Physico - Chemical Processes for Wastewater Treatment

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Lecture - 06

Water Quality Monitoring: Chemical Parameters - II

So, good day everyone, welcome to this lecture on Understanding the Chemical Parameters while doing the water quality monitoring in the course on Physico Chemical Processes for Wastewater Treatment. So, in the last class, we were discussing regarding hardness and various other elements in particular, like sodium, which has important parameter and for

understanding the usage of various types of water, in particular, for irrigation.

Now, we will be continuing the chemical parameters in this lecture as well. And there are important parameters like alkalinity which are not well understood. So, in particular, so, alkalinity is one of the important parameters along with pH. And that actually not only helps us in determining which method has to be used, also many times it is inherently we must have

sometimes alkalinity in the water for any treatment process to work sufficiently well.

So, many times we have to use the alkalinity, add the alkalinity from outside. And that way when a particular alkalinity value is not present, then the treatment process may not work. So, for this reason, alkalinity is one of the important parameters and it has to be within certain limits to how to find out the alkalinity, what is its importance, this is the first parameter that we are going to study in this lecture.

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ALKALINITY (A_T)

 Alkalinity is a measure of the ability of a solution to neutralize acids to the equivalence point of carbonate or bicarbonate.

- It is the water's ability to absorb hydrogen ions without significant pH change, i.e., the buffering capacity of water.
- Alkalinity is equal to the stoichiometric sum of the bases in solution.
- In natural environment, carbonate alkalinity makes up most of the total alkalinity due to the common occurrence and dissolution of carbonate rocks and presence of carbon dioxide in the atmosphere.
- Other natural components that contribute to alkalinity include hydroxide, borate, phosphate, silicate, nitrate, dissolved ammonia, conjugate bases of some organic acids and sulfide.



So, if I ask anybody sometimes to very common students like if we have 2 water and one water is having, one water sample is having pH 7 and another having pH 7.5. So, is it always necessary that pH 7.5 water will have always higher alkalinity? So, it is not correct, any higher pH water may have lower alkalinity also. So, this is a possibility.

So, alkalinity is not directly related to pH. It is related but it may still be changed their alkalinity value may change or differ with respect to waters having same pH or otherwise. So, what is the alkalinity? It is a measure of the ability of a solution to neutralize acids to the equivalence points of carbonate or bicarbonate. So, here alkalinity is like a buffering capacity.

So, if you add acids actually it will neutralize the acid. So, it is the waters ability to absorb hydrogen ions without significant pH change. So, if the alkalinity value is high, so, that means that water has more buffering capacity. And if any acid rain or anything happens, it will not change the pH of that water.

So, this is very important parameter and alkalinity in general is it is equal to the stoichiometric sum of all the bases present in the solution. So, that base may not be only hydroxyl radical, that base may be other types of anions also. So, this is possible in natural environment which is commonly there, if any water body is there and which is open to atmosphere.

So, it will always contain some carbonate alkalinity, this is so, because some amount of CO2 will always get dissolved into the water up to its solubility limit depending upon the pH of the water. So, alkalinity, natural alkalinity is always present in any water which is under the atmospheric condition because the CO2 will always get dissolved. So, this is always present.

Other natural components also may contribute to the alkalinity and that may be like hydroxyl hydroxide ions, borate, phosphate, silicate, nitrate, dissolved ammonia, conjugate basis of some of the organic basic, organic acids and sulphide.

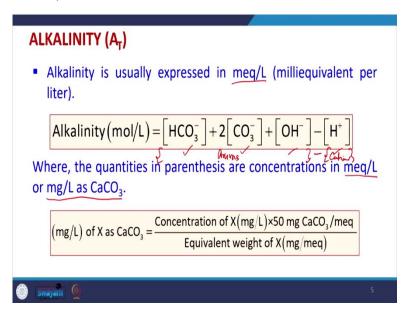
So, all these things add to the alkalinity. And these alkalinity is very, very important and how to determine this alkalinity we are going to learn in this particular lecture. Now, higher alkalinity of water protects the faeces and aquatic animals from any rapid change in pH due to acid rain.

Because any acid rain which will occur, so, the hydroxyl ions will be neutralized by this alkalinity. So, pH change will not happen. So, it will protect the fish and aquatic animals. Large amount of alkalinity present in more than the required amount. So, it will impart some bitter taste to the water.

Also precipitates may form because of the reaction between cations in the water and alkalinity if more amount of alkalinity is there. But it is in some other treatment like coagulation, this is what is that is why if alkalinity is not present, we have to add alkalinity because we want precipitate to form and if alkalinity is not there precipitate will not form.

So, in natural water precipitation may not be good. In the treatment process we want precipitation to occur. So, we had to add alkalinity from outside. Alkalinity present in the water can corrode pipes in water distribution systems also. So, this is an undesirable thing with respect to usage of water, which is having higher amount of alkalinity in industrial cases, so this is there.

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Now how to determine the alkalinity and how it is defined? So, alkalinity is usually expressed in milliequivalent per liter as it has been done and it is like all the anions are added together. So, here we can see the bicarbonate, carbonate and then we have OH and finally, subtracting the H plus. In general we can put it like this also all the anions together in form of adding them together minus all the cations but then only we consider H plus only, so this is there.

Alkalinity is usually expressed in meq/L (milliequivalent per liter).

Alkalinity
$$(mol/L) = \lceil HCO_3^- \rceil + 2\lceil CO_3^{-2} \rceil + \lceil OH^- \rceil - \lceil H^+ \rceil$$

where, the quantities in parenthesis are concentrations in meq/L or mg/L as CaCO₃.

$$(mg/L)$$
 of X as $CaCO_3 = \frac{Concentration of X(mg/L) \times 50 mg CaCO_3/meq}{Equivalent weight of X(mg/meq)}$

And what we do is that we always report try to find out in milliequivalent per liter, but for water treatment uses as well as for our common knowledge by so that we can understand that how much amount of alkalinity is present, we always convert this milliequivalent per liter into milligram per liter as CaCO3.

So, what we do is that we use this formula. So, initially what we do is that we calculate the concentration in milliequivalent per liter or if it is in milligram per liter also we can calculate and then we can convert it into milligram per liter CaCO3. You will understand it better when we solve the problem, so, in today itself.

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Determination of Alkalinity (A_r)

- If a water sample having pH > 4.5 is titrated with any acid to lower the pH to 4.5, all the natural anions, i.e., OH⁻, CO₃²⁻ and HCO₃⁻ get neutralized.
- It means that if the sample is having pH < 4.5, it has no alkalinity because of natural ions.
- If a water sample having pH > 8.3 is titrated with any acid to lower the pH to 8.3, alkalinity due to all OH⁻ ions and half of the CO₃²⁻ ions gets neutralized.

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Now, determination of alkalinity, so, in natural environment already we have added this. Now, if a water sample, what we do is that for determining the alkalinity, we take the water sample. We go on adding some amount of indicators and then we add H2SO4 or any other acid can also be used but generally H2SO4 is used. And we go on adding the H2SO4 and measuring the amount of H2SO4 that has been used.

So, and it will depend upon the molarity of H2SO4 which is being used for titration, so, this

is there. And we have two important pH up to which we determine that how much amount of

H2SO4 has been used and those pH are like pH 8.3 and pH 4.5. So if any wastewater is there,

suppose it is having pH 10. So, what we do is that? That water sample we will take.

We will add some indicators, and then we will determine that how much of H2SO4 of

particular molarity or normality has been used to lower the pH up to 8.3. Similarly, we will

measure up to 4.5. So, two important volume of a particular molar H2SO4 or normal H2SO4

which has been used to lower the pH of that wastewater up to 8.3 and 4.5 it is determined.

And from that we can calculate the all different types of alkalinities. Now, if a, what are the

basis why we choose 4.5 and 8.3 it is written in this. And if a water sample is having pH

greater than 4.5 and it is titrated with any acid to lower the pH up to 4.5. At 4.5, all the

natural anions which are present like hydroxyl, carbonate, bicarbonate, they get neutralize.

So, what does it mean? If a sample of water is having pH lower than 4.5 it will have no

alkalinity et al. So, if any H plus is added further, it will lower the pH very quickly, there will

be no buffering capacity of that water which is having a pH less than 4.5. Above 4.5. It will

be having some buffering capacity.

Now, if a water sample is having pH more than 8.3 it is titrated with any acid to lower the pH

up to 8.3. So, at 8.3 equivalence point it is known that all the OH ions and half of the

carbonate ions get neutralized. So, these two important knowing's are there through which

we calculate the different types of alkalinity as well as the total alkalinity. Now, how the

titration works?

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Determination of Alkalinity (A_T) In any water sample (having pH > 8.3), addition of phenolphthalein indicator will change the sample color to pink. This pink color is due to presence of hydroxyl ions. Addition of sulfuric acid to the sample will result in disappearance of the pink color indicating neutralization of all OH- ions. Now addition of mixed indicator will change the color to blue indicating the presence of CO₃-2, and HCO₃- ions. Further addition of sulfuric acid will change the color from blue to red, indicating neutralization of CO₃-2 and HCO₃- ions has been neutralized. This is the end point (pH = 4.5).

So, in any water sample, what we do is that, suppose pH is having it is having pH more than 8.3. So, we add phenolphthalein indicator and as soon as we add the phenolphthalein indicator, it will change the color of the water to pink. This pink color is because of the presence of hydroxyl ion. So, phenolphthalein with hydroxyl ions gives pink color. Now, if we add sulfuric acid to this sample, so, at around 8.3 the disappearance of the pink color will be there and that will be because of the neutralization of all the OH minus ions.

Now, that tells that we have reached the 8.3. Here half of the carbonate alkalinity also gets removed. Now, addition of, at this point now, we add another indicator, mix indicator and as soon as we add that, it will change the color to blue indicating still the carbonate, carbonate ions are present as well as bicarbonate ions are present.

Now, we again go on adding the sulfuric acid to that and it will change the color from blue to red, add 4.5 equivalents point and add that point all the other alkalinities because of carbonate and bicarbonate everything will get neutralized. So, this is the end point which is pH 4.5. So, this is how we go on.

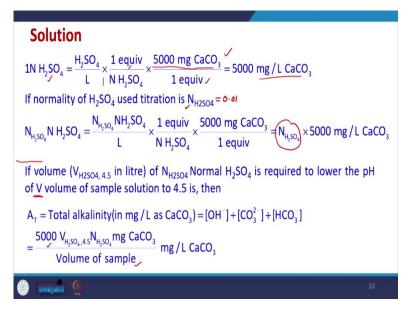
So, we have to note the value of acid, volume of acid used, sulfuric acid used till 8.3 pH point as well as that 4.5 equivalence points. So, 2 equivalence points are important, one is 8.3, another is 4.5. Now, one example, we will solve today itself.

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Problem A 50 ml sample of water has an initial pH of 11.2. Determine the species and the quantity of each species of alkalinity if the 8.3 equivalence point is reached at 8 ml of 0.01 N H₂SO₄ and 4.5 equivalence point is reached at 18 ml of 0.01 N H₂SO₄.

So, a 50 ml sample of water is having an initial pH of 11.2, determine the species and the quantity of each species of alkalinity present. If the 8.3 equivalence point is reached at by using 8 ml of 0.01 normal H2SO4 and 4.5 equivalence point is reached using 18 ml of 0.01 normal H2SO4. So, this is the problem and we have to determine the total alkalinity as well as the individual alkalinities also. The hydroxyl alkalinity, the carbonate alkalinity and the bicarbonate alkalinity. So, all three we have to determined. Now, here some calculations are shown.

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So if suppose one normal H2SO4 is there, so how we can write this? So, this is we want to convert one normal H2SO4 into milligram per liter of CaCO3. Because alkalinity is always

reported in milligram per liter. Now, we can easily calculate this using the tricks which are

given here.

So, one this is one normal, so that means 1 equivalent per liter of H2SO4, and this is one

normal. And one normal H2SO4 is equivalent to 1 equivalent and for one CaCO3, 1

equivalent is equal to 5000 milligram of CaCO3.

Because we can easily calculate for calcium carbonate. It is having atomic weight of calcium

is 40 plus 12 for carbon and plus 48 for oxygen, so, it is 100 in total. Now 100 divided by 2

because we have 2 valency, so that is why it is 50. And for this 1 equivalence point is equal to

5000 milligram CaCO3.

So, one normal H2SO4 is actually equal to 5000 milligram per liter of CaCO3 in terms of

calculation. Now, if the normality of H2SO4 used for titration is n, so, for the present

question, it is we have taken as 0.01, but here the normal calculation is given any other value

may be there.

Now, if n normal H2SO4 is used. So, it will be having we have to multiply by the normality

only to this, so this is there. Now, so, up till here this was a general idea is given. Now, if

volume of the n normal H2SO4 which is required to lower the pH to up to 4.5 is total volume

which is required is V.

So, the total alkalinity in milligram per liter will be equal to using the formula which is given

here. So, 5000 into volume of, we are using the trick of V1, N1 is equal to V2N2. So, through

that we are finding out the total alkalinity. And this is the volume of sample which was taken.

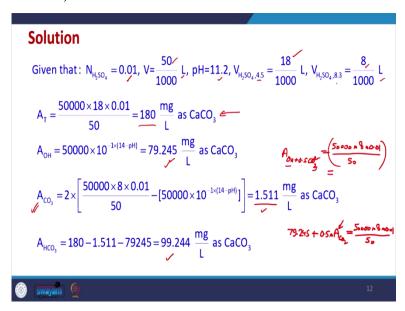
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So, in the previous example, the volume of sample which was taken was 50 ml. So, this volume was 50 ml and 5000 is the conversion ratio and V is the volume of the H2SO4 up to 4.5. N is the normality of H2SO4 and through that we can calculate the total alkalinity. So, now, for OH alkalinity what we do is that the pH is already given. So, from pH we can find out the pOH.

So, like and from that we can directly calculate and what we have to do is that we had to multiply by this only to convert into corresponding calcium carbonate milligram per liter value. Similarly, with respect to if same normal H2SO4 used and volume required up to 8.3 equivalence point this is, this is sorry this is 8.3, so up to 8.3 whatever is the value required from that we calculate the total hydroxyl alkalinity as well as half of the carbonate alkalinity.

So, we can from here we can determine this and through that we can perform the calculation. So, we can we know this total value and then we can find out the carbonate alkalinity by subtraction. So, we will solve the problem now.

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So, in this present case what is given is that normality is 0.1, volume is 50 divided by 1000 because we have to take the value in liter. pH is 11.2, volume up to H2SO4 equivalence point of 4.5 is 18. So, we again divide by 1000 to convert it into ml and for 8.3 equivalence point the volume required was 8 ml, so, we convert into liter. So, total alkalinity will be using this 18 value. So, from 18 we use a normality, the volume of sample is 50.

So, we use the formula total alkalinity and we can directly find out that 180 milligram per liter of CaCO3 as alkalinity is the total alkalinity. Now, next step what we find out is that what is OH alkalinity because up to 8 pH from pH also we can get the OH alkalinity and now for pH is for this case it was 11.2. So, 14 minus pH will give pOH and from pOH we can easily determine that 79.245 is the OH alkalinity in this water.

Now, once this is determined, then what we do is that we determine the alkalinity with respect to OH plus half of the CO3 2 minus. And that can be obtained using this this formula itself, but in place of 18 it will be 8, which will be there. So, this will be like 50,000 into 8 into 0.01 divided by 50. So, this will whatever is the value, this will give total OH alkalinity minus, plus half of this.

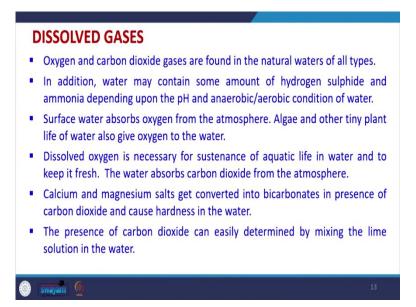
So, we can directly determine the carbonate alkalinity via subtracting, so this is what is shown, so total value is already known to us, this OH alkalinity is already known to us, so, we can write in this formula like 79.245 plus 0.5 of the carbonate alkalinity is this will be equivalent to this particular value, what is, whatever is given here, so this will be 50,000 into 8 into 0.01 divided by 50.

And from this we can directly determine the carbonate alkalinity what is given here and this is what has been done. So, here only in terms of formula it is written that directly also we can find. So, this value is 1.511. And once OH alkalinity and carbonate alkalinity are known, we can subtract these from total alkalinity and we can get the value of bicarbonate alkalinity.

So, this way, we can determine all the 3 types of alkalinity values which are given in this case. So, this is that total alkalinity and all the species alkalinity have been determined and they will be used further also. So, alkalinity is one of the important parameter.

Now, there are many dissolved gases may be present in the water, already we learned about carbon dioxide. So, carbon dioxide will always be dissolved in the natural water. Also oxygen will also be dissolved. So, depending upon the solubility limit, so, how to calculate that how much amount of any gas can get dissolved in the water at any temperature that we will learn later on using the Henry's constant values. But we will try to understand the what are the importance of dissolved gases in the water. Already for CO2 we learned.

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Water may also contain some other amount of gases in addition to oxygen and carbon dioxide and those are dangerous gases generally hydrogen sulphide, ammonia depending upon the pH, anaerobic or aerobic condition of the water and what are the various organic species present in the water. So, that will depend upon that.

The surface water always absorbs oxygen from the atmosphere and algae and other tiny plants and other life species which are there in the water they use that water for their purposes. But if dissolved gases, dissolved oxygen is necessary for sustenance of life that is there.

So, and the water also absorbs carbon dioxide from the atmosphere and the calcium and magnesium salts if they are there in the water, they will get converted into bicarbonate, if carbon dioxide is present and they cause hardness.

So, they are very interrelated thing that which gases are present, how much concentration whether other types of ions and minerals are present. So, they are weathering their precipitation, everything will be dependent upon pH upon how much amount of gases are present and how they react with each other. So, they are very, very interesting topics to understand. We will not be going further.

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CHLORINE

- Dissolved free chlorine is never found in natural waters.
- It is present in the treated water resulting from disinfection with chlorine.
- The chlorine remains as residual in treated water for the sake of safety against pathogenic bacteria.
- Residual chlorine is determined by the starch-iodide test.
- In starch-iodide test, potassium iodide and starch solutions are added to the sample of water due to which blue color is formed.



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- This blue color is then removed by titrating with sodium thiosuplhate solution, and the quantity of chloride is calculated.
- On the addition of ortho-iodine solution if yellow color is formed, it indicates the presence of residual chlorine in the water.
- The intensity of this yellow color is compared with standard colors to determine the quantity of residual chlorine.
- The residual chlorine should remain between 0.5 to 0.2 mg/L in the water so that it remains safe against pathogenic bacteria.



Similarly, chlorine may also be present sometimes generally it is not there. So, dissolved free chlorine is never found in the natural water. But in the water which is like discharged from the industrial premises they may contain chlorine. Also a disinfection we do in the water that we take out from the ground before actually using the water for drinking.

So, some amount of chlorine may be there because hypochlorite, etc., is used. So, if chlorine is there residual chlorine is there in the treated water. So, it is not good, up to a certain value it will kill the pathogenic bacteria. But if it is used beyond the desired value, then it will cause problem.

So, residual chlorine has to be determined in the water and that is determined by using the starch iodide test. And in this test actually we use potassium iodide along with the starch solution and if blue color is found we say that okay residual chlorine is present in the water and that should be determined and so, what we have to do?

We have to remove this blue color. So, what we do is that we titrate by the sodium thiosulfate solution and via using the calculations we can determine the quantity of chloride which is present in this particular water. And there are intensity of the color actually is compared with the standard colors to determine the residual chlorine. There is a limit that the residual chlorine should always be less than 0.5 milligram per liter. So, point it is between 0.05 to 0.02 milligram per liter in the water and so that it remains in the safe limit against pathogenic bacteria.

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METALS AND OTHER CHEMICAL SUBSTANCES Water contains various types of minerals and metals such as iron, manganese, copper, lead barium, cadmium, selenium, fluoride, arsenic, etc. Arsenic, selenium are poisonous, therefore they must be removed totally. Human lungs are affected by the presence of high quantity of copper in the • Fewer cavities in the teeth will be formed due to excessive presence of fluoride in water. The quantity of the metals and other substances can be done indirectly by colorimetric methods using UV-visible spectrophotometer or directly by the use of sophisticated instruments such as Atomic Absorption Spectrophotometer (AAS), Atomic Emission Spectrophotometer (AES), Inductively Coupled Mass Spectrophotometer (ICP-MS), etc. **LEAD & ARSENIC** These are not usually found in natural waters. But sometimes lead is mixed up in water from lead pipes or from tanks lined with lead paint when water moves through them. These are poisonous and dangerous to the health of public. The presence of lead and arsenic is detected by means of chemical tests.

There are other types of metals and other chemical substances may be present in the water and different types of metals such as iron, manganese, copper, lead, barium, cadmium, selenium, fluoride, arsenic, etc., may be present. So, and all these metals, most of these metals are highly toxic and poisonous and they must be removed in totally.

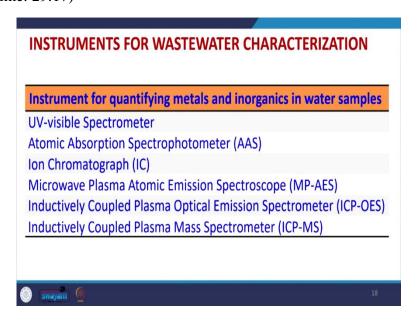
So, and the treatment process should work to remove these toxic elements of the water. So, one thing is that how to determine the presence of these metals and many other organic compounds in the water. So, there are many sophisticated instruments which are there which can be used for determining the quantity of metals and other organic substances present in the water and one of the important element which is there is like fluoride.

So, if fluoride is present it will cause excessive cavities in the teeth, etc. So, we have to remove the fluoride. So, that testing has to be done. There are many approaches for determining all these metals and organic substances also. But, these lab based methods have limits and they can determine the concentration if the concentration amount of the substances present in the water is high. However, the standards which have been set for drinking or otherwise are very, very low.

So, these titration methods and other methods cannot work. So, we have to use lots of sophisticated instruments for determining the concentration of these in the water. Lead and arsenic is one of the element which is very common. And in particular arsenic is present in many places in our country in particular in Bengal and nearby places. And they are usually not found in natural water, but because of the weathering of the rocks that happens and this is so, because our water tables are going down.

So, more amount of CO2 and other gases, they go inside the soil and they do the weathering of these rocks. And because of that they cause problem. And these arsenic and other things or other metals like selenium, lead, etc., are highly toxic and they must be detected and they must be removed before drinking. So, how to remove these things we will discuss later. But how to determine, so we have to use a lot of sophisticated instruments for determining the concentration of these things.

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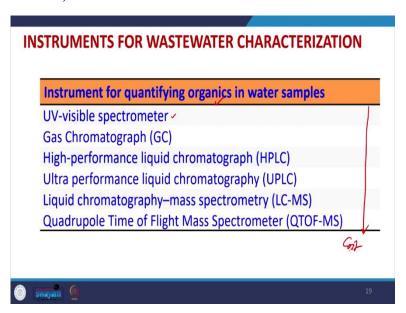
So, there are some of the instruments I have listed here, which can be helpful in quantifying the metals inorganics in water sample at very low concentration. So, the simplest one is like UV visible spectrophotometer for determining metals and inorganics what we use is called a colorimetric method.

So, what we do is that we use some chemicals, which after combination with the metals and other thing they impart color. And based upon that color, we try to determine the concentration. So, we have to make standards and a calibration graph and from that we can determine. But again, this will be higher having a lot of limitations and the concentration up to which UV visible spectrophotometer can be used are very less.

Then we have atomic absorption spectrophotometer which is commonly called there is double AAS, then ion chromatograph can be used for determining all types of cations-anions in the water. Then we have microwave plasma atomic emission spectrometer. Then we have inductively coupled plasma optical emission spectrometer, then inductively coupled plasma mass spectrometer.

So, there are many instruments which are there. As we go down a concentration we can determine is low enough and but the cost will also be high. So, as we go down the cost goes up and the concentration which can be determined easily maybe up to PPT levels also using these instruments.

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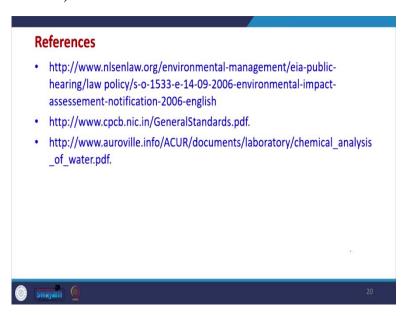
Similarly, for quantifying organics in the water, many types of organic compounds are coming and these are coming from cosmetic industry, these are coming from pharmaceutical industry, then antibiotics, all those things can also be determined in the water sample using

many sophisticated instruments like UV visible spectrophotometer, it can easily work in the UV range.

Many of these organics may not be having color, but they still they will be having some absorbance in the UV range. So, it is possible to determine them, then we have gas chromatograph then high performance liquid chromatograph, ultra performance liquid chromatograph, liquid chromatograph in combination with mass spectrometry.

Then quadrupole time of flight mass spectrometer. So, as again as we go down, the cost is increasing of each of them and it is increasing exponentially. Right now, the for example, we can buy a good UV visible spectrometer in rupees 5 lakh or INR value of rupees 5 lakhs, but quadrupole will take not more money around 5, around 2.5 to 3 crore rupees. So, this is the cost increases exponentially, but the concentration limit also goes down exponentially, so, we can determine the concentration at much lower values also.

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So, this is it. Thank you very much and we will continue with other water quality parameters in particular the biological or biochemical parameters in the next lecture. Thank you.