

**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 $\xrightarrow[\text{chromic acid}]{\text{acidic oxidizing agent}}$ $\text{CO}_2 + \text{H}_2\text{O} + \text{NH}_3, \text{HX}, \text{H}_2\text{S}$

(C, H, O, N)
 S, X

Excess method

ferrous ammonium sulphate (FAS) titrates the excess $(\text{H}_2\text{SO}_4 + \text{Cr}_2\text{O}_3)$

\rightarrow Ferrin Indicator \rightarrow

So the other now the method that is used is called as chemical oxygen demand. So here I think we did not rely on biodegradation, there is a direct oxidizing agent that is used. So under acidic conditions so you have the equation maybe not write this equation. So, we have organic compounds or we call it an organic load the presence of acidic and oxidizing conditions use you $\text{CO}_2 + \text{H}_2\text{O}$ plus organic compounds contains a C, H, O, and N generally and some ratio.

So you are going 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 and something else. But this is the main reaction to a strong acid is used 1 method standard method calls for the use of $\text{Cr}_2\text{O}_3 + \text{H}_2\text{SO}_4$ it is called chromic acid chromium trioxide with concentrated sulfuric acid.

And usually what is used this it is what, is the back titration is called excess method. So you had a large amount of acid you did not 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 called as what we add is ferrous ammonium sulfate FAS. So this titrate the excess $\text{H}_2\text{SO}_4 + \text{Cr}_2\text{O}_3$. So what we do is we take some amount of sulfuric acid, this chromium trioxide some say we have some volume of what we add into.

So, the method for this is you take again a certain volume of water, you add the oxidizing agent and the and then let it digest for a long time so long time is again relative think now, the standard method will half an hour or 45 minutes, 2 hours the slack related method also and then at the end of it whatever is the unreacted as acid will react with a FAS you add FAS and then that will go and then there is a an indicator that is added in order to calculate how much of an indicator is added.

And we essentially calculate how much of FAS is was used. The amount of FAS is used 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 samples only sulfuric acid and FAS. Then you have a sample which is water plus sulfuric acid and the FAS and this the difference between these 2 will give you the there is a formula for doing it and not give it here you would not be doing any calculation for this.

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

Sometimes these interferences you will only know if you do the full analysis of the water. So, the 1 problem with the sulfuric acid method is, if there is something else in the water that is also consuming sulfuric acid, you would not know that so you will know that so you must have other

method by which you only look at organic load, you are looking 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, that is why you are interested, that is fine.

But if you are looking at organic load, specifically, carbon issues, you are talking about carbon compounds. But then you cannot be sure it will only carbon that the acid is reacting with it could be few other things to 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. I am correct for the COD.

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There is another method which is called us TOC just call it total organic carbon to, obviate to correct whatever we said in the COD, we are only interested in carbon here sometime because a lot of things see when you do waste for analysis we do we are interested in total nitrogen, phosphorus, carbon, everything sulfur, 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 what are we talked about now, in terms of partitioning and all that this is a very important parameter. Organic Carbon is also important because, sometimes and when people are analyzing whether a particular method is

working or not working, they look at total organic carbon in the water they want to see, especially when they are looking at degradation in the water.

We are biodegradation or any other degrees we would like TOC what is going on. And the one of the ways in which people check is also using this, it is very clear. The biggest difference between this and the other 2 methods are that those are surrogate methods, you are not you will get milligrams per liter, but that milligrams per liter is not direct carbon. This will give you carbon is actual carbon.

If I am saying it is total organic carbon, where I am saying BOD is 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 is not 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 so TOC will give you if it says milligrams of carbon, if milligrams per liter, it is milligrams per liter of carbon, whatever is the carbon is here.

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

So, you got to get total organic carbons is TC equals to TOC plus TIC inorganic carbon OC plus IC total carbon OC plus IC for the instrument itself does not care about OC, IC you have to remove IC before you do OC. So, the way we move IC we add something that will convert all the 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 had a little bit of it will go to CO₂ will come out you have to bubble it out and then the rest of the carbon that is there is all organic carbon.

So, the organic carbon the water is added to a catalyst added to a reactor is added to a which basically does oxidation, all the carbon is oxidize its catalytic oxidation at high temperature and

it will release it will give you carbon dioxide or carbon monoxide and this is measured using near infrared detector IR detected. So, this part I will explain a little bit later and the next section this is what is what we call a spectroscopy.

And there are different kinds of spectroscopy, there is atomic spectroscopy molecular spectroscopy as a word. What it means is that we are using a in this case we are using something to the material that is there going through behaves interacts with radiation in this case, in this case infrared, it interacts with infrared and gives some signal and that signal is inferred in terms of CO₂ or CO whatever it is.

So, each of these spectroscopy techniques ourselves specific characteristic that you can prove and based on that you can learn more about the sample we 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 and 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.

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, this instrument, so, we measured the total carbon and if it only contains OC call it has total organic carbon subtract, IC there is also our other with the IC can be analyzed also by using some other as you know and so that that is also possible. Some other reactive some other catalyst but this is general mechanism.

So the total Organic Carbon instrument is expensive. It is more expensive it is cost in a few years back it was cost about several lakhs I think 10's of lakhs compared to BOD and COD which are very cheap, you are only the 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 we get more information or more cost. In this there is another category called NPOC. Just call us non

purgeable organic carbon and just take 5 more minutes we are done. What this means they are still doing the same thing you are adding samples, but before it goes into the sample, I can I will push 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 this information when you go in one very good source for how instruments work is that catalog is there the catalog and their manual and if you give sometime 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 they will not tell lot of; interferences are not mentioned expressly. People like you, whoever is using it have to find this out sometimes.

Somebody will say the instrument works well. When 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 and instrument cannot be used for these conditions. You will see a lot of examples, when you see the next list. So, you also have to calibrate this instrument. Calibration of this is done by putting carbon no amounts of carbon into your water and getting a signal.

So, you will put actual infrared signal versus carbon mass. So, in this case carbon mass is in terms of volume you are making a concentration of a certain instrument will take a certain volume say it will take 10 ml is injected into this catalyst. So, 10 ml offer solution multiplied by the concentration and give you the mass of carbon that is present in this. So, the calibration is done in terms of concentration rather than mass but it is more convenient for us to nobody are going to calculate.

And since you are not adding your next you are just adding a fixed volume of offer a particular listing, you did not need to calibrate mass you can calibrate concentration directly, we would not have to worry about recalculating the concentration of its directly concentration calibration. So, you will get a listing 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.standard methods.org. This refers to this method the BOD method that is, there was mentioned standard method for the examination of water and wastewater. This is the standard methods and wastewater.