Number of mL of N/10 $Na_2CO_3$ × 0.515 = $CO_2$ grains per gallon.

## FREE CHLORINE (RESIDUAL CHLORIDE)

Chlorine determination is necessary in those samples of water that have been treated with chlorine or hypochlorites. This is carried out with the help of orthotoluidine reagent which can be prepared by first preparing a paste of one gm of orthotoluidine in 5 mL of 25% HCl. The paste is then dissolved in 200 mL of water and transferred to a litre measuring flask. It is further diluted to 505 mL with water and finally made upto the mark with 25% HCl. Mix the contents well and store the reagent in a coloured bottle at room temperature. At pH less than four, chlorine gives a colour with this reagent changing from pale yellow at low concentrations to an orange at higher concentrations. The presence of chloramines can also be tested by this reagent. The test is, however, interfered by the presence of oxidising agents, manganic compounds, nitrites, algae, ligno cellulose and organic iron compounds etc. The formation of yellow colour indicates the presence of residual chlorine. **The deeper the colour, the greater is the amount of residual chlorine.** The exact amount of residual chlorine can be ascertained by referring to the colour standards.

For potable water, a lemon yellow colour has been considered to be safe. When water is highly alkaline, a blue tinge is produced by this test. In such a case the amount of ortho toluidine solution should be doubled. No modification is required in the test if chloramines are present in water, because chloramines act in the same manner as free chlorine. If chlorine alone is used, the colour of water should be observed in 5 minutes after ortho toluidine solution is added and if chloramine is adopted as a disinfecting agent, the deepest colour of water in 15 minutes after ortho toluidine solution is added should be recorded for the analysis of chlorine content in water. The free residual chlorine forms colour in first 5 seconds of the test, while the combined residual chlorine goes on forming the colour upto about 5 minutes.

**Estimation of free chlorine in water** - It is based on the oxidation of KI by free chlorine. When water sample is treated with an excess of KI solution, the free chlorine, present in water sample oxidises KI and liberates $I_2$ in equivalent amounts. The iodine so formed is dissolved in excess of KI giving a deep violet complex $KI_3$.

$$2KI + Cl_2 \rightarrow 2KCl + I_2$$

$$KI + I_2 \rightarrow KI_3$$

The amount of liberated iodine is then titrated against a standard solution of sodium thiosulphate using starch as an indicator.

$$I_2 + 2Na_2S_2O_3 \rightarrow 2NaI + Na_2S_4O_6$$

$$I_2 + \text{Starch} \rightarrow \text{Complex having deep blue colour}$$

**Reagents** :

**(a) Sodium thiosulphate solution ( 0.1 N)** - It can be prepared by dissolving 24.82 g sodium thiosulphate in boiled and cooled distilled water in 1000 mL measuring flask. Standardise it against standard potassium dichromate solution ( 0.1 N). It can be preserved by adding a few mL of chloroform.

**(b) Glacial acetic acid.**

**(c) Potassium iodide crystals.**

**(d) Starch.**

**(e) Sodium thiosulphate solution (0.0025N).**

**Standardisation of sodium thiosulphate :**

(a) *Dissolve 1.226 g. potassium dichromate in distilled water in 250 mL volumetric flask.*

(b) *Dissolve 3g potassium iodide and 2g sodium bicarbonate in 100 mL boiled and cooled distilled water in a 500 mL conical flask.*

(c) *Add 6 mL conc. HCl followed by 25.0 mL standard potassium dichromate solution (0.1N). Keep it for 5 minutes in dark.*

(d) *Dilute it with 300 mL water. Titrate the liberated iodine with hypo solution. When the colour becomes yellowish green, add 2 mL starch solution. Titrate it until the colour changes to light green.*

(e) *Determine the normality of sodium thiosulphate solution.*

**Procedure** – Take 500 mL of the sample in a conical flask. Add 1g of KI and 5 mL acetic acid. Titrate with 0.0025N hypo solution until the colour of iodine is discharged. Add 1 mL starch indicator and titrate until the blue colour disappears.

**Modified method when manganese, nitrite and ferric iron (2 mg/L) are present** – The pH is adjusted from 4.5 to 8.0 by adding acetic acid. Add 1g KI and titrate with 0.0025N hypo solution.

**Calculations** –

$$\text{mg/L Chlorine} = \frac{\text{mL 0.0025 N sodium thiosulphate} \times 0.0887 \times 1000}{\text{mL sample taken for estimation}}$$

**Result** – Excess of chlorine in water can accelerate corrosion, deteriorate lumber, may cause tastes in canned foods or frozen products. Therefore residual chlorine content in pure water should not exceed 2 mg/L.

**Estimation of dissolved chlorides** – A sample of hard water containing chlorides of calcium and magnesium, gives an instant white precipitate of AgCl with $AgNO_3$ solution. The process continues as long as $Cl^-$ ions are there.

The completion of the chloride precipitate can be checked by adding a few drops of potassium chromate solution as indicator which suddenly gives a red precipitate when chloride removal is complete. This appearance of red precipitate of silver chromate only after complete removal of the dissolved chloride is due to wide difference in the solubility product values of AgCl ($1.82 \times 10^{-10}$) and $AgCrO_4$($1.1 \times 10^{-12}$).

The sample of water after neutralisation with N/50 $H_2SO_4$ using methyl orange as indicator is taken. Few drops of potassium chromate indicator are added to it and then the sample is titrated against N/50 $AgNO_3$ solution till the colour changes from white yellow to reddish brown.

The number of c.c. of $AgNO_3$ solution added is calculated as parts per $10^6$ parts of sodium chloride (as $CaCO_3$), as

$$\frac{x \times N \times 10^6}{1000 \times 50 \times 100}$$

where x is the number of c.c. of N/50 $AgNO_3$ and N is the equivalent weight of $CaCO_3$.

## CHLORINE DEMAND

Polluted waters such as sewage, effluents, trade wastes, industrial wastes, and water highly contaminated from organic sources frequently require chlorination to control odour and bacterial growth. A measure of **chlorine demand** may be required in order to estimate the quantity of chlorine necessary to add to a given volume of water.

**Chlorine demand** may be defined as the quantity of chlorine required to produce a residual chlorine content between a trace and 0.1 ppm after 10 minute contact. The measurement of chlorine demand helps in estimating the quantity of chlorine necessary to add to a given volume of water. Take a reagent bottle containing 250 mL of the sample and add to it standard chlorine water containing 0.5 mg of chlorine from a burette.

Stir the mixture well and withdraw 0.25 mL of the solution with a pipette on a spot plate and immediately test it for free chlorine with a drop of orthotoluidine reagent. Continue adding the standard chlorine water in 0.5 mL portions, mixing, and testing as before until there is a slight excess of chlorine which is indicated by light yellow colour. The quantity of chlorine required is regarded as the immediate chlorine demand.

Now again take a similar sample and add to it standard chlorine water in an amount equivalent to the immediate chlorine demand plus 0.5 mL. more. Agitate the mixture well and allow it to stand for exactly 10 minutes. After completion of ten minutes, immediately test a portion for residual chlorine as described above.

**Calculation –**

mL of standard chlorine water × grams chlorine per litre in standard chlorine water $\times \frac{1000}{250}$ = ppm. chlorine demand.

**Reagents (i) Standard chlorine solution :** Weigh 350 mg of 30% bleaching powder and transfer its paste to a 1000 mL volumetric flask. Make up the solution to the mark with distilled water. The solution contains about 100 mg/L chlorine. Standardise it against 0.025 N sodium thiosulphate solution using starch as an indicator. Calculate chlorine as follows :

$$\text{mg chlorine per mL solution} = \frac{\text{mL 0.025 N Sodium thiosulphate} \times 0.885}{\text{mL sample used for determination}}$$

**Method** – Measure 200 mL portions of well mixed sample into each of ten bottles. Add increasing amounts of chlorine solution in increaments of 0.1 mg/L. After contact period (10 minutes) determine free available chlorine and combined available chlorine by starch iodide method.

**Calculation** – mg/L chlorine demand = mg/L chlorine added–mg/L residual chlorine.

**Determination of residual chlorine** - Iodometric and orthotoludine methods are used for the determination of residual chlorine in potable water, moderately polluted water, cooling water and water treatment effluents. Iodometric method is considered to be the standard one and is best suited to samples containing chlorine more than 1 mg/L only.