Environmental Quality:
Monitoring and Analysis
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Lecture No. 20
Analysis Methods – Water Quality Parameters

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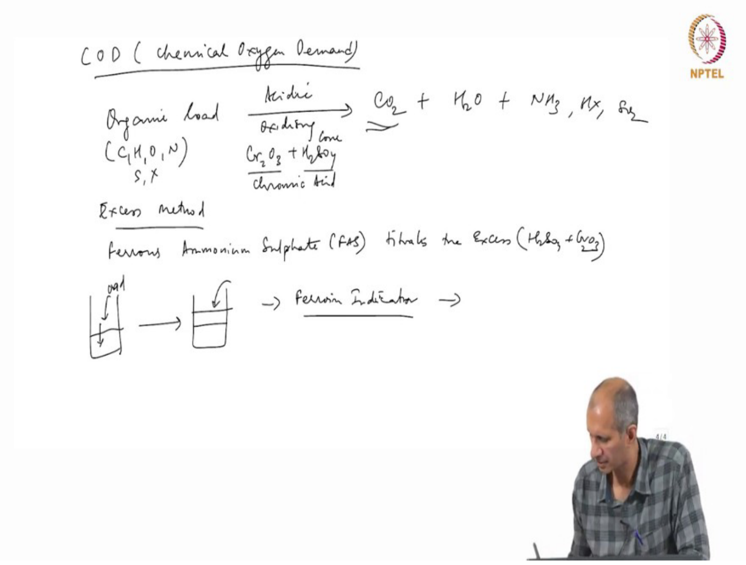

COD (chemical Oxygen Demand)

Organic load (C, H, O, N) S, X $\xrightarrow[\text{Oxidising}]{\text{Acidic}}$ CO_2 + H_2O + NH_3, HX, SO_2

Cr_2O_3 + H_2SO_4 Conc

Chromic Acid

Excess method

Ferrous Ammonium Sulphate (FAS) titrates the Excess (H_2SO_4 + CrO_3)

→ Ferroin Indicator →

So the other method that is used is called as chemical oxygen demand. So here I think we don't rely on biodegradation, there is a direct oxidizing agent that is used. So, you have organic compounds or we call it as organic load in the presence of acidic and oxidizing conditions gives you CO_2 plus H_2O plus organic compounds contains a C, H, O, and N generally some ratio, ok.

$\underbrace{organic\ load}_{(C,H,O,N,S,X)}\ acidic\ , \underset{\rightarrow}{oxidizing}\ conditions\ CO_2+H_2O+NH_3+HX+H_2S+SO_2$

So can either get NH_3 or if you have other compounds like S and X all that you get HX, you can get a H_2S or you can get SO_2 depending on what is forming. Typically, you may get SO_2 or something else. But this is the main reaction. So standard method calls for the use of Cr_2O_3 + H_2SO_4 it is called chromic acid, chromium trioxide with concentrated sulfuric acid. And usually back titration is used which is called excess method. So you add a large amount of acid, you don't know how much acid to add for it to react. So you had an excess of acid and you also add another reagent so it is ferrous ammonium sulfate or FAS. So this titrates the excess H_2SO_4 + Cr_2O_3.

So, the method for this is you take again a certain volume of water, you add the oxidizing agent and then let it digest for a long time, the standard time is about 2 hours. And then at the end of it whatever is the unreacted acid will react with a FAS and then there is an indicator that is added in order to calculate essentially calculate how much of FAS was used. So amount of FAS used is estimated and from there what is the amount of acid that is used is estimated. So you have a blank sample which has no water sample only sulfuric acid and FAS. Then you have a sample which has water plus sulfuric acid and FAS then the difference between these two will give you the there is a formula for doing it I will not give it here you won't be doing any calculations for this.

So, I think the COD is more an indicator, it does not relay on the conditions that you have and it's also faster than the BOD. You can do it fairly quickly, you can also do it simultaneously, there are equipment to do that. There are of course, other interferences in COD also there's something which is a chemical reaction. So, sulfuric acid react with a lot of things, something there in the water may interfere with it and with the FAS, those interferences must be separately dealt with.

Sometimes you will know about these interferences only if you do the full analysis of the water. So, the one problem with the sulfuric acid method is, if there is something else in the water that is also consuming sulfuric acid, you won't know that, so you must have another method by which you only look at organic load. So we are looking at chemical oxygen demand in general, it will take everything, it is taking care of all the compounds, if that is what you are interested, that is fine. But if you are looking at organic load, specifically, carbonaceous, we are talking about carbon compounds. But then you can't be sure if it is only carbon that the acid is reacting with, it could be few other things, it could be something else, whatever is there in the water. So it is a bit of a tricky question. So you have to analyze a lot of things and correct for the COD, yeah, ok.

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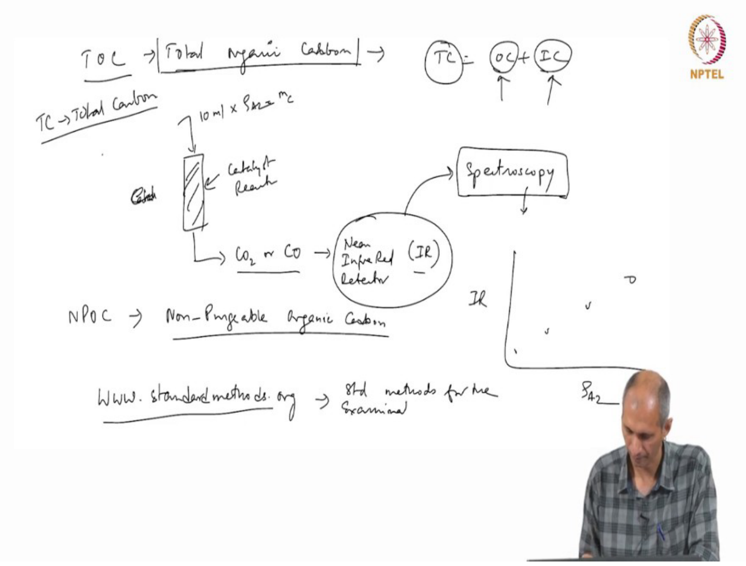

There is another method which is called as total organic carbon (TOC) to correct whatever we said in the COD. We are only interested in carbon here. See when you do wastewater analysis we are interested in total nitrogen, phosphorus, carbon, sulfur, everything all those things are important from a water quality perspective when we are interested in the overall what is happening in the chemistry of the water. But from the context we are looking at the course we talked about whatever we talked about now, in terms of partitioning and all that, this is a very important parameter, Organic Carbon. This is also important because, sometimes when people are analyzing whether a particular method is working or not working, they look at total organic carbon in the water so they want to see, especially when they are looking at degradation in the in water.

We have biodegradation or any other degradation we would like to see what's going on. And one of the ways in which people check is also using this, it is a very clear thing. The biggest difference between this and the other two methods are that those are surrogate methods, you will get milligrams per liter, but that milligrams per liter is not direct carbon. This will give you carbon this is actual carbon.

If I am saying it is total organic carbon it is total organic carbon, there I am saying is BOD biological oxygen demand, it is a concentration of oxygen you are measuring and it is a concentration of sulfuric acid that you are measuring. It does not directly reflect on the amount unless you calibrate BOD and COD with something actual amount of carbon. So they have to be used in that context only. But in TOC if it says if milligrams per liter, it is milligrams per liter of carbon, whatever is the carbon that is there.

So the analysis of this is a little more sophisticated and there we go down to much lower concentrations in this. So, I will just briefly describe the method to you. So, this in this TOC is organic carbon what we measure is initially what is called as total carbon TC because carbon in water can also be inorganic, in the form of carbonates. So, if you are looking at total organic carbon.

$$TC = OC + IC$$

So the instrument itself doesn't care about OC or IC you have to remove IC before you do the OC. So, the way we remove IC is we add something that will release all the carbon dioxide that is their associated with carbonate usually we do it with some acid or something like HCl or something we add a little bit of it, CO_2 will come out you have to bubble it out and then the rest of the carbon that is there is all organic carbon, yeah.

So, the organic carbon is added to a catalyst which basically does oxidation, all the carbon is oxidized. It's catalytic oxidation at high temperature and it will release carbon dioxide or carbon monoxide and this is measured using near infrared detector (IR) detector which we call as spectroscopy. So, this part, I will explain a little bit later in the next section ok.

And there are different kinds of spectroscopies, there is atomic spectroscopy, molecular spectroscopy. As a word what it means is the material that's there is going to interact with radiation, in this case infrared, and gives some signal and that signal is inferred in terms of CO_2 or CO whatever it is.

So, each of these spectroscopy techniques have a specific characteristic that you can prove and based on that you can learn more about the sample. Will talk about this little bit more as we go deeper into this, is again does not give you any specific breakup of the carbon that is going in. it is taking all the carbon is doing something a little more than it is doing exactly what COD and

BOD reactions are doing, but it is not changing the form we are measuring what is coming out, ok.

But by way of process, we are doing the same thing we are oxidizing everything making it CO2 and the CO2 and CO is measured physically. So, we measure the total carbon and if it only contains OC we call it as total organic carbon, we subtract IC. There is also another way with which IC can be analyzed, also by using some other acid and that is also possible. Some other catalyst but this is general mechanism.

So the total Organic Carbon instrument is expensive. It is more expensive. A few years back it used to cost about several lakhs I think 10's of lakhs, ok. Compared to BOD and COD which are very cheap, you need only DO meter and you need a few small things you can get it done maybe a couple of lakhs, and you can run it continuously. So, you get more information and more cost, you get less information but less cost.

So this is typically the way in which analysis runs, all analysis, protocol is like that so you get more information you have more cost, ok. In this there is another category called NPOC which is called as non-purgeable organic carbon. What this means is that you are still doing the same thing you are adding samples, but before it goes into the sample, I can I will purge my sample what it means is any volatile organic compounds are all gone, they are taken away whatever is there is the non-volatile part which is then sent through the catalyst. And then carbon dioxide comes from out. Anyway this is for your information and one very good source for how instruments work is the catalog and their manual so it will give you the theory of by which the instrument is supposed to work and all that, so you can get a lot of information about that. And the interferences, a lot of interferences are not mentioned expressly. People like you, whoever is using it have to find this out sometimes.

So somebody will say the instrument works well. But then you find out it does not work well for some set of conditions that there are interferences that, so you have to report it. And somebody like the CPCB, or the US EPA will catch that and say verify it and then say so these instrument cannot be used for these conditions. You will see a lot of examples. So, you also have to calibrate this instrument, ok. Calibration of this is done by putting known amounts of carbon into your water and getting a signal.

So, this is infrared signal versus carbon mass. So, in this case carbon mass is in terms of volume. This instrument will take a certain volume say it will take 10 ml, 10ml is injected into this catalyst. So, 10 ml of a solution multiplied by the concentration will give you the mass of carbon that is present in this. So, the calibration is done in terms of concentration rather than mass so that's more convenient for us to do nobody is going to calculate. And since you are just adding a fixed volume of a particular listing, you don't need to calibrate mass you can calibrate concentration directly, because you don't have to worry about recalculating the concentration and all that. Its directly concentration calibration. So, you will get a relation by changing the concentration of carbon in your standard, prepare different standards for different carbon. So, there are some standard methods of what to use and all that. So, you can go and look at this website called www.standardmethods.org. This refers to this BOD method that is mentioned, standard method for the examination of water and wastewater.