

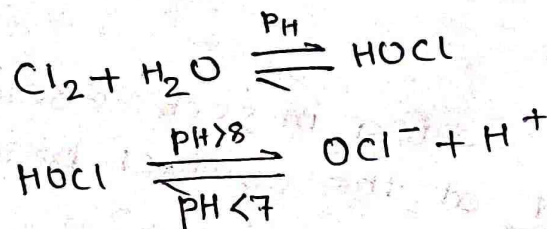
Major method of Disinfection.

(i) Treatment with chlorine (Cl)

→ When chlorine added with water reacts it at $\text{pH} > 5$ & heads to formation of highly unstable Hypochlorous acid (HOCl) which further dissociates into Hypochlorite ion (OCl^-) at $\text{pH} > 7$.

→ Here all three above forms of chlorine are collectively termed as freely available chlorine and is capable of carrying out disinfection. But HOCl is most destructive disinfectant amongst them. (Sometimes more effective than hypochlorite ion) Hence pH during disinfection is maintained slightly less than < 7 .

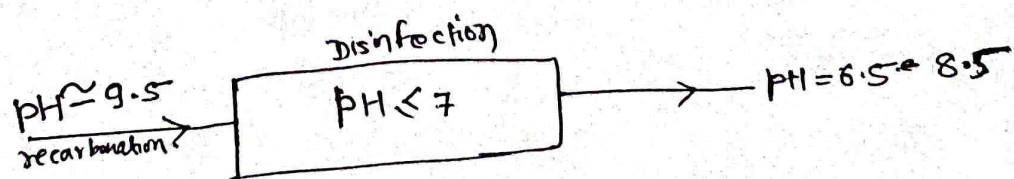
→ Chlorine enters into cell wall of m/o and destroy the enzyme responsible for metabolism in them in order to carry out disinfection. **"ENZYMATIC HYPOTHESIS"**



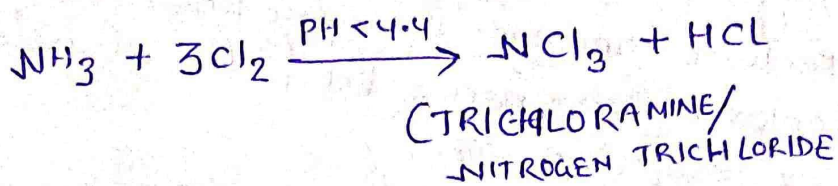
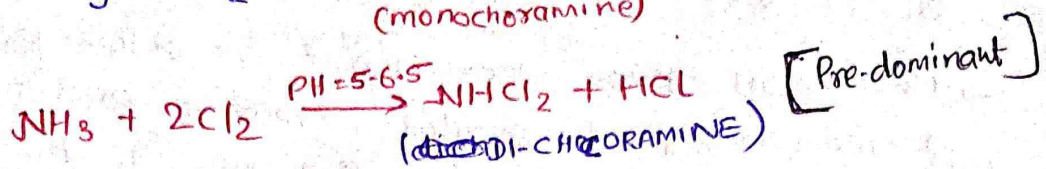
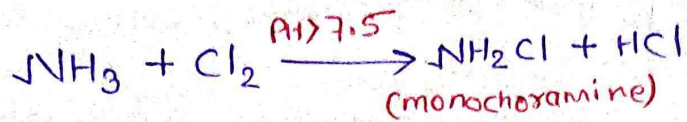
metabolism = Catabolism + Anabolism
Metabolism is the process in which bigger nutrients consumed by living organism are broken into lighter nutrients and energy is released (CATABOLISM) and this energy is further used by body for the growth of new cell (ANABOLISM)

$\text{Cl}_2, \text{HOCl}, \text{OCl}^-$
Free available chlorine

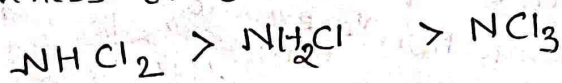
pH	form of chlorine.
< 5	Cl_2
<u>5-7</u>	<u>HOCl</u>
7-8	$\text{HOCl}, \text{OCl}^-$
> 8	OCl^-



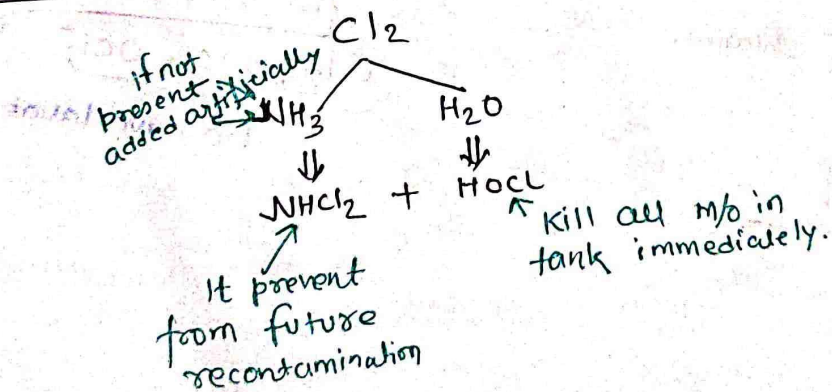
→ Chlorine when added in water immediately reacts with ammonia and form chloramine which are also termed as combined form of chlorine and are capable of carrying out disinfection but are 25 times less effective than free chlorine.



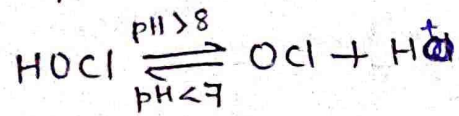
→ Effectiveness of chloramine in killing M/O.



→ Dose of chlorine is added in such a residual of 0.2 mg/l is insured at the contact period of 10 minutes.



Q 20mg/lit of chlorine is added in water to carry out disinfection equilibrium of which is governed by following reaction. R



$$K = 2.5 \times 10^{-7} \text{ moles/lit.}$$

(i) compute

(ii) fraction of HOCl in water at pH=7.

(iii) Concentration of OCl⁻ at this pH, considering chlorine added dissociates in HOCl & OCl⁻.

(iv) At what pH of water 0.7 fraction of OCl⁻ would be available in water.

(i) pH=7 $\Rightarrow [\text{H}^+] = 10^{-7} \text{ moles/lit}$

$$K_f = \frac{[\text{OCl}^-][\text{H}^+]}{[\text{HOCl}]}$$

$$2.5 \times 10^{-7} = \frac{[\text{OCl}^-][10^{-7}]}{[\text{HOCl}]}$$

$$[\text{HOCl}] = 0.4 [\text{OCl}^-]$$

$$f[\text{HOCl}] = \frac{[\text{HOCl}]}{[\text{HOCl}] + [\text{OCl}^-] + [\text{H}^+]} \xrightarrow{\text{neglect.}}$$

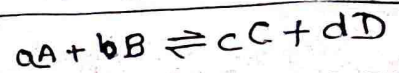
$$= \frac{0.4}{1.4} = 0.285$$

$$f[\text{HOCl}] = 0.285 \\ = 0.285 \times 100 \\ = 28.5\%$$

$$K_f = \frac{[\text{OCl}^-][\text{H}^+]}{[\text{HOCl}]}$$

$$K_b = \frac{[\text{HOCl}]}{[\text{OCl}^-][\text{H}^+]}$$

$$K_f \cdot K_b = 1$$



$$K_f = \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b}$$

where a, b, c, d are no. of moles.

At pH < 7
OCl⁻ HOCl
Both present

(i) At $\text{pH} = 7$

$$[\text{HOCl}] = 0.4 [\text{OCl}^-] \quad \text{--- (i)}$$

moles of chlorine added. $= [\text{Cl}_2] = [\text{HOCl}] + [\text{OCl}^-]$

$$\frac{20 \times 10^{-3}}{71} = [\text{HOCl}] + [\text{OCl}^-] \quad \text{--- (ii)}$$

$$\frac{20 \times 10^{-3}}{71} = 0.4 [\text{OCl}^-] + [\text{OCl}^-]$$

$$[\text{OCl}^-] = \frac{20 \times 10^{-3}}{71 \times 1.4} = 2.01 \times 10^{-4} \text{ moles/lit}$$

(iii) $f[\text{OCl}^-] = 0.7$

$$\frac{[\text{OCl}^-]}{[\text{OCl}^-] + [\text{HOCl}] + [\text{H}^+]} = 0.7 \quad \text{--- neglect}$$

$$[\text{OCl}^-] = 0.7 [\text{OCl}^-] + 0.7 [\text{HOCl}]$$

$$0.3 [\text{OCl}^-] = 0.7 [\text{HOCl}]$$

$$\frac{[\text{OCl}^-]}{[\text{HOCl}]} = \frac{7}{3}$$

$$\Rightarrow K_f = \frac{[\text{OCl}^-][\text{H}^+]}{[\text{HOCl}]}$$

$$2.5 \times 10^{-7} = \frac{7}{3} [\text{H}^+]$$

$$[\text{H}^+] = 1.07 \times 10^{-7} \text{ moles/lit.}$$

$$\text{pH} = -\log_{10}(1.07 \times 10^{-7})$$
$$= 6.97$$

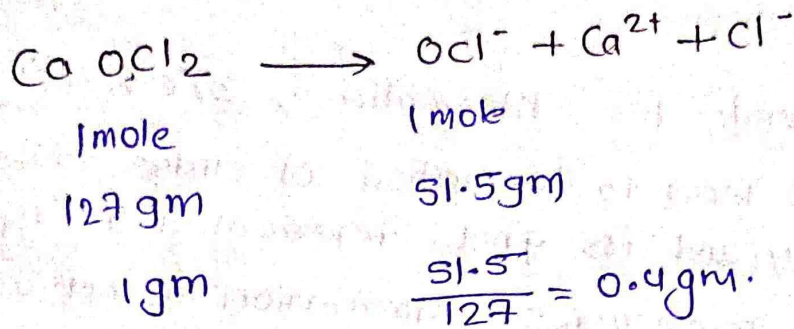
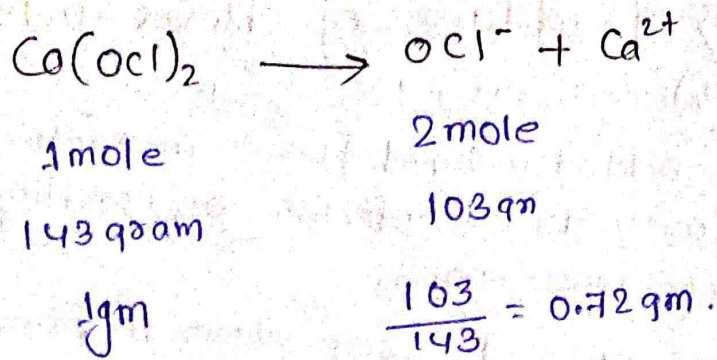
Different forms of addition of Chlorine in Water.

(i) Free chlorine (Cl_2) (solid, liquid, gas)

- Free chlorine is added in liquid phase in treatment plant in order to carry out disinfection as handling of liquid chlorine is much easier.
- It is highly sensitive to temperature. It freezes below 10°C and burns the container above 92°C in which it is kept for storage.
- Optimum temp. for chlorination is 32°C to 48°C .
- It does not lead to formation of sludge while disinfection and its quality ~~and~~ is not deteriorated during storage.
- Temperature problem, so chlorination is not used in European countries (Distribution system temp.).

(ii) Hypochlorites and Bleaching Powder.

- In this case either hypochlorite ion and ~~hyp~~ HOCl carries out the disinfection depending upon the pH of water.
- For 100% pure calcium hypochlorite freely available chlorination availability is approximately 72% which also goes on decreasing with time.
- For 100% pure bleaching powder, freely available chlorination availability is approximately 40% which also goes on decreasing with time.
- Use of these forms also leads to formation of sludge while disinfection. Hence it is not suitable for treatment in plant but can be used for swimming pool.

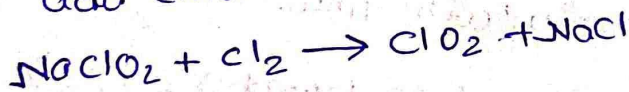


(iii) Chloramine

→ It is added in treatment plant for disinfection in case when phenol is present in water.

(ii) Chlorine dioxide (ClO₂)

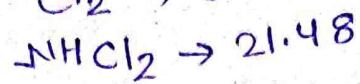
When we add chlorine is sodium chloride



→ It is strong oxidising reagent (2.5 times more effective than free chlorine.) which can remove ~~not~~ both microorganism and OM from water but it is not capable of safeguarding water against future recontamination.

→ It can also be used when phenol is present in water.

Q freely available Unit oxidising power of free chlorine is 35.5 and that of dichloramine is 21.48. Find the % of free Cl_2 in dichloramine.



$$\% (35.5) = 21.48$$

$$\% = \frac{21.48}{35.5} = 0.6$$
$$= 60\%$$

Q A city with the population of 50000 is to be provided disinfected water @ of 250 l/c/d. Find the amount of 25% pure bleaching powder required for treatment of this water @ dose of 20 mg/lit.

$$\text{Qty of CaOCl}_2 = \frac{5 \times 10^4 \times 250 \times 20 \times 10^{-6}}{0.25}$$
$$= 1000 \text{ kg/day}$$

Factor effecting efficiency of chlorination

- (i) Turbidity ↑ ↓
(ii) Presence of metallic ion. (Fe, Mn²⁺) ↑ ↓
(iii) Presence of ammonia (NH₃) ↑ ↓
(iv) pH ↑ ↓ (optimum pH = 5-7)
(v) Temperature ↑ ↑
(vi) Time of contact ↑ ↑

Types of chlorination:-

1) Plain chlorination.

- If the only treatment given to water is chlorination it is termed as plain chlorination.
- It removes taste, colour, odour and micro-organism from water.
- It is not done if turbidity of water is beyond permissible limit.
- Normal dose of chlorine in this case is 0.5 mg/lit.

2) Pre-chlorination:-

- If chlorination is done during coagulation and or during filtration. it is termed as pre-chlorination.
- It is adopted when quality of water is poor with respect to organic matter and micro-organism.
- Pre-chlorination is always succeeded by post chlorination but vice-versa not.
- Dose of chlorine in this case depend upon point of addition of chlorine.
- In ~~coagulation~~ ^{filtration} it is 0.1-0.5 mg/lit and in ~~filtration~~ ^{coagulation} it is 5-10 mg/lit

(iii) Post-chlorination

- If chlorination is done after filtration or it is the last treatment given to water it is termed as post chlorination
- Does of chlorine in ~~each~~ this case such a residual of 0.2 mg/lit of free Cl_2 is insured at contact period of 10 min to safeguard the water against future contamination.

(iv) Double-chlorination

- If both pre and post chlorination is done it is termed as double-chlorination.
- It is adopted when higher efficiency of chlorination is required

(v) Super-chlorination

- ~~Whenever a para~~
- If excess of chlorine is added in the range of $5-15 \text{ mg/lit}$ so as to ensure residual of $1-2 \text{ mg/lit}$ at contact period of 10 minute during epidemic, it is termed as super-chlorination.

(vi) De-chlorination

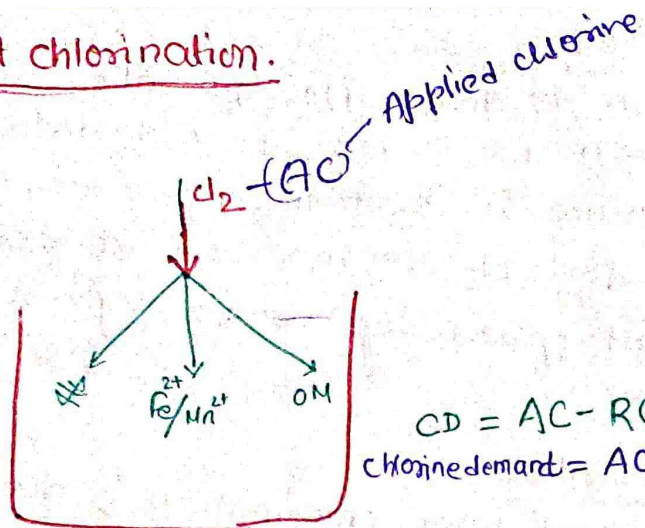
It is process of removal of excess chlorine from the water. It can be achieved by any of following chemicals.

Effective → NaAs ✓
cheap → $\text{Na}_2\text{S}_2\text{O}_3$

→ NH_4OH
→ Activated carbon
→ SO_2

} De-chlorinating Reagent

190 (ii) Break Point chlorination.

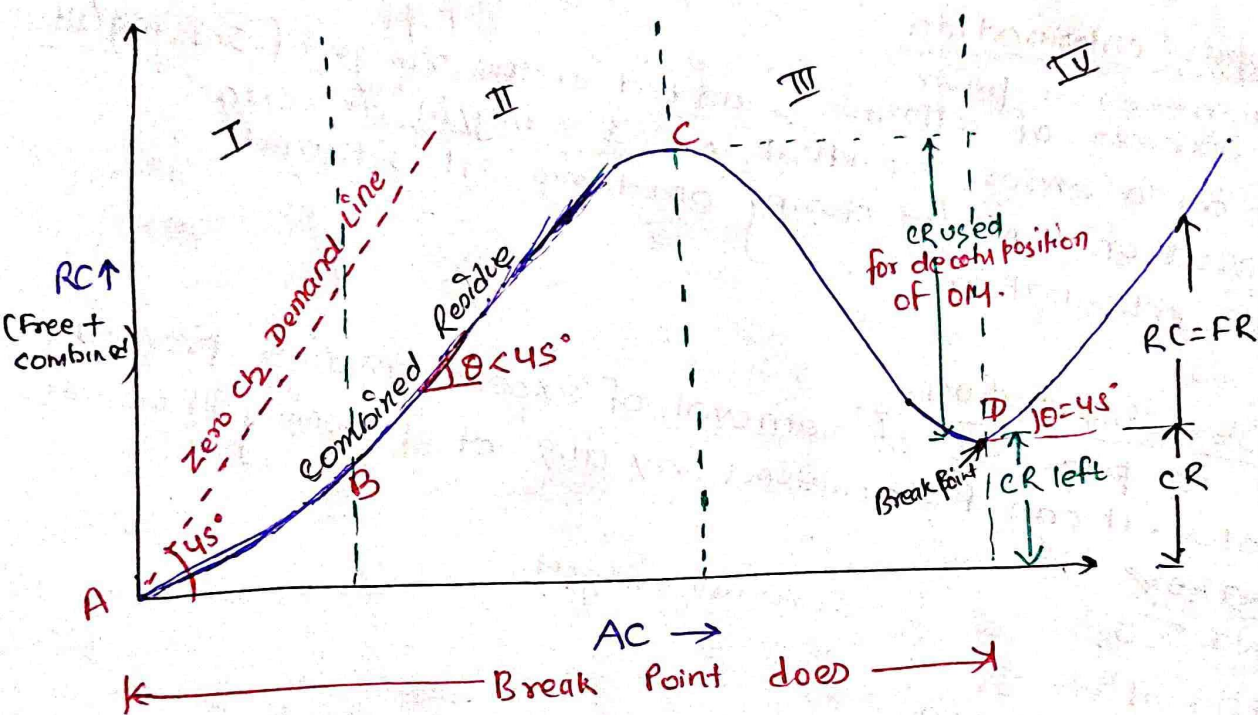


$$\text{CD} = \text{AC} - \text{RC}$$

Chlorine demand = AC - RC

$$\text{RC} = \text{FR} + \text{CR}$$

Residual chlorine = Free Residual + Combined residual



- In phase-I, chlorine first performs the function of disinfection and oxidation of mineral in the water resulting in high chlorine demand and leading to lesser residual chlorine in water.
- As most of the demand for disinfection and oxidation of mineral is satisfied in phase-I, residual chlorine increase in phase-II.

- At no point in phase II, residual chlorine equals applied chlorine as some amount of disinfection still takes place in this phase
- At the end of this phase i.e., at point C, bad smell oxidation of organic matter started by chlorine.
- As the result of this high chlorine demand, destruction of chloramines and chloroorganic compounds takes place in this phase.
- At the end of this phase i.e., point D, bad smell stop coming out of the water indicate complete decomposition of organic matter.
- After this point D, whatever chlorine is added breaks free from water i.e., appear as a residual chlorine, hence this point is termed as break point & the amount of chlorine required to reach upto this point is termed as break point dose.
- Theoretically no chlorine is required to be added in water after this point but practically chlorine is added to ensure the residual of 0.2 mg/lit after the contact period of 10 minutes.

	I	II	III	IV
AC	10	10	10	10
CD	9.8	0.3	8.5	0
RC	<u>0.2</u> CR	<u>9.7</u> CR	<u>6.9</u> CR	<u>16.9</u> FR + CR

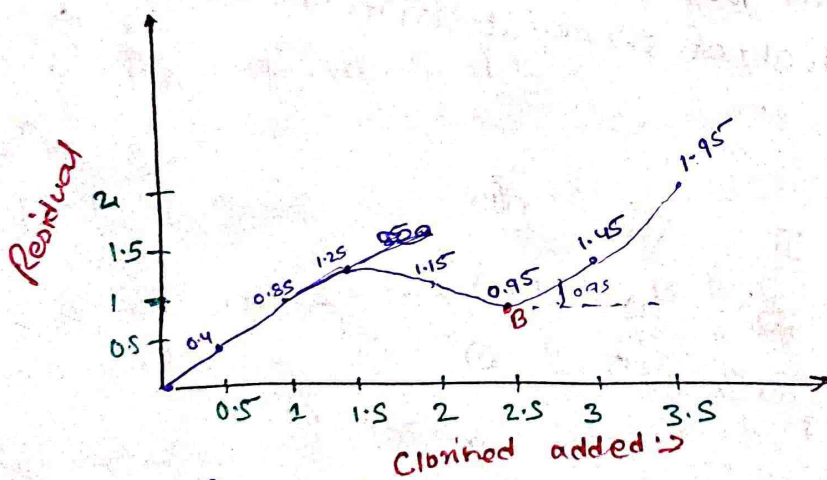
$$3CR \rightarrow 3FR \rightarrow 75CR.$$

Q For the given data, Compute (i) CD (ii) Break point Does, (iii) CD at does of 3mg/lit. (iv) Does of chlorine required for free residual of 0.75

Ac (mg/lit)	RC (mg/lit)	CD'	CD
0.5	0.4	$0.5 - 0.4 = 0.1$	$0.5 - 0.4 = 0.1$
1.0	0.85	$0.5 - 0.45 = 0.05$	$1 - 0.85 = 0.15$
1.5	1.25	$0.5 - 0.4 = 0.1$	$1.5 - 1.25 = 0.25$
2.0	1.15	$0.5 - (-0.15) = 0.65$	$2 - 1.15 = 0.85$
(ii) <u>2.5</u> Break point	0.95	$0.5 - (-0.2) = 0.7$	$2.5 - 0.95 = 1.55$ (i)
3.0	1.45	$0.5 - 0.5 = 0$	$3 - 1.45 = 1.55$ (ii)
3.5	1.95	$0.5 - 0.5 = 0$	$3.5 - 1.95 = 1.55$

(iv) Break point

after = Free residual of 0.75, chlorine demand = 1.55



B = Break point

(i) Chlorine demand = $2.5 - 0.95 = 1.55$

(ii) Break point does = 2.5

(iii) Chlorine demand @ 3 mg/lit = it is after Break point
= 1.55 mg/lit.

(iv) Does of chlorine required for free residual of 0.75

$$= 1.55 + 0.75$$

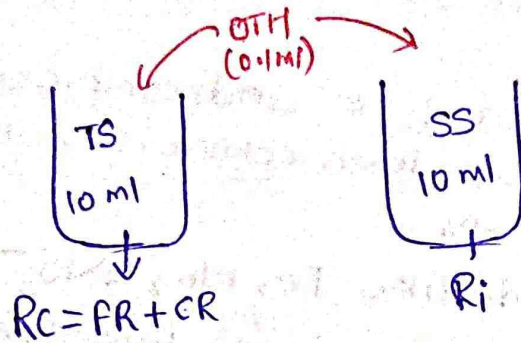
Testing of chlorine Residual.

Testing of chlorine residual can be done by any one of following methods -

① ORTHOTOLIDINE TEST

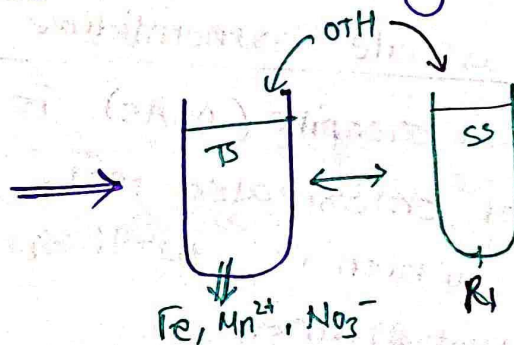
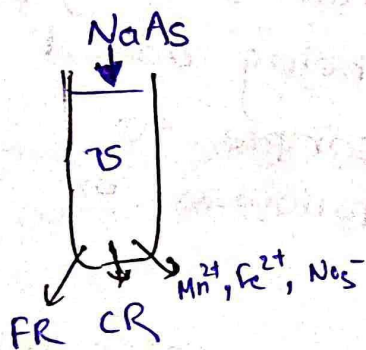
→ This test is based upon colour matching technique. & the colour is induced by addition of orthotolidin.

(i)

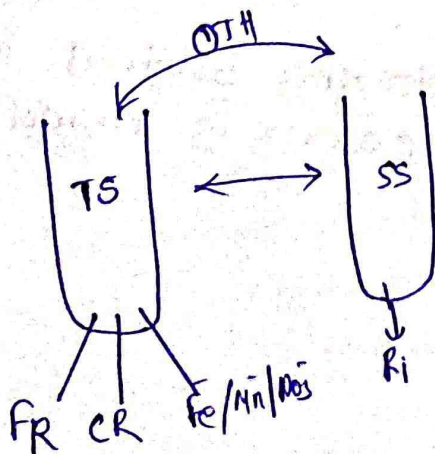


$$\begin{aligned} \text{5 sec} \\ FR &= R_1 \\ \text{5 min} \\ FR + CR &= R_2 \\ CR &= R_2 - R_1 \end{aligned}$$

ii) If colour causing compound ^(Fe, Mn) are present in water orthotolidine arsenite test is being performed. (OTA).



$$Fe^{2+}, Mn^{2+}, NO_3^- = R_1$$



$$\begin{aligned} FR + Fe^{2+}/Mn^{2+}/NO_3^- &= R_2 \\ FR &= R_2 - R_1 \end{aligned}$$

$$\begin{aligned} \text{5 min} \\ FR + CR + Fe^{2+}/Mn^{2+}/NO_3^- &= R_3 \\ CR &= R_3 - R_2 \end{aligned}$$

→ Practically this test obsolete now.

Procedure

→ In this test 10ml of chlorinated water sample is mixed with 0.1ml of orthotolidine which gives yellow colour in it. Intensity of which is further matched with that

→ Orthotolidine or 2-Tolidine is $C_{14}H_{16}N_2$ of standard

sample. If the intensity of colour of test sample is same with that of the standard sample, then chlorine in standard sample is also same as that of test sample.

→ With separate concentration of free and combined chlorine in residual form is desired, then colour is noted after 35 and 5min respectively.

→ If colour causing compounds like Fe, Mn, NO_3^- , are also present in the water, they give false yellow colour during the test resulting in higher value of residual chlorine than actual.

→ In such case, arsenite orthotolidine test is being performed in which sodium arsenite (NaAs) is being added to the original chlorinated test sample to dechlorinate it which is further followed by addition of orthotolidine.

→ Intensity of the colour induced by these colour causing compound is matched with that of the standard sample

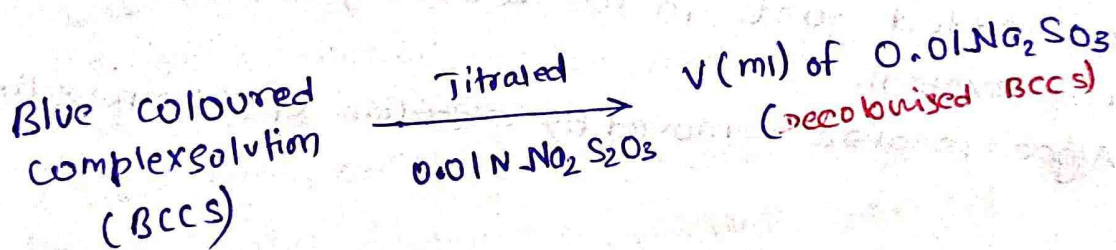
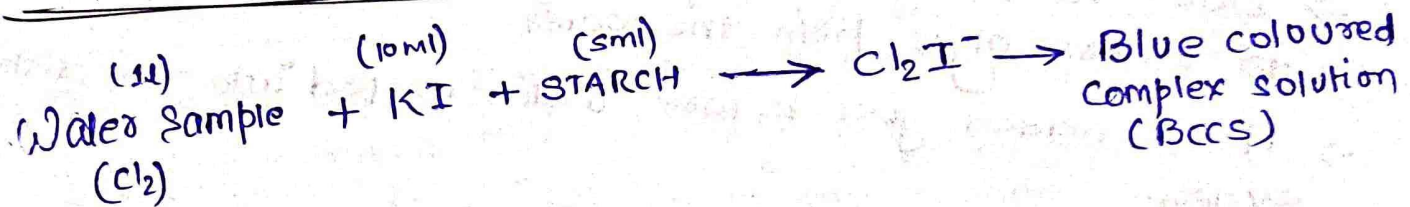
→ Orthotolidine is also added to the original chlorinated test sample and colour is noted after 5 minute respectively.

In today's time Orthotolidine test DPD (Diethyle phenylene diamine) and chloroex test is used which are also based upon colour matching technique. and are more accurate than orthotolidine test but are also comparatively costlier.

→ These two reagent DPD and chloroex are also termed as BDH (British Drug house) reagent.

Note:- Orthotolidine test may also be referred as ~~orthotolidine~~ method of SNORT (stabilized neutral-o-tolidine) method

(ii) Starch Iodide Test. (Iodimetric Test)



$$\text{gm. equivalent of } Na_2S_2O_3 \text{ used} = \frac{0.01}{10^3} \times V = \text{gm. eq. of } Cl_2$$

$$Cl_2 (\text{mg/lit}) = \frac{0.01}{10^3} \times V \times 35.5 \times 10^3 = 0.355 V$$

* Starch reacts with complex of halogen gases. [Chlorine, fluorine, bromine, iodine, astatine].