Environmental Quality:
Monitoring and Analysis
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Lecture No. 19
Analysis Methods – Introduction and Water Quality Parameters

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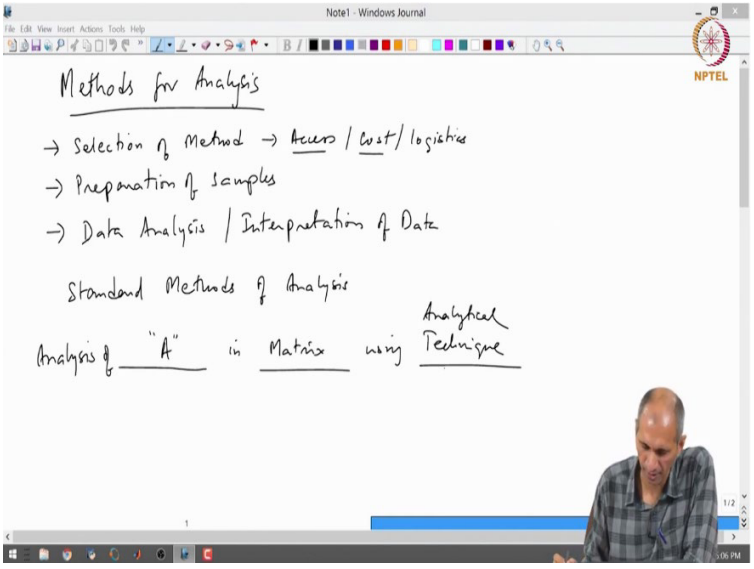

Okay, so today we are talking about the analysis method just an overview, because each one of these methods will take a long time to completely understand. So, at the level of for environmental analysis one needs to know 2 things the objective of doing this is to a selection of method and then it also helped in your preparation of samples. In other words, you are you can tailor your sampling methods to the instrument that is being based on the selection of the method of analysis.

Because there are a large number of options available and sometimes the selection of method is governed by access to the instrument and also the cost and the logistics of doing it. Sometimes it may be very difficult to do some analysis, sometimes you do not have access to it so sometimes prohibitively expensive. Second, it may also help you in sampling methodology. So, preparation of if you know the method, what are the methods available? You need to you can also prepare then the third is data analysis what we call us interpretation of the data.

This requires you to know something about the instrument. So you do not need to know the how the instrument works and how it can be optimized, you need to know at least what it is giving you and whether it is reasonable it is what you are looking for, it is reasonable, it is completely pointing in some direction that mislead you. So, you have to know a little bit of the overview of the instrumentation for this purpose.

So this is the objective of doing it not to give you complete information about the working of an instrument. So it will take you an entire course to just look at 1 particular type of instrument to understand the intricate things. So our goal is not to do that. It is just to give some overview of what are available and why it is used simple so this is a mistake. So, in that context so, and we will also look at different analysis. So, last class as I mentioned.

So, we have standard methods and I will go over that again of analysis. So, the 3 things are important in the standard methods is the analysis of or measurement of the pollutant in matrix using an analytical instrument using a technique. So, this is what so if you know these 3 things that constitutes one complete methodology that is used to doing it.

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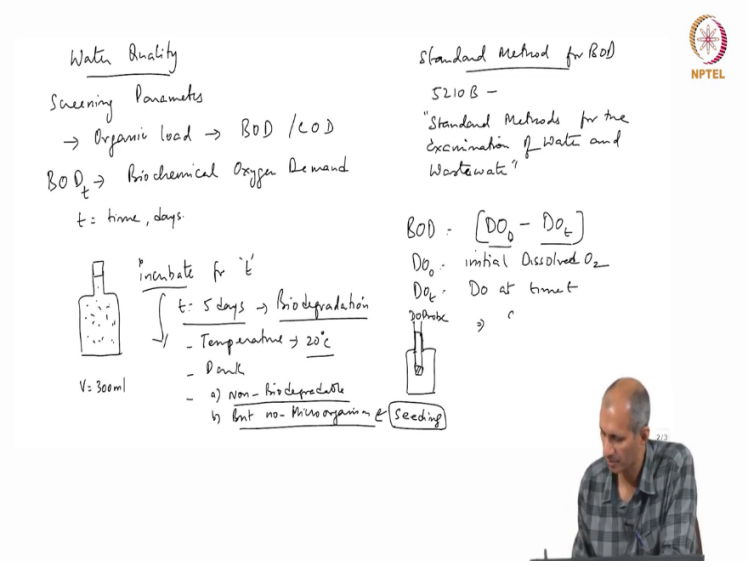

So, we will go from we go back to our analysis method. So, we are looking at water quality, the way we are going to do this is first we will I will just do certain things that are specific to water and specific to air and then we will move on to something that is more generic. It applies to all

matrices. And then looking at examples of some of these so water quality so we are looking at the first thing we look in water quality is screening parameters.

Screening parameters for organic load, we are looking at BOD and COD mainly so, BOD is, we had discussed briefly earlier is biochemical oxygen demand. We had discussed some of this before let us go over this again biochemical oxygen demand usually there is a time below the series it can be anything, but typically time in whatever units typically these days, but it can be anything. So, what it the way the BOD works is there is a standard method for it the standard method is using one of these.

One of the methods standard methods for release is method number 5210 from compilation this is called as a standard methods for examination of water and wastewater. I think this is there are methods to large number of methods in this I will show you the website. So in this method according to this method, and is very generic method and there is a, what is known as a BOD bottle.

It is so designed in such a way that this is a typical volumes of this bottle is about 300 ml. This is all standard. So, you have to understand that this you can do this whichever way you want. But because it is a standard method, the objectives of many of the standard methods is for people to be able to use it without any prior knowledge of this particular thing. So, for example, I can do a BOD analysis in whichever way I want as long as I understand what I am doing and why I am doing.

But the lot of people who are just or just come into blindly they will analyze the sample. For them the standard methods gives you all instructions step by step instruction you follow blindly it should give you the correct answers, you don't have to apply your mind to it. So, there is something called as a BOD bottle, which has the volume of 300, ok, volume of 300 you completely fill it, no headspace, ok. The reason it is called a BOD bottle is because the measurement of BOD is essentially the dissolved oxygen at initial time t equals to zero minus dissolved oxygen at some time.
This is essentially the biological oxygen demand. So it measures 0 this initially DO is 0 is initial. So the BOD analysis the weight done is a 300 ml sample bottle you take a sample from somewhere

taking water from say a river or a lake or any anything you fill this up. So, you have the analysis of BOD is dissolved oxygen at the 0 minus dissolved oxygen at some time for DO0 is the initial DO or dissolved oxygen and DOt is the DO at time t now at zero t what we do usually is the there is a DO probe that is placed in in the into the water.

So this BOD bottle is so designed that the standard DO pro goes nicely in this without allowing any air to pass in or any oxygen to escape. And then you measure and then you take it out. So in this you can also see that there is a lot of chances of error associated with were as talking about oxygen. So, there is if the reaction is going on here, oxygen can also be consumed and oxygen can get infused. So the idea is, you close it, you open it could be probe inside measure, wait for the do DO reading to show up.

And once you are satisfied with the reading, you take it out and close the bottle again and keep it somewhere. This is the idea. So in this time, if there is a loss you have to check for that. Sir water don't go out? What you assume that water is not going out so that's the other thing. So the so you have to estimate how much water is going on this as you are pulling in and out, some water will stick to the probe and come out. So, out of 300 ml if people are determining what.

So usually what they do is they will fill it up, they will almost overflow it then they will take out slowly or sometimes you can just leave it as it is, but it is not convenient. So DO probe is expensive. You cannot have DO one DO probe for every DO bottle that would be nice to have it sitting in the probe bottle. But unfortunately, we don't have that many do you have to take it out and use it for 100 other samples.

So some of these groups can cost up to I think they can get a cheap probe of 50; 60,000 rupees but it can also go up to maybe a lack or more. So depending on the characteristics of the group. So those are quality control questions, I think so if you think they are important to you have to worry about corrections for that otherwise does not matter. So the volume is not really important that much here the only way volume is important here is if it creates a headspace then it is a problem because oxygen will now go and equilibrium there.

And available oxygen for us in the BOD is not enough, ok. So then once you do the initial thing you take the BOD bottle and incubate it for t whatever time t is, typically t is 5 days in the standard method t is 5 days. Now, this is not set in stone, this is also not a fixed thing, because it can vary from waste to waste it can vary from a composition of the waste. So, what happens in t days is the microorganisms that are present in the water consume oxygen to degrade whatever is the organic compounds called as for the degradation of organic compounds that are present in the in the water, yeah. So what are the possible errors in this? We are talking about quality control, what are the possible this thing, so after 5 days you take out and measure the probe DO again. So, you are going to get a decrease in the DO from the initial to the final, which means that corresponding to the amount of organic load that is present there is certain amount of degradation that has happened oxygen has been utilized for the degradation of organic compounds.

And therefore this is difference is expressed as a less BOD oxygen demand, yeah. What errors could be there in this so it's not I am not giving you full information this is not standard method means they will tell you everything. You know, whether you should move your hand this much keep it there, keep it here all that everything is included. So, a lot of missing information here like I give you a BOD bottle and water sample and DO probe, what will you do? You will add this take the BOD then what do you do where do you incubate it? The word incubate means it is kept at what are the different things we are we are doing biodegradation here right we are doing biological degradation. Then you have to think about what are the things that affect biodegradation and also things that affect oxygen consumption, the oxygen in the water, , if you talk about biodegradation one thing that biodegradation is influenced by is temperature.

So, you have to keep it at some temperature. So, this BOD can different biodegradations can happen rates that can happen at different temperatures. So at 5 days I can consume one level of oxygen and it can change if I my temperature changes. So, you have to standardize this you have to tell everybody that all you all people do the incubation at some temperature and not do it whichever temperature you want.

So, if I keep it outside temperature in Chennai is 35, 33 degrees and temperature in somewhere else, somewhere some other some other part of the world is different. Temperature in Delhi in

winter is 20 degrees, 30 degrees' difference between Chennai and Delhi all these things are there so, you can't have that, this is what we call a standardization when you say standardization, it means everybody follows the same method which means you have to do it at some temperature.

Typically, the temperature is 25 or 30 degrees, I think the standard method asks for 25, 25 or 30? 20. 20? Ah, 20 you are right, 20 degrees centigrade. One may argue, this 20 degrees never happens in India often is India. Temperature in South India is always 20 plus night or day it does not really apply to India. So it does not the point the BOD is a surrogate measurement, it is not a real measurement. It is already a surrogate measurement. Because it is measuring oxygen, it is not measuring organic compound.

It is also a reference point at 20 degrees centigrade and for 5 days. So you have to understand it in that context that you have to map this to an actual concentration of some chemical. So the the value of BOD is to give you a parameter that will indicate the quality of water that is all so there are standards based on this, to tell you that if the BOD level is above some value, the water is considered to be unhealthy you know considered to be polluted.

So, these are all the same references this is important why everybody follows the standard method. Irrespective of you know, if you don' t have the equipment to follow a standard method, you should not call it a standard method, you should say that I measured BOD at 35 degrees centigrade using, you know, some other instrument or you can develop your own method for it is not standard method of BOD that's also because everything will change a lot of things will change. And the second problem is is that you can also get oxygen production using by photosynthesis is something is there in the water including microorganisms including some biological matter which will contribute to oxygen production during photosynthesis. You don't want that you want oxygen neutral systems in reference to that so, that will cause problems.

So, when you are only looking at oxygen demand by for degradation. This entire thing is done in the dark. You put it away from sunlight, dark, ok. So there is another problem here these are these are general two conditions for very highly polluted water you can use t as one day and all that. So that is that is also possible. But everything else remains the same. But typically when somebody says BOD it is BOD 5 days 5 days of incubation, ok.

The third another another factor that influences the analysis, the results for BOD is what if you do not see any change or you see very small change, does that mean what could it mean two possibilities? If you see a very small change in the oxygen content of the of between the 0 and DOt, what does it what does it mean? What could it mean? There are no microorganisms. There are no microorganisms. Bottle is not sealed. Bottle is not? Sealed properly. Why but oxygen is not changing from initially means, oxygen is not going out anywhere, it is not been consumed.

One is there are no microorganisms that is one possibility that there is no microorganisms in the wastewater to do the micro biodegradation that is one possibility. So what is the second possibility? No organic matter. Ah? No biodegradable organic matter. That is there, is any other possibility? Ah, no biodegradable organic matter so that covers it. So there could be organic matter, but it is non-biodegradable. So it is quite possible that it is non-biodegradable. It is biodegradable but does not contain no microorganisms.

If it is non-biodegradable, you can't do anything about it. You can't use this method no matter what. But to if there is no microorganisms can be addressed by adding microorganisms from outside so this is called as seeding. We will seed the system by adding mechanisms, which are again standard, but this is more tricky because standard means somebody has to sell you those microorganisms.

To tell that this is even more, trickier because there is a specific species of microorganism and microorganism profiles in different places across the world are very different. It may be very different here compared to what is then 10 kilometers away from here. There is a wide variation depending on what is the substrate available here and all that. So that is a very complex problem, so people don't get into that. So instead, they will add whatever is available. They'll so this is again not standardized, but I think you have to be very careful when you are doing the seeding you have to do with all references must be same in the same seeding. This is a bit of a tricky thing that we will not get into that. So that analysis of that requires you to analyze the population all that. So if it is generally there is some recommendation of a seed, but people may not have access to that sometimes they will just add whatever is available.

So, what we call a general microbial populations. So, the idea of a seed is that natural water have some microbial populations that are there already so, it will degrade. So, the idea behind it is that it will degrade by itself things will bio biodegrade naturally, which means that you have to rely on whatever is there naturally, it could not it need not be one particular bacterial strain or microbial strain it could be multiple family of them depending on what is there in the water they will eat something will survive and will grow metabolic metabolize whatever is there.

So, you seed, so, let us say that so, ideally what you would hope is that, at the end of 5 days, all your biodegradation is done, finished. And so, you start so, you take an example. We'll write the example in the next page.

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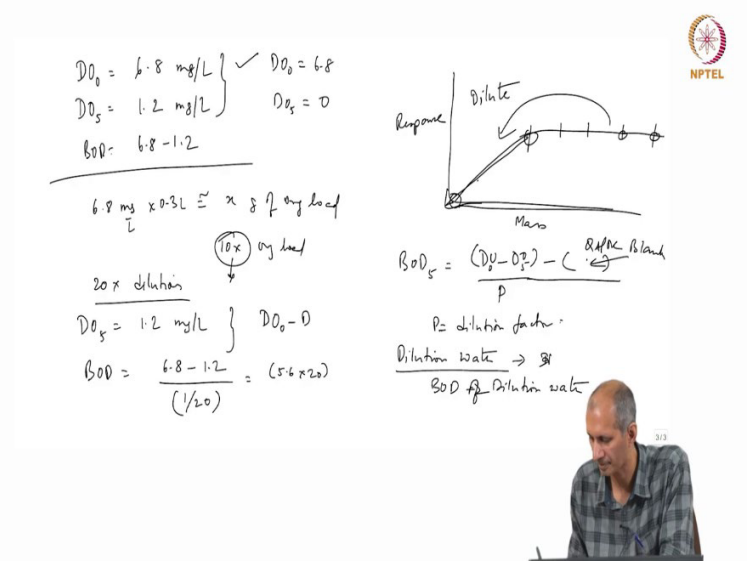

Let us say that the DO initial is the 9.8 milligrams per liter not 9.8, 6.8 and DO 5 is 1.2 is very straight forward. BOD is the difference between these 2 is 6.8 - 1.2 over. Suppose I get instead of this thing. DO0 is 6.8, DO5 is 0. What does this mean? What could this mean? Zero is a problem, because in our case of when we are doing calibration if you recall calibration, we have response verses mass or something, if your calibration does this, 0 is equivalent to this part.

I have no idea where this is. what does mean? zero means all oxygen is consumed, which means 6.8 grams of oxygen can be consumed by some x grams of organic load, what if there is 10x

organic load, ok. 6.8 milligrams per liter worth for 6.8 milligrams multiplied by 0.3 liters is the amount of oxygen you have in there this corresponds to x grams of organic load. What if there are 10 x organic load? You have no idea it will still be zero you once this x is gone.

The remaining 9 x is still sitting there. Your analysis is incomplete, yeah. So what do you do? BOD 5, is there an easier method? Whatever happens in the first 10 minutes? Now, whenever we do is what do we do if you have a signal response like this, if you are in this range, what do we have to do? We have to bring it into the range where it is measurable. So, what do we do in this case? Dilute. We dilute, so we dilute so here how much will you dilute your 10 x you are diluting at least 10 times you bring it below 6.8 below the range where it is going happen.

So I will dilute it by a lot large amount. So I can do multiple dilution this is what people do, they have no idea what the concentration is, they dilute 10 times, 20 times, 30 times, 100 times somewhere his value will be above 0. Then they take that value as the reference. So, if you dilute this in fact, I dilute say 20 times and my DO5 is 1.2 milligrams per liter. My actual DO will now we DO0 minus DO my BOD will be 6.8 - 1.2.

But this 6.8 - 1.2 corresponds to 1 / 20th of the sample. So I have to divide by 1 / 20. 20th dilution this is this is the dilution factor that goes in there. So this actual BOD of the sample is 6.8 - 1.2 is what 5.6 multiplied by 20 typically, this is what is done. You don't have very few samples which are BOD of 15 and 10 and all that. It is always more so, dilution is inevitably done. So, the standard method equation straightaway the standard method equation is DO0- DO5 divided by what is called as P is known as the dilution factor in this case is 1 / 20 so, you have to. Sir what is used for dilution? Distilled water or? Yeah, good question. So, you use, it is called what do you use for dilution is a dilution water whatever call it now this could be whatever is the purest water that you have now, what is the quality control here? So, there is a matrix effect now, if I am diluting 20 times or 100 times which means that in the 300 mL sample 300mL bottle 3 mL is actual sample rest of it is my dilution water, yeah. So, the dilution water is the matrix is the is the water.

$$BOD_5 = \frac{DO_0 - DO_5}{p}$$

p is dilution factor

So, now you have to check if what is the BOD of dilution water? This is a matrix blank; this is the matrix blank. You have to do this matrix blank because the the water you are adding for dilution can have a BOD of its own. So, you have to you have to calculate that separately you have to calculate that separately. So this must be subtracted, something must be subtracted from this it's a DO is a change in DO of the blank of the dilution water, yeah. How much value is that so that you have to divide that and then do the dilution there is another possibility that the seed that you are adding also has its own its own BOD.

You are saying it is microorganism, but it may also accumulate BOD, it may also have some some consumption going on. So, along with this blank, if you are adding a seed, you put that seed also you put some amount of seed and then calculate the consumption of oxygen for the seed. So, these are the this is a quality control, this is a QA/QC blank the blank term goes here so you do not consider that as part of the sample.

It is part of your method, your sample dilution water or the seed or anything else. Oxygen leaks all these are like the way we do with blanks what we do with blanks some false positive and all that you have to do here also. If you want to look at leak of oxygen leaking of oxygen across the way we do is we have a standard what is the standard here? What could be a standard there is no standard here what is the standard here oxygen is a standard we are we are measuring oxygen.

So, you have to calibrate the instrument using oxygen your dissolved oxygen probe is measuring oxygen from 1 point to 1 point the DO probe usually, so we operate at which means you have to make standards at multiple concentrations of oxygen very very difficult to do. So what people do is they have maximum what is the maximum concentration of oxygen in water that is highest you can get is the the solubility saturation.

So they will bubble oxygen or air through water for a long time, 1 day, 2 days they will measure keep measuring what is the solubility of oxygen and what dissolved oxygen solubility roughly 8 could be. 8 yeah, surround between 9 9 10 around that milligram per litre. Don't say a ppm is a

very I don't I would suggest you use absolute units always because there is a lot of confusion ppm, ppb, ppt and all that. If you don't if you forget you make a mistake. It will cost you 1000 factors. The factor of 1000. Milligrams per liter is around 10, 9, 10, 25 degrees 30 degrees is around 10, 8 between 9 and 10 depending on the water. So it is not very high, ok.

So you can make it so whatever you get the highest value you if you if you know what the value is you keep it at one. The other end you completely remove oxygen from water, which is also not easy. Because you are now exposed to oxygen whenever you expose water to oxygen, oxygen always wants to go in. So you have to purge the oxygen out of it, there are ways to do it. One way is to add an oxidizing an agent that will react with oxygen, all oxygen can be taken away.

There are methods to do it we will not go into it but you have to prepare this and it is not trivial to prepare this. One way is to just purge with nitrogen will remove all oxygen and that is one way of doing it. It is a lengthy process it takes time this mass transfer of nitrogen using oxygen and then that is one end so you have a 2-point calibration is 2-point calibration is very dangerous, but that is the best you can do as of now because any anything else in between is not stable oxygen is by the time you prepare everything system open it put the do probe gone, it is not the same different so it's a bit tricky. Ok, any questions? This is just a overview of this?
Student: Sir we are keeping seed for consumption only how will that interfere.
Professor: No no, so, sometimes the seed may also have, you are taking seed from somewhere that could have some organic load that will also consume microorganisms when you are collecting it practically it may have something else in it unless you are using pure culture and all that.

So, this is this may or may not give you any value. So, it is this the same quality control is done just to ensure any such artifacts. Sometimes it may be important especially because of the dilution factor. So, the reason you are if you are using dilution factor of 100 and all that any small error there will magnify by 100 times here so that is the reason why worried about small small things like otherwise it is not a need not be a big issue.