Environmental Quality & Pollution Monitoring Techniques

Water Quality Parameters

Hardness in Water

- What ?
- Why ?
- How ?

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Water Quality Parameters – Hardness

- **Hardness** in water is related to an effect caused by presence of certain cations.
- **Hardness** is defined as the concentrations of di or multivalent cations, mostly calcium and magnesium, expressed in terms of calcium carbonate.
- These minerals in **water** can cause some everyday problems. ...
- When **water** containing calcium carbonate is heated, a hard scale is formed that can plug pipes and coat heating elements.

Water Quality Parameters – Hardness

Hardness

- Hard waters have many disadvantages, primarily scale formation (i.e., $CaCO_3$ deposition) and enhanced capacity to precipitate soap. Thus measurement of water hardness is very necessary.
- Total hardness of water is the sum of Ca^{++} and Mg^{++} concentration in water. The results are expressed as calcium carbonate, in mg/L, i.e., "mg/L as $CaCO_3$".
- Cations (sodium, calcium, magnesium, ……) and Anions (hydroxyl, bicarbonates, carbonates, chlorides, sulphates, ……..).
- When total hardness is numerically greater than the sum of carbonate and bicarbonate alkalinity for a water sample, the amount of hardness equivalent to the carbonate plus bicarbonate alkalinity is called "**carbonate hardness**". The amount of hardness in excess of this is called "**noncarbonate hardness**". When hardness numerically is equal to or less than the sum of carbonate and bicarbonate alkalinity, all hardness is carbonate hardness, and noncarbonate hardness is absent.

Water Quality Parameters – Hardness

Total Hardness Determination

- Total hardness may be determined by performing a complexometric titration with EDTA as the chelating agent.
- The indicator Eriochrome Black-T (EBT) is normally blue in colour, but becomes red in colour when it forms complex with calcium or magnesium. Thus when EBT is added to a solution containing hardness, it complexes Ca^{++} and/or Mg^{++} and becomes red in colour.
- When EDTA, which has much stronger affinity for Ca^{++} and Mg^{++} than EBT, is added to the solution, it chelates the Ca^{++} and Mg^{++}ions complexed with EBT. When all such ions are chelated, i.e., the endpoint of the titration is reached; EBT reverts to its original blue colour.
- Relevant equation: **EDTA + Ca^{++} → Ca – EDTA**

Water Quality Parameters – Hardness

Procedure for Total Hardness Determination:

- Dissolve 1.179 g of EDTA disodium salt of EDTA dihydrate and 780 mg $MgSO_4.7H_2O$ or 644 mg $MgCl_2.6H_2O$ in 50 mL of distilled water. Add this solution to 16.9 g NH_4Cl and 143 mL conc. NH_4OH with mixing and dilute to 250 mL with distilled water. Store in a plastic bottle. Label, "**Buffer solution for hardness determination**".
- Dissolve 3.723 g analytical reagent grade EDTA disodium salt dihydrate in distilled water and dilute to 1000 mL. Label**, "EDTA titrant for hardness determination, 0.01 M**".
- Pour 1.0 g $CaCO_3$ powder in a 500 mL conical flask. Add, a little at a time 1+1 HCl until $CaCO_3$ is dissolved. Add 200 mL of distilled water. Add a few drops of methyl red indicator, and if necessary, adjust the colour to orange using acid/base. Dilute to 1000 mL. Label, "**$CaCO_3$ standard for hardness determination, 1000 mg/L**".

Water Quality Parameters – Hardness

- Prepare 50 mL aliquots by diluting the standard $CaCO_3$ solution. The hardness values of these aliquots should be 100, 200, 300,and 500 mg/L as $CaCO_3$ respectively.
- To each aliquot add 1-2 mL of the buffer solution.
- To each aliquot add a pinch of Eriochrome Black-T powder (indicator). The aliquots are red in colour.
- Titrate each aliquot using the standard EDTA solution (in burette).
- At the end point the aliquots change colour from red to blue.
- Draw a calibration curve of Hardness vs mL of EDTA required.
- Repeat the procedure with 50 mL of sample.
- Use the calibration curve to determine the hardness of sample. Express the results as hardness in mg/L as $CaCO_3$.
- What is the carbonate and noncarbonate hardness in sample? (You need the alkalinity value of sample determined earlier for this purpose)

Water Quality Parameters – Hardness

Calcium Hardness Determination

- Calcium hardness, i.e., the calcium ion concentration in water expressed in mg/L as $CaCO_3$ may be determined by performing a complexometric titration with EDTA as the chelating agent, and ammonium purpurate (murexide) as the indicator.
- The pH of the sample is first raised to 11-12 by the addition of strong base. All the magnesium present in the sample precipitates at this pH as $Mg(OH)_2$ (s).
- Murexide powder is added to the solution at this point as an indicator. Murexide combines with calcium and the resulting complex is pink in colour.
- When EDTA, which has much stronger affinity for Ca^{++} than murexide is added to the solution, it chelates the Ca^{++} ions complexed with murexide. When all such ions are chelated, i.e., the endpoint of the titration is reached, murexide reverts to its original purple colour.

Water Quality Parameters – Hardness

Procedure for Calcium Hardness Determination

- Take a 50 mL aliquot of sample.
- Add 2 mL of the 6 N NaOH solution.
- Add a pinch of ammonium purpurate (murexide) powder (indicator).
- Titrate using the standard EDTA solution (in burette) until colour change occurs from pink to purple.

Water Quality Parameters – Hardness

- Why as $CaCO_3$?
- Comparison with Alkalinity
- To assess Carbonate and Non-Carbonate Hardness
- Why assess Carbonate and Non-Carbonate Hardness?
- Chemistry of Carbonate and Non-Carbonate Hardness

Water Quality Parameters – Hardness

Calculation of Carbonate and Non-Carbonate Hardness
H = Total Hardness (Calcium + Magnesium) in mg/L as $CaCO_3$
T = (Carbonate Alkalinity + Bicarbonate Alkalinity) in mg/L as $CaCO_3$

Case I: If, $H > T$
Non-Carbonate Hardness = H - T
Carbonate Hardness = T

Case II: If, $H < T$
Carbonate Hardness = H
Non Carbonate Hardness = 0