

Titrimetric Procedures – ALKALINITY HARDNESS, Ca, Mg and CHLORIDES

D.S.S.SRINIVAS

QUALITY MANAGER

Environment Protection Training & Research
Institute, (EPTRI)

METHODS OF ANALYSIS

• Mainly the following techniques are used for the determination of Physico-Chemical Parameters in the water and waste water.

1. Electrometry-PH, E.C,

2. Titrometry-Total Alkalinity, Total Hardness

Calcium Hardness, Chlorides, N-NH₃

TKN, COD, Bio-Chemical oxygen demand

3. Gravimetry-T.S, T.D.S, T.S.S, T.V.S, T.D.V.S, T.F.S, & Oil and Grease

METHODS OF ANALYSIS

- 4. Colourimetry- NO₂-, NO₃-, PHOSPHATES,
FLOURIDE,
- 5. Turbidometry- Turbidity, Sulphates
- 6. Ion selective Electrodes: F-, Cl, CN,
N-NH₃,
- 7. INSTRUMENTAL ANALYSIS: METALS
PESTICIDES
PAHS, VOC, S,

ALKALINITY

Introduction: The alkalinity of water is a measure of its capacity to neutralise acids. The alkalinity of natural waters is due to the salts of carbonates, bicarbonates, borates, silicates and phosphates along with the hydroxyl ions in the Free State. However the major portion of the alkalinity in natural waters is caused by hydroxide, carbonate and bicarbonate, which may be ranked in order of their association with high pH values. Alkalinity values provide guidance in applying proper doses of chemicals in water and wastewater treatment processes, particularly in coagulation, softening and operational control of anaerobic digestion.

A. Titrimetric method The alkalinity in sample can be determined by titrating at room temperature with 0.02N sulphuric acid by using phenolphthalein and methyl orange indicator. Alkalinity of sample can be estimated by titrating with standard sulphuric acid (0.02N). Titration to decolourisation of phenolphthalein indicator will indicate complete neutralisation of OH^- and $1/2$ of CO_3^{--} while sharp change from yellow to orange of methyl orange indicator will indicate total alkalinity, (complete neutralisation of OH^- , CO_3^{--} , HCO_3^-).

Apparatus 5

- a. Beakers - The size and form will depend upon the electrode and the size of the sample to be used for determination of alkalinity
- b. Pipettes (volumetric)
- c. Flasks (volumetric): 1000 mL, 200 mL, 100 mL

Reagents and standards

- a. Standard H₂SO₄, 0.02 N: Prepare 0.1 N H₂SO₄ by diluting 3.0 mL conc. H₂SO₄ to 1000 mL. Standardise it against standard 0.1N Na₂CO₃ solution. Dilute appropriate volume of H₂SO₄ to 1000 mL to obtain standard 0.02 N H₂SO₄.
- b. Phenolphthalein indicator: Dissolve 0.5 g in 500 mL 95% ethyl alcohol. Add 500 mL distilled water. Add dropwise 0.02 N NaOH till faint pink colour appears (pH 8.3)
- c. Methyl orange indicator: Dissolve 0.5 g and dilute to 1000 mL with CO₂-free distilled water (pH 4.3-4.5). OR Bromo-cresol green indicator: Dissolve 0.1 g bromocresol green, sodium salt, in 100 mL distilled water (pH 4.5).

PREPARATION OF KNOWN STRENGTHS FROM STOCK SOLUTIONS

REQUIRED STRENGTH X REQUIRED VOLUME

STRENGTH OF THE STOCK SOLUTION

EX:PREPARATION OF 0.1 N SULPHURIC ACID

REQUIRED STRENGTH=0.1N

REQUIRED VOLUME =1000mL

STRENGTH (NORMOLITY)

OF THE AVAILABLE CON H₂SO₄=36N

$$\frac{0.1 \text{ N} \times 1000}{36 \text{ N}} = 2.78 \text{ ML or } 3 \text{ mL}$$

PROCEDURE

Take 25 or 50 mL sample in a conical flask and add 2-3 drops of phenolphthalein indicator

- b. If pink colour develops titrate with 0.02 N H₂SO₄ till it disappears or pH is 8.3. Note the volume of H₂SO₄ required.
- c. Add 2-3 drops methyl orange to the same flask, and continue titration till yellow colour changes to orange. Note the volumes of H₂SO₄ required.
- d. In case pink colour does not appear after addition of phenolphthalein continue as above.
- e. Alternatively, perform potentiometric titration to preselected pH using appropriate volume of sample and titration assembly. Titrate to the end point pH without recording intermediate pH. As the end point is approached make smaller additions of acid and be sure that pH equilibrium is reached before adding more titrant. The following pH values are suggested as equivalence points for corresponding alkalinity concentration as mg CaCO₃/L

Data analysis and calculations

Calculate total (T), phenolphthalein (P) alkalinity as follows:

P - alkalinity, as mg CaCO₃/L = A x 1000/mL sample

T - alkalinity, as mg CaCO₃/L = B x 1000/mL sample In case H₂SO₄ is not 0.02 N apply the following formula:

In case H₂SO₄ is not 0.02 N apply the following formula

$$\text{Alkalinity, as mg CaCO}_3/\text{L} = \frac{A/B \times N \times 50000}{\text{mL of sample}}$$

where,

A = mL of H₂SO₄ required to bring the pH to 8.3

B = mL of H₂SO₄ required to bring the pH to 4.5

N = normality of H₂SO₄ Once, the phenolphthalein and total alkalinities are determined, three types of alkalinities i.e. hydroxide, carbonate and bicarbonate are easily calculated from the table given as under:

ALKALINITY RELATIONSHIPS

RESULT OF TITRATION	HYDROXIDE ALKALINITY AS CaCO_3	CARBONATE ALKALINITY AS CaCO_3	BICARBONATE CONCENTRATION AS CaCO_3
1. $P=0$	0	0	TOTAL ALKALINITY
2. $P < 1/2 T$	0	$2P$	TOTAL- $2P$
3. $P = 1/2 T$	0	$2P$	0
4. $P > 1/2 T$	$2P - T$	$2(T - P)$	0
5. $P = T$	TOTAL.ALK	0	0

Hardness

Water hardness is a traditional measure of the capacity of water to precipitate soap. Hardness of water is not a specific constituent but is a variable and complex mixture of cations and anions. It is caused by dissolved polyvalent metallic ions. In fresh water, the principal hardness-causing ions are calcium and magnesium which precipitate soap. Other polyvalent cations also may precipitate soap, but often are in complex forms, frequently with organic constituents, and their role in water hardness may be minimal and difficult to define. Total hardness is defined as the sum of the calcium and magnesium concentration, both expressed as CaCO_3 , in mg/l.

• Degree Of Hardness Of Drinking Water

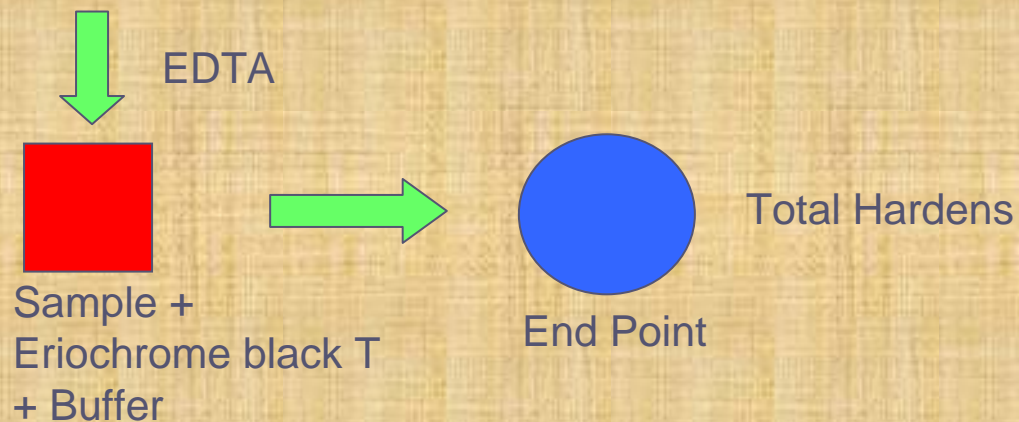
- Soft 0-60 mg/L
- Medium 60-120 mg/L
- Hard 120-180 mg/L
- Very hard >180 mg/L

Carbonate and Non – carbonate Hardness

- Carbonate (temporary / equivalent to total alkalinity,)
- Non-carbonate (permanent / excess of total alkalinity)
- When total hardness is numerically greater than that of total alkalinity expressed as CaCO_3 , the amount of hardness equivalent to total alkalinity is called 'carbonate hardness'.
- When the hardness is numerically equal to less than total alkalinity, all hardness is carbonate hardness.
- Carbonate hardness refers to the amount of carbonate and bicarbonates in solution that can be removed or precipitated by boiling. This type of hardness is responsible for the deposition of scale in hot water pipes and kettles
- When total hardness is numerically greater than that of total alkalinity expressed as CaCO_3 , the amount of hardness which is more than the total alkalinity is called 'non carbonate hardness'.
- Non-carbonate hardness is caused by the association of the hardness-causing cation with sulfate, chloride or nitrate and is referred to as "permanent hardness". This type of hardness cannot be removed by boiling.

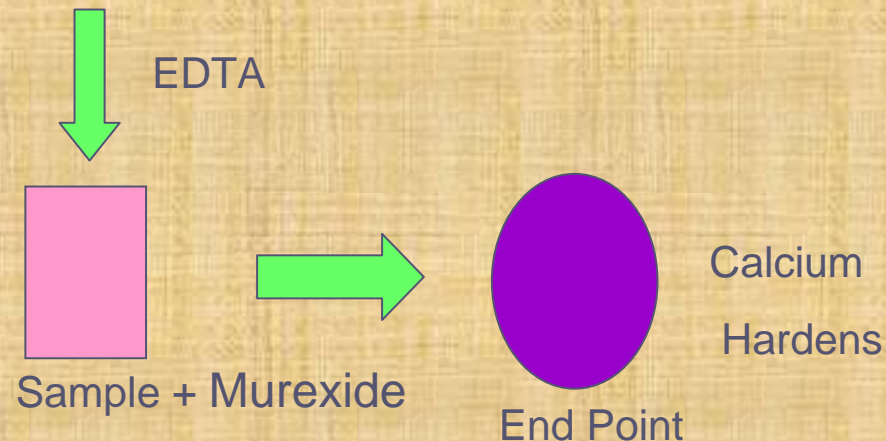
Total Hardness

- EDTA method in alkaline condition
- EDTA and its sodium salts form a soluble chelated complex with certain metal ions.
- Calcium and Magnesium ions develop wine red colour with Eriochrome black T in aqueous solution at $\text{pH } 10.0 \pm 0.1$.
- When EDTA is added as a titrant, Calcium and Magnesium divalent ions get complexed resulting in a sharp change from wine red to blue which indicates end-point of the titration.
- Mg ion must be present to yield end point, neutral Mg salt of EDTA is added to the Buffer



Calcium Hardness

- At a higher pH i.e. at about 12.0 Mg^{++} ions precipitate and only Ca^{++} ions remain in solution.
- At this pH Murexide (ammonium purpurate) indicator forms a pink colour with Ca^{++} . When EDTA is added Ca^{++} gets complexed resulting in a change from pink to purple which indicates end point of the reaction.
- To minimize the tendency towards $CaCO_3$ precipitation limit the duration of titration period to 5 minutes.



Interferences

- Some metal ions interfere by causing fading or indistinct end points or by stoichiometric consumption of EDTA but can be reduced by addition of inhibitors. Suspended or colloidal organic matter may also interfere with the end point. This interference can be eliminated by evaporating 50 mL sample to dryness on a steam bath and then heating in a muffle furnace at 550°C. Residue may be dissolved in 20 mL of 1N hydrochloric acid and on neutralisation to pH 7 with 1N sodium hydroxide, volume be made to 50 mL with distilled water. Run a reagent blank following the same procedure.

Analytical Instruments

- a. Conical flasks 100 mL
- b. Burette
- c. Pipette
- d. Spatula

Reagents and Standards

- Buffer solution
- Inhibitor
- MgCDTA
- Eriochrome black T indicator
- Murexide indicator
- NaOH 2N
- Standard EDTA Solution 0.01 M
- Standard calcium solution

• Calibration and Standardization

- The EDTA solution needs be standardised against standard calcium solution such that the strength of EDTA will be $1\text{ml} = 1\text{ mg as CaCO}_3$.

Procedure for Total hardness

- Take 25 or 50 mL well mixed sample in porcelain dish or conical flask
- Add 1-2 mL buffer solution followed by 1 mL inhibitor.
- Add a pinch of Eriochrome black T and titrate with standard EDTA (0.01M) till wine red colour changes to blue, note down the volume of EDTA required (A).
- Run a reagent blank. Note the volume of EDTA (B).
- Calculate volume of EDTA required by sample, $C = (A-B)$

- For natural waters of low hardness, take a larger sample volume, i.e. 100-1000 mL for titration and add proportionately larger amounts of buffer, inhibitor and indicator. Add standard EDTA titrant slowly from a microburette and run a blank using redistilled, deionized water of the same volume as
- sample. Apply blank correction for computing the results.

Calcium hardness

- Take 25 or 50 mL sample in a porcelain dish
- Add 1 mL NaOH to raise pH to 12.0 and a pinch of Murexide indicator.
- Titrate immediately with EDTA till pink colour changes to purple. Note the volume of EDTA required (A)
- Run a reagent blank. Note the mL of EDTA required (B) and keep it aside to compare end points of sample titrations.
- Calculate the volume of EDTA required by sample, $C = (A-B)$.
- Standardise the EDTA (0.1 M) solution following the procedure of calcium hardness from 1 to 4, using standard calcium solution.

Data Analysis And Calculations

- TH as CaCO₃ mg/l = $\frac{C \times D \times 1000}{\text{ml sample}}$
- Where, C = volume of EDTA required by sample
- D = mg CaCO₃ equivalent to 1.0 mL EDTA titrant
- CaH as CaCO₃ mg/l = $\frac{C \times D \times 1000}{\text{ml sample}}$
- where C = volume of EDTA used by sample
- D = mg CaCO₃ equivalent to 1.0 mL EDTA titrant

☞ **Magnesium Hardness**

☞ Magnesium Hardness = TH as CaCO₃ mg/l – Ca H as CaCO₃

☞ **Alkaline (Carbonate) hardness and non-alkaline (non-carbonate) hardness**

☞ These types of hardness can be calculated from total hardness and total alkalinity as follows:

☞ If total hardness as CaCO₃ > Total alkalinity as CaCO₃

☞ Then,

☞ a. Alkaline hardness = Total alkalinity

☞ b. Non-alkaline Hardness = Total hardness – Total alkalinity

☞ If total hardness as CaCO₃ < Total alkalinity as CaCO₃

☞ Then,

☞ 1. Alkaline hardness = Total hardness

☞ 2. Nonalkaline hardness = Nil

Chloride

- The presence of chloride in natural waters can be attributed to dissolution of salt deposits, discharges of effluents from chemical industries, oil well operations and seawater intrusion in coastal areas. Each of these sources may result in local contamination of both surface water and groundwater. The salty taste produced by chloride depends on the chemical composition of the water. A concentration of 250 mg/L may be detectable in some waters containing sodium ions. On the other hand, the typical salty taste may be absent in water containing 1000 mg/L chloride when calcium and magnesium ions are predominant. High chloride content may harm metallic pipes and structures as well as agricultural plants.

Analytical Apparatus for Argentometric Method

- a. Porcelain dish 200 mL
- b. Pipettes
- c. Burettes
- d. Glass rod

Reagents and Standards

- Potassium chromate indicator
-
- Silver nitrate, 0.0141N
- Sodium chloride, 0.0141N

Calibration and Standardization

- The silver nitrate solution should be standardized against sodium chloride solution of 0.0141 N. It gives the strength of silver nitrate solution $1 \text{ mL} = 0.5 \text{ mg}$ chloride as Cl^- .

Procedure

- Take 50 mL well mixed sample adjusted to pH 7.0-8.0 and add 1.0 mL K_2CrO_4 .
- Titrate with standard $AgNO_3$ solution till Ag_2CrO_4 starts precipitating
- Standardise $AgNO_3$ against standard $NaCl$
- For better accuracy titrate distilled water (50 mL) in the same way to establish reagent blank.

Data analysis and Calculations

- Chloride mg/l as Cl⁻
- $$\frac{(A-B) \times N \times 35.45 \times 1000}{\text{mL sample}}$$
- where, A = mL AgNO₃ required for sample
- B = mL AgNO₃ required for blank, and
- N = Normality of AgNO₃ used
- Ag⁺ + Cl⁻ = AgCl (white ppt)
- Ag⁺ + CrO₄⁻ = Ag₂CrO₄ (Red ppt)

Interferences

- Bromide, iodide and cyanide are measured as equivalent of chloride ions, if the sample contains sufficient thiosulfate, thiocyanate, cyanide, sulfite and sulfide to interfere seriously with the determination.
- If the sample is too coloured or turbid to allow the end point to be readily detected, this interference may be reduced by the following treatment with a suspension of aluminium hydroxide.

FLAME PHOTOMETER

FLAME--- LENCE---FILTER----PHOTOCELL
AMPLIFIER
READ-OUT

BURNER

GAS---

NEBULISER

MIXING CHAMBER

Drain

Air

Sample

Sodium

- Sodium can be estimated by two methods
- By A.A.S AT 589.6 WAVE LENGTH
- DETECTION LIMIT-0.002 Mg/L
by Flame Photometer

Stock solution: 2.542 of NaCl dried at 140 degrees

Working standards: 0-25, 50, 75, 100 ppm

POTASSIUM

- Potassium can be estimated by two methods
- By A.S.S. AT 766.5 nm
- Detection limited: 0.01 mg/L

by Flame photometer

Dissolve 0.1907 gr of KCl dried at 110 degrees

Working standards 0,25,50,75,100 mg/L

THANK YOU

