BE 2ND SEMESTER PREACTICAL

QUANTITATIVE INORGANIC ANALYSIS

Syllabus

1. **Estimation of Fe^{2+} by standard $KMnO_4$**
2. **Estimation of Fe^{3+} by standard $K_2Cr_2O_7$**
3. **Estimation of Cu^{2+} by iodometric method**

Experiment No.: 1

Aim of experiment: Estimation of Fe^{2+} from supplied solution by standard $KMnO_4$

Theory: This process was presented by Mabride in 1912. When oxalic acid acidified with dil. H_2SO_4 is titrated with potassium permanganate solution at $60\text{-}70^{O}C$ temperature, an oxidation-reduction reaction takes place between these substances. The chemical reaction is

$$\begin{array}{l}
2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O] \\
H_2C_2O_4 + [O] \longrightarrow 2CO_2 + H_2O\ ] \times 5 \\
\hline
\end{array}$$

$$2KMnO_4 + 3H_2SO_4 + 5H_2C_2O_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 10CO_2$$

Similarly, the ionic reaction is

$$MnO_4^- + 16H^+ + 5C_2O_4^{2-} \longrightarrow 2Mn^{2+} + 10H_2O + 10CO_2$$

When solution of Fe^{2+} ion acidified with dil. H_2SO_4 is titrated with potassium permanganate solution at room temperature, an oxidation-reduction reaction takes place between these substances. The chemical reaction is

$$\begin{array}{l}
2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O] \\
2FeSO_4 + H_2SO_4 + [O] \longrightarrow Fe_2(SO_4)_3 + H_2O\ ] \times 5 \\
\hline
\end{array}$$

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

Similarly, the ionic reaction is

$$MnO_4^- + 5Fe^{2+} + 8H^+ \longrightarrow Mn^{2+} + 5H_2O + 4Fe^{3+}$$

Required materials and solutions: Burette, pipette (20 mL), 250 mL conical flask, 250 mL volumetric flask, oxalic acid, potassium permanganate, etc.

Preparation of 0.1 N potassium permanganate solution

Take 3.2 g of potassium permanganate crystals in a 2 litre beaker. Add 1 litre of distilled water and stir until all the crystals dissolve in it. Boil the solution for about 15 minutes. After cool, filter the solution with the help of glass wool and kelp in coloured bottle. This solution is called a decinormal solution. The strength of this solution can be determined by titrating with standard Mohr's salt solution or standard solution of oxalic acid.

Preparation of 0.1 N solution of oxalic acid

Weigh accurately 1.575 g of oxalic acid in a chemical balance (or electronic balance) and transfer it to a 250 mL volumetric flask. Add 100 mL distilled water and shake vigorously until all the crystal is dissolved. Add again distilled water upto the mark of flask and it is labelled as 0.1N oxalic acid solution

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[Note: It may not be possible to weigh exact amount of crystals. Sometime few more crystals may be transferred or sometime fewer crystals may be transferred to the volumetric flask. If such situation is happen then strength of the solution will be high or less than what is expected. To get the exact strength of the solution in these cases a simple formula is employed.

$$\text{Actual strength} = \frac{\text{Weight taken}}{\text{Weight to be taken}} \times 0.1\ N$$

So, if amount of oxalic acid is 1.6000, then the actual strength of the solution is

$$= 1.6000/1.575 \times 0.1\ N = 0.1015N]$$

Standardization of KMnO4 by standard solution of oxalic acid

1. Take a clean burette and rinse it with potassium permanganate solution, support it with a burette clamp. Close the stopcock and with the help of a funnel fill potassium permanganate solution to just above the zero mark. Open the stopcock to remove any air bubbles in the tip.

2. In a 250 mL conical flask, take 20 mL oxalic acid by using a graduated pipette and 5 mL conc. H_2SO_4. Heat the flask to about 60-70 ^{O}C temperature on a wire gouge. When it becomes unbearable to touch, the required temperature is reached.
3. Read the upper meniscus of burette reading containing $KMnO_4$ solution.
4. Place a white paper below the burette and place the titration flask and run the $KMnO_4$ solution from the burette. During titration, operate the stopcock with left hand and constantly stir the flask with the right hand.
5. Stop addition of the $KMnO_4$ solution when the end point is reached (pink colour of the solution) and note the final reading of the burette. The difference between the final and initial readings gives the volume of the solution used for completion of the reaction.
6. Repeats the same titration for 3-4 times so that atleast the concordant reading (difference not more than 0.05 mL) are observed.

Observations:

Sl. No.	**Initial burette reading (mL)**	**Final burette reading (mL)**	**Volume of $KMnO_4$ (mL)**	**Concordant reading (mL)**
1	0	--	--	--
2	0	--	--	
3	0	--	--	

Calculation:

Volume of pipette = 20 mL

20 mL 0.1N oxalic acid $\equiv$ V volume of $KMnO_4$ (burette reading)

Or, $= 20 \times N/10 = V \times N_{KMnO_4}$

Or, $N_{KMnO_4} = 2N/V$

$= 0.1f$ N (say)

Estimation of Fe^{2+} by standard solution of $KMnO_4$ solution

1. Fill potassium permanganate solution to just above the zero mark of burette. Open the stopcock to remove any air bubbles in the tip.

2. In a 250 mL conical flask, take 20 mL Mohr's salt solution by using a graduated pipette and add 5 mL conc. H_2SO_4, 5 mL syrupy phosphoric acid.
3. Read the upper meniscus of burette reading containing $KMnO_4$ solution.
4. Place a white paper below the burette and place the titration flask and run the $KMnO_4$ solution from the burette. During titration, operate the stopcock with left hand and constantly stir the flask with the right hand.
5. Stop addition of the $KMnO_4$ solution when the end point is reached (faint pink colour lasting for 30 seconds) note the final reading of the burette. The difference between the final and initial readings gives the volume of the solution used for completion of the reaction.
6. Repeats the same titration for 3-4 times so that atleast the concordant reading (difference not more than 0.05 mL) are observed.

Observations

Sl. No.	**Initial burette reading (mL)**	**Final burette reading (mL)**	**Volume of $KMnO_4$ (mL)**	**Concordant reading (mL)**
1	0	--	--	--
2	0	--	--	
3	0	--	--	

Calculation:

1mL of 0.1 N $KMnO_4 \equiv 0.005585$ g of Fe^{2+}

1 mL of 0.1f N $KMnO_4 \equiv (0.005585 \times 0.01f)$ g of Fe^{2+}

V mL of 0.1f N $KMnO_4 \equiv (0.005585 \times 0.01f \times V)$ g of Fe^{2+}

Hence, the amount of Fe^{2+} present in 20 mL solution is = $(0.005585 \times 0.01f \times V)$ g

Hence the amount of Fe^{2+} present in 250 mL solution is = $(0.005585 \times 0.01f \times V \times 25)/2$ g

Some important points and precautions of titration

1. Before preparation of any standard solution all the glassware should be washed properly so that there no any contamination.
2. Do not use excess titrant, because even one more drop of titrant may disturb in determination of end point.

3. Reaction conditions are important factor of redox titration. For example, titration between $KMnO_4$ and Oxalic acid, the temperature of acid should not less than $60^{O}C$ and medium should be acidic.
4. Examine the stopcock of burette before use. Loose or damage stopcock cannot control.
5. It is important to know how to take the reading of burette. The eye level and liquid surface in the burette should be parallel.

Experiment No.: 2

Aim of experiment: Estimation of Fe^{3+} from supplied solution by standard $K_2Cr_2O_7$ solution

Theory: Since Fe^{3+} ions do not react with potassium dichromate, they are reduced to Fe^{2+} state by using $SnCl_2$ and HCl. The solution is then titrated with standard $K_2Cr_2O_7$ solution.

$$2Fe^{3+} + Sn^{2+} \longrightarrow 2Fe^{2+} + Sn^{4+}$$

$$6Fe^{2+} + Cr_2O_7^{2-} + 14H^{+} \longrightarrow 6Fe^{3+} + Cr^{3+} + 7H_2O$$

The estimation of Fe^{2+} is done by using diphenylamine indicator in presence of H_3PO_4

Required materials and solutions: Burette, pipette (20 mL), 250 mL conical flask, 250 mL volumetric flask, potassium dichromate, $SnCl_2$, HCl, diphenylamine, etc.

Preparation of 0.1N potassium dichromate solution

Weigh accurately 1.225 g of potassium dichromate in a chemical balance (or electronic balance) and transfer it to a 250 mL volumetric flask. Add 100 mL distilled water and shake vigorously until all the crystal is dissolved. Add again distilled water upto the mark of flask and it is labeled as 0.1 N $K_2Cr_2O_7$ solution.

Estimation of Fe^{3+} by standard 0.1N potassium dichromate solution

1. Fill potassium dichromate solution to just above the zero mark of burette. Open the stopcock to remove any air bubbles in the tip.
2. In a 500 mL conical flask, take 20 mL Fe^{3+} ion solution by using a graduated pipette, add 20 mL conc. HCl, heat the flask to about 70-80°C on an wire gauge.
3. Add $SnCl_2$ drop wise with constant shaking until the yellow colour of solution just disappears. Add few drops of $SnCl_2$ in excess.
4. Cool the flask rapidly under tap water to room temperature.
5. Add 10 mL of 5% $HgCl_2$ solution once at a time, shake and allow to stand for 5-10 minutes when a slight silky white precipitate appears, which indicates the reduction of Fe^{3+} to Fe^{2+}.
6. Dilute the solute by adding 150 mL water and add 5 mL conc. H_2SO_4, 5 mL syrupy phosphoric acid and 3-4 drops of diphenylamine indicator.
7. Read the upper meniscus of burette reading containing potassium dichromate solution.

8. Place a white paper below the burette and place the titration flask and run the potassium dichromate solution from the burette until the permanent red-violet colouration.
9. Repeats the same titration for 3-4 times so that atleast the concordant reading (difference not more than 0.05 mL) are observed.

Sl. No.	**Initial burette reading (mL)**	**Final burette reading (mL)**	**Volume of $K_2Cr_2O_7$ (mL)**	**Concordant reading (mL)**
1	0	--	--	--
2	0	--	--	
3	0	--	--	

Suppose V mL

Calculation:

1 mL of 0.1 N $K_2Cr_2O_7$ solution ≡ 0.005585 g Fe^{3+}

V mL of 0.1 N $K_2Cr_2O_7$ solution = (0.005585 × V) g Fe^{3+}

Hence, 20 mL of solution contain = (0.005585 × V) g Fe^{3+}

Hence, 250 mL of solution contain = (0.005585 × V × 25)/2 g Fe^{3+}

Experiment No.: 3

Aim of experiment: Estimation of Cu^{2+} from the supplied solution by iodometric method

Theory: Copper is estimated iodometrically. In this titration iodine is liberated which is titrated against sodium thiosulphate solution using starch as indicator,

$$CuSO_4.5H_2O + 4KI \longrightarrow 2CuI_2 + K_2SO_4 + 5H_2O$$

$$2CuI_2 \longrightarrow Cu_2I_2 + I_2$$

$$Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2NaI$$

The ionic equation is

$$2Cu^{2+} + 2I^- \longrightarrow Cu_2^{2+} + I_2$$

$$I_2 + S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2I^-$$

Required materials and solutions: Burette, pipette (20 mL), 250 mL conical flask, 250 mL volumetric flask, potassium dichromate, sodium thiosulphate, starch solution, HCl (1:1), ammonia solution, ammonium thiocyanate or potassium thiocyanate , etc.

Preparation of 0.1 N sodium thiosulphate solution

Weigh 6.2 g of sodium thiosulphate in a chemical balance (or electronic balance) and transfer it to a 250 mL volumetric flask. Add 100 mL distilled water and shake vigorously until all the crystal is dissolved. Add again distilled water upto the mark of flask and it is labeled as 0.1N $Na_2S_2O_3$ solution.

Preparation of 0.1 N potassium dichromate solution

See in experiment no.1

Standardization of sodium thiosulphate solution by standard potassium dichromate solution

1. Take a clean burette and rinse it with sodium thiosulphate solution, support it with a burette clamp. Close the stopcock and with the help of a funnel fill sodium thiosulphate solution to just above the zero mark. Open the stopcock to remove any air bubbles in the tip.
2. In a 500 mL conical flask, take 20 mL potassium dichromate by using a graduated pipette. 2 g of KI dissolved in 10 mL water, 5 mL conc. HCl. Shake the mixture and kept in dark covering the mouth of the flask with a watch glass for 5 minutes.
3. Wash the watch glass and side of the flask with sufficient distilled water and add 150 mL more distilled water to the mixture.

4. Place a white paper below the burette and place the titration flask and run the thiosulphate solution from the burette rapidly until the brown colour of the solution fades to straw-yellow colour.
5. Add 2 mL freshly prepared starch solution, the colour of the solution turns deep blue. Titrate the solution again with continuous stirring until the blue colour just disappears leaving a bright green solution.
6. Repeats the same titration for 3-4 times so that atleast the concordant reading (difference not more than 0.05 mL) are observed.

Observations:

Sl. No.	**Initial burette reading (mL)**	**Final burette reading (mL)**	**Volume of $K_2Cr_2O_7$ (mL)**	**Concordant reading (mL)**
1	0	--	--	--
2	0	--	--	
3	0	--	--	

Suppose V mL

Calculation:

Volume of pipette = 20 mL

20 mL 0.1N oxalic acid = V volume of thiosulphate (burette reading)

Or, = 20 × N/10 = V × $N_{Na_2S_2O_3}$

Or, $N_{Na_2S_2O_3}$ = 2 N/V

= 0.1f N (say)

Estimation of Cu^{2+} by standard solution of $Na_2S_2O_3$ solution

1. In a 500 mL conical flask, take 20 mL copper solution by using a graduated pipette. Add (1:1) NH_4OH solution drop wise with constant shaking until a slight greenish white precipitate appears. Add 5 mL glacial acetic acid to dissolve the precipitate.
2. Add 2 g of KI dissolved in 10 mL water, 5 mL and kept the mixture in dark covering the mouth of the flask with a watch glass for about 2 minutes.
3. Wash the watch glass and side of the flask with sufficient distilled water and add 100 mL more distilled water to the mixture.

4. Place a white paper below the burette and place the titration flask and run the thiosulphate solution from the burette rapidly until the brown colour of the solution fades to straw-yellow colour.
5. Add 2-3 mL freshly prepared starch solution, the colour of the solution turns deep blue. Again titrate the solution with continuous stirring until the blue colour fades to pale blue. Add 20 mL of 2% ammonium thiocyanate or potassium thiocyanate. Now titrate it again very slowly with constant shaking until the pale blue colour just disappears leaving the milky white solution.
6. Repeats the same titration for 3-4 times so that atleast the concordant reading (difference not more than 0.05 mL) are observed.

Sl. No.	**Initial burette reading (mL)**	**Final burette reading (mL)**	**Volume of thiosulphate solution (mL)**	**Concordant reading (mL)**
1	0	--	--	--
2	0	--	--	
3	0	--	--	

Suppose V mL

Calculation:

1mL of 0.1 N sodium thiosulphate solution ≡ 0.006357 g of Cu^{2+}

V mL of $0.1\times f$ N sodium thiosulphate solution = $(0.006357 \times V \times 0.1 \times f)$ g of Cu^{2+}

Hence, the amount of Cu^{2+} in 20 mL of solution = $(0.006357 \times V \times 0.1 \times f)$ g of Cu^{2+}

Hence, the amount of Cu^{2+} in 250 mL of solution = $(0.006357 \times V \times 0.1 \times f \times 25)/2$ g of Cu^{2+}

Physical Experiment

Experiment No.: 4

Aim of experiment: Study the kinetics of the reaction between $S_2O_3^{2-}$ and HCl

Theory: Sodium thiosulphate reacts with mineral acid like HCl to form elemental sulphur by the following reaction

$$Na_2S_2O_3 + 2HCl \longrightarrow 2NaCl + H_2O + SO_2 + S$$

The sulphur precipitated is marked by turbidity in the solution which indicates the progress of the reaction. The acid is taken in excess to keep its concentration more or less and solutions of various concentrations of thiosulphate are used to study the reaction kinetics.

Required materials and solutions: Five 250 mL beakers, measuring cylinder**,** 0.5N HCl, sodium thiosulphate

Procedure

a) Weigh accurately 0.1, 0.3, 0.5, 0.7 and 0.9 g sodium thosulphate and transfer to five 250 mL beakers. Dissolve in water and make each upto 100 mL with distilled water. Label them I to V.

b) Make a big cross mark (x) on a white paper and put the first beaker on it. Add 20 mL of 0.5N HCl and run the stopwatch. Observe the cross mark from the top of the solution. When the cross mark becomes invisible, stop the stopwatch and note the time needed.

c) Repeat the same experiments with remaining four thiosulphate solutions.

d) Plot a graph taking amount of thiosulphate per 100 mL of solution on *y* axis against reciprocal of the time needed to bring turbidity on *x* axis.

Results

Experimental temperature: ......°C

Sl. No	Amount of thiosulphate in gram per 100 mL	Volume of 0.5 N HCl (mL)	Time (t) needed for turbidity (sec)	Reciprocal of time (1/t)
1	0.1	20	...	...

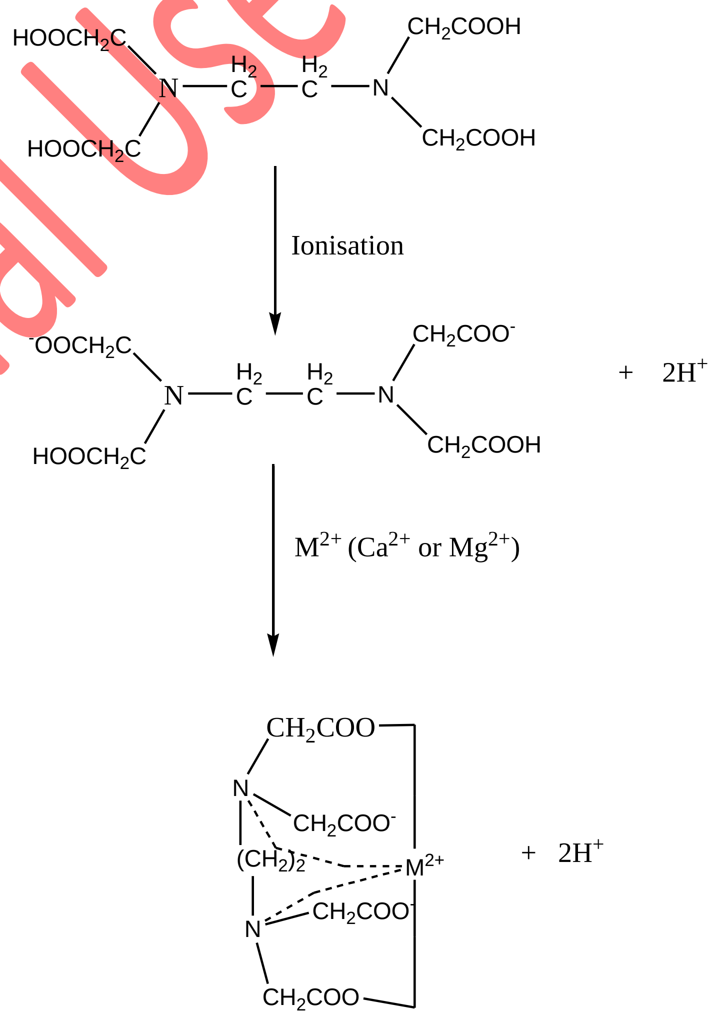
2	0.3	20	...	...
3	0.5	20	...	...
4	0.7	20	...	...
5	0.9	20	...	...

Conclusion

The above data and graph indicates that the reaction between sodium thiosulphate and HCl is a first order reaction because the reciprocal of time needed for turbidity is proportional to initial concentration of the thiosulphate.

Experiment No.:5

Aim of Experiment: Determination of hardness of water by complexometric titration.



Theory: Hard water is saturated with calcium, iron, magnesium and many other inorganic minerals. Water hardness is determined by the concentration of multivalent cations in the water. Common cations found in hard water include Ca^{2+} and Mg^{2+}. The total hardness is the sum of the molar concentrations of Ca^{2+} and Mg^{2+} in mg/L or mmol/L. It is generally measured by complexometric titration method. EDTA (Ethylenediamine tetraaceticacid) is one of the important reagents which form complexes with metals such as Ca^{2+} and Mg^{2+}.

The ionisation of this complex depends in the pH of the solution. In the estimation of Ca^{2+} and Mg^{2+}

with EDTA, an azo dye known as Eriochrome Black-T [1-(1-hydroxy-2-naphthylazo)-6-nitro-2-naphthol-4-sulphonate] is used as indicator. This forms a metal indicator complex. The solution is initially red. As the titration is proceeds, the metal ions form stable complex with EDTA, hence the indicator anion goes on solution and the colour changes from red to blue at the end point. Since the reaction is pH sensitive, so pH of the solution is maintained by adding suitable buffer.

Required solutions: Water sample, EDTA solution, $CaCl_2$ or $CaCO_3$, Eriochrome Black-T indicator

Standardization of EDTA

Preparation of standard 0.01M EDTA solution:

The estimation of the total hardness can be done by using disodium dihydrogenethylenediaminetetra-acetate (EDTA) of analytical grade. Anhydrous analytical grade EDTA (Na_2H_2 C_{10} $H_{12}O_8$ N_2 $.2H_2O$) should not be used as a primary standard as it contains moisture. The solution can be standardized by using standard $CaCl_2$, $ZnSO_4$ or $Zn(CH_3COO)_2$ solution. Weigh 9.3 g EDTA (3.73 g for disodium EDTA) and dissolve in distilled water in a 250 mL volumetric flask. Make up the volume to the mark of volumetric flask and labeled as 0.01M EDTA solution. This solution must be stored in a polythene bottle.

Preparation of standard 0.01M Zinc sulphate solution:

An amount of 0.1634 g granulated zinc is accurately measure and put in a beaker. Dissolve in dil. H_2SO_4, neutralize the solution with sodium hydroxide solution. Transfer it to a 250 mL volumetric flask and make up the volume up to the mark with distilled water.

Preparation of standard 0.01M Zinc acetate solution:

An amount of 0.5475 g of zinc acetate measure accurately and transfer it to a 250 mL volumetric flask containing 2 g ammonium chloride dissolve in10 mL of distilled water. Dissolve the salt and make up the volume up to the mark with distilled water.

Preparation of ammonia-ammonium chloride solution as buffer (pH = 10):

This solution may be prepared by adding 142 mL concentrated ammonia solution of specific gravity 0.90 to 17.5 g ammonium chloride and diluted to 250 mL volume with deionized water. The second solution may be prepared by dissolving 1.179 g of EDTA and 0.780 g of $MgSO_4.7H_2O$ in 50 mL deionized water. Now mix both the solutions and make the volume of 250 mL.

Preparation of Eriochrome black-T:

Prepare Eriochrome black-T solution by dissolving 0.2 g of it in 15 mL of triethanolamine and then dilute with 5 mL of ethanol. This indicator solution is unstable hence must be prepare freshly.

Or grind a solid mixture of 0.05 g Eriochrome black-T and about 4.9 g KNO_3.

Procedure

Take 50 mL of given water sample and add 1 mL of buffer solution and 0.40 g of indicator mixture. Now, titrate the mixture with standard EDTA solution until the colour changes from red to blue. Sometime, Mg may not be present in the given water sample, then it is necessary to add 0.1 mL Mg-EDTA solution before adding the indication mixture. In some cases, hard water may contains interfering ions in trace amount which may be overcome by adding 4 mL of the buffer solution followed by 0.30 g of hydroxylammonium chloride and then 0.5 g KCN (analytical grade) before applying indicator. Repeat the process to get concordant results.

Results

Sl. No	Initial burette reading (mL)	Final burette reading (mL)	Volume of EDTA (mL)	Concordant results (mL)
1				
2				
3				

Calculation

25 mL of 0.01M zinc acetate or zinc sulphate solution ≡ V mL EDTA

$$\text{Hence, strength of EDTA} = \frac{25 \times 0.01}{V}$$

$$= f \times 0.01 \text{ M (suppose)}$$

Determination of Total hardness of water

Hardness is expressed in parts of $CaCO_3$ equivalent of Ca and Mg salts per million part (ppm) of water.

Procedure

Pipette out 50 mL of water sample into a 250 mL conical flask. Dilute it to 100 mL with distilled water. Add 5 mL ammonia-ammonium chloride buffer and 30-35 mg indicator (EBT + KNO_3). The mixture is shaken vigorously to obtain wine-red colour. Titrate the mixture with standard EDTA solution until the colour changes to blue. Repeat the process to get concordant results.

Results:

Sl. No	Initial burette reading (mL)	Final burette reading (mL)	Volume of EDTA (mL)	Concordant results (mL)
1				
2				
3				

Suppose V mL

Calculation

1000 mL of 0.01 M EDTA solution $\equiv$ 1000 mL of 0.01 M $CaCO_3$

$\equiv$ 1 g of $CaCO_3$ (mol. wt. of $CaCO_3$ = 100)

$$\text{V mL of f 0.01 M EDTA solution} \equiv \frac{1 \times V \times f}{1000}\ \text{g of } CaCO_3$$

$\equiv V \times f \times 10^{-3}$ parts of $CaCO_3$

Hence, 10^6 parts of hard water contain $(V \times f \times 10^{-3} \times 10^6)/50$ parts of $CaCO_3$

Total hardness = $(V \times f \times 10^2)/5$ ppm = $V \times f \times 20$ ppm

Determination of permanent hardness of water

Boil 250 mL of the same water sample in a 500 mL beaker for 30 minutes. Cool and filter it, collect the filter in a 250 mL of volumetric flask without washing the filter paper containing precipitate. Make up the solution up to the mark with distilled water.

Pipette out 50 mL of the solution into a 250 mL conical flask and titrate by using same procedure as described above. Repeat the process to get concordant results.

Determination of temporary hardness of water

Subtraction of permanent hardness from total hardness of water as calculated above gives the temporary hardness of water in ppm.

Reference

Undergraduate Practical Chemistry, J. Borah and R. Ojah, Assam Book Depot, Guwahati-1

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