JECRC

Department of Chemistry

(Session- 2020-2021)

Subject: Engineering Chemistry (CODE : 1FY2-03)

Year/Semester: 1st Year/ 1st Semester

COURSE OUTCOMES

Students will be able to:

CO1: Explain the impurities of water (mainly hardness) and boiler troubles

Chapter 1:WATER:Lecture 2:Topic 1: Units of Hardness

1.2.1 Units of Hardness: There are four different units used for hardness as

- 1. Parts per million (ppm)
- 2. Milligrams per litre (mg/L)
- 3. Degree Clark (°*Cl*)
- 4. Degree French (°*Fr*)

1. Parts per million (ppm) : It is the parts of $CaCO_3$ equivalent hardness present per million or 10^6 parts of water.

1ppm = 1 part of CaCO₃ equivalent hardness present per million or 10^6 parts of water

2. Milligrams per litre (mg/L) : It is the number of milligrams of CaCO₃ equivalent hardness present per litre of water

 $1 \text{mg/L} = 1 \text{ mg of CaCO}_3$ equivalent hardness present per litre of water

1 mg/L = 1 ppm

It can be proved.

 $1L= 1 \text{kg of water} = 1000 \text{ x } 1000 \text{ mg} = 10^6 \text{ mg}$

1mg/L=1 mg of CaCO₃ equivalent per 10⁶ mg of water

= 1 part of CaCO₃ equivalent per 10^6 mg of water

1 mg/L = 1 ppm

3. Degree Clark (**Cl*) : It is the number of grains (1/7000 lb) of CaCO₃ equivalent hardness per gallon (10lb or 70,000 grains) of water.

1 Clark = 1 grain of CaCO₃ equivalent hardness per gallon of water

1 Clark = 1 part of CaCO₃ equivalent hardness per 70,000 part of water

4. Degree French (•*Fr*) : Is the parts of CaCO₃ equivalent hardness per lac (10⁵) parts of water

1•French = 1 part of CaCO₃ equivalent hardness per 10^5 parts of water.

Unit/unit	Ррт	mg/L	•Cl	•Fr
Ppm	1	1	0.07	0.1
mg/L	1	1	0.07	0.1
•Cl	14.3	14.3	1	1.43
•Fr	10	10	0.7	1

Table1: Relation among different units of hardness

Chapter 1:WATER: Lecture 2:Topic 2: Determination of hardness by EDTA method

1.2.2.Determination of Hardness of Water:

There are two methods which are most commonly used for determination of hardness

- 1. Clark's Method (Soap titration method)
- 2. EDTA Method (Complexometric titration method)

EDTA Method (Complexometric titration method):

This method is more accurate for determining the hardness of water mainly caused by dissolved calcium and magnesium salts.

This is a complexometric method. Since EDTA has limited solubility in water the disodium salt of EDTA is taken for titration. Ethylene Diamine Tetraacetic Acid (EDTA) is a strong complexing agent.



Structure of EDTA

It acts as a tetra dentate or hexadentate ligand and binds with metal ions to give colorless, soluble and very stable 1: 1 complexes (chelates)



Hexadentate form

 $M = Ca^{++} \text{ or } Mg^{++}$

(i) **Basic Principal :**EDTA (Ethylenediamine tetra acetic acid) forms colorless stable complexes with Ca^{2+} and Mg^{2+} ions present in water at pH = 9.8-10.

The indicator used in this titration is Eriochrome Black-T (E.B.T).

EBT indicator forms unstable, wine-red colored complexes with Ca^{2+} and Mg^{2+} ions present in hard water.

At the endpoint of the titration, when all the Ca^{2+} and Mg^{2+} ions are consumed, the next drop of EDTA displaces EBT from the weak complex and color changes from wine red to blue due to free EBT in the solution.



Eriochrome Black-T

Determine the hardness of given water sample by complexometric method using EDTA.

(ii) Procedure :

(A) Preparation of solutions:

(A-1)Preparation of standard hard water

(A-2) Preparation of M/100 EDTA solution

(A-3)Preparation of buffer solution(NH₄Cl- NH₄OH) of pH10

(A-4) Preparation of Erichrome Black- T indicator

(A-1) Preparation of standard hard water: 1.0 g pure and dry CaCO₃ is dissolved in little quantity of HCl. The solution is then heated till it becomes dry (to remove CO₂ and excess acid).Dry residue is then dissolved in distilled water to make one litre solution.

1 ml of standard hard water = 1 mg $CaCO_3$

(A-2)Preparation of M/100 EDTA solution: 3.722 g of disodium salt of EDTA is dissolved in distilled water to make up to 1 litre solution.

(A-3)Preparation of NH₄Cl- NH₄OH of pH10: 67.5 gm of A.R.NH₄Cl and 570 ml concentrated ammonia solution is taken and diluted to 1 litre with de-ionized water.

(A-4)Preparation of Erichrome Black- T indicator: 0.5 gm of Erichrome Black-T indicator is dissolved in 100 ml ethyl alcohol.

(B)Standardization of EDTA Solution: 50 ml of standard hard water is taken into a conical flask, 8-10 ml of buffer solution and 3-4 drops of indicator EBT is added to it. Then it is titrated with EDTA solution till wine red color of the mixture changes to blue. This is end point. Let the volume of EDTA solution consumed here is V_1 ml.

(C) Determination of Total hardness: 50 ml of sample hard water is taken into a conical flask,8-10 ml of buffer solution and 3-4 drops of indicator EBT is added to it. Then it is titrated with EDTA solution till wine red color of the mixture changes to blue. This is end point .Let the volume of EDTA solution consumed here is V_2 ml.

(D) Determination of permanent hardness: 250 ml of sample hard water is boiled till it reduces to 50 ml. The precipitate is filtered off and is washed with distilled water. Both the filtrate and washings are collected in a 250 ml capacity flask and volume is again made 250ml by adding distilled water.50 ml of this boiled water is taken into a conical flask and it is titrated with EDTA solution same as above. Let the volume of EDTA solution consumed here is V_3 ml.

(iii) Calculations:

(i) <u>Standardization of EDTA solution :</u>

50 ml standard hard water= V_1 ml EDTA solution

 $(1 \text{ ml of standard hard water} = 1 \text{ mg CaCO}_3)$

V₁ ml EDTA solution= 50 mg CaCO₃

Or 1 ml EDTA solution= $(50/V_1)$ mg CaCO₃

(ii) Total hardness:

50 ml sample hard water= V2 ml EDTA solution

- Or 1 ml sample hard water= $(V_2/50)$ ml EDTA solution= (V_2/V_1) mg CaCO₃
- Or 1000 ml sample hard water (<u>Total hardness</u>) = $(V_2 * 1000 / V_1)$ mg CaCO₃
 - (iii) Permanent hardness:

50 ml boiled hard water= V₃ ml EDTA solution

- Or 1 ml boiled hard water= $(V_3/50)$ ml EDTA solution= (V_3 / V_1) mg CaCO₃
- Or 1000 ml boiled hard water (**Permanent hardness**) = $(V_3 * 1000 / V_1)$ mg CaCO₃

Total hardness = $V_2/V_1 x$ 1000 ppm

Permanent hardness = $V_3/V_1 \ge 1000$ ppm

Temporary hardness = Total hardness - Permanent hardness

(iv) Advantages of EDTA Method :

- (i) More accurate
- (ii) Convenient
- (iii) More rapid Procedure.

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Chapter 1: WATER: Lecture 3: Topic: Municipal Water Supply (Water for Domestic Supply):

1. <u>Requisite of Drinking water:</u> The essential requirements for drinking/potable water should satisfy the following characteristics.

(i) Physical :

- 1. Drinking water should be colorless, perfectly cool and pleasant in taste.
- 2. The range of pH should be within 6.5 8.5 (alkaline).
- 3. Its turbidity should not exceed the permissible limit given by BIS (5ppm).

(ii) Chemical :

- 1. It should be free from objectionable gases like H₂S.
- 2. Total dissolved solids should be less than 500ppm.
- 3. Total hardness should be less than 200ppm.
- 4. It should be free from harmful toxic metals like As, Hg, Pb, Cd, etc.
- 5. Fluoride content should be less than 1.5ppm.

6. Chloride and Sulphate contents should be less than 250ppm, and 150ppm respectively.

(iii) Biological :

- 1. Coliform organisms should be less than 10MPN/100mL(No E. Coli in 100mL)
- 2. It should be free from pathogens.

B. Purification of Water (Treatment of Water for Municipal Supply):

Municipality supply drinking water uses the natural sources of water such as rivers, wells, etc. Water from these sources is not as per specifications of drinking water. So to make the water fit for human consumption, water from the sources have to be treated by the methods which are dependent on the nature of impurities in raw water.

The usual methods used in making raw water potable are Screening, Sedimentation, Coagulation, Filtration and Disinfection as discussed below:

S. No.	Impurity	Process Employed]
1	Floating matter like leaves, twigs	Screening	1
2	Suspended particles(large)	Plain Sedimentation	ni
3	Fine Suspended particles	Sedimentation with coagulation	is
4	Microorganisms & colloidal impurities	Filtration	in
5	Microorganisms including pathogens	Disinfection	wa
6	Hardness	Softening	thr

(Coarse, Medium and Fine) to remove impurities. The raw water is passed through these screens having large number of holes, where floating materials like leaves, twigs, etc. are held by them and water, free from floating material is obtained.

2. **Sedimentation:** It is the process, which requires the flow of water at low velocities or the retention of water for a certain period in a tank. During this process most of the suspended particles are settled down and removed. The retention period may vary from an hour to multiple hours. In this process 70-75% suspended impurities are removed.

- It is of two types:
- (i) Plain Sedimentation
- (ii) Sedimentation with Coagulation



(i) Plain Sedimentation :

In this process water is kept undisturbed in large rectangular tanks about 5m deep, where most of the suspended impurities settle down at the bottom, due to gravitational force. The clear supernatant water is then drawn from tank with the help of pump. The retention period is about 2-6 hours depending upon the particle size of the suspended matter.

(ii) Sedimentation with Coagulation :

The colloidal impurities will not settle by plain sedimentation, therefore, the coagulants are added to water tank before sedimentation. The coagulants react with colloidal particles which are oppositely charged, hence, neutralizing them, so that these smaller particles come closer and their size becomes larger. The force of gravity acts on these larger particles and they settle down or precipitate in the tank as floc rapidly. The most commonly used coagulants in this process are as follows:

(a)K₂SO₄.Al₂(SO₄)₃.24H₂O (Alum)

(b)Fe SO₄.7 H₂O (Ferrous sulphate)

(c)NaAlO₂ (Sodium aluminate)

(i) K₂SO₄.Al₂(SO₄)₃.24H₂O (Alum): For water having pH=6.5-8.5

 $Al_2(SO_4)_3 + 3Ca(HCO_3)_2 \quad \rightarrow Al(OH)_3 \downarrow + CaSO_4 + CO_2 \uparrow$

(ii) Fe SO4.7 H₂O (Ferrous sulphate): For water having pH > 8.5

Fe SO₄ + Mg (HCO₃)₂ \rightarrow Fe (OH) ₂ \downarrow + MgSO₄ +CO₂ \uparrow

 $4Fe~(OH)_2 \textbf{+} \textbf{2H}_2\textbf{O} \textbf{+} O_2 \rightarrow 4Fe(OH)_3 \downarrow$

(iii) NaAlO₂ (Sodium Aluminate): For water having pH 5.5-8.0

It can be used for treating acidic waters. The aluminium hydroxide floc causes sedimentation. The NaOH produced during the reaction precipitate magnesium salt as Mg(OH)₂. Thus, sodium aluminate decreases hardness due to removal of magnesium ions from water.

 $NaAlO_2 + 2H_2O \rightarrow Al \ (OH)_3 \downarrow \quad + \ NaOH$

 $MgSO_4 + 2NaOH \rightarrow Mg(OH)_2 \downarrow + Na_2SO_4$