Hardness

Hard water: Is that water which requires a considerable amount of soap to produce foam and causes scale in boilers and pipes.

Hardness in water is caused by the divalent cataions:

Calcium (Ca++) and magnesium (Mg++) and polyvalents Aluminum (Al+++), Iron (Fe+++), Manganese (Mn+++) and Strontium (Sr +++). The polyvalents, however, are too low in fresh water to produce significant hardness. For this reason it will be assumed here that hardness is caused entirely by calcium and magnesium ions. These divalent have the ability to react with soap, forming insoluble compounds, thus reducing foaming and with anion forming scale; most of the calcium and magnesium are present in water as bicarbonates, sulphates, and sometimes as chlorides or nitrates.

The source of water hardness;

The main source of hardness in water is the limestone present in the earth’s surface. As rain water falls on the earth’s crust, it is incapable of dissolving limestone by itself, when rain attacks the soil it takes up CO2 which is released by bacterial action. The limestone will react with water containing CO2 forming calcium bicarbonate which is soluble compound.

 CaCO3 + H2O + CO2 Ca (HCO3)2.

Limestone is not pure carbonate but includes impurities such as sulphates and chlorides. These are water soluble as well.

Types of hardness:

Water hardness can be classified in two ways:

1. With respect two metallic ions.
2. Calcium hardness: caused by calcium ions.
3. Magnesium hardness: caused by Magnesium ions.

Calcium plus magnesium hardness equal total hardness.

1. With respect to the anions associated with the metallic ions.
2. Carbonate hardness: Is that hardness caused by the presence of calcium and magnesium carbonate (CO3) and bicarbonate (HCO3). This type of hardness is also called temporary hardness of these compounds precipitate when the water is boiled.
3. Non carbonate hardness: caused by the presence of calcium and magnesium sulfates (SO4-2) and or chloride (Cl-). This type of hardness is considered permanent as these compounds do not precipitate by boiling the water.

Carbonate hardness plus non- carbonate hardness equal total hardness

 Degree of hardness: water can be classified according to following hardness classes.

Ca and Mg hardness hardness degree (or classes)

0-75 mg/l soft water

75-150 mg/l moderately hard water

150 – 300 mg/l hard water

More than 300 mg/l very hard water.

EDTA Method for hardness determination:

 PRINCIPLE:

The original color of Eriochrome black T is blue. When about 10.0 it added to hard water sample of a pH combines with hardness producing cataions (Ca and Mg) and forming a weak complex ion that is wine red in color.

Ca and Mg + Eriochrome black T (Eriochrome black T) wine red.

EDTA is chelating agent, during titration, it forms a stable complex with calcium and magnesium ion.

Ca and Mg + EDTA M.EDTA complex.

This reaction liberate the Eriochrome black T is blue then all cataions react with EDTA, the wine red color will change to distinct blue color.

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Then determining the amount of calcium in the sample a buffer solution (pH 12) is added. This strong basic solution will lead to precipitation magnesium ion as Mg(OH)2. What remains or the indicator (murexide) to react with is mainly Ca ions.

Reagents:

1. 0.01 N EDTA titrant

Dissolve 3.723 g of EDTA (ethylene diamine tetraacetic acid disodium salt), (Na2H2C10H12O8H2.2H2O) in distilled water, then dilute to 1 liter.

1. Eriochrome black T indicator. To prepare a dry powder of this dye mix 0.5g Eriochrome black T with 100g of NaCl.
2. Murexide indicator.

To prepare a dry powder mix 200g of Murexide with 100g of NaCl.

1. Buffer solution pH (10).

Add 18.3 ml 0.1 M NaOH to 50 ml of 0.025 N Borax.

1. Buffer solution pH (12).

Add 96.9 ml of 0.1 M NaOH to 50 ml 0.05 M Na2HPO4.

Procedure:

1. For total hardness
2. Pipette 50 ml of sample into conical flask.
3. Add 1-2 ml of buffer solution pH (10), shake well.
4. Add 0.2g Eriochrome black T indicator, shake well, the solution will have a wine red color.
5. Titrate against 0.01 M EDTA (disodium salt) solution until the color change from wine red to pure blue.



Calculation:

Total hardness as mg CaCO3/L = A\*B\*1000/sample size

A= volume of titrated EDTA for total hardness.

B= 1 ml of EDTA eq. 1 ml CaCO3.

B= 1

1. For calcium hardness.
2. Pipette 50 ml of sample into conical flask.
3. Add 1-2 ml of buffer solution pH (12), shake well.
4. Add 0.2g Murexide indicator, shake well, the solution will have a pink color.
5. Titrate against 0.01 M EDTA (disodium salt) solution until the color change from pink to purple.



Calculation:

Calcium hardness as mg CaCO3/L = A\*B\*1000/sample size

A= volume of titrated EDTA for total hardness.

B= 1 ml of EDTA eq. 1 ml CaCO3.

B= 1

Calcium as mg/l = A\*B\*400.8/sample size

A= volume of titrated EDTA for total hardness.

B= 1 ml of EDTA eq. 1 ml CaCO3.

B= 1

1. For magnesium hardness:

Magnesium hardness as mg CaCO3/L.= Total hardness as mg CaCO3/L - Calcium hardness mg CaCO3/L.

 To change Mg ++ hardness as mg CaCO3/L for Mg++ as mg/l use this equation.

Mg++ as mg/L= Mg ++ hardness as mg CaCO3/L \* 0.243