Environmental Quality & Pollution Monitoring Techniques

Water Quality Parameters - Chlorine

Free and Combined Residual Chlorine

- What ?
- Why ?
- How ?

Dr Vinod Tare
Department of Civil Engineering
IIT Kanpur

Environmental Quality & Pollution Monitoring Techniques

Water Quality Parameters - Chlorine

Chlorine and Chloride

- What ?
- Why ?
- How ?

Water Quality Parameters – Chlorine

Disinfection - Chemical Methods

Mostly Oxidising Agents

Large Scale:
Chlorine
Sodium / Calcium hypochlorite
Chloramine
Chlorine dioxide
Ozone

Small Scale:
Silver
Iodine
Potassium permanganate
Chlorine compounds

Water Quality Parameters – Chlorine

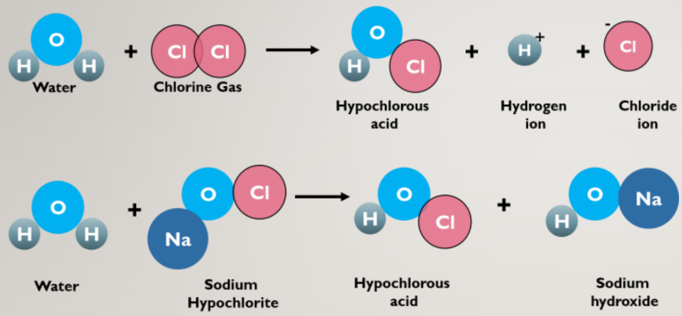
Chlorine Compounds Used in Disinfection

- Chlorine gas Cl_2
- Calcium Hypochlorite $Ca(OCl)_2$
- Sodium hypochlorite NaOCl
- Chlorine dioxide ClO_2

  (Cl^- is not a disinfectant)

Water Quality Parameters - Chlorine

Addition of Chlorine to Water



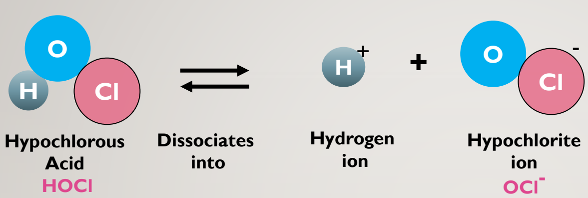
Hypochlorite salts : $Ca(OCl)_2 + 2H_2O \leftrightarrow 2HOCl + Ca(OH)_2$

$NaOCl + H_2O \leftrightarrow HOCl + NaOH$

- Hypochlorous acid is the primary disinfectant used in drinking water
- Chlorine gas added to water causes a decrease in pH (increase in hydrogen ions)
- The chlorine gas reaction is extremely fast (rate constant = $5x10^{14}$)
- Sodium Hypochlorite added to water increases pH (sodium hydroxide)

Water Quality Parameters - Chlorine

Dissociation of HOCl



This reaction is pH dependent

The ionization constant is: $$K_i = \frac{[HOCl]}{[OCl^-][H^+]}$$

The value of K_i varies with temperature

At 15^0C, K_i is 2.32×10^{-8}

pH is critical in disinfection

- The concentration of HOCl for a given measured free chlorine residual is 80% at pH 7, *and decreases to only 30% at pH 8.*
- At pH 6, *98% of the free chlorine residual is hypochlorous acid.*
- *Disinfection is far more efficient at low pH (6.5) as compared to higher pH (8).*
- Temperature has an effect as well...but it is offsetting with disinfection mechanism

Water Quality Parameters - Chlorine

- Chlorine readily combines with chemicals dissolved in water, microorganisms, small animals, plant material, tastes, odors, and colors.
- These components "use up" chlorine and comprise the **chlorine demand** of the treatment system.
- It is important to add sufficient chlorine to the water to meet the chlorine demand and provide residual disinfection.

1. **Chlorine demand** is the amount of chlorine required to kill bacteria, oxidize iron or other elements in the water.
2. **Free available chlorine residual** is the amount of chlorine remaining in the water after the chlorine demand has been met.
3. **Contact time** is the amount of time that the chlorine is present in the water. The combination of chlorine residual and contact time determines the effectiveness of the chlorination treatment.

Water Quality Parameters - Chlorine

(1) Free Chlorine

Chlorine Gas i.e. Cl_2 + Pure water

a) <u>Hydrolysis</u> $Cl_2 + H_2O \rightleftharpoons HOCl + HCl$

b) <u>Ionisation</u> $HOCl \rightleftharpoons H^+ + OCl^-$

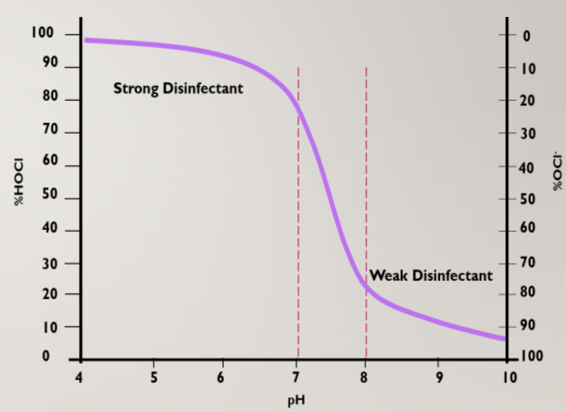
Hypochlorous Acid Hypochlorite Ion

(Free Chlorine Residuals)

Form of Free Chlorine depends on pH

$K = [HOCl]\,[H^+]\,[Cl^-] / [Cl_2] = 4.5*10^{-4}$ @ 25 °C

$K = [H^+]\,[OCl^-] / [HOCl] = 2.9*10^{-8}$ @ 25 °C



Water Quality Parameters - Chlorine

Reaction of Chlorine with Ammonia

Weight Ratio $Cl:NH_3$

$HOCl + NH_3 \Leftrightarrow NH_2Cl + H_2O$	< 5:1
$HOCl + NH_2Cl \Leftrightarrow NHCl_2 + H_2O$	< 10:1
$HOCl + NHCl_2 \Leftrightarrow NCl_3 + H_2O$	> 10:1

Ultimately:

$\mathbf{2\ NH_3 + 3\ Cl_2 \quad N_2 + 6\ HCl}$

Mole ratio **2 : 3** gives complete oxidation = **Breakpoint**

i.e. Weight Ratio **1 : 7.6** gives complete oxidation = **Breakpoint**

If NH_3 concentration in water (including organic nitrogen) is known, amount of HOCL required for "breakpoint" can be calculated

Theoretically Chlorine requirement = Weight NH_3-N x 7.6; However, in practice > Weight NH_3-N x 10

High $Cl:NH_3$ ratios also give increased rate of breakdown reactions

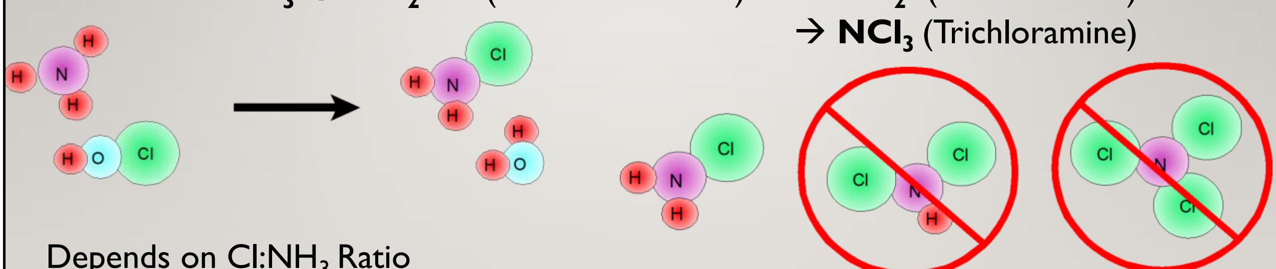
Other products of oxidation include: NO_3^- (Nitrate ion); Organo- chloramines (protein amino groups)

Water Quality Parameters - Chlorine

(II) Combined Chlorine

$Cl_2 + NH_3$ Sequential substitution of H in NH_3

$\mathbf{NH_3 \rightarrow NH_2Cl}$ (Monochloramine) $\rightarrow$ $\mathbf{NHCl_2}$ (Dichloramine) $\rightarrow$ $\mathbf{NCl_3}$ (Trichloramine)



Depends on $Cl:NH_3$ Ratio

NH_2Cl & $NHCl_2$ also serve as disinfectant but nasty to taste in water

NCl_3 does not serve as disinfectant and is particularly offensive

Water Quality Parameters – Chlorine

Total Chlorine

Free chlorine
Available to inactivate diseases causing-organisms

Combined chlorine
Reacts with nitrates and unavailable for disinfection

Residual chlorine is usually tested in finished water which is ready to be released into the distribution system, although operators must also ensure that there is adequate residual at the extreme ends of the distribution system.

Water Quality Parameters - Chlorine

Nitrogen Forms of Concern

- Ammonia, NH_3 or Ammonium ion, NH_4
  - In neutral or acidic natural waters, ammonia is present as ammonium ion
- Nitrite, NO_2
- Nitrate, NO_3
- Kjeldahl Nitrogen, TKN
  - TKN = Organic nitrogen + ammonia
- For systems adding ammonia
  - Ammonium sulfate, ammonium hydroxide, or others

Water Quality Parameters - Chlorine

Chlorine reacts with **H_2S, Fe(II), Mn(II)**

$$H_2S + 4\,Cl_2 + 4\,H_2O \longrightarrow H_2SO_4 + 8\,HCl$$

$$H_2S + Cl_2 \longrightarrow S + 2HCl$$

$$2Fe(HCO_3)_2 + Cl_2 + Ca(HCO_3)_2 \longrightarrow 2Fe(OH)_{3\,(s)} + CaCl_2 + 6\,CO_2$$

Associated pH rise, useful for iron removal & coagulant production

$$MnSO_4 + Cl_2 + 4\,NaOH \longrightarrow MnO_{2\,(s)} + 2\,NaCl + Na_2SO_4 + 2\,H_2O$$

Precipitate takes 2-4 hours to form, longer for complex Mn ions

Where H_2S, Mn or Fe present, PRECHLORINATION + FILTRATION are used for their removal. However, due to THM formation, it is used with caution.

Water Quality Parameters - Chlorine

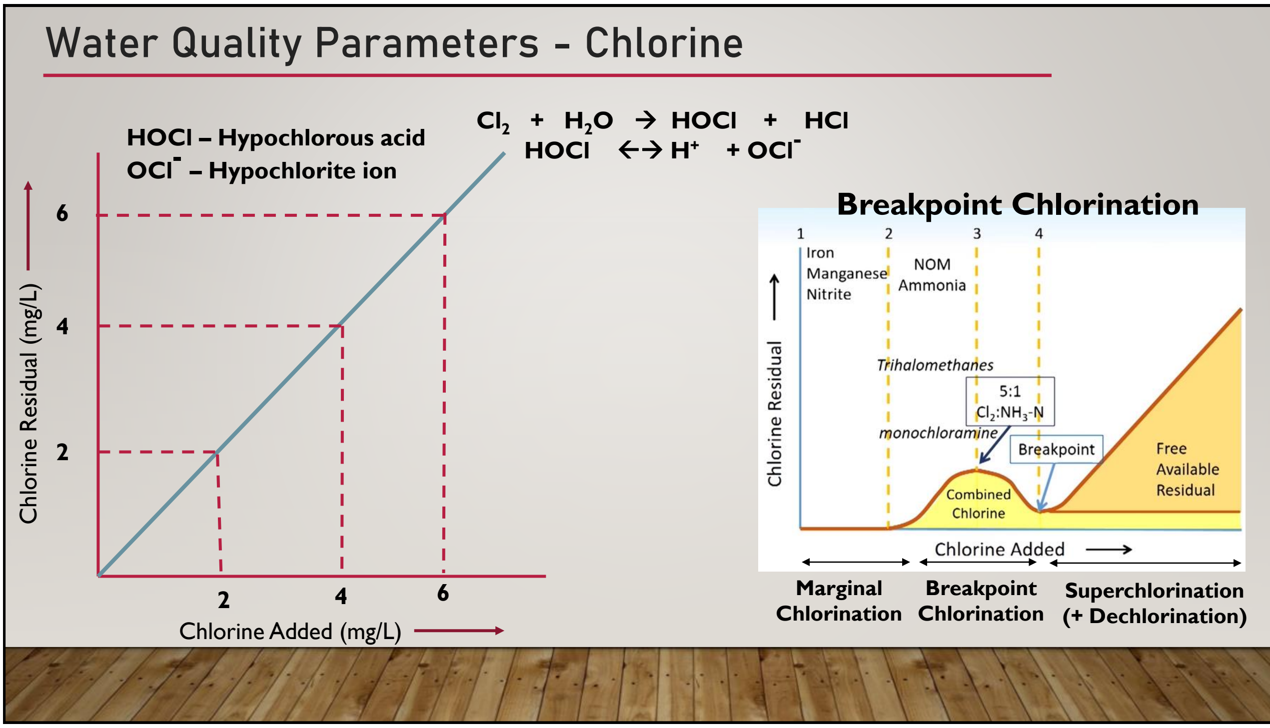
Chlorine Demand

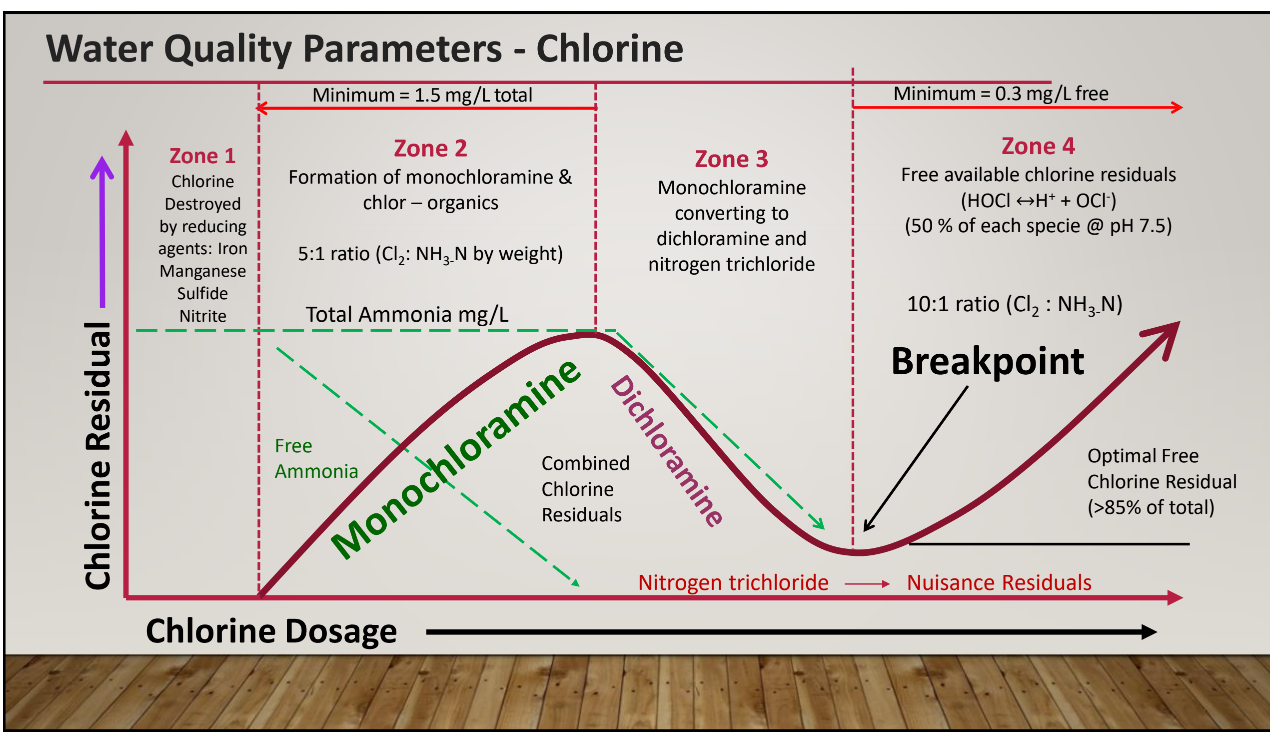
Chlorine added to water is not necessarily available for disinfection.

- Chlorine Reacts with:
  - Ammonia
  - Organic Matter (Dissolved, Colour causing substances; Particulate
  - Metal ions (Pipe materials; From source water)

Lowland surface waters

- Chlorine demand of 6 - 8 mg/l


Water Quality Parameters - Chlorine
HOCl – Hypochlorous acid
OCl- – Hypochlorite ion
Cl2 + H2O → HOCl + HCl
HOCl ←→ H+ + OCl-
Chlorine Residual (mg/L)
Chlorine Added (mg/L)
2
4
6
Breakpoint Chlorination
1 2 3 4
Iron
Manganese
Nitrite
NOM
Ammonia
Trihalomethanes
5:1
Cl2:NH3-N
monochloramine
Breakpoint
Combined Chlorine
Free Available Residual
Chlorine Residual
Chlorine Added
Marginal Chlorination
Breakpoint Chlorination
Superchlorination
(+ Dechlorination)


Water Quality Parameters - Chlorine
Minimum = 1.5 mg/L total
Minimum = 0.3 mg/L free
Zone 1
Chlorine Destroyed by reducing agents: Iron Manganese Sulfide Nitrite
Zone 2
Formation of monochloramine & chlor – organics
5:1 ratio (Cl2: NH3-N by weight)
Total Ammonia mg/L
Zone 3
Monochloramine converting to dichloramine and nitrogen trichloride
Zone 4
Free available chlorine residuals
(HOCl ↔H+ + OCl-)
(50 % of each specie @ pH 7.5)
10:1 ratio (Cl2 : NH3-N)
Breakpoint
Free Ammonia
Monochloramine
Dichloramine
Combined Chlorine Residuals
Optimal Free Chlorine Residual (>85% of total)
Nitrogen trichloride → Nuisance Residuals
Chlorine Residual
Chlorine Dosage

Water Quality Parameters - Chlorine

Zone 1: Initial chlorine demand is caused by reducing agents (Fe^{+2}, Mn^{+2}, H_2S, NO_2) that consume most of the chlorine applied prior to forming combined residuals.

Zone 2: Additional chlorine combines with available total ammonia and reactive organics until forming maximum monochloramine residual. At the same time, uncombined free ammonia is being depleted until it reaches zero.

Zone 3: More chlorine dosage converts monochloramine into odorous dichloramine and nitrogen trichloride. Total combined chloramine residual decreases and ammonia concentration approaches zero at the breakpoint.

Zone 4: True free chlorine residual is obtained and provides the least nuisance odor when free residuals make up 85 percent of the total chlorine concentration. Nuisance combined chlorine residuals survive and the potential for disinfection by-products (trihalomethane and haloacetic acid) formation remains, as free chlorine residual develops further.

Water Quality Parameters - Chlorine

Chlorine Residuals

Minimum Levels Dependent on where you are on the Curve

- Levels throughout the distribution system
- Minimum of 0.3 mg/L free chlorine residual if on the breakpoint side of the curve
- Minimum of 1.5 mg/L total chlorine residual if chloraminating
- Maximum of 4.0 mg/L total chlorine
  - Based on Running Annual Average (RAA) = MRDL

Water Quality Parameters - Chlorine

Chlorination Practice

Combined Residual

(a) **Simple, Marginal chlorination** → Suitable for Upland waters

(b) **Ammonia-chlorine treatment** → Add NH_3, then HOCl

Suitable for groundwaters

Ensures combined residuals in distribution.

Free Residual

(a) **Breakpoint chlorination** → Suitable for Lowland surface waters.

(b) **Superchlorination + Dechlorination** (SO_2, $S_2O_3^{2-}$ or Act. Carbon.)

- For industrially polluted surface waters
  - destroys tastes + odours + colour

Desirable to have chlorine Residual in the Distribution System;
Combined chlorine preferable
Most persistent.

Water Quality Parameters - Chlorine

Taste, Odour and Health Issues Due to Chlorination

Hypochlorous Acid	20 mg/L
Monochloramine	5 mg/L
Dichloramine	0.8 mg/L
Trichloramine	0.02 mg/L

- Typically "swimming pool" or other "chemical" or "chlorine" type smell
- "Burning" of eyes, particularly in shower or other hot water uses

Water Quality Parameters - Chlorine

Taste, Odour and Health Issues Due to Chlorination

Hydrogen Sulfide + Chlorine + Oxygen Ion Elemental ⟶ Sulfur + Water + Chloride Ions

$$H_2S + Cl_2 + O^{2-} \longrightarrow S + H_2O + 2Cl^-$$

In the first reaction, hydrogen sulfide reacts with chlorine and oxygen to create elemental sulfur, water, and chloride ions. The elemental sulfur precipitates out of the water and can cause odor problems.

Hydrogen Sulfide + Chlorine + Water ⟶ Sulfuric Acid + Hydrochloric Acid

$$H_2S + 4Cl_2 + 4H_2O \longrightarrow H_2SO_4 + 8\,HCl$$

In the second reaction, hydrogen sulfide reacts with chlorine and water to create sulfuric acid and hydrochloric acid.

Water Quality Parameters - Chlorine

Taste, Odour and Health Issues Due to Chlorination

- Phenols react with Chlorine:

Cl_2 + Phenols →Produce mono-, di-, Trichlorophenols → produce taste & odor

- Chlorine reacts with other halogens:

$$\mathbf{Br^- + HOCl \rightarrow HOBr + Cl^-}$$

HOBr : Hypobromous acid

- Cl_2 and HOBr reacts with humic substance

→ Halogenated organics. THMs → Suspected human carcinogens.

- Alternative disinfectants ?

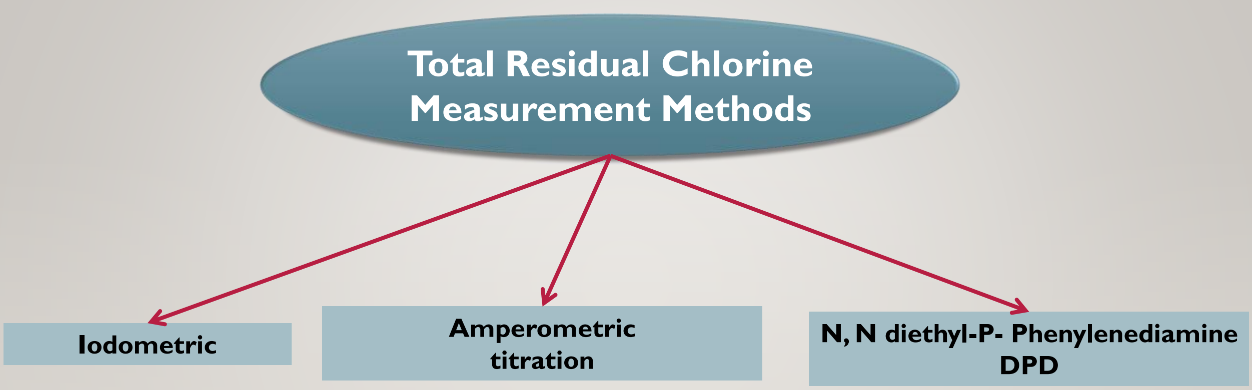
Water Quality Parameters - Chlorine

Sampling and Sample Handling and Preservation

- As a general guide, the World Health Organization (WHO, 2006) recommends that one sample per 1000 persons served should be examined each month for water supply system that serves up to 100,000 persons.
- Preservation of the sample is not desirable. Because biological activity will continue after sample has been taken, changes may occur during handling and storage.
- If analysis is to be carried out within 2 hours of collection, cool storage is not necessary.
- If analysis can not be started within 2 hours of sample collection keep the sample at $4^{0}C$.
- Do not allow sample to freeze.
- Do not open the sample bottle before analysis.
- Begin analysis within 6 hours of sample collection.

Temperature (°C)	Solubility (kg Cl_2/m^3 of water)
0	14.4
20	7.25
40	4.6

Water Quality Parameters - Chlorine



Environmental significance: Active chlorine (free and combined) should be determined at each stage in the treatment process of drinking water and in the water mains in order to guarantee bacteriological impeccable water.

Water Quality Parameters - Chlorine

Determination of the Strength of the Stock Chlorine Solution: NaOCl vs $Na_2S_2O_3$

Theory

Based on your understanding of oxidation-reduction titrations; write down the relevant equations for determination of the strength of an unknown chlorine stock solution using a $Na_2S_2O_3$ solution of known strength.

Water Quality Parameters - Chlorine

Procedure:

- Prepare "**Standard Chlorine Solution**" by taking10 mL of stock chlorine solution and diluting to 1000 mL.
- Prepare 1000 mL 0.1 M $Na_2S_2O_3$ solution.
- To 25 mL of standard chlorine solution, add **5 mL of glacial acetic acid** and **1 g of KI**. Dilute to 100 mL. Titrate using **0.1 M $Na_2S_2O_3$** for iodine quantification.
- Determine the strength of the unknown chlorine solution in mg/L as Cl_2.

Water Quality Parameters - Chlorine

Determination of the Strength of the Stock Chlorine Solution: NaOCl vs FAS

Theory

Based on your understanding of oxidation-reduction titrations; write down the relevant equations for determination of the strength of an unknown chlorine stock solution using a FAS solution of known strength.

How Colour is formed?

Free chlorine complexes instantly with DPD indicator to produce red colour. This red colour is discharged when chlorine in the solution is consumed by FAS, thus signifying the end-point of the titration.

Water Quality Parameters - Chlorine

Procedure:

- Prepare 0.0028 M FAS solution with freshly boiled distilled water. Add 0.25 mL concentrated H_2SO_4 to the bottle. Label, "**Standard FAS Solution**".
- Dissolve 24g anhydrous Na_2HPO_4 and 46 g KH_2PO_4 in distilled water. Combine with 100 mL of distilled water to which 800 mg of disodium EDTA has been dissolved. Dilute the mixture to 1000 mL and add 20 mg $HgCl_2$ to the solution. Label, "**Phosphate Buffer Solution for Chlorine Measurement**".

Water Quality Parameters - Chlorine

- Dissolve 1 g of DPD Oxalate or 1.5 g of DPD sulfate pentahydrate or 1.1 g of DPD sulfate in 6 mL of distilled water containing 2 mL concentrated H_2SO_4 and 200 mg EDTA disodium salt. Make up to 1000 mL. Store in a brown bottle in the dark. Label, "**DPD Solution for Chlorine Determination**".
- Add 5 mL of buffer solution and 5 mL of DPD reagent and mix in a conical flask. Take appropriate quantity (in mL) of the standard chlorine solution and dilute to 100 mL (after dilution the chlorine concentration should be in the range 1-4 mg/L). Add this diluted solution to the conical flask. Titrate rapidly with FAS until the red color is discharged.
- Determine the strength of the unknown chlorine solution in mg/L as Cl_2.

Compare the strengths obtained from two different experiments done.

Water Quality Parameters - Chlorine

STARCH – IODIDE METHOD

- **Oxidizing power of free and combined chlorine to convert iodide to iodine.**

$$Cl_2 + 2I^- \rightarrow I_2 + 2Cl^-$$

$$I_2 + \text{starch} \rightarrow \text{blue color}$$

- **Blue color → Shows the presence of free chlorine.**

Water Quality Parameters - Chlorine

Determination of Free and Combined Residual Chlorine in Water

Theory

Free chlorine complexes instantly with DPD indicator to produce red color. This red color is discharged when the chlorine in solution is consumed by FAS, thus signifying the endpoint of the titration.

Subsequent addition of about 1 g of KI causes the combined chlorine to complex with DPD (the iodide ion acts as a catalyst in this complexation process). Further titration with FAS to a colorless endpoint results in quantification of combined chlorine.

Water Quality Parameters - Chlorine

Procedure:

- Take 5 BOD bottles and two conical flasks.
- Based on determination of the average strength of the chlorine solution **in earlier part of the experiment** prepare 100 mL of a 100.0 mg/L stock chlorine (as Cl_2) solution.
- Pour 100 mL of the sample water in each of the 5 BOD bottles.
- Add appropriate concentrations of the chlorine stock solution to each BOD bottle such that the added chlorine(as Cl_2) concentrations in the bottles are approximately 0, 1, 4, 8, and 10 mg/L. Mix well. Space the chlorine additions 5 minutes apart.

Water Quality Parameters - Chlorine

- Wait for 30 minutes (this gives time for chlorine to react), before titrating each solution by the **DPD Ferrous Titrimetric Method**.
- Chlorine quantification is done in this case by the **DPD Ferrous Titrimetric Method**, which involves the following steps:
  - Place 5 mL each of the buffer reagent and the DPD indicator solution in a conical flask
  - Add 100 mL of sample (or diluted sample) to this flask and mix.
  - Titrate rapidly (this is very important) with the standard FAS solution until the red color is discharged. This reading (A) is equivalent to the free chlorine concentration.
  - Add a small amount (1 g approximately) KI to the sample, and mix to dissolve. Let stand for 2 minutes. If the red color returns, titrate until the color is discharged again. This reading is equivalent to the combined chlorine (B) concentration.

Water Quality Parameters - Chlorine

- Titrate
  - full 100 mL of solutions with 0 and 2 mg/L chlorine dose,
  - 50 mL of the solution diluted to 100 mL for the solutions with chlorine doses of 4 and 8 mg/L.
  - 25 mL of the solution diluted to 100 mL for the dilution with chlorine dose of 10 mg/L.
- Record the volume of titrant required in each case.
- For each chlorine dose, determine the concentration of Free Chlorine (A), Combined Residual Chlorine (B)
- Also determine the amount of chlorine consumed by other reactions in each case. This will be given by the difference between the added chlorine concentrations and the sum of free and combined chlorine concentration.