are different physical and chemical parameters like pH, conductivity, total hardness, temporary and permanent hardness, magnesium hardness, alkalinity, dissolved oxygen, chemical oxygen demand (COD) and biological oxygen demand (BOD), etc., which are used to assess the quality of water. It may not be possible for you to evaluate all these parameters. In this unit you would determine the following parameters in a water sample using chemical methods:

i) Total hardness
ii) Temporary and permanent hardness
iii) Alkalinity
iv) Dissolved oxygen

Objectives

After performing water analysis experiments, you should be able to:

- list different substances present in water obtained from natural sources,
- define total, temporary and permanent hardness,
- describe the formation of a complex of metal ions with ethylenediamine tetraacetic acid (EDTA),
- discuss the role of the buffer and the indicator in complexometric titrations,
- estimate total, temporary and permanent hardness in water by complexometric titration,
- define alkalinity of water,
- estimate total alkalinity or methyl orange alkalinity and phenolphthalein alkalinity,
- state the principle of Winkler's method for determination of dissolved oxygen in water, and
- estimate the dissolved oxygen in a sample of water by Winkler's method.

6.2 EXPERIMENT 9: DETERMINATION OF TOTAL HARDNESS OF WATER BY COMPLEXOMETRY

Determination of the hardness of water is necessary for determining the quality of water for household and industrial uses. As we have stated earlier that hardness of water is due to the presence of salts of calcium and magnesium in it. When we add simple soap (not a synthetic detergent) to hard water, an insoluble substance commonly known as "soap scum" is produced. Therefore, we also sometimes define

hardness as the soap consuming capacity of water. There are two types of hardness:

i) **Temporary hardness:** This is due to bicarbonates of calcium and magnesium. Temporary hardness gets removed on boiling water, when soluble bicarbonates decompose to give insoluble carbonates, however, $MgCO_3$ is partially soluble.

Hard water causes formation of deposits or scales inside the water pipes of boilers and other water conditioning equipment.

$$Ca(HCO_3)_2 \longrightarrow CaCO_3 + H_2O + CO_2$$
$$Mg(HCO_3)_2 \longrightarrow MgCO_3 + H_2O + CO_2$$
(partially soluble)

ii) **Permanent hardness:** It is so called because it does not get removed on boiling. Permanent hardness is due to chlorides and sulphates of calcium and magnesium. Total hardness is temporary and permanent hardness together.

$$\text{Total hardness} = \underset{\text{hardness}}{\text{Temporary}} + \underset{\text{hardness}}{\text{Permanent}}$$

It is necessary to know temporary and permanent hardness separately to devise a suitable treatment for water softening. Hardness of water is expressed in terms of mg of $CaCO_3$ per dm^3 of water or as ppm.

Hardness is expressed in ppm of $CaCO_3$ although in Experiment 9 the hardness may be due to magnesium or other cations.

Hardness of a water sample can be determined by titration with soap solution or by complexometric titration with EDTA (Ethylenediamine tetraacetic acid) or by conductometric methods. EDTA method is accurate, simple and fast. We shall first discuss the principle of complexometric titrations.

It is usual to know $CaCO_3$ equivalent to some common salts causing hardness. 100 parts of $CaCO_3$ are equivalent to:
162 parts $Ca(HCO_3)_2$
111 parts $CaCl_2$
95 parts $HgCl_2$
136 parts $CaSO_4$
120 parts $MgSO_4$

6.2.1 Principle

In complexometric titration we use, EDTA as complexing reagent, which forms soluble complexes with metal ions like Ca^{++} and Mg^{++}. **End point** in this titration is detected by colour change of eriochrome black T indicator. As the stability of the complex and colour change of the indicator are sensitive to pH changes, the solution to be titrated must be well buffered by ammonium hydroxide-ammonium chloride buffer solution of pH 10. Let us study complexation action of EDTA and the role of metal ion indicators in detail.

Complexation Reaction

A complexation reaction with a metal ion involves the replacement of one or more of the coordinated solvent molecules by other nucleophilic groups. The groups bound to the central ion are called **ligands**. In aqueous solution, the reaction can be represented by the following equation:

$$M(H_2O)_n + nL \longrightarrow ML_n + nH_2O$$

where, L = Ligand, e.g., NH_3, CN^-, EDTA

n = Coordination number of the metal ion and represents the maximum number of monodentate ligands that can be bound to it.

In this experiment EDTA is used as the ligand. The structure of EDTA is given in Fig. 6.1. EDTA has very wide general application in analysis because of its powerful complexing action and commercial availability.

Ligands may be classified according to the number of points of attachment to the central metal ions. Monodentate ligand—with one point of attachment, e.g., cyanide ions, halide ions, molecules of water and ammonia, Bidentate ligand—with two points of attachment, e.g., oxalic acid, Polydentate ligand—with more than two points of attachment, e.g., EDTA.

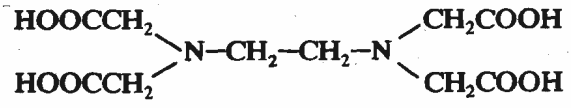


Fig. 6.1: Structure of EDTA

Abbreviation H_4Y is often employed in representing EDTA. The disodium salt of EDTA, Na_2H_2Y, also called sodium versenate, is generally used in EDTA titrations. The sodium salt is stable, can be obtained in high purity as a dihydrate and is soluble in water, whereas EDTA itself is quite insoluble. Na_2H_2Y undergoes extensive hydrolysis in solution giving H_2Y^{2-} ions. The disodium salt reacts with metal ions in 1 : 1 ratio. The reaction with cations, e.g., M^{2+}, may be written as,

$$M^{2+} + H_2Y^{2-} \longrightarrow MY^{2-} + 2H^+$$

It is apparent from the above equation that there is always a competition in the solution between the metal ions and hydrogen ions seeking the negative sites on EDTA. The equilibrium situation is determined by the strength of the bond between the metal ion and the ligand and the relative concentrations of metal ion versus hydrogen ion. In other words, we can say that the stability of a metal–EDTA complex will be governed by the hydrogen ion concentration or pH of the solution.

Table 6.1, gives minimum pH values for the stability of EDTA complexes of some selected metals.

Table 6.1: Stability with respect to pH of some metal-EDTA complexes

Minimum pH at which complex is stable	Selected Metals
1 – 3	Zr^{4+}, Hf^{4+}, Th^{4+}, Bi^{3+}
4 – 6	Pb^{2+}, Cu^{2+}, Zr^{2+}, Co^{2+}, Sb^{2+}, Mn^{2+}, Fe^{2+}
8 – 10	Ca^{2+}, Sr^{2+}, Ba^{2+}, Mg^{2+}

You can see that in general, EDTA complexes with alkaline earth metal ions are stable in alkaline solution, whilst complexes with tri- and tetravalent metal ions may exist in solution of much higher acidity. This is the reason why complexometric titrations for determining total hardness, i.e., Ca^{2+} and Mg^{2+}, are carried out at pH 10.

Metal Ion Indicators

We can titrate a metal-ion solution directly with standard EDTA solution. At the end point, the concentration of metal ion decreases abruptly. This is generally determined by change in the colour of a metal ion indicator which responds to change in metal ion concentration.

The end point may also be determined by conductometric, colorimetric, or in some cases, by potentiometric methods. Since in this experiment, we would be using metal ion indicators, we will briefly discuss them. A metal ion indicator forms a complex with a metal ion.

$$M^{2+} + HIn^{2-} \longrightarrow MIn^{-} + H^{+}$$

Where HIn^{2-} represents indicator form at a particular pH.

However, metal ion indicator complexes are generally less stable than the metal–EDTA complexes. The indicator releases the metal ions at the end point, and this shows a change in colour.

In the determination of the hardness of water, we use eriochrome black T or solochrome black as metal ion indicator. Eriochrome black T is sodium 1–(1–hydroxy–2–napthylazo)–6–nitro–2–napthol–4–sulphonate. Its structure is given in Fig. 6.2.

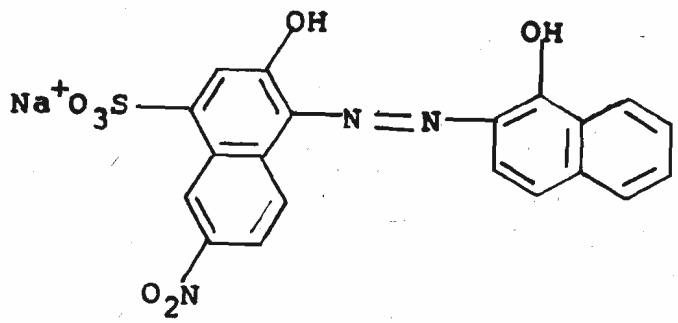


Fig. 6.2: Structure of eriochrome black-T.

In the presence of metal ions, eriochrome black–T forms a wine red complex. The colour changes to blue of the free indicator when the metal ions are fully complexed with EDTA at the end point in a titration.

$$MIn^- + H_2Y^{2-} \longrightarrow MY^{2-} + HIn^{2-} + H^+$$
(wine red) (colourless) (blue)

Where H_2Y^{2-} represents disodium salt of EDTA and HIn^{2-} represents eriochrome black T in a buffer solution of pH 10.

In the determination of the total hardness by EDTA titration, since Ca/Mg–EDTA complexes are stable at pH 8–10, the pH of the solution during the titration must be maintained at pH 10 by adding a suitable buffer like NH_4Cl/NH_4OH solution. In this titration, calcium ions do not form a sufficiently strong complex with eriochrome black T, Mg–EDTA complex is added to the titration flask, if the sample either does not contain sufficient magnesium ions or does not contain these ions at all to provide a sharp colour change at the end point.

Eriochrome black T has acid-base properties, which are summarised as follows,

$H_2In^- \overset{pH\ 8.1}{\rightleftharpoons} HIn^{2-} \overset{pH\ 12.4}{\rightleftharpoons} In^{3-}$
(red) (blue) (orange)

Since it forms metal complexes with red form only, eriochrome black T is a useful metal-ion indicator only in the pH range 8.1 – 12.4.

Chemical changes during titration may be written as:

$$Ca^{2+} + H_2Y^{2-} \longrightarrow CaY^{2-} + 2H^+ \quad .....(6.1)$$
$$Mg^{2+} + H_2Y^{2-} \longrightarrow MgY^{2-} + 2H^+ \quad .....(6.2)$$
$$Mg^{2+} + HIn^{2-} \longrightarrow MgIn^- + H^+$$
$$MgIn^- + H_2Y^{2-} \longrightarrow MgY^{2-} + HIn^{2-} + H^+ \text{ (at the end point)}$$
Wine red Colourless Colourless Blue

From the Eq. 6.1 and Eq. 6.2, it is clear that one mole of the disodium salt of EDTA reacts with one mole of Ca^{2+}/Mg^{2+} ions. Therefore, the molarities are related as per the following equation.

$$\frac{M_1V_1}{M_2V_2} = \frac{1}{1}$$

$$M_1V_1 = M_2V_2 \quad .... (6.3)$$

Where M_1 and M_2 are the molarities of EDTA salt and metal-ion solutions, respectively. V_1 and V_2 are the volumes of EDTA salt and metal-ion solutions, respectively.

In the next section we are going to give you experimental details for determination of the total hardness of water and the method of calculation. Before that try the following SAQs.

SAQ 1

Why is water sample buffered at pH 10 before titration with EDTA?

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SAQ 2

Explain why Mg^{2+} ion may be added when water sample is titrated with EDTA using eriochrome black T as indicator.

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6.2.2 Requirements

You will need the following apparatus, chemicals and solutions for this experiment.

Apparatus
Burette (50 cm^3) – 1
Pipette (20 cm^3) – 1
Conical flask (250 cm^3) – 2
Weighing bottle
Volumetric flask (250 cm^3) – 1
Funnel–1
Burette stand with clamp – 1

Chemicals
Disodium salt of EDTA

Solutions Provided
Water sample
NH_4OH–NH_4Cl Buffer solution, pH 10
It is prepared by dissolving 64g of NH_4Cl in distilled water, adding 570 cm^3 of ammonia solution (sp.gr. 0.88) and diluting to 1 dm^3 with distilled water.

Eriochrome black T (0.5% mass/volume)

0.50g indicator is weighed and dissolved in 100 cm^3 ethanol.

Mg–EDTA complex (0.005 *M*) solution
It is prepared by adding stoichiometric amounts of 0.01 *M* disodium salt of EDTA and 0.01 *M* $MgCl_2$. A portion of Mg–EDTA solution, when treated with a few drops of eriochrome black T at pH 10 should change to a wine red colour, which should change to pure blue on the addition of one drop of 0.01 *M* EDTA solution and wine red on addition of a single drop of 0.01 *M* $MgCl_2$ solution.

6.2.3 Procedure

The experimental procedure involves the following steps:

1) **Preparation of standard 0.01 *M* EDTA solution:** As said earlier, EDTA is available as its disodium dihydrate salt ($Na_2H_2Y.2H_2O$). First take already dried disodium salt of EDTA from the counsellor. Then take rough mass of a glass weighing bottle and transfer about 0.95 g of the salt to the weighing bottle and weigh accurately. Transfer the salt to a clean and dry volumetric flask of 250 cm^3 capacity through a glass funnel. Find out the accurate mass of the weighing bottle after transferring the salt. The difference between two masses gives the actual amount of EDTA salt taken. Record these values in your observation note book to calculate exact concentration according to the mass of the EDTA salt taken. Now, dissolve the salt in deionised or distilled water. Make up to the mark with distilled water and shake thoroughly to make a homogeneous solution.

2) **Titration of water sample**
   i) Fill the burette with the EDTA salt solution after rinsing it with this solution and mount the burette on a stand, also insert a parallex card. Note the reading in the burette and record it in the observation Table I under the 'Initial reading' column.
   ii) Pipette out 60 cm^3 of the water sample using a 20 cm^3 pipette in a 250 cm^3 conical flask, add 2 cm^3 of the buffer solution, 0.5 cm^3 of Mg–EDTA complex solution–mandatory , and five drops of eriochrome black T indicator. Colour of the mixture at this stage must be wine red.
   iii) Titrate with 0.01 *M* EDTA from the burette with constant swirling. End point is detected by the colour change from wine red through purple to a clear blue. The solution should be stirred thoroughly and the titrant added slowly near the end point.

A white crystalline precipitate of calcium carbonate may appear after the buffer is added, if the water is very hard. This should dissolve during the course of the titration. The precipitate may dissolve slowly, however, it must dissolve before the end point is reached.

In some cases, where the alkalinity of the water sample is very high, it is recommended to boil a known volume of the water sample with a few drops of HCl to remove CO_2. Cool, add a few drops of methyl red and neutralise with NaOH solution till the red colour is discharged.

iv) Note the burette reading and record in the observation Table I under the 'Final reading' column. The difference of the two readings gives the volume of EDTA salt solution used in the titration. Repeat the titration to get at least two concordant readings.

The volume of EDTA salt solution used for the titration should not be less than 10 cm^3. Adjust the volume of the water sample accordingly.

6.2.4 Observations

Approximate mass of the weighing bottle = m_1 = ...g

Mass of the weighing bottle + EDTA (before transferring the salt) = m_2 = ...g

Mass of the weighing bottle (after transferring the salt) = m_3 = ...g

Amount of EDTA salt transferred = $m_2 - m_3 = m$ = ...g

Molar mass (M_m) of sodium salt of EDTA = 372.3 g mol^{-1}

Volume of EDTA salt solution prepared = 250 cm^3

Molarity of EDTA salt solution

$$= M_1 = \frac{m \times 1000}{M_m \times 250} \text{ mol dm}^{-3}$$

$$= \frac{m \times 4}{372.31} \text{ mol dm}^{-3}$$

Observation Table I
Water sample vs EDTA salt solution

Sl. No.	Volume of water sample in cm^3	Burette reading		Volume of EDTA salt in cm^3 (Final − Initial)
		Initial	Final	
1	60			
2	60			
3	60			

6.2.5 Calculations

Estimation of total hardness of water sample

Molarity of EDTA salt solution = $M_1 = m \times 4/372.3$ = ... mol dm^{-3}

Volume of EDTA salt solution used (From Table I) = V_1 = ... cm^3

Volume of water sample = V_2 = 60 cm^3

Molarity of Ca^{2+}/Mg^{2+} in the water sample = M_2 = ?

Using Eq. 6.3,

$$M_1 V_1 = M_2 V_2$$

Molarity of Ca^{2+}/Mg^{2+} in water sample

$$M_2 = \frac{M_1 V_1}{V_2} \text{ mol dm}^{-3}$$

= ..... mol dm^{-3}

Total hardness of water sample in mg of $CaCO_3$ in one dm^3 of water

= M_2 × Molar mass of $CaCO_3$ × 1000

Molar mass of $CaCO_3$ = 100.09

For all the practical purposes this may be taken as 100.00 for the sake of convenience in calculations. Now, we have,

Total hardness of water sample = $M_2 \times 100 \times 1000$ = ... ppm of $CaCO_3$.

6.2.6 Result

Total hardness of the given sample of water = ... ppm of $CaCO_3$

Hardness of more than 300-500 mg dm^{-3} of $CaCO_3$ is considered excessive for public water supply and results in high soap consumption as well as objectionable scale in heating vessels and pipes. Keeping these points in view, discuss the suitability of water sample given to you.

6.3 EXPERIMENT 10: DETERMINATION OF PERMANENT AND TEMPORARY HARDNESS OF WATER

In Experiment 9, you have determined the total hardness of water, i.e., temporary + permanent hardness. As we have discussed earlier if a water sample is boiled for sometime, bicarbonates of calcium and magnesium which cause temporary hardness are precipitated as carbonates and can be removed by filtration. If you now titrate the filtered water sample with EDTA salt, this gives you the permanent hardness only. Once permanent hardness is determined, you can easily calculate temporary hardness by subtracting the permanent hardness from the total hardness.

In this experiment, you will first remove the temporary hardness by boiling and then titrate water sample for permanent hardness. Finally you will calculate permanent and temporary hardness.

6.3.1 Principle

You are again going to use EDTA titration method, therefore, the principle involved is same as in the case of Experiment 9.

SAQ 3

Define permanent and temporary hardnesses of water and also list the compounds which are responsible for them.

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6.3.2 Requirements

You can use the apparatus, chemicals and solutions which you have prepared for Experiment 9, besides that you will need a 400 cm^3 beaker, a 250 cm^3 volumetric flask, burner, funnel and filter paper.

6.3.3 Procedure

1) First determine the total hardness of the water sample by performing Experiment 9. If you are using the same water sample, there is no need to repeat this experiment.

2) Measure 250 cm^3 of the same water sample with the help of a volumetric flask and transfer it to a 400 cm^3 beaker. Boil it for 30 minutes. Cool the sample and filter it through a filter paper, Whatman No. 1 into a 250 cm^3 volumetric flask. Magnesium and calcium carbonates, which are precipitated on boiling are filtered off. Make up the filtered sample to the mark by adding distilled or deionised water. Now, the temporary hardness has been removed and you can titrate the filtered sample with EDTA salt for permanent hardness.

3) Pipette out 60 cm^3 of the filtered sample using a 20 cm^3 pipette into a 250 cm^3 conical flask, add 2 cm^3 of buffer solution, 0.5 cm^3 of Mg – EDTA complex solution – mandatory, and five drops of eriochrome black T indicator. The colour at this stage must be wine red.

4) Fill the burette with the EDTA salt solution which is prepared for Experiment 9. Note its initial reading and record it in the observation Table I.

5) Titrate the contents of the conical flask with EDTA salt solution as directed under the procedure for total hardness and note the final reading in the observation Table I. The difference of the final and initial readings gives the

volume of EDTA salt solution used in the determination of permanent hardness. Repeat the titration to get at least two concordant readings.

6.3.4 Observation

Observation Table I
EDTA salt solution vs water sample (after boiling)

Sl. No.	Volume of water sample in cm^3	Burette reading		Volume of EDTA salt solution in cm^3 (Final − Initial)
		Initial	Final	
1	60			
2	60			
3	60			

6.3.5 Calculations

(a) **Permanent hardness of water sample**
Molarity of EDTA salt solution = M_1 = ... mol dm^{-3}
(From Experiment 9, if you are using the same EDTA solution).
Volume of EDTA solution = V_1 = ... cm^3
used (From Table I)
Volume of water sample = V_2 = 60 cm^3
Molarity of Ca^{2+}/Mg^{2+} in water sample = M_2 = ?
after boiling
Molarity of Ca^{2+}/Mg^{2+} in water sample
after boiling

$$= M_2 = \frac{M_1 V_1}{V_2}$$
= ..... mol dm^{-3}

Permanent hardness of water sample in mg of $CaCO_3$ in one dm^3 of water
= M_2 × Molar mass of $CaCO_3$ × 1000
= M_2 × 100 × 1000 = ... ppm of $CaCO_3$

(b) **Temporary hardness of water sample**
= Total hardness − Permanent hardness
(From Experiment 9) (From Experiment 10)
= ..... ppm of $CaCO_3$

6.3.6 Result

Permanent hardness of the given water sample = ... ppm of $CaCO_3$
Temporary hardness of the given water sample = ... ppm of $CaCO_3$

6.4 EXPERIMENT 11: DETERMINATION OF ALKALINITY OF WATER

In the previous two experiments you were introduced to the complexometric titration methods. Now, we are again going to discuss acid-base or neutralisation titration method to estimate alkalinity of water. As you may recollect neutralisation titration was discussed in Units 2 and 3.

The alkalinity of water is a measure of its quantitative capacity to neutralise a strong acid to a designated pH. The alkalinity of many surface waters is primarily due to carbonate, bicarbonate and hydroxide ions and less frequently borates, silicates and phosphates. It is, however, taken as an indication of the concentration of former.

Alkaline waters containing bicarbonates of calcium and magnesium when heated, form crust like scales in pipes thus restricting the flow of fluids. Carbon dioxide released in the reaction is corrosive.

Alkalinity values provide guidance in applying proper doses of chemicals in water and waste water treatment plants, particularly in coagulation, softening and operational control of anaerobic digestion. Alkalinity in excess of the permissible concentration is significant in determining the suitability of water for irrigation. High alkalinity in water can damage root hairs of plants.

6.4.1 Principle

As mentioned above, the primary species contributing to alkalinity are carbonate, bicarbonate and hydroxide ions. Alkalinity is determined by titration with standard solution of a strong acid using phenolphthalein and methyl orange indicators similar to Experiment 4. Besides bicarbonates, waters having a pH above 8.3 contain, normal carbonates and hydroxides also. Titration to an end point of pH 8.3 determines the alkalinity contributed by hydroxide and half that of the carbonate present as you know, at this pH carbonate gets converted to bicarbonate. This is obtained by using phenolphthalein as an indicator.

The alkalinity fraction equivalent to the amount of acid required to lower the pH of the water sample to 8.3 is called phenolphthalein alkalinity.

The total alkalinity is determined by titration of the sample to the end point using a suitable indicator like methyl orange having a colour change at about pH 4.5.

The amount of acid required to lower the pH to 4.5 of water sample determines the total alkalinity or methyl orange alkalinity.

The reactions which take place can be summed up as follows:

$OH^- + H^+ \rightleftharpoons H_2O$

$CO_3^{2-} + H^+ \rightleftharpoons HCO_3^-$] end point with phenolphthalein (phenolphthalein alkalinity)

$HCO_3^- + H^+ \rightarrow H_2CO_3$] end point with methyl orange (total or methyl orange alkalinity)

Alkalinity results are expressed in terms of concentration of $CaCO_3$. You know that one mole of $CaCO_3$ is neutralised by 2 moles of HCl as shown in the following equation:

$$CaCO_3 + 2HCl \longrightarrow CaCl_2 + H_2O + CO_2$$

Alkalinity is taken primarily as an indication of the concentration of carbonate, bicarbonate, and hydroxide ions. Presence of these ions is shown as follows,
i) Carbonate ion (CO_3^{2-}) is present when phonolphthalein alkalinity is not zero but is less than total alkalinity.
ii) Hydroxide ion (OH^-) is present if phenolphthalein alkalinity is more than half the total alkalinity.
iii)Bicarbonate ion (HCO_3^{2-}) is present if phonolphthalein alkalinity is less than half the total alkalinity.

Therefore, the molarity equation for the alkalinity can be written as,

$$M_{HCl}\ V_{HCl} = 2M_{CaCO3}\ V_{CaCO3} = 2M_{WS}\ V_{WS} \quad \text{..... (6.4)}$$

Where M_{WS} is the molarity of alkalinity in water sample in terms of $CaCO_3$ and V_{WS} is the volume of water sample.

We use above molarity equation to calculate phenolphthalein and methyl orange alkalinity.

A minimum quantity of 0.1 *M* sodium thiosulphate solution is added to the sample to remove traces of residual chlorine that would otherwise interfere in colour change in the determination of total alkalinity.

6.4.2 Requirements

You will need the following apparatus and chemicals for this experiment.

Apparatus
Burette (50 cm^3) – 1
Pipette (20 cm^3) – 1
Conical flask (250 cm^3) – 1
Weighing bottle
Volumetric flask (250 cm^3) – 1
Funnel – 1
Burette stand with clamp – 1

Chemicals
Sodium carbonate

Solutions Provided

Water sample

Hydrochloric acid (approximately *M*/50)
It is prepared by diluting 2 cm^3 of concentrated HCl to 1 dm^3 with distilled water to make an approximately *M*/50 solution.

Phenolphthalein indicator solution
It is prepared by dissolving 0.5 g of phenolphthalein in 50 cm^3 of ethanol and diluting to 100 cm^3 with distilled water.

Methyl orange indicator solution
0.1 g of methyl orange is dissolved in 200 cm^3 of distilled water.

Sodium thiosulphate (0.01 *M*)
2.48 g of $Na_2S_2O_3{\cdot}5H_2O$ is dissolved in distilled water and diluted to 100 cm^3.

Distilled water
Use distilled water having a pH higher than 6.0. If the water has a lower pH, it should be boiled for at least 15 minutes and allowed to cool to room temperature. This water should be used for the preparation of all standard solutions.

6.4.3 Procedure

As given above, you are provided with an approximate *M*/50 hydrochloric acid solution. The exact concentration of hydrochloric acid solution is determined by titrating against a standard solution of Na_2CO_3.

1) **Preparation of standard sodium carbonate solution (*M*/100):** Weigh accurately 0.26 – 0.27 g Na_2CO_3 (previously dried) in a weighing bottle. Transfer it to a clean 250 cm^3 volumetric flask. By weighing the weighing bottle again, find out by difference, the accurate mass of the salt transferred. Dissolve the salt in 100 cm^3 freshly boiled and cooled distilled water and make up the solution to the mark. Shake the solution till it is completely homogeneous.

2) **Standardisation of HCl solution:** Pipette out 20 cm^3 of the given Na_2CO_3 solution into a 250 cm^3 conical flask. Add 2–3 drops of methyl orange indicator. Your solution will turn yellow on the addition of this indicator. Titrate with HCl taken in the burette. Swirl the flask after each addition till a permanent red colour is obtained at the end point. Record your observations in observation Table I. Repeat the titration till you get two concordant readings.

3) **Titration of water sample with HCl solution**

i) Pipette 60 cm^3 of the water sample in a 250 cm^3 conical flask. Add a drop of 0.1 *M* sodium thiosulphate to the water sample to remove possible chlorine residues. Add 2-3 drops of phenolphthalein indicator and slowly titrate with HCl from the burette with constant swirling till the colour just disappears (pH 8.3). Record your observations in observation Table II. Repeat the titration to get at least two concordant readings.

Note: If no pink colour develops on addition of phenolphthalein to the water sample, do not titrate the sample for phenolphthalein alkalinity.

ii) Again take 60 cm^3 of the water sample as above and titrate with HCl using methyl orange indicator till a red colour is obtained (pH 4.5).

Record your observations in observation Table III. Repeat the titration to get at least two concordant readings. Adjust the volume of water sample so that the volume of HCl required is about 15 to 20 cm^3.

6.4.4 Observations

Mass of the weighing bottle = m_1 = ... g
Mass of weighing bottle + Na_2CO_3 (before transferring the salt) = m_2 = ... g
Mass of the bottle (after transferring the salt) = m_3 = ... g
Amount of Na_2CO_3 transferred = $m_2 - m_3 = m$ ..... g
Molar mass of Na_2CO_3 = 106 g mol^{-1}
Volume of Na_2CO_3 solution prepared = 250 cm^3
Molarity of Na_2CO_3 solution = M_1

$$= \frac{m \times 1000}{M_m \times 250}$$

$$= \frac{m \times 4}{106}$$

= ..... mol dm^{-3}

Observation Table I
Na_2CO_3 solution vs HCl solution

Sl. No.	Volume of Na_2CO_3 sample in cm^3	Burette reading		Volume of HCl in cm^3 (Final − Initial)
		Initial	Final	
1	20			
2	20			
3	20			

Observation Table II
Water sample vs HCl solution (Phenolphthalein indicator)

Sl. No.	Volume of water sample in cm^3	Burette reading		Volume of HCl in cm^3 (Final − Initial)
		Initial	Final	
1	60			
2	60			
3	60			

Observation Table III
Water sample vs HCl solution (Methyl orange indicator)

Sl. No.	Volume of water sample in cm^3	Burette reading		Volume of HCl in cm^3 (Final − Initial)
		Initial	Final	
1	60			
2	60			
3	60			

6.4.5 Calculations

(a) Estimation of the strength of HCl solution

Morality of Na_2CO_3 solution = $M_1 = m \times 4/106$ = ... mol dm^{-3}
Volume of Na_2CO_3 solution = V_1 = 20 cm^3
Volume of HCl solution (from Table I) = V_2 = ... cm^3
Molarity of HCl solution = M_2 = ?

Using Eq. 3.6 (Unit 3)

$$2M_1V_1 = M_2V_2$$

$$M_2 = \frac{2M_1V_1}{V_2}$$

= ..... mol dm^{-3}

In this titration, one mole of Na_2CO_3 reacts with two moles of HCl.

(b) Estimation of Phenolphthalein alkalinity of water sample

Molarity of HCl solution = $M_3 = M_2$ = ... mol dm^{-3}
Volume of HCl solution (From Table II) = V_3 = ... cm^3
Volume of water sample = V_4 = 60 cm^3
Molarity of phenolphthalein-alkalinity in water sample in terms of $CaCO_3$ = M_4 = ?

Using Eq. 6.4

$$M_3V_3 = 2M_4V_4$$

$$M_4 = \frac{M_3V_3}{2V_4}$$

= ..... mol dm^{-3}

Phenolphthalein alkalinity of water sample in mg of $CaCO_3$ in one dm^3 of water
= M_4 × Molar mass of $CaCO_3$ × 1000
Molar mass of $CaCO_3$ = 100 g mol^{-1}

Phenolphthalein alkalinity of water sample
= $M_4 \times 100 \times 1000$ ppm $CaCO_3$
= ..... ppm $CaCO_3$

Simply, we can define phenolphthalein alkalinity as:

Phenolphthalein alkalinity

$$\text{mg of } CaCO_3 \text{ dm}^{-3} \text{ or ppm} = \frac{\left(\text{Volume of HCl (cm}^3\text{) to phenolphthalein end point}\right) \times M_{HCl} \times 100{,}000}{2 \times \text{Volume of water sample (cm}^3\text{)}}$$

(c) Estimation of methyl orange (total) alkalinity of water sample

Molarity of HCl $= M_5 = M_2 =$ ..... mol dm^{-3}
Volume of HCl $= V_5 =$ ..... cm^3
Volume of water sample $= V_6 = 60$ cm^3
Molarity of methyl orange-alkalinity in water sample in terms of $CaCO_3$ $= M_6 = ?$

Using Eq. 6.4
$M_5 V_5 = 2M_6 V_6$

$$M_6 = \frac{M_5 V_5}{2V_6}$$
$$= \text{.....} \text{ mol dm}^{-3}$$

Methyl orange alkalinity of water sample in mg of $CaCO_3$ dm^{-3}
$= M_6 \times$ Molar mass of $CaCO_3 \times 1000$
$= M_6 \times 100 \times 1000$
$=$ ..... ppm of $CaCO_3$

Simply, we can define methyl orange alkalinity as:

Total alkalinity or methyl orange alkalinity

$$\text{mg of } CaCO_3 \text{ dm}^{-3} \text{ or ppm} = \frac{\left(\text{Volume of HCl (cm}^3\text{) to methyl orange end point}\right) \times M_{HCl} \times 100{,}000}{2 \times \text{Volume of water sample (cm}^3\text{)}}$$

6.4.6 Result

Phenolphthalein alkalinity = ... ppm of $CaCO_3$
Methyl orange alkalinity = ... ppm of $CaCO_3$

6.5 EXPERIMENT 12: DETERMINATION OF THE DISSOLVED OXYGEN (DO) IN A GIVEN WATER SAMPLE

In the previous experiment, you have determined the alkalinity of a water sample. In this experiment you will be determining dissolved oxygen (DO) in a given water sample.

While oxygen itself is not a pollutant in water, its presence, particularly, its deficiency, is an indicator of several types of pollution in waters. Dissolved oxygen is necessary for life of fish and other aquatic organisms. When its concentration is less than 4 ppm, the fresh water systems are unsuitable for aquatic life, especially the game fish like trout. Oxygen is also needed to enable bacteria to oxidise organic matter present in water. Low concentration or absence of oxygen is an indicator of pollution in water. Further dissolved oxygen in boiler feed water causes corrosion of boiler plate. Its determination is, therefore, essential.

The rate at which oxygen is consumed by a sample of water is called the biochemical oxygen demand (BOD), which for polluted water is usually much higher than for clean waters. This is because of the large consumption of oxygen by bacteria as they decompose organic waste material in polluted water. BOD is used to indicate the amount of organic matter in water.

Both chemical and instrumental methods are available for determination of dissolved oxygen. There are sensors available, which could be lowered into the water sample at any location and which would rapidly furnish a readout related to the *in situ* concentration of oxygen at that exact time and place. Oxygen electrode also has its limitations and is quite unselective for oxygen in the presence of other oxidants.

There are problems in sampling and storing water for chemical determination of dissolved oxygen, especially so if microflora remains active in the sample. Titrimetric procedure is also inconvenient for field work.

Winklers azide method for determination of dissolved oxygen in water is perhaps the most well-known of all the chemical methods used for estimation of dissolved oxygen in water. In this experiment, you will use this method to estimate dissolved oxygen in a water sample.

6.5.1 Principle

Winklers azide method of determining dissolved oxygen in water was developed in 1888 by Winkler. It involves introducing first a concentrated solution of manganese (II) sulphate, sodium hydroxide and potassium iodide — azide reagent into the water sample. The white precipitate of manganese (II) hydroxide $Mn(OH)_2$ is formed, and is oxidised by dissolved oxygen in the water sample to give a brown precipitate of manganese (III) hydroxide, $Mn(OH)_3$. The sample is then said to be fixed and can be stored in this condition indefinitely. In the presence of sulphuric acid, manganese (III) hydroxide dissolves and liberates free iodine from the potassium iodide added, in an amount exactly equivalent to the amount of dissolved oxygen in the water sample. In the presence of excess iodide ions, the liberated iodine (I_2) is present in the form of I_3^-. The amount of liberated iodine is then estimated by titrating against sodium thiosulphate using starch as an indicator.

The series of reactions which take place can be summarised by the following equations:

$$MnSO_4 + 2NaOH \longrightarrow Mn(OH)_2 + Na_2SO_4$$
$$4Mn(OH)_2 + O_2 + 2H_2O \longrightarrow 4Mn(OH)_3$$
$$Mn(OH)_3 + H_2SO_4 \longrightarrow MnSO_4 + 2H_2O + O$$
$$2KI + H_2SO_4 + O \longrightarrow K_2SO_4 + H_2O + I_2$$
$$2Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2NaI$$

The ratio between the moles of dissolved oxygen in the sample and the moles of thiosulphate needed to react with liberated I_2 can be deduced from the following:

$$4Mn(OH)_2 + O_2 + 2H_2O \longrightarrow 4Mn(OH)_3$$
$$4Mn(OH)_3 + 4I^- + 12H^+ \longrightarrow 4Mn^{2+} + 2I_2 + 12H_2O$$
$$2I_2 + 4S_2O_3^{2-} \longrightarrow 2S_4O_6^{2-} + 2I^-$$

From the above equations, it is clear, two moles of I_2 are liberated per mole of O_2 and since each I_2 reacts with two $S_2O_3^{2-}$, one mole of O_2 will be equivalent to four moles of sodium thiosulphate that the stoichiometric ratio between the moles of oxygen in the water sample and moles of thiosulphate used is 1 to 4, i.e.,

$$O_2 = 2I_2 = 4S_2O_3^{2-}$$

Therefore , if $M_{Na_2S_2O_3}$ is the molarity of sodium thiosulphate solution, M_{DO} is the molarity of dissolved oxygen in the water sample and $V_{Na_2S_2O_3}$ is the volume of sodium thiosulphate used for the titration of water sample and V_{DO} is the volume of water sample, respectively, substituting these values for p and q in Eq. 1.8 the molarities are related as per the following equation.

$$\frac{M_{Na_2S_2O_3}\, V_{Na_2S_2O_3}}{M_{DO}\, V_{DO}} = \frac{4}{1}$$

$$\text{or } M_{Na_2S_2O_3}\, V_{Na_2S_2O_3} = 4 M_{DO}\, V_{DO} \qquad ...(6.5)$$

The main interference in this process is due to the presence of nitrites. These react with KI and liberate iodine according to the following equation,

$$2HNO_2 + H_2SO_4 + 2KI \longrightarrow 2NO + K_2SO_4 + 2H_2O + I_2$$

This liberated iodine will also use up thiosulphate. Sodium azide is, therefore, used in this process to take care of any nitrite present in the water sample, it distroys the nitrite when the sample is acidified,

$$2NaN_3 + H_2SO_4 \longrightarrow 2HN_3 + Na_2SO_4$$
(Hydrazoic acid)

$$HNO_2 + HN_3 \longrightarrow NO_2 + N_2 + H_2O$$

Standardisation of sodium thiosulphate solution

This method is based on the principle of iodometry, which has been discussed in Unit 5. In this case, potassium dichromate oxidises iodide to iodine in the acidic medium according to the reaction,

$$Cr_2O_7^{2-} + 14H^+ + 6I^- \longrightarrow 2Cr^{3+} + 3I_2 + 7H_2O \quad ...(6.6)$$

The librated iodine, similar to iodometric titration, is titrated with sodium thiosulphate solution according to the reaction,

$$2S_2O_3^{2-} + I_2 \longrightarrow S_4O_6^{2-} + 2I^- \quad ...(6.7)$$

On combining Eq. 6.6 and 6.7, we get,

$$Cr_2O_7^{2-} + 6S_2O_3^{2-} + 14H^+ \longrightarrow 2Cr^{3+} + 3S_4O_6^{2-} + 7H_2O \quad ...(6.8)$$

We see from Eq. 6.8, that one mole of potassium dichromate reacts with 6 moles of sodium thiosulphate. Therefore, substituting the values for p and q in Eq. 1.8, the molarities are related as per the following equation:

$$\frac{M_{K_2Cr_2O_7}\ V_{K_2Cr_2O_7}}{M_{Na_2S_2O_3}\ V_{Na_2S_2O_3}} = \frac{1}{6}$$

$$6M_{K_2Cr_2O_7}\ V_{K_2Cr_2O_7} = M_{Na_2S_2O_3}\ V_{Na_2S_2O_3} \quad ...(6.9)$$

SAQ 4

Mark the following as true (T) or false (F).

a) Dissolved oxygen is necessary for life of fish and other aquatic organisms.
b) Concentration of dissolved oxygen less than 4 ppm is unsuitable for aquatic life.
c) Concentration of oxygen is a good indicator of polluted waters.
d) Dissolved oxygen is desirable ior industrial water supply.

SAQ 5

What is the role of manganese (II) sulphate and alkaline potassium iodide solution in the detection of dissolved oxygen?

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6.5.2 Requirements

Apparatus

Burette (50 cm^3) – 1
Pipette (20 cm^3) – 1
Conical flask (250 cm^3) – 1
Weighing bottle
Volumetric flask – 1
Stoppered bottle (250 cm^3) – 1.
Dropper (2 cm^3) – 1
Burette stand with clamp – 1

Chemicals

Sodium bicarbonate
Conc. sulphuric acid or
Phosphoric (V) acid

Potassium iodide

Solutions Provided

Water sample.

Manganese (II) sulphate solution: It is prepared by dissolving 50 g of manganese (II) sulphate pentahydrate in distilled water and making up to 100 cm^3.

Alkaline iodide-azide solution: It is prepared from 40 g of sodium hydroxide, 20g of potassium iodide and 0.5g of reagent grade sodium azide (NaN_3) made up to 100 cm^3 with water. Sodium azide is added to the cooled solution

Caution: Sodium azide is poisonous, it may also explode if exposed to heat. Handle with care.

Note: Both manganese (II) sulphate and alkaline iodide-azide solutions are added to the water sample just below the surface of water with the help of the jet arrangement attached to the burette (see Fig. 6.3).

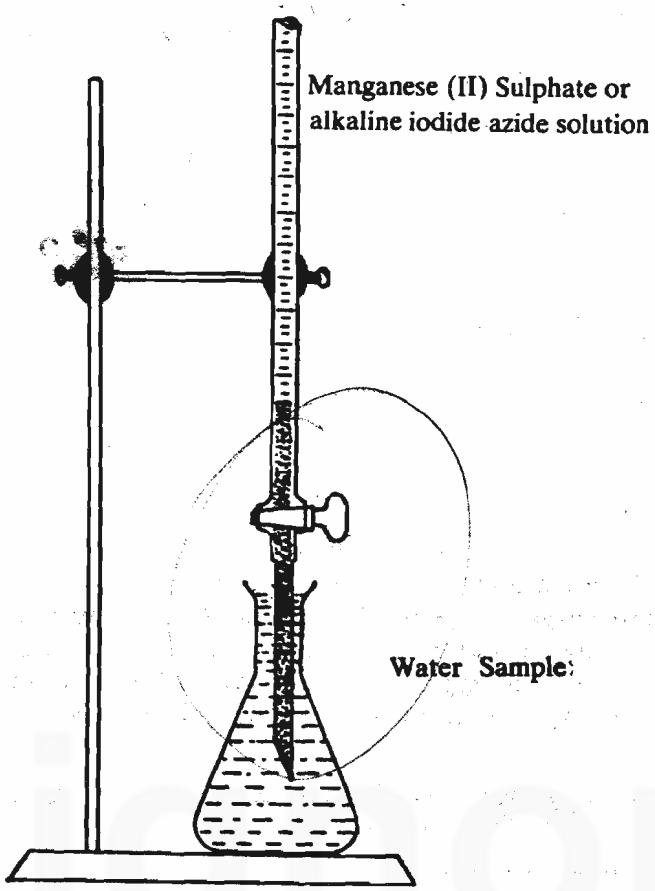

Fig. 6.3: Arrangement for the addition of manganese (II) sulphate and alkaline iodide-azide solution.

Sodium thiosulphate solution (*M*/80): Prepared by dissolving 3.15g sodium thiosulphate ($Na_2S_2O_3.5H_2O$) in distilled water and making up to the mark in a $1dm^3$ volumetric flask with distilled water. If the solution is to be kept for more than a few days, 0.1g sodium carbonate or three drops of chloroform may be added to avoid decomposition of sodium thiosulphate.

Standard potassium dichromate solution (*M*/480): It is prepared by accurately weighing about 0.125g of dry potassium dichromate in a weighing bottle by the usual method, transferring it into a $1dm^3$ volumetric flask, dissolving in a small quantity of water, making it up to the mark with distilled water, and mixing thoroughly.

Dilute Sulphuric acid: As mentioned in Experiment 7

Starch solution: A smooth paste of 2g of soluble starch is made and added a little at a time to $1dm^3$ of boiling water with constant stirring. Heating is continued until the solution becomes clear. The solution is cooled and preserved by adding 1.25 g salicylic acid or a few drops of toluene.

6.5.3 Procedure

As you know, sodium thiosulphate is not a primary standard, therefore, you would first have to standardise it by titrating with a standard solution of potassium dichromate.

Solid sodium bicarbonate is added to make a cover of carbon dioxide in the reaction flask during the titration to prevent oxidation of hydroiodic acid by oxygen of air.

1) **Titration of standard potassium dichromate with given thiosulphate solution:** Fill the burette with the given solution of sodium thiosulphate. Note the initial reading of the burette and record it in the observation Table I. Pipette out 20 cm^3 of the given standard solution of potassium dichromate into a conical flask, add 10 cm^3 of 10% KI solution, 2g sodium bicarbonate and 15 cm^3 dilute sulphuric acid. Cover the flask and keep it in dark for 2-3 minutes. Titrate

against sodium thiosulphate with constant stirring. When the solution acquires a greenish yellow colour, add 2.0 cm^3 of starch solution. Continue the addition of the thiosulphate solution dropwise till a light green colour is formed. This indicates the end point of the titration. Note the burette reading and record it in the observation Table I under the 'Final Reading' column. The difference of the two readings gives the volume of sodium thiosulphate solution used. Repeat the titration till concordant values are obtained.

2) **Titration of water sample:**

i) Fill a 250 cm^3 stoppered bottle with the water sample supplied. Insert the stopper carefully by allowing it to displace the water in the bottle neck without trapping air bubbles which could raise oxygen level by aerating the sample.

ii) Remove the stopper, and by using a jet attached to the burette (see Fig.6.3), add 1cm^3 of manganese (II) solution. Similarly add 1 cm^3 of alkaline iodide - azide solution. Point of the jet should be below the surface of water so that the dense reagent solutions sink to bottom displacing water. Restopper the bottle and shake the mixture well.

iii) Allow the brown precipitate of manganese (III) hydroxide to settle completely for 15 minutes and add 2 cm^3 of concentrated sulphuric acid or 2 cm^3 of concentrated phosphoric (V) acid with the help of a 2 cm^3 dropper or measuring pipette after removing the stopper. Restopper and gently shake to dissolve the precipitate. This should produce the characteristic brownish red colour of iodine. Whole of the precipitate should dissolve. If some of the dark brown precipitate persists after a few minutes, a few drops more of sulphuric acid can be added.

iv) With a pipette, transfer 100 cm^3 of the above solution for titration in a 250 cm^3 conical flask and titrate the liberated I_2 with standardised sodium thiosulphate solution until the sample solution becomes pale yellow. Add 2 cm^3 of starch solution and continue the titration till the blue colour disappears. Repeat the titration to get another reading.

6.5.5 Observations

Molarity of potassium dichromate solution $M_1 = M/480$

Observation Table I
Potassium dichromate vs sodium thiosulphate

Sl. No.	Volume of potassium dichromate solution in cm^3	Burette reading		Volume of sodium thiosulphate in cm^3 (Final − Initial)
		Initial	Final	
1	20			
2	20			
3	20			

Observation Table II
Water sample vs sodium thiosulphate

Sl. No.	Volume of water sample in cm^3	Burette reading		Volume of sodium thiosulphate in cm^3 (Final − Initial)
		Initial	Final	
1	100			
2	100			

6.5.6 Calculations

a) **Determination of the strength of sodium thiosulphate solution.**
Molarity of potassium dichromate solution = $M_1 = M/480$
Volume of potassium dichromate solution = $V_1 = 20$ cm^3
Volume of sodium thiosulphate solution (from Table I) = V_2 = ... cm^3
Molarity of sodium thiosulphate solution = M_2 = ?
Using Eq. 6.9,

$$6M_1V_1 = M_2V_2$$

$$M_2 = \frac{6M_1V_1}{V_2}$$

$$= \text{.....} \text{ mol dm}^{-3}$$

b) **Determination of the dissolved oxygen (DO) in the water sample**
Molarity of sodium thiosulphate solution = $M_3 = M_2$ = ... mol dm^{-3}
Volume of sodium thiosulphate solution (from Table II) = V_3 = ... cm^3

Volume of water sample used for titration = V_4 = 100 cm^3
Molarity of dissolved oxygen = M_4 = ?
Using Eq. 6.5.

$$4M_4V_4 = M_3V_3$$

$$M_4 = \frac{M_3V_3}{4V_4}$$

$$= \text{.....} \text{ mol dm}^{-3}$$

Dissolved oxygen (DO) in water sample in mg dm^{-3}

$= M_4 \times$ Molar mass of $O_2 \times 1000$
$= M_4 \times 32 \times 1000$ ppm
= ..... ppm

6.5.7 Result

Molarity of oxygen in the water sample = ... mol dm^{-3}
Amount of dissolved oxygen in the water sample in ppm = ...

In general, the minimum dissolved oxygen level needed to support a population of fish is 4 ppm, on this basis tell whether the water sample is suitable for the purpose of fisheries or not.

6.6 ANSWERS TO SAQs

Self-assessment Questions

1) In water sample hardness is due to the Ca^{2+} and Mg^{2+} ions. From Table 6.1, you can see that EDTA complexes with these ions are stable at pH 8-10. Further, metal ion indicator, eriochrome black T is worked in pH range 8.1-12.4. Therefore, water sample should be well buffered at pH 10.

2) Ca^{2+} ions do not form a sufficiently strong complex with eriochrome black T, so, in absence of Mg^{2+} ions in water sample we could not observe an accurate end point during titration with EDTA.

3) **Temporary hardness:** This hardness is removed on boiling, therefore, it is called as temporary hardness. This is due to bicarbonates of calcium and magnesium. **Permanent hardness:** It is so called because it does not get removed on boiling. Permanent hardness is due to chlorides and sulphates of calcium and magnesium.

4) (a) T (b) T (c) T (d) F (DO causes corrosion).

5) Role of these chemicals can be summarised in the form of following chemical equations:

$$MnSO_4 + 2NaOH \longrightarrow Mn(OH)_2 + Na_2SO_4$$
$$4Mn(OH)_2 + O_2 + 2H_2O \longrightarrow 4Mn(OH)_3$$
$$Mn(OH)_3 + H_2SO_4 \longrightarrow MnSO_4 + 2H_2O + O$$
$$2KI + H_2SO_4 + O \longrightarrow K_2SO_4 + H_2O + I_2$$
$$2Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2NaI$$

Further Reading

1) Vogel's *Text Book of Quantitative Chemical Analysis* revised by G.H. Jeffery, J. Bassett, J. Mendham and R.C. Denny, ELBS, 5th edition, 1989.

2) *Quantitative Analysis,* V. Alexayev, MIR publishers, 2nd edition, 1985.

3) *An Introduction to Practical Chemistry,* K.K. Sharma and D.S. Sharma, Vikas Publishing House Pvt. Ltd., 1988.

4) *Text Book of Quantitative Inorganic Analysis,* I.M. Kolthoff and E.B. Sandell, The Macmillan Company, New York, 3rd edition, 1967.