Environmental Chemistry and Microbiology

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Module - 5
Lecture - 25
Chlorine Chemistry and Disinfection (Part-C)

Welcome everyone to our online NPTEL course, Environmental Chemistry and Microbiology. This course will be taught by Professor Sudha Goel and myself, Professor Anjali Pal. We both are from Civil Engineering Department, IIT Kharagpur. We have divided this course into 2 parts. The first part, Environmental Chemistry will be covered by me and the second part, i.e., Environmental Microbiology will be taught by Professor Sudha Goel.

In my first module, I discussed about the acids, bases and salts. In the second module, I discussed about the chemical equilibrium. In the third module, I discussed about the chemical kinetics. In the fourth module, I covered the catalysis and this is my fifth module. This is my lecture number 25. I am covering chlorine chemistry and disinfection, Part C.

In the last 2 lectures also I discussed about chlorine and how we can disinfect the water with chlorine. I discussed about the chemistry of chlorine and also the chloramine formation, the chlorine demand, breakpoint chlorination curve, etc. In this lecture, I will cover the determination methods.

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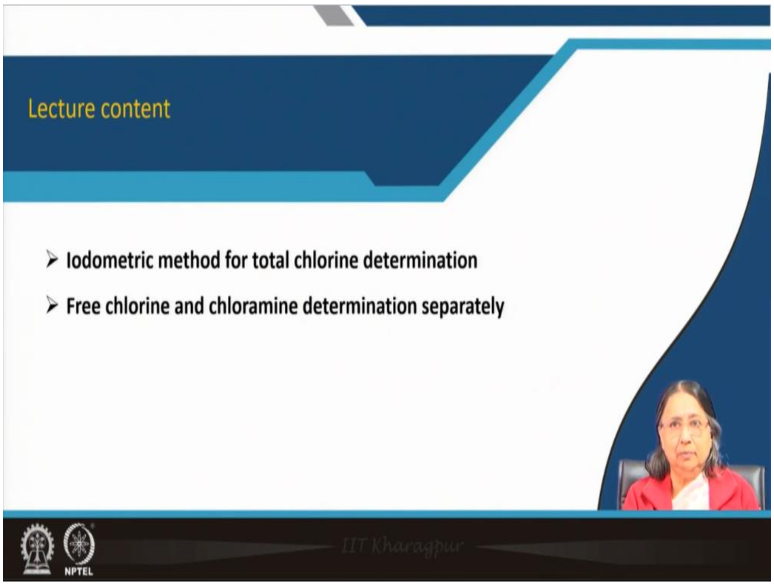

Lecture content

- Iodometric method for total chlorine determination
- Free chlorine and chloramine determination separately

That content of this lecture are as follows:.

The iodometric method for total chlorine determination.

Free chlorine and chloramine determination separately.

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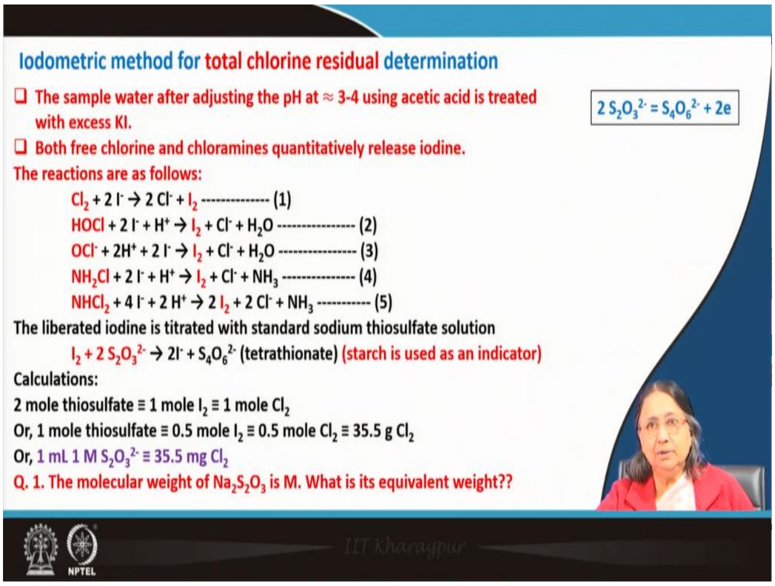

Iodometric method for total chlorine residual determination

$2\,S_2O_3^{2-} = S_4O_6^{2-} + 2e$

- ☐ The sample water after adjusting the pH at ≈ 3-4 using acetic acid is treated with excess KI.
- ☐ Both free chlorine and chloramines quantitatively release iodine.

The reactions are as follows:

$Cl_2 + 2\,I^- \rightarrow 2\,Cl^- + I_2$ ------------- (1)

$HOCl + 2\,I^- + H^+ \rightarrow I_2 + Cl^- + H_2O$ --------------- (2)

$OCl^- + 2H^+ + 2\,I^- \rightarrow I_2 + Cl^- + H_2O$ --------------- (3)

$NH_2Cl + 2\,I^- + H^+ \rightarrow I_2 + Cl^- + NH_3$ -------------- (4)

$NHCl_2 + 4\,I^- + 2\,H^+ \rightarrow 2\,I_2 + 2\,Cl^- + NH_3$ ---------- (5)

The liberated iodine is titrated with standard sodium thiosulfate solution

$I_2 + 2\,S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$ (tetrathionate) (starch is used as an indicator)

Calculations:

2 mole thiosulfate ≡ 1 mole I_2 ≡ 1 mole Cl_2

Or, 1 mole thiosulfate ≡ 0.5 mole I_2 ≡ 0.5 mole Cl_2 ≡ 35.5 g Cl_2

Or, 1 mL 1 M $S_2O_3^{2-}$ ≡ 35.5 mg Cl_2

Q. 1. The molecular weight of $Na_2S_2O_3$ is M. What is its equivalent weight??

Let us see the iodometric method for total chlorine residual determination. Total chlorine means free chlorine residual and combined chlorine residual. The pH of the sample water is adjusted to 3 to 4 first. It is maintained by acetic acid. Then it is treated with excess potassium iodide. When we add KI, then you see the reactions shown from (1) to (5):

$Cl_2+2I^- \rightarrow 2Cl^-+I_2$…………………..(1)

$HOCl+2I^-+H^+ \rightarrow I_2+Cl^-+H_2O$……….(2)

$OCl^-+2H^++2I^- \rightarrow I_2+Cl^-+H_2O$……….(3)

$NH_2Cl+2I^-+H^+ \rightarrow I_2+Cl^-+NH_3$…………(4)

$NH_2Cl+4I^-+2H^+ \rightarrow 2I_2+2Cl^-+NH_3$……(5)

To determine the iodine quantity, it is titrated with thiosulphate and the balanced equation is:

$I_2+2S_2O_3^{2-} \rightarrow 2I^-+S_4O_6^{2-}$ (tetrathionate)……………………(6)

Starch is the indicator. So, we all know that for this type of iodometric titration, we start the reaction with thiosulfate solution in the burette. We take the solution where iodine is generated i.e., in the conical flask. But when we will add starch? We all know that iodine has the brown colour. If its concentration is less, then it is yellow colour. If it is brown colour, then in the beginning we will not add starch. We will start with addition of thiosulfate. Then slowly the colour will become less intense. That means, initially if it is brown, then it will slowly become yellow. Then when we see the straw yellow colour (very faint yellow colour) then we will add the starch indicator. Immediately we will see the blue colour formation. When lot of iodine is already transformed into iodide, then only little amount of iodine is there showing the straw yellow colour, then we will add the starch. We will then continue the titration with thiosulfate. Within a few drops, the colour will disappear. That is the end-point. Now, the question is, why from the beginning we have not added the starch? Why after almost at the end of the titration we have added this? We can see here that 2 moles of thiosulfate is equivalent to 1 mole of iodine. So, 1 mole of thiosulfate is equivalent to 0.5 mole of iodine and 0.5 mole of chlorine (35.5 gram of chlorine). Hence, 1 mL 1M thiosulfate is equivalent to 35.5 milligram of chlorine. Now, for thiosulphate molecular weight and the equivalent weight are the same as evident from (7):

$2S_2O_3^{2-}=S_4O_6^{2-}+2e$…….(7)

So, when something is like redox reaction, then you have to think about how many electrons are involved in transfer. When you think about the acid, then you have to think that how many H is present. For e.g., in H_2SO_4 equivalent weight will be molecular weight divided by 2, in HCl it will be molecular weight divided by 1. For salt, say for example calcium carbonate, the molecular weight is 100, but its equivalent weight is 50. As 1 calcium is there and the valency of calcium is 2, so, it will be divided by 2.

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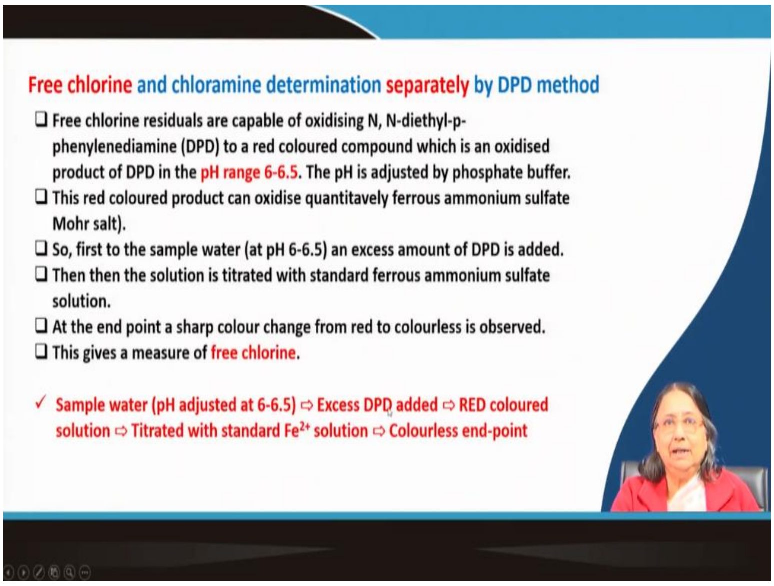

Free chlorine and chloramine determination separately by DPD method

- ☐ Free chlorine residuals are capable of oxidising N, N-diethyl-p-phenylenediamine (DPD) to a red coloured compound which is an oxidised product of DPD in the pH range 6-6.5. The pH is adjusted by phosphate buffer.
- ☐ This red coloured product can oxidise quantitavely ferrous ammonium sulfate Mohr salt).
- ☐ So, first to the sample water (at pH 6-6.5) an excess amount of DPD is added.
- ☐ Then then the solution is titrated with standard ferrous ammonium sulfate solution.
- ☐ At the end point a sharp colour change from red to colourless is observed.
- ☐ This gives a measure of free chlorine.

✓ Sample water (pH adjusted at 6-6.5) ⇨ Excess DPD added ⇨ RED coloured solution ⇨ Titrated with standard Fe^{2+} solution ⇨ Colourless end-point

You have understood that the iodometric method can be used in low pH condition. It can be used for total residual chlorine determination. Now, we will see free chlorine and chloramine determination separately by DPD method. It is a very interesting method. Free chlorine residuals are capable of oxidising N, N diethyl paraphenylene diamine (DPD) to red coloured compound which is an oxidised product of DPD. The pH range should be 6 to 6.5. pH is adjusted by phosphate buffer. In my first module I had explained buffer. The amount of DPD oxidised is quantitative to the chlorine concentration. This red coloured product can oxidise quantitatively ferrous ammonium sulfate, which is also known as Mohr salt. Fe^{2+} can go to Fe^{3+}. So, this red coloured product which is the oxidised product of DPD can oxidise the ferrous ammonium sulfate. Rather you can tell that ferrous ammonium sulfate can reduce this red coloured product. Moreover, ferrous ammonium sulfate is a primary standard. So, you can prepare the standard with known concentration of Fe^{2+} and you can titrate the red coloured complex. Then you can find out how much Fe^{2+} is required. Consequently, you can easily calculate how much chlorine was needed to oxidise the DPD. At the end-point sharp colour change from red to colourless is observed. This gives a measure of free chlorine.

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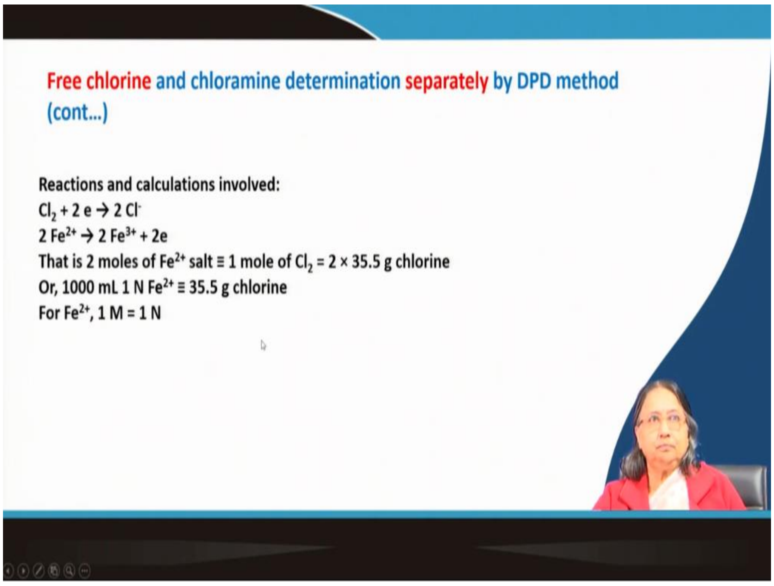

Free chlorine and chloramine determination separately by DPD method (cont...)

Reactions and calculations involved:

$Cl_2 + 2\,e \rightarrow 2\,Cl^-$

$2\,Fe^{2+} \rightarrow 2\,Fe^{3+} + 2e$

That is 2 moles of Fe^{2+} salt ≡ 1 mole of Cl_2 = 2 × 35.5 g chlorine

Or, 1000 mL 1 N Fe^{2+} ≡ 35.5 g chlorine

For Fe^{2+}, 1 M = 1 N

The reactions involved are expressed as:

$Cl_2+2e\rightarrow 2Cl^-$……………..(8)

$2Fe^{2+}\rightarrow 2Fe^{3+}+2e$…………(9)

The calculation involved is that 2 moles of Fe^{2+} salt I equivalent to 1 mole of chlorine (71g).

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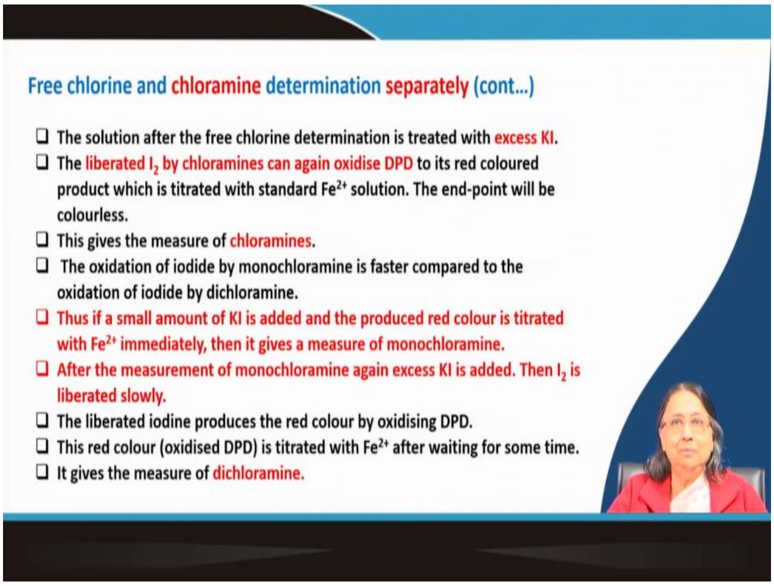

Free chloride and chloramine determination separately (cont...)

- ☐ The solution after the free chlorine determination is treated with excess KI.
- ☐ The liberated I_2 by chloramines can again oxidise DPD to its red coloured product which is titrated with standard Fe^{2+} solution. The end-point will be colourless.
- ☐ This gives the measure of chloramines.
- ☐ The oxidation of iodide by monochloramine is faster compared to the oxidation of iodide by dichloramine.
- ☐ Thus if a small amount of KI is added and the produced red colour is titrated with Fe^{2+} immediately, then it gives a measure of monochloramine.
- ☐ After the measurement of monochloramine again excess KI is added. Then I_2 is liberated slowly.
- ☐ The liberated iodine produces the red colour by oxidising DPD.
- ☐ This red colour (oxidised DPD) is titrated with Fe^{2+} after waiting for some time.
- ☐ It gives the measure of dichloramine.

After the free chlorine determination, the solution is treated with excess KI. Then, iodine will be liberated by chloramine. That liberated iodine can again oxidise DPD to red coloured product. Then again you are titraing with Mohr salt. The end-product will be colourless. It is the same way like the previous one. So, it will give the measure of chloramines. Now, if there is monochloramine and dichloramine both, then how you can determine? Again kinetics is coming. If a small amount of KI is added and the produced red colour is titrated with Fe^{2+} immediately, then it gives a measure of monochloramine. Now, after the measurement of monochloramine, again add excess KI. Then iodine is liberated slowly. The liberated iodine produces the red colour by oxidising DPD. But it is produced slowly by dichloramine and quickly by monochloramine.

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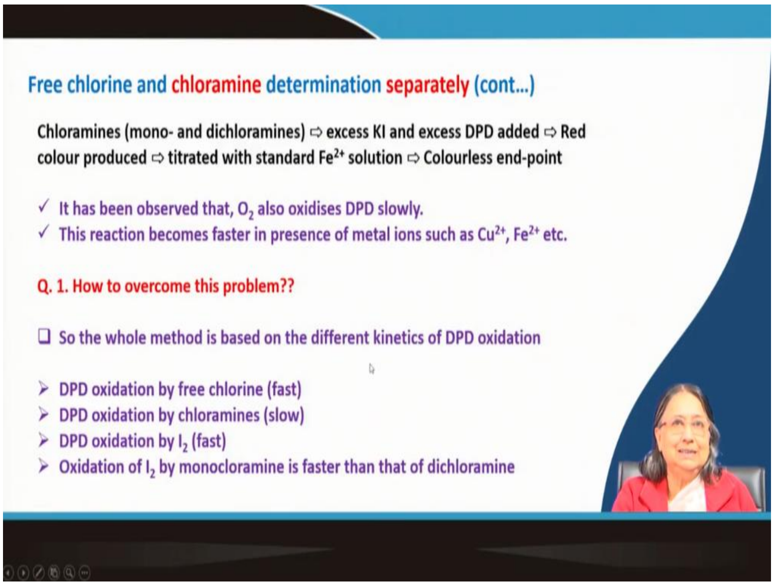

Free chlorine and chloramine determination separately (cont...)

Chloramines (mono- and dichloramines) ⇨ excess KI and excess DPD added ⇨ Red colour produced ⇨ titrated with standard Fe^{2+} solution ⇨ Colourless end-point

- ✓ It has been observed that, O_2 also oxidises DPD slowly.
- ✓ This reaction becomes faster in presence of metal ions such as Cu^{2+}, Fe^{2+} etc.

Q. 1. How to overcome this problem??

- ☐ So the whole method is based on the different kinetics of DPD oxidation

- ➢ DPD oxidation by free chlorine (fast)
- ➢ DPD oxidation by chloramines (slow)
- ➢ DPD oxidation by I_2 (fast)
- ➢ Oxidation of I_2 by monocloramine is faster than that of dichloramine

Oxygen is also an oxidising agent, right. So, it can oxidise DPD also. This reaction becomes faster in presence of metal ions. Again, if metal ion is there, it catalyses. So, how will you resist it? It can be done by adding EDTA. You know EDTA is a very good complexing agent. It can complex with metal ions. So, if you can complex these metal ions with EDTA, then it is no more a catalyst. So, this reaction will be slowed down and oxidation will not happen. Titration in nitrogen atmosphere or some other inert atmosphere is not possible. So you have to allow oxygen. But you can do this way to minimize error.

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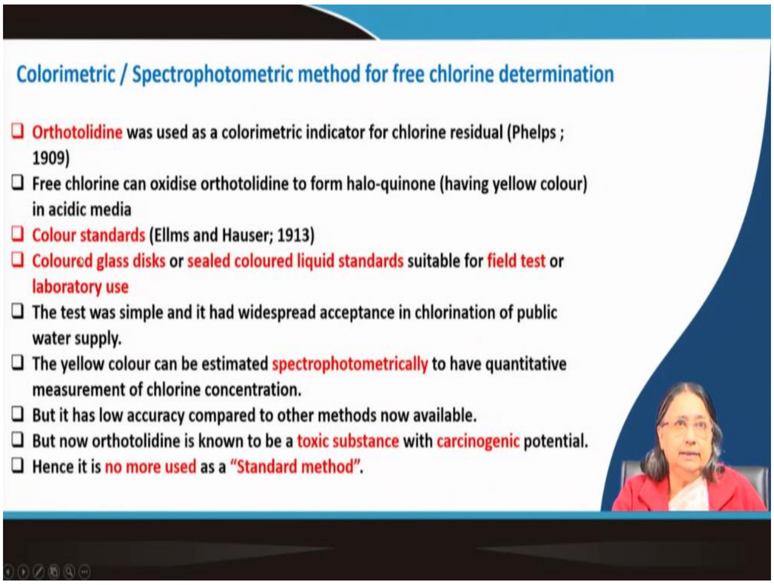

Colorimetric / Spectrophotometric method for free chlorine determination

- Orthotolidine was used as a colorimetric indicator for chlorine residual (Phelps ; 1909)
- Free chlorine can oxidise orthotolidine to form halo-quinone (having yellow colour) in acidic media
- Colour standards (Ellms and Hauser; 1913)
- Coloured glass disks or sealed coloured liquid standards suitable for field test or laboratory use
- The test was simple and it had widespread acceptance in chlorination of public water supply.
- The yellow colour can be estimated spectrophotometrically to have quantitative measurement of chlorine concentration.
- But it has low accuracy compared to other methods now available.
- But now orthotolidine is known to be a toxic substance with carcinogenic potential.
- Hence it is no more used as a "Standard method".

Other method such as Orthotolidine method is also there. This is an old method (Colorimetric or spectrophotometric). In colorimetric method you just standards of different concentrations having different intensity of colour. Then you compare your sample with the standards. Spectrophotometric means, you have to prepare standard curve. Then, with the sample also you have to develop the colour and measure the absorbance value. Put it in the calibration curve and get the concentration. It is more accurate.

Orthotolidine was used as a colorimetric indicator for chlorine residual (Phelps, 1909). Free chlorine can oxidise orthotolidine to form a halo-quinone. I told that sometimes that it has yellow colour in acidic medium. Why this is important? You know, at that time spectrophotometer was not there. So, simple methods were used. So, you can prepare some standards with known concentration of chlorine. Then you add the reagents and some colour is developed. Then you seal it. For your sample you do the same thing and compare the colour. Sometimes we have used chloroscope (disc has colour). You put there your prepared solution. It is giving some colour. So, you match with the discs and then you will know what is the concentration. These are very used for field test, because in the field you cannot carry the instrument. Only the test kit is suitable to carry.

Orthotolidine method is not very accurate method. Orthotolidine is known to be a toxic substance. It is carcinogenic compound. We are very much concerned about our health also. I told you the green chemistry approach in catalysis. So, we do not want to use toxic substances.

In the Standard Methods (there is a book where all the standard methods are there for determining) it was there. But due to toxicity it is no more used in the standard method. It is not that accurate also. But it is a very old method. It has the history.

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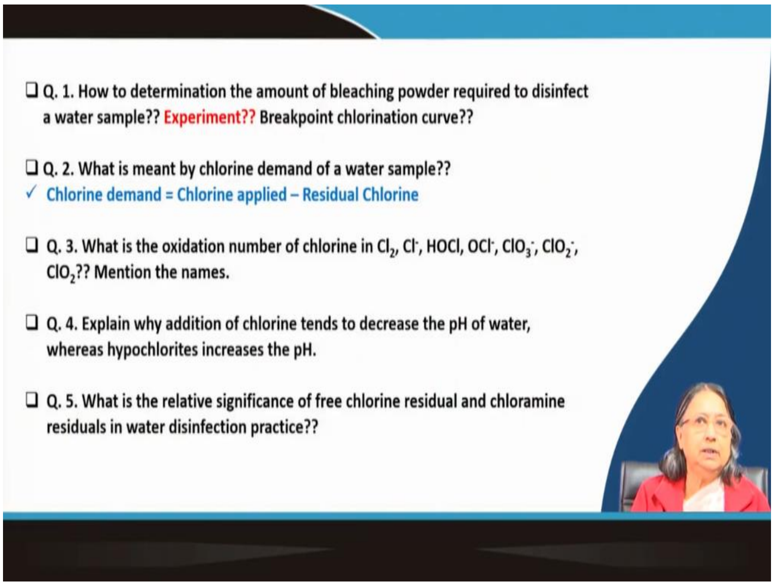

☐ Q. 1. How to determination the amount of bleaching powder required to disinfect a water sample?? Experiment?? Breakpoint chlorination curve??

☐ Q. 2. What is meant by chlorine demand of a water sample??

✓ Chlorine demand = Chlorine applied – Residual Chlorine

☐ Q. 3. What is the oxidation number of chlorine in Cl_2, Cl^-, HOCl, OCl^-, ClO_3^-, ClO_2^-, ClO_2?? Mention the names.

☐ Q. 4. Explain why addition of chlorine tends to decrease the pH of water, whereas hypochlorites increases the pH.

☐ Q. 5. What is the relative significance of free chlorine residual and chloramine residuals in water disinfection practice??

Now, there are some questions.

How to determine the amount of bleaching powder required to disinfect a water sample? you have to draw breakpoint chlorination curve. You have to do some experiments by varying the dose. In different containers you take same volume water and add the different doses of chlorine. Keep it for some time and then measure the residual chlorine. Prepare the graph and then you will know how much is the demand. Then you apply that type of chlorine dose to be in the safe side.

What is chlorine demand? Chlorine demand is defined as the difference of applied chlorine and residual chlorine.

What is the oxidation number of chlorine in Cl_2, Cl^-, HOCl, OCl^-, ClO_3^-, ClO_2^-, ClO_2 gas and what are the names?

Explain why addition of chlorine tends to decrease the pH of water and hypochlorous increases the pH. I already answered.

What is the relative significance of free chlorine residual and chloramine residual in water disinfection practice?

I told you, during transport the residual combined chlorine residual is very important. Although being better disinfectant, free chlorine residual is dissipated fast.

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References

1) Sawyer CN, McCarty PL, Parkin GF (2000) Chemistry for Environmental Engineering, Tata McGraw Hill, New Delhi
2) Das AK (2010) Environmental Chemistry with Green Chemistry, Books & Allied (P) Ltd., Kolkata

Now, for references you can follow books by Sawyer and McCarty and AK das. You can also go through the Standard Methods.

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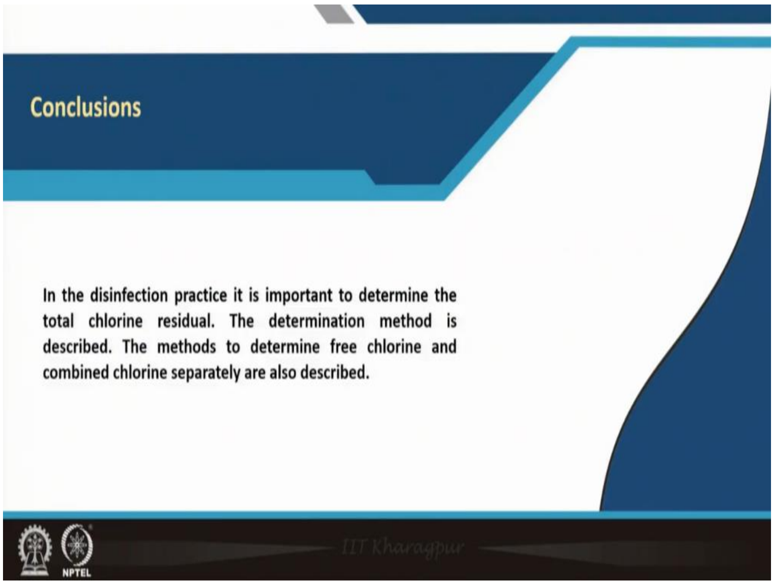

Conclusions

In the disinfection practice it is important to determine the total chlorine residual. The determination method is described. The methods to determine free chlorine and combined chlorine separately are also described.

As a conclusion I can tell from this lecture, in the disinfection practice, it is important to determine the total chlorine residual. The determination method is described. The methods to determine the free chlorine and combined chlorine separately are also described. There are different methods. You can choose which one we apply. Thank you.