

Water Technology

“Without food, human can survive for number of days, but water is such an essential that without it one cannot survive”.

“Although water is nature’s most wonderful, abundant and useful compound yet it is also the most misused one”.



Pocket Digital Tds Meter For RO Filter Purifier

Module: 1: Water Technology

5 hrs

Module: 1

Hardness of water; Hardness Causing Impurities,
TDS, pH, DO, COD and BOD of water;

Estimation of hardness by EDTA method- numerical problems.

Boiler troubles –

Scale, sludge,
priming, foaming,
Caustic embrittlement and boiler corrosion;

Internal conditioning– Phosphate and
Calgon conditioning methods;

Sources of Water

A) Surface Waters

Rain Water - Pure but contaminated with gases

River Water - High dissolved salts moderate organics

Lake Water - Const. composition but high organics

Sea Water - High salinity and organics

B) Underground Waters

Spring/Well Water - Crystal clear but high dissolved salts and less impurity from organics

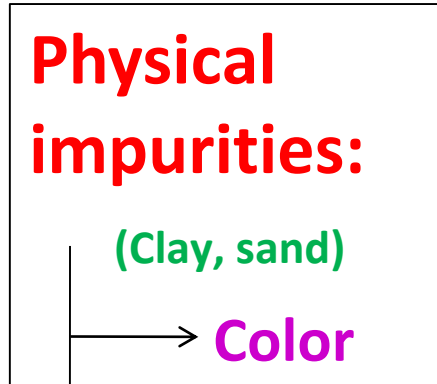


Natural water is contaminated mostly by three types of impurities:

(a) **Physical impurities**

(b) **Chemical impurities**

(c) **Biological impurities**



Can be removed by Sedimentation, Coagulation, Adsorption or Filtration

Can be removed by Chemical treatment.

Can be removed by chlorination.

Municipal water supplied to Homes: Physical and Biological impurities (major removal) + Chemical impurities (minor removal)

Water supplied to Industries: Physical and Chemical impurities (major removal) + Biological impurities (negligibly removed)

Impurities in water

○ **Physical** (Colour, Odour Turbidity and Taste)

- Inorganic such as clay, sand
- Organic such as oil globules, vegetable/animal matter
- Colloidal such as $\text{Fe}(\text{OH})_3$, Complex proteins, amines etc

○ **Chemical**

- Anions: Cl^- , SO_4^{2-} , CO_3^{2-} , HCO_3^- , NO_3^- of Ca & Mg
 - Cations: Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Fe^{3+} , Al^{3+}
 - Dissolved gases: O_2 , N_2 , CO_2 , H_2S , NH_3
- (Not all the above chemical impurities causes hardness in water)

○ **Biological**

- Micro-organisms such as algae, fungi, bacteria
(Pathogenic causing malaria, diarrhea, typhoid etc.)

Effect of impurities on water

Bad taste, colour & odour

- Hardness, corrosiveness, staining
- Decrease in DO level
- Increase in BOD/COD
- Causes various diseases and infections.

Classification of Impurities in water

- ❧ Physical Impurities - Dissolved Solids/Salts
- ❧ Chemical Impurities - Inorganic & Organic Chemicals
- ❧ Biological Impurities - Pathogens, algae, fungi, viruses...

- 1) Colour
- 2) Turbidity
- 3) Taste
- 4) Odour
- 5) Conductivity
- 6) *Temperature*

- 1) Acidity (pH)
- 2) Gases (CO_2 - O_2 , NH_3)
- 3) Minerals
- 4) Salinity
- 5) Alkalinity
- 6) Hardness

- 1) Microorganisms
- 2) Algae
- 3) fungi

Impurities in Water

Colour:

- ❖ Colour in water is due to metallic salts of Fe, Mn and due to organic substances like humus, algae, weed ...
- ❖ Industrial activities such as textile, paper & pulp, dyeing, tanneries
- ❖ Colour intensities of water sample can be measured using tintometer using Platinum cobalt standard colour complex.

Turbidity:

It is due to colloidal, extremely fine suspension such as clay, slit, finely divided matters, sometimes microorganisms...

Taste

- Presence of dissolved salts and gases imparts bitter, soapy, brackish and palatable taste which is normally co-related with odour.
- Bitter (Fe, Al, Mn, SO_4^{2-} , $\text{Ca}(\text{OH})_2$)
- Soapy (NaHCO_3)
- Brackish (High salt content - NaCl)
- Palatable (CO_2 and NO_3^-)

Odour

- Domestic and industries activities cause undesirable odour to water.
- Industrial effluent of organics, sewage discharge, presence of N, S and P contains compounds, metal ion pollution like Fe
- Substances like algae, bacteria
- Grassy odour, offensive odour.

MAJOR IMPURITIES OF WATER

Ionic and dissolved

Hardness	Cationic	Alkalinity	Anionic	Nonionic and undissolved	Gases
	Calcium Magnesium		Bicarbonate Carbonate Hydroxide		
	Sodium		Sulfate	Color, Plankton	CO ₂
	Potassium		Chloride	Organic matter,	H ₂ S
	Ammonium		Nitrate	Colloidal silica,	NH ₃
	Iron		Phosphate	Microorganisms,	CH ₄
	Manganese			Bacteria	O ₂

Total Dissolved Solids (TDS)

Total Dissolved Solids (TDS) are the total amount of charged ions, including minerals, salts or metals dissolved in a given volume of water.

It is expressed in units of mg per unit volume of water (mg/L), also referred as parts per million (ppm).

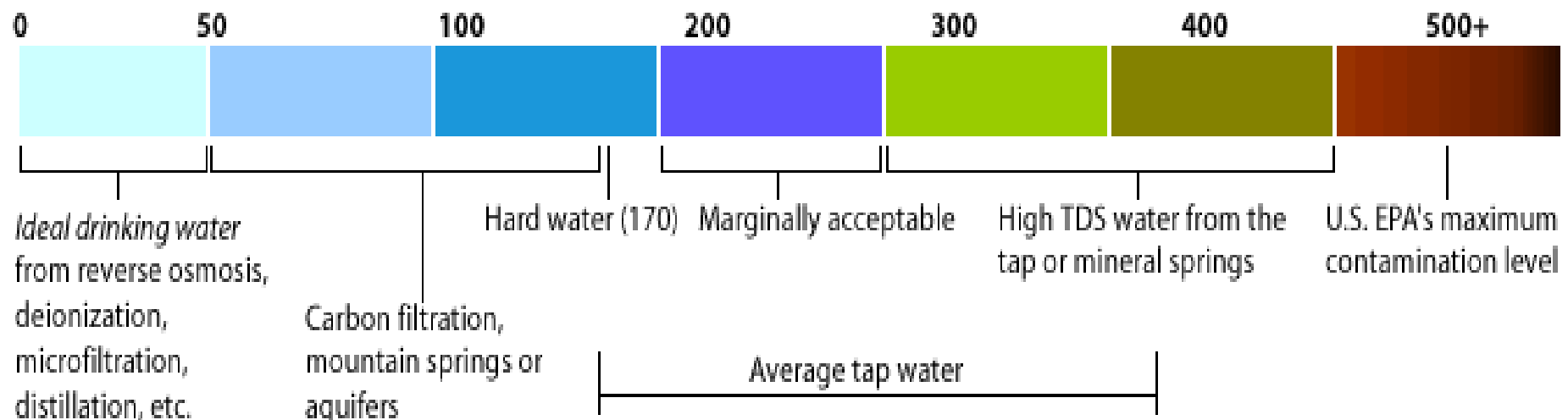
TDS is a measure of the combined content of all inorganic and organic substances contained in a liquid in molecular, ionized or micro-granular (colloidal sol) suspended form.

The principal constituents are usually

Cations : Calcium, magnesium, sodium, and potassium and

Anions.: Carbonate, Bicarbonate, chloride, sulfate, and nitrate.

TDS in parts per million (PPM)



Total Dissolved Solids (TDS)

TDS are normally discussed only for freshwater systems, as salinity includes some of the ions constituting the definition of TDS.

The principal application of TDS is in the study of water quality for streams, river sand lakes, although **TDS is not generally considered a primary pollutant** (e.g. it is not deemed to be associated with health effects).

Primary sources for TDS in receiving waters are agricultural and residential runoff, leaching of soil contamination and point source water pollution discharge from industrial or sewage treatment plants.

More exotic and harmful elements of TDS are pesticides arising from surface runoff.

Water can be classified by the amount of TDS per liter:

- ❖ Fresh water < 1000 mg/L TDS
- ❖ Brackish water 1000 to 10,000mg/L TDS
- ❖ Saline water 10,000 to 30,000mg/L TDS
- ❖ Brine> 30,000mg/L TDS

▣ The two principal methods of measuring total dissolved solids are gravimetry and conductivity.

Electrical conductivity of water is directly related to the concentration of dissolved ionized solids in the water, which can be measured using a conventional conductivity meter or TDS meter.

TDS values of different waters

Rain water	→ 1 – 150 mg/L
Surface water in Hills	→ 10 – 100 mg/L
Surface water in Plains	→ 100 – 1000 mg/L
Ground water	→ 500 – 5000 mg/L
Ground water polluted	→ 2000 – 20000 mg/L
Sea water	→ 35000 mg/L
Mineral (bottled water)	→ 100 – 200 mg/L
Permissible Limit	→ 500 mg/L
Maximum allowable Limit	→ 2000 mg/L



pH and Water Quality

Water pH is 7 at 25°C, but varies with temperature.

pH of pure water is 6.55

Rainfall generally has a pH value between 5 - 6.5.

Since pH can be affected by chemicals in the water, pH is an important indicator of water that is changing chemically.

Acidic: Water that has more free hydrogen ions is acidic

Due to dissolved carbon dioxide, Carbonic acid and air pollutants, such as sulphur dioxide or nitrogen oxides.

Basic: water that has more free hydroxyl ions is basic.

If the rainwater flows over soil containing hard-water minerals, its pH usually increases.

Bicarbonate ions, HCO_3^- resulting from limestone deposits react with the water to produce OH^- ions, according to the equation:

OH^- ion



As a result, streams and lakes are often basic, with

pH values between 7- 8, sometimes as high as 8.5.

pH and water quality

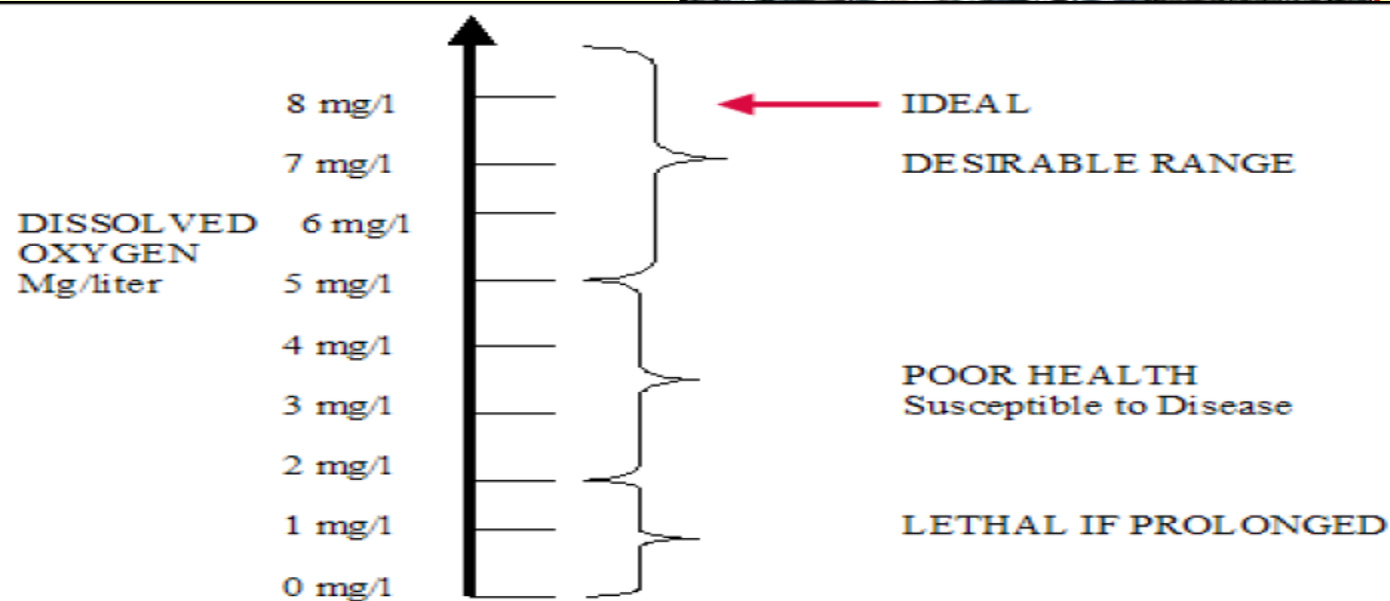


- ❑ Water pH 7 at 25 °C; value varies with temperature.
pH of pure water at 50 °C is 6.55.
- ❑ When an acid or base is dissolved in water, the pH will be less or greater than pure water, pH will be 0 to 14,
- ❑ water that has been exposed to air is mildly acidic as it absorbs carbon dioxide and converted into bicarbonate and hydrogen ions (essentially creating carbonic acid).
- ❑ The pH of seawater plays an important role in the ocean's carbon cycle, ocean acidification caused by carbon dioxide emissions
- ❑ High pH causes a bitter taste, water pipes and water-using appliances become encrusted with deposits, Low-pH water will corrode or dissolve metals and other substances.
- ❑ Pollution can change pH, which in turn can harm animals and plants living in the water. For instance, water coming out of an abandoned coal mine can have a pH of 2, which is very acidic

DO (Dissolved Oxygen)

Another indicator of water quality is its *level of (DO)*.

- Number of molecules of O_2 dissolved in one Liter of water – Expressed as mg/L (ppm).
- One of the best indicators to understand the health of the water body and life sustaining ability.
- Most life supporting water systems – 4-6 mg/L of DO
- Factors affecting DO levels
 - *Water temperature*
 - *Organic waste*
 - *Aquatic plant populations*
 - *Water flow*
 - *Altitude (atm. Pressure)*
 - *Human activities*



Methods to measure water quality: *dissolved oxygen (DO)*.

Another indicator of water quality is its *level of dissolved oxygen (DO)*.

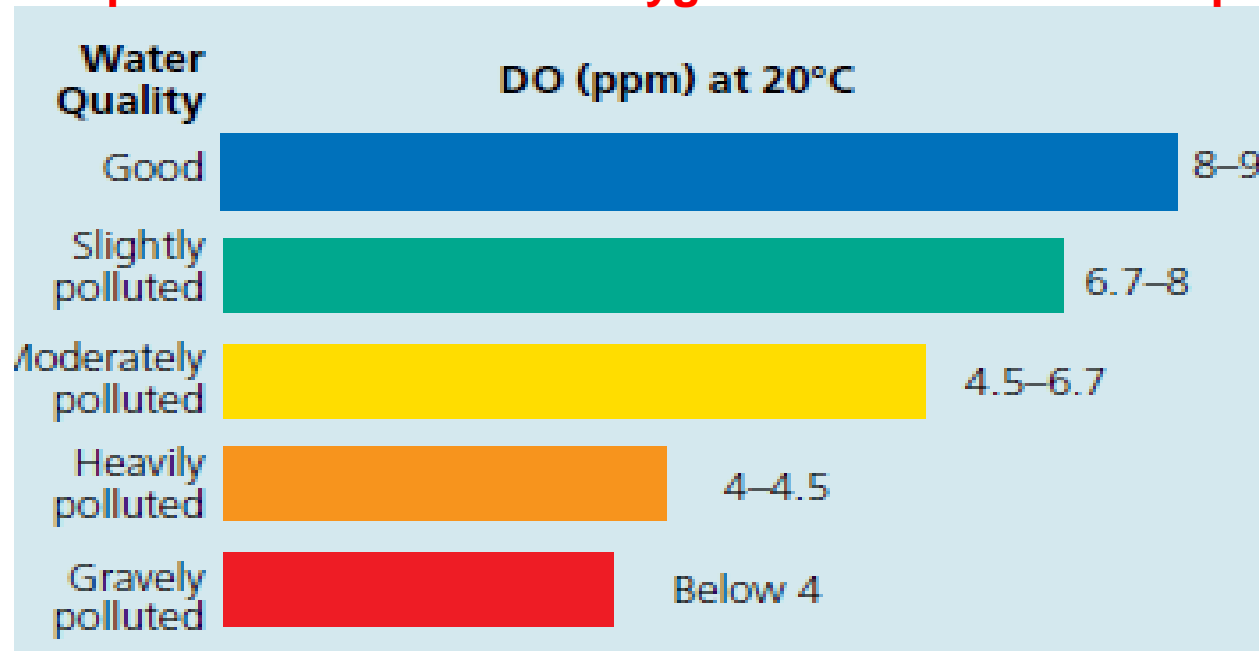
Excessive inputs of oxygen-demanding wastes can deplete DO levels in water.

Scientists can use chemical analysis to determine for the presence and concentrations of specific organic chemicals in polluted water.

The dissolved oxygen (DO) content is measured in parts per million (ppm) at 20°C (68°F) as an indicator of water quality.

Only a few fish species can survive in water with less than 4 ppm of dissolved oxygen at this temperature.

Relationship between dissolved oxygen content and water quality.



DO determination - Winkler's method

Dissolved oxygen is usually determined by **Winkler's method** of **Iodometric titration**

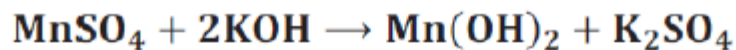
It is based on the fact that **dissolved oxygen** oxidized **potassium iodide (KI)** to **iodine**.

The liberated **iodine** is titrated against **standard sodium thiosulphate solution** using **starch indicator**.

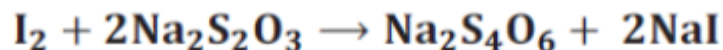
Since dissolved oxygen in water is in molecular state.

It as such cannot oxidize KI. Hence Manganese Hydroxide is used as an oxygen carrier to bring about the reaction between KI and Oxygen.

Manganese hydroxide, in turn, is obtained by the action of NaOH on MnSO₄.



$2\text{Mn(OH)}_2 + \text{O}_2 \rightarrow 2\text{MnO(OH)}_2$ Basic manganic oxide which on acidification gives



Calculation - DO

1 mole of O_2 = 2 moles of I_2 = 4 moles of $Na_2S_2O_3$

1 mole of $Na_2S_2O_3$ = $\frac{1}{4}$ mole of O_2 = 8 g of O_2

1mL of 1N $Na_2S_2O_3$ = 8 mg of O_2

'V' mL of ' N_1 'N $Na_2S_2O_3$ = $8 \times V \times N_1$

$$\text{DO of water sample} = \frac{8 \times \text{Vol. of } Na_2S_2O_3 \text{ consumed} \times \text{Normality of } Na_2S_2O_3 \times 1000}{\text{Volume of water sample taken}}$$

DO of the water sample is expressed in mg/L (ppm)

Biological oxygen Demand

Biological oxygen demand (BOD) is the amount of dissolved oxygen needed by aerobic biological organisms in a water body to break down organic material present in a given water sample at certain temperature over a specific time period.

The BOD value is most commonly expressed in milligrams of oxygen consumed per litre of sample **for the biologically oxidizable impurities** during 5 days of incubation at 20 °C and is often used as a robust surrogate to determine the degree of biodegradable organic pollution in water.

BOD is similar in function to COD, in that both measure the amount of organic compounds in water. However, COD is less specific, since it measures everything that can be chemically oxidized, rather than just levels of biologically active organic matter.

BOD Level (in ppm)	Water Quality
1 - 2	Very Good There will not be much organic waste present in the water supply.
3 - 5	Fair: Moderately Clean
6 - 9	Poor: Somewhat Polluted Usually indicates organic matter is present and bacteria are decomposing this waste.
100 or greater	Very Poor: Very Polluted Contains organic waste.

Chemical oxygen demand (COD)

Chemical oxygen demand (COD) test is commonly used to indirectly measure the amount of organic compounds in water.

Most applications of COD determine the amount of organic pollutants found in surface water (e.g. lakes and rivers) or waste water, making COD a useful measure of water quality.

Chemical Oxygen Demand (COD)

The chemical oxygen demand determines the amount of oxidizable organic pollutants found in surface water, making COD a useful measure of water quality.

It is expressed in milligrams per litre (mg/L), which indicates the mass of oxygen consumed per litre of solution.

The basis for the COD test is that nearly all organic compounds can be fully oxidized to carbon dioxide with a strong oxidizing agent under acidic conditions.

The amount of oxygen required to oxidize an organic compound to carbon dioxide, ammonia, and water.

COD Estimation

The COD is determined by refluxing the sample in the presence of excess $\text{K}_2\text{Cr}_2\text{O}_7$, which serves as oxidizing agent.

The solution is acidified with H_2SO_4 , and Ag_2SO_4 is added as a catalyst to speed the oxidation of **low-molecular-weight fatty acids**.

Mercuric sulfate, HgSO_4 , is added to complex any chloride that is present, thus preventing the precipitation of the Ag^+ catalyst as AgCl .

After refluxing for 30min, the solution is cooled to room temperature, and the excess Cr_2O_7 is determined by a **back titration**, using **ferrous ammonium sulphate as the titrant** and **ferroin as the indicator**.

The difference in the amount of FAS needed to titrate the blank and the sample is proportional to COD.

$$\text{COD of water (mg/L)} = \frac{(\text{B}-\text{S}) \times \text{N} \times 8 \times 1000}{\text{V}}$$

B = FAS used for Blank (mL)

S = FAS used for sample (mL) = unreacted dichromate

N = Normality of FAS

V = Volume of water sample (mL)



Parameter	COD	BOD
Oxidant Used	$K_2Cr_2O_7$ $Mn_2(SO_4)_3$	Oxidation by microorganisms
Most Suitable Use	Rapid and frequent monitoring of treatment plant efficiency and water quality	Modeling treatment plant process and the effects of organic compounds on the dissolved oxygen content of receiving waters
Test Completion Time	1-1/2 to 3 hours	5 days (for standard BOD test)
Accuracy and Precision	5 - 10% relative standard deviation; may be higher when samples contain suspended solids; sample homogenization can be important	15% relative standard deviation; not considered highly accurate
Advantages	<ul style="list-style-type: none"> • Correlates with BOD on waste with constant composition. • Toxic materials do not affect oxidant. • Changes in the COD value between influent and effluent may parallel BOD content and supplement BOD results • Short analysis time 	<ul style="list-style-type: none"> • Most closely models the natural environment when used with the proper "seed"
Disadvantages	<ul style="list-style-type: none"> • Interference from chloride ions • Some organic compounds are not oxidized completely 	<ul style="list-style-type: none"> • Toxic materials kill microorganisms • Microorganisms do not oxidize all materials present in waste • Inaccuracies when used with improper "seed" • Lengthy test period

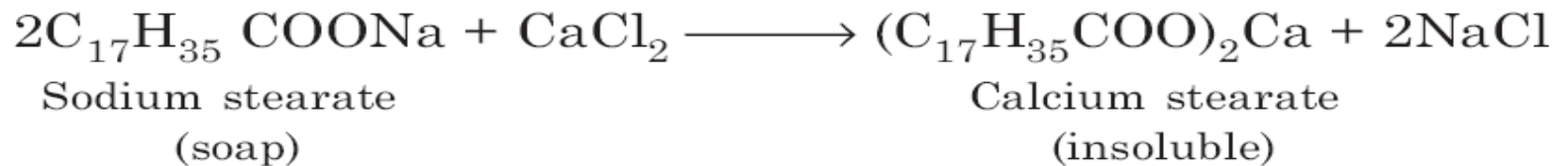
Hardness of water

What is Hard water?

Hard water is water that contains an appreciable quantity of dissolved minerals (like calcium and magnesium).

Water that does not produce lather with soap solution readily but forms an insoluble white precipitate is called **HARD WATER**.

Hard water containing Mg^{2+} , Ca^{2+} or Fe^{2+} salts when treated with soap (sodium or potassium salts of stearic acid) does not produce lather but forms an insoluble white precipitate of calcium or magnesium stearate.



Soft water is surface water that contains **low concentrations of ions** and in particular is **low in ions of calcium and magnesium**.

As rainwater falls, it is naturally soft.

Practically speaking, measurement of:

- Calcium (Ca) ions
- Magnesium (Mg) ions

Hardness as calcium carbonate

	<i>mg/L (ppm)</i>
Soft	0-17
Moderately hard (Medium)	60-120
Hard	120-180
Very hard	180 & over

Hardwater and Soap



Hardness of water: Causes

✚ Hardness in water is caused by the presence of certain dissolved salts such as **bicarbonates, chlorides, and sulfates of Mg^{2+} , Ca^{2+} or Fe^{2+}** which under certain conditions of temperature, pressure or reactions with other chemicals results in the formation of insoluble scales and sludges.

✚ Whereas, **hardness in water is not caused by the salts of Na^+ or K^+ ions**.

Eg.: **Na_2CO_3 (washing soda) is used as a water softener to reduce the hardness in water.**

They are soluble in water under all conditions except when they reach the saturation level.

Why be concerned about Hard Water?



- Originally, water hardness was defined as the measure of the **capacity of the water to precipitate soap**
- Hard water does cause soap scum, **clogs pipes and clogs boilers as lime scale**

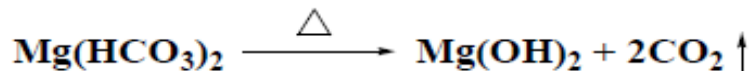
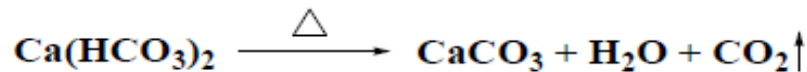
In steam generation in boilers

If the hard water is fed directly to the boilers, which led to the many problems such as
i) scale and sludge formation (ii) corrosion (iii) priming and foaming and (iv) caustic embrittlement

Types of Hardness

Temporary Hardness (or) carbonate hardness

- Dissolved **bicarbonate** salts of Ca and Mg and other heavy metals such as iron
- Can be removed easily by boiling



Permanent Hardness (or) noncarbonate hardness

- presence of chlorides and sulphates of Ca, Mg and other heavy metals)
- Can't be removed by simple boiling

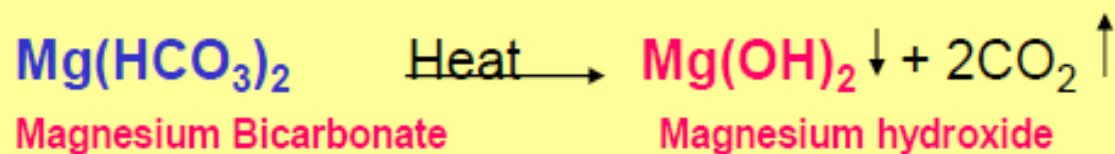
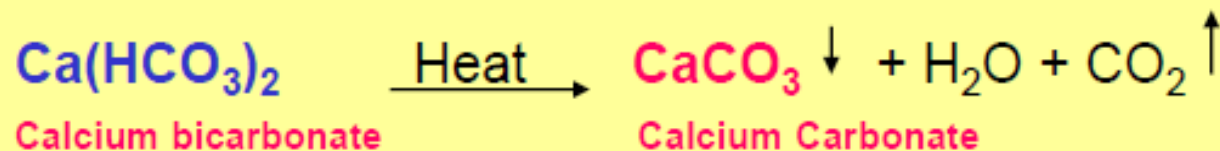
Can be removed through zeolite, Lime-soda, ion-exchange processes.

The dissolved bicarbonates in the water are decomposed into insoluble carbonates or hydroxides which are deposited as crust (as scales) at the bottom of vessel.

Temporary Hardness (Alkaline hardness)

- Temporary Hardness is caused by the presence of dissolved *bicarbonate of calcium, magnesium*

It is mostly destroyed by more boiling of water, when bicarbonates are decomposed yielding insoluble carbonates.



Permanent Hardness (Non-alkaline hardness)

Non-Carbonate Hardness is due to the presence of chlorides, sulfates of calcium, Magnesium

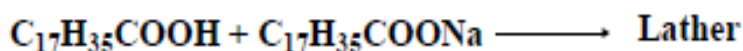
Permanent hardness cannot be removed by boiling

Disadvantages of Hard water

Domestic Use

✓ Washing

do not lather with soap, silky precipitates of Mg and Ca



✓ Bathing

Cleansing quality of soap is poor

✓ Cooking

elevated boiling point; more fuel for cooking

✓ Drinking

bad effect in digestive system; possibility of forming **calcium oxalate** crystals in urinary tracks

Industrial Use

➤ Textile industry

(wastage of soap, precipitates of Ca & Mg adhered to the fabric- which don't produce the exact shades)

➤ Sugar Industry

(water containing sulphates, nitrates, alkali carbonates etc. causes difficulties in sugar crystallization)

➤ Concrete making

(hydration of cement as well as concrete strength)

➤ Pharmaceutical Industry

(May produce undesirable substance)

HOW TO EXPRESS HARDNESS OF WATER ?

Equivalents of Calcium Carbonate

Hardness as well as non-hardness constituting ions are generally expressed in terms of equivalent amount of CaCO_3

Why CaCO_3

- Most insoluble salt in water treatment
- Molecular weight = 100; Equivalent Weight = 50

CaCO_3 equivalent hardness

$$\text{Calcium carbonate equivalent} = \frac{\text{Mass of hardness producing substance} \times \text{Molecular weight of } \text{CaCO}_3}{\text{Molecular weight of hardness producing substances}}$$

Problem 1

Calculate the calcium carbonate equivalent hardness of a water sample containing 204mg of CaSO_4 per litre

Solution :

$$\text{Calcium carbonate equivalent hardness} = \frac{204 \times 100}{136} = 150 \text{ mg of } \text{CaCO}_3/\text{L} \\ = 150 \text{ ppm}$$

Note : Mol. Weight of CaCO_3 = 100
Mol. Weight of CaSO_4 = 136

Units of Hardness

Most Commonly used

- **Parts per million (ppm)**

1ppm=1 part of CaCO_3 equivalence hardness causing substance present in 10^6 parts of water

- **Milligrams per liter (mg/litre)**

1mg/L=1mg of CaCO_3 equivalence hardness causing substance present in one liter of water

1mg/L=1ppm

Relationship; 1L water = 1Kg = 1000 g = 1000 X 1000 mg = 10^6 mg

1mg/L = 1mg of CaCO_3 eq per 10^6 mg of water

= 1 part of CaCO_3 eq per 10^6 parts of water = 1ppm

- **Clare's Degree($^{\circ}\text{Cl}$)**

1 $^{\circ}$ Clarke= 1part of CaCO_3 equivalent hardness in 70000 parts of water

- **Degrees French ($^{\circ}\text{Fr}$)**

1 $^{\circ}$ Fr = 1 part of CaCO_3 eq per 10^5 parts of water

$1^\circ \text{Fr} = 1 \text{ part of } \text{CaCO}_3 \text{ equivalent hardness per } 10^5 \text{ parts}$
 $1^\circ \text{ppm} = 1 \text{ part per } 10,00,000 \text{ parts of water}$
 $1^\circ \text{cl} = 1 \text{ part per } 70,000 \text{ parts of water}$

$$\frac{100 \text{ ppm}}{100} = \frac{7^\circ \text{cl}}{100} = \frac{10^\circ \text{Fr}}{100}$$

$$1 \text{ ppm} = 0.07^\circ \text{cl} = 0.1^\circ \text{Fr}$$

$$1^\circ \text{cl} = 1.42^\circ \text{Fr} = 14.2 \text{ ppm}$$

$$1^\circ \text{Fr} = 0.7^\circ \text{cl} = 10 \text{ ppm}$$

Problem:

If the hardness of water is 210.5 ppm Calculate its hardness in $^\circ \text{cl}$.

$$1 \text{ ppm} = 0.07^\circ \text{cl}$$

$$210.5 \text{ ppm} = 0.07 \times 210.5 = 14.735^\circ \text{cl}$$

Relation between various units of hardness

1 ppm	= 1 mg/l	= 0.1°Fr	= 0.07°Cl
1 mg/l	= 1 ppm	= 0.1°Fr	= 0.07°Cl
1°Cl	= 1.43°Fr	= 14.3 ppm	= 14.3 mg/l
1°Fr	= 10 ppm	= 10 mg/l	= 0.7°Cl .

Calcium carbonate equivalence conversion during hardness calculation

Hardness producing substance	Molecular weight	Multiplication factor (in terms of CaCO_3 equivalence)
$\text{Ca(HCO}_3)_2$	162	100/162 or 50/81
$\text{Mg(HCO}_3)_2$	146	100/146 or 50/73
CaSO_4	136	100/136 or 50/68
CaCl_2	111	100/111 or 50/55.5
MgSO_4	120	100/120 or 50/60
MgCl_2	95	100/95 or 50/47.5
CaCO_3	100	100/100 or 50/50
MgCO_3	84	100/84 or 50/42
CO_2	44	100/44 or 50/22
HCO_3^-	61	100/61 or 50/61
OH^-	17	100/17 or 50/17
CO_3^{2-}	60	100/60 or 50/30

Problems

1. A water sample from an industry in Bombay had the following data

$\text{Mg}(\text{HCO}_3)_2 = 16.8\text{mg/L}$, $\text{MgCl}_2 = 19\text{ mg/L}$, $\text{Ca}(\text{HCO}_3)_2 = 20\text{ ppm}$, $\text{MgSO}_4 = 24.0\text{mg/L}$ and $\text{KOH} = 1\text{ ppm}$. Calculate the temporary, permanent and total hardness of the water sample.

Solution

Step 1 conversion in to CaCO_3 equivalent

Constituent present	quantity	Conversion factor	Hardness
$\text{Mg}(\text{HCO}_3)_2$	16.8 mg/L	100/146	$16.8 \times 100/146 = 11.50$
MgCl_2	19.0 mg/L	100/95	$19 \times 100/95 = 20.0$
$\text{Ca}(\text{HCO}_3)_2$	20 ppm	100/162	$20 \times 100/162 = 12.34$
MgSO_4	24.0 mg/L	100/120	$24 \times 100/120 = 20.0$

Calculation

Temp. Hardness = 23.8 ppm

P. Hardness = 40 ppm

Tot. Hardness = 63.8 ppm

Example 2. Calculate the temporary hardness and permanent hardness of a sample water containing $\text{Mg}(\text{HCO}_3)_2 = 7.3 \text{ mg/L}$; $\text{Ca}(\text{HCO}_3)_2 = 16.2 \text{ mg/L}$; $\text{MgCl}_2 = 9.5 \text{ mg/L}$; $\text{CaSO}_4 = 13.6 \text{ mg/L}$ (atomic weight of Mg and Ca are 24 and 40 respectively, Cl and S are 35.45 and 32 respectively)

Solution: Conversion into CaCO_3 equivalent:

Constituent	Multiplication factor	CaCO_3 equivalent
$\text{Mg}(\text{HCO}_3)_2 = 7.3 \text{ mg/L}$	$100/146$	$7.3 \times 100/146 = 5 \text{ mg/L}$
$\text{Ca}(\text{HCO}_3)_2 = 16.2 \text{ mg/L}$	$100/162$	$16.2 \times 100/162 = 10 \text{ mg/L}$
$\text{MgCl}_2 = 9.5 \text{ mg/L}$	$100/95$	$9.5 \times 100/95 = 10 \text{ mg/L}$
$\text{CaSO}_4 = 13.6 \text{ mg/L}$	$100/136$	$13.6 \times 100/136 = 10 \text{ mg/L}$

Temporary hardness, due to $\text{Mg}(\text{HCO}_3)_2$ and $\text{Ca}(\text{HCO}_3)_2$
 $= (5 + 10) \text{ mg/L} = 15 \text{ mg/L}$ or 15 ppm

Permanent hardness, due to MgCl_2 and CaSO_4
 $= (10 + 10) \text{ mg/L} = 20 \text{ mg/L}$ or 20 ppm

Total hardness = Temporary hardness + Permanent hardness

Example 3. Calculate the temporary hardness and total hardness of a sample water containing $\text{Mg}(\text{HCO}_3)_2 = 73 \text{ mg/L}$; $\text{Ca}(\text{HCO}_3)_2 = 162 \text{ mg/L}$; $\text{MgCl}_2 = 95 \text{ mg/L}$; $\text{CaSO}_4 = 136 \text{ mg/L}$ (atomic weight of Mg and Ca are 24 and 40 respectively, Cl and S are 35.45 and 32 respectively)

Solution: Calculation of CaCO_3 equivalent:

<i>Constituent</i>	<i>Multiplication factor</i>	<i>CaCO_3 equivalent</i>
$\text{Mg}(\text{HCO}_3)_2 = 73\text{mg/L}$	100/146	$73 \times 100/146 = 50\text{mg/L}$
$\text{Ca}(\text{HCO}_3)_2 = 162\text{mg/L}$	100/162	$162 \times 100/162 = 100\text{mg/L}$
$\text{MgCl}_2 = 95\text{mg/L}$	100/95	$95 \times 100/95 = 100 \text{ mg/L}$
$\text{CaSO}_4 = 136\text{mg/L}$	100/136	$136 \times 100/136 = 100\text{mg/L}$

Temporary hardness, due to $\text{Mg}(\text{HCO}_3)_2$ and $\text{Ca}(\text{HCO}_3)_2$
 $= (50 + 100) \text{ mg/L} = 150 \text{ mg/L}$ or 150 ppm

Total hardness, $= (50 + 100 + 100 + 100) \text{ mg/L} = 350 \text{ mg/L}$ or 350 ppm

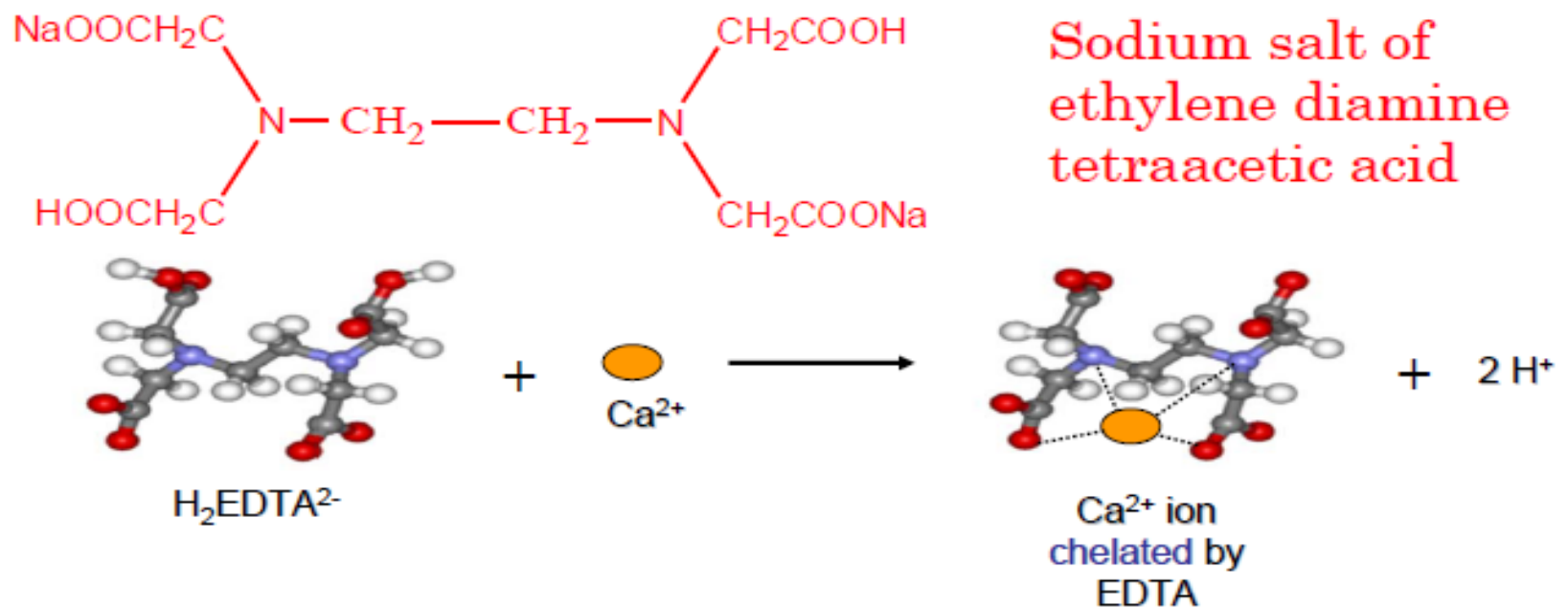
Permanent hardness = Total hardness - Temporary hardness

Estimation of Hardness

Essential for the water to be used in Industry and boilers for steam generation

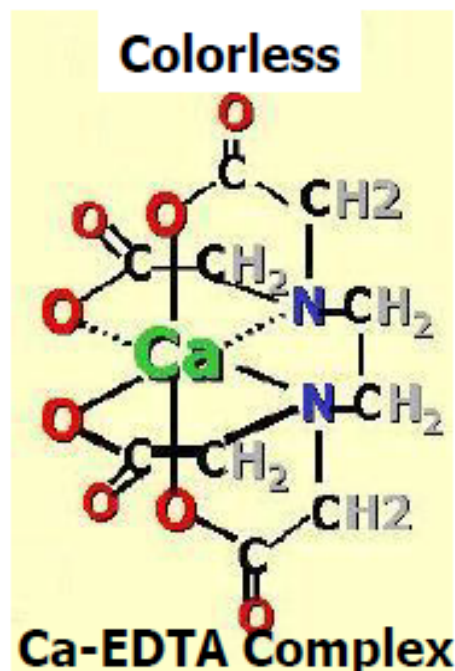
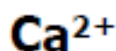
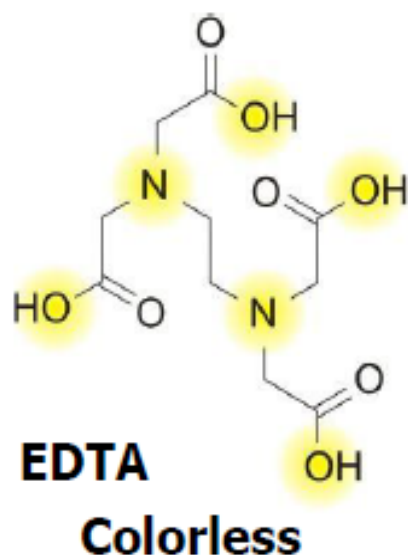
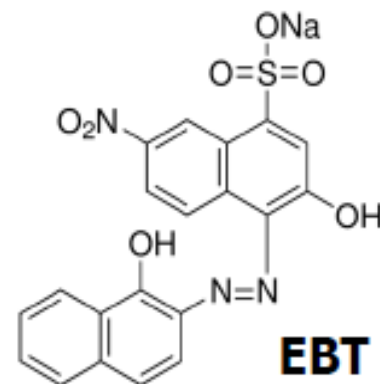
EDTA method

EDTA forms permanent complex with Ca^{2+} and Mg^{2+} present in the hard water



EDTA method: Hardness

- Complexometric titration.
- Pipette solution: water sample
- Titrant: **EDTA** (Strong complexing agent)
- Condition for titration: **pH-9-10** – Ammonia-ammonium chloride buffer added.
- Indicator: **Eriochrome Black – T (EBT)**
- End point: **wine red to steel blue**

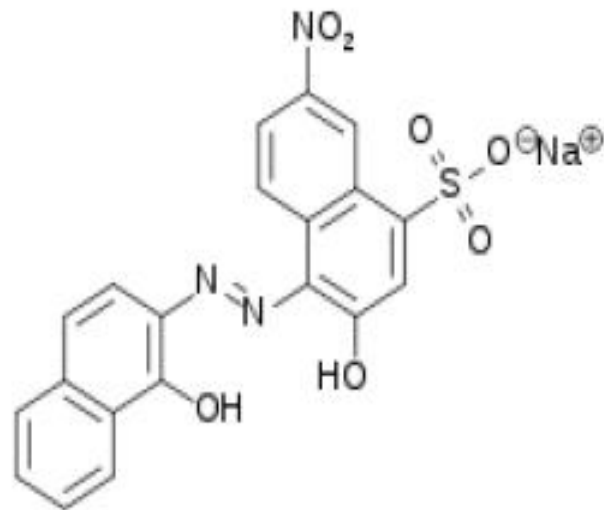


Color of Ca-EBT

Color of free EBT

EDTA forms permanent complex with Ca^{2+} and Mg^{2+} present in the hard water

EDTA: Colorless solution

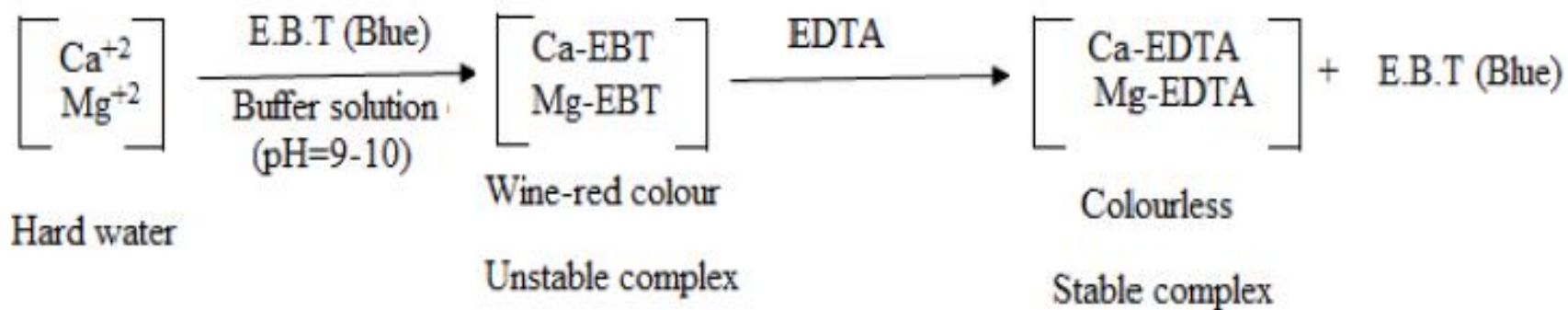


Eriochrome Black T

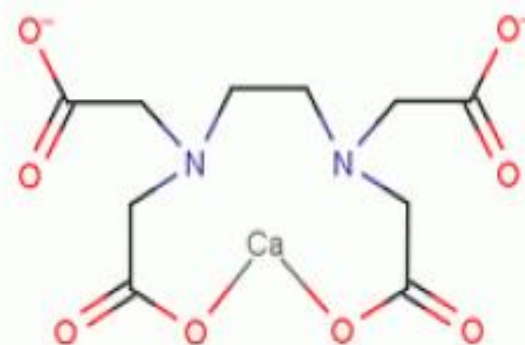


EBT is blue in a buffered solution at pH 10, it turns red when Ca^{2+} ions were added

The characteristic blue end-point is reached when sufficient EDTA is added and metal ions are chelated by EDTA, leaving the free indicator molecule



Na⁺



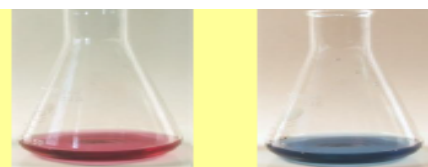
Na⁺

Experiment- Numerical Problems

1. Preparation of EDTA solution (0.01 M)
i.e. dissolve 3.72 g of sodium salt of EDTA crystals in 1 litre of distilled water
2. Preparation of standard Hard Water
 - a. Dissolve 1.0 g of pure, dry CaCO_3 in small quantity of conc. HCl and evaporate the solution to dryness
 - b. Dissolve the residue in distilled water (1 litre)
1 ml of this solution contains 1 mg of CaCO_3 equ. hardness
3. Preparation of buffer solution
Add 67.5 g of NH_4Cl to 570 ml of conc. Ammonia soln. and dilute with distilled water to 1 litre
4. Preparation of indicator
Dissolve 0.5 g of EB-T in 100 ml alcohol

5. Standardization of EDTA solution

Burette - EDTA solution (0.01 M)



Conical Flask - 50 ml of std. hard water + 10-15 ml of ammonia buffer + few drops of EB-T indicator

Volume of EDTA consumed = V_1 ml

6. Estimation of total Hardness

Conical Flask - 50 ml of sample hard water + 10-15 ml of ammonia buffer + few drops of EB-T indicator

Volume of EDTA consumed = V_2 ml

7. Estimation of permanent Hardness

Conical Flask - 50 ml of boiled sample hard water + 10-15 ml of ammonia buffer + few drops of EBT indicator

Volume of EDTA consumed = V_3 ml

Boiled water preparation:

250mL of Hard water – boiled it – reduced the volume about 50mL

Bicarbonates are decomposed to insoluble CaCO_3 and $\text{Mg}(\text{OH})_2$

Filter, wash the precipitate with distilled water – collect the filtrate – make up to 250mL

Calculation: Estimation of Total Hardness

50ml of standard hard water = V_1 mL of EDTA

1mL of EDTA = $50 / V_1$ mg of CaCO_3 eqvt.

50ml of given hard water = V_2 mL of EDTA

= $V_2 \times 50 / V_1$ mg of CaCO_3 eqvt.

1mL of Given hard water = $V_2 \times 50 / V_1 \times 50$ mg of CaCO_3 eqvt.

1000mL of Given hard water = $1000 V_2 / V_1$ mg of CaCO_3 eqvt.

Total Hardness of water = $1000 V_2 / V_1$ mg/L
= $1000 V_2 / V_1$ ppm

Calculation: Estimation of Permanent Hardness

50ml of boiled water = V_3 mL of EDTA

$$= V_3 \times 50 / V_1 \text{ mg of CaCO}_3 \text{ eqvt.}$$

1mL of boiled water = $V_3 \times 50 / V_1 \times 50$ mg of CaCO₃ eqvt.

1000mL of boiled water = $1000 V_3 / V_1$ mg of CaCO₃ eqvt.

$$\begin{aligned}\text{Permanent Hardness of water} &= 1000 V_3 / V_1 \text{ mg/L} \\ &= 1000 V_3 / V_1 \text{ ppm}\end{aligned}$$

Temporary Hardness of water = [Total – Permanent] hardness

$$\begin{aligned}&= \frac{V_2}{V_1} - \frac{V_3}{V_1} \times 1000 \text{ ppm} = \frac{V_2 - V_3}{V_1} \times 1000 \text{ ppm}\end{aligned}$$

$$= 1000 \{(V_2 - V_3) / V_1\} \text{ ppm}$$

1. 0.5 g of CaCO_3 was dissolved in HCl and the solution made up to 500 ml with distilled water. 50 ml of the solution required 48 ml of EDTA solution for titration. 50 ml of hard water sample req. 15 ml EDTA and after boiling and filtering req. 10 ml of EDTA solution calculate the hardness.

1 ml of hard water contain 1 mg of CaCO_3

50 ml of hard water contain 50 mg of CaCO_3

50 ml of hard water consumes 48 ml of EDTA (V_1)

48 ml of EDTA	= 50 mg of CaCO_3 equivalent hardness
1 ml of EDTA	= 50 mg of CaCO_3 equivalent hardness
	= $\frac{50}{48}$ mg of CaCO_3 equivalent hardness

Calculation of total hardness: $= 1000 \bar{V}_2 / \bar{V}_1 \text{ ppm}$

50 ml of water sample consumes 15 ml of EDTA (V_2)

Total Hardness = $(15/48) \times 1000 \times 1 \text{ mg of } \text{CaCO}_3$

= 312.5 ppm

Permanent hardness: (non – carbonate hardness)

= $1000 V_3 / V_1 \text{ ppm}$

50ml of water sample = 10 ml of EDTA (V_3)

Permanent Hardness = $(10/48) \times 1000 \times 1 \text{ mg of } \text{CaCO}_3$

= 208.4 ppm

Temporary Hardness (1L) = Total hardness – Permanent hardness

= $312.5 - 208.4 = 104.1 \text{ ppm}$

2. In an EDTA titration, 50 ml of standard hard (1mg CaCO_3 in 1ml) water sample consumed 25 ml of EDTA, 50 ml of hard water sample consumed 35 ml of EDTA and the 50ml sample hard water (after boiling, cooling and filtering) required 10ml EDTA . Calculate the permanent and temporary hardness of the given water sample.

1 mL std. hardwater = 1mg CaCO_3

50 mL std. hardwater = 25 mL EDTA (V_1)

Therefore, 1 mL EDTA = $(50/25) \times 1\text{mg } \text{CaCO}_3$

50 ml of hard water = 35 ml of EDTA (V_2)

1000 mL of hardwater contains = $(35/25) \times 1000 \times 1\text{mg } \text{CaCO}_3$

Total hardness = 1400 ppm

After boiling, EDTA consumed = 10 mL

50 mL of sample hardwater = 10 mL of EDTA (V_3)

1000 mL of hardwater after boiling contains = $(10/25) \times 1000 \times 1\text{mg } \text{CaCO}_3$

Permanent hardness = 400 ppm

Therefore, temp. hardness = $1400 - 400 = 1000$ ppm

3. Calculate Total, Temporary and Permanent hardness of the given hard water sample with following analysis report:-

[i] 50 mL of standard hard water sample consume 42 mL of EDTA solution.

[ii] 50 mL of hard water sample consume 19.9 mL of EDTA solution before boiling.

[iii] 50 mL of hard water sample consume 8.9 mL of EDTA solution after boiling.

Standard hard water is prepared by dissolving 1.5 gram of CaCO_3 per Litre.

Solution:

1mL of SHW contains 1.5mg of CaCO_3

[i] total hardness: 710.7 ppm

[ii] permanent hardness: 317.8 ppm

[iii] Temporary hardness: 392.9