Environmental Quality:
Monitoring and Analysis
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Lecture No. 22
Analysis Methods – Organics in Water

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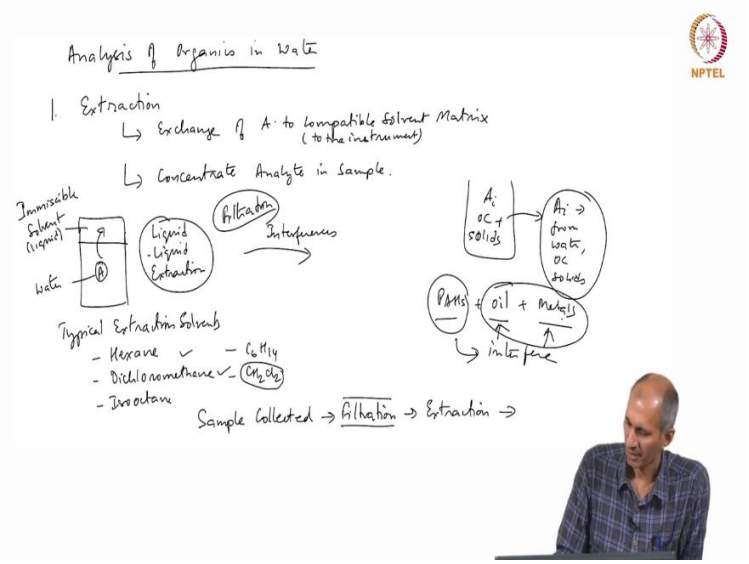

So, we look at analysis of organics in water. So, the first thing is the extraction, we look about extraction. Extraction means, we are talking about something which is at very low levels, typically, we are talking about nanogram per liter or microgram per liter that level of concentration. So, we want to pull it out. So, as if you recall the objectives of extraction are, use of compatible solvent for exchange of A to compatible solvent matrix, that is compatible means it to the instrument.

Second, it gives you an opportunity to concentrate the sample. So you can do this in multiple ways. So, one of the common methods in which people do this is, one is your water sample which contains A to which they add another solvent. This is another liquid and then A will transfer to this. So, this is directly using what is called as liquid - liquid extraction. So the second solvent liquid that we use, by definition if you are going to do liquid - liquid extraction it must be immiscible in water predominantly.

So, use an immiscible when we say immiscible, we are not talking from environmental point of view, all of them have some solubility, but bulk in solubility is very small. So, if you add 100 ml or 50 ml of solvent to 1 liter of water, you can recover most of it, 40 ml you can recover at least. So, we did that calculation last time. So, this is one of the reasons, you can only recover some of it. You cannot recover all of it because some of it may have already dissolved in it.

So, that is possible we did not worry about that. Our goal is to extract us much as possible. So, typically immiscible solvent which can now has a greater solubility of A in it. So, if some inorganic some organic solvent that can hold A in a larger quantity, typical extraction solvents are hexane, Dichloromethane. These are 2 very commonly used, also you can use Iso-octane and things like that, but, typically these 2 you will see mostly.

Dichloromethane is CH_2Cl_2, you know this is C_6H_{14} this is a very hazardous compound. Dichloromethane is a chlorinated organic solvent but this is one of the strongest solvents that there is, many of the chlorinated solvents organic solvents are very powerful, they will extract a lot of things. Okay, but they also are listed among, if you go and look at the priority chemicals of concern organic, you will find some of them there.

You will find some of them there because they are used in large quantities so the opportunity of exposure is very high. So, industry and all the people use solvents for all kinds of things, they use for painting, cleaning of things because it is a very good extractor, so you want to clean something it will come out very easily. So, for this kind of extraction, we are not using large quantities but we are using small quantities.

And that is why you have a section in your analysis method it's called waste management which means you will end up at the end with some Dichloromethane or hexane which is not supposed to be there and you can't throw it down the down the drain. You have to dispose it properly. Okay. This this is one point in which you have to do method selection properly. So, there is a waste management associated with it because you are introducing some hazardous chemical here.

You have to understand this principle, we are not discussing it in this course but when you are discussing treatment processes or remediation, you have to remember that maybe sometimes it is very effective to use some chemical for treatment or clean up but then that you will be creating more problems for environment for everyone. But here the usage is so small, quantities are very small and the purpose is to analyze. So, it is not considered as hazardous, we will search for methods which are more sustainable, but if it is not its not, so we do whatever is the best available to us.

So, when you extract water as it is raw water, sometimes you will get everything, all the interferences in your sample and this is true mostly for samples that are coming from waste water treatment plants or sewage treatment plants. Such thing you want to know what is the concentration, there you may find some other material there and that may also get extracted and that will introduce interferences.

One example is this so, when normally say I collect a water sample of water from a very turbid lake, I do not do anything I just add hexane or dichloromethane, it will extract everything, it will extract the organic carbon and it will extract all of that. So, if the original water contains A plus organic carbon plus some other solids say let us not call it A we call it as bunch of A, Ai, I will call it as Ai which means there are lots of chemicals.

It is not only extracting this Ai from water, it is also extracting from OC and from the solids and Ai will contain a few things. So, here comes the definition of an interference very interesting now, because if your goal is to find out what is there in the water whatever is there in the water is going to come out so none of it is really an interference, the interference is very specifically defined for one analyte or a group of analytes that you are focusing on.

For example, if I have PAHs plus oil plus some other things let us say metals in the water. I am interested to know all of this. Right! How much of PAHs are there and how much of oil is there but if I am analyzing PAHs specifically, these 2 may interfere with my analysis of PAH, the oil and the metals will interfere. So in my method for analysis of PAHs if this is seen as an

interference, these are interference. So I must do something with these 2 before I go on the analysis PAHs.

So, you have to interpret the interference like that so there is no absolute interference. Interference is relative to whatever you are trying to analyze. All of these are important for analysis. So, the other interference is from what we talked about in the last class. When I am analyzing water, I want concentration of A, in water alone. If this is associated with solids, and I know I am getting the wrong information. Yeah. So, before this you have to do liquid - liquid extraction, if you don`t want that information, you have to filter the samples.

So filtration must be done before LLE. Okay. So normal sequence of events that you will see is the sample is collected then we move on, after this we do the next step. Okay.

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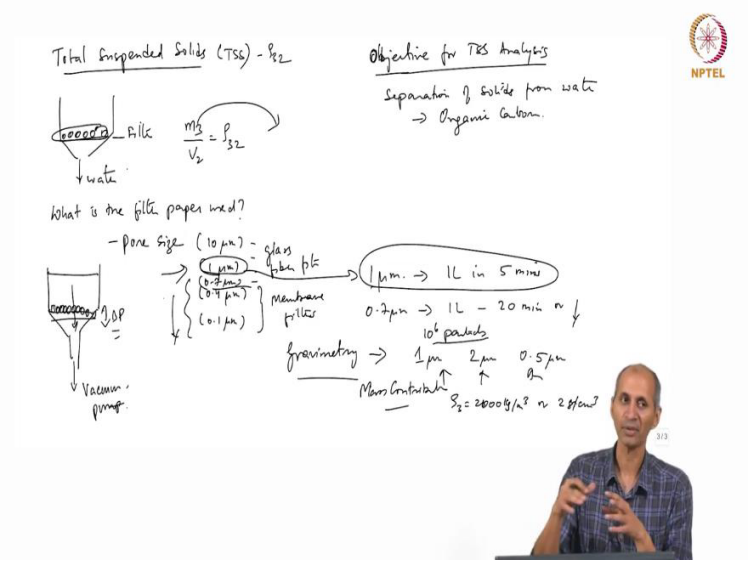

I want to sidestep a little bit here and talk about filtration a little bit. So, we have discussed something called total suspended solids. I think we have not discussed it in detail. So, is it a good base to do this now, when you say total suspended solids it is we are taking a water sample and filtering it through a filter paper and all the solids are trapped on here and you get water and the mass of filter that is collected here divided by the volume of water will give you ρ_{32} this total suspended solids, ρ_{32}.

There is one piece of information that is needed here is, what is the filter paper that we use? Professor: Have we discussed this in the class? No, I don't think so, what filter paper we will use? So, if you go and open a catalog for filter papers, you will find a lot of papers, you have used filter papers from high school for various things. What is the definition of the filter paper that we use here? What kind of filter paper do we use? What is the characteristic of filter papers typically when you say filter paper? Predominantly you'll say pore size. So the pore size say is in some microns. So, it will say 10 microns or it will say 1 micron you can go up 0.4 microns, 0.2 microns, 0.1 microns all of them are there. Up to about 0.7 microns you have glass fiber filters from somewhere around o.4 or 0.1 microns and you have membrane filters and you have more specialized filters.

So, you have a wide selection of filter paper and filter materials, what will you use? Is there a qualitative rational decision? Why do we want to use some particular filter paper? People who have done filtration will know what is the difference. what is your objective? we had all these example analysis problems because for this question what is your objective in doing this, in analyzing TSS? Objective is very simple answer, i.e, separation of solids.

So, what are the solid sizes from that needs to separate or fully like separate. Based on the example in the last week, what would you like to separate doing if you are doing organic analysis? What would you like to separate if you are analyzing an organic chemical in the water? I would like to separate some component which will accumulate a lot of organic compounds. So mainly I am interested in separating organic carbon for that purpose.

But TSS does not differentiate when organic carbon and the suspended solds, it does not care anything, all particles down to whatever the size. So, ideally what would I want to use if I have filter papers available for 0.1 pore size. Can I use 0.1 pore size? It will stop everything bigger than 0.1 because colloids organic carbon is in the size range of 0.4, 0.2. I will definitely remove all of them. Then why do you have filter papers have 1 micron and 4 microns and 10 microns.

For one is easier to make, that is one reason but they are still there in the market and people sell it for one reason. As the pore size goes down. what is the other consequence in filtration? It takes longer, it takes an enormous amount of pressure drop to push liquid through that filter. So it takes

very long to do this. Second, so let us say I use a filter say I use 1 micron glass fiber filters. I am able to do it in filtration of 1 litre in 5 minutes.

I take 0.7 micron filter, it takes for 1 liter 20 minutes or sometimes depending on the amount of solids, I may not even be able to finish it, filter will get clogged. I cannot do so the way we do filtration here. I get a little filtration if I just put it on a filter paper and leave the pressure drop across the filter paper to itself. Because pressure drop is so much that the moment the first drop of particles come and collect there it will not go through by gravity.

So you have to put some negative pressure here, so you have to apply a vacuum to do this. You have to use it, otherwise by gravity alone, it will not happen. You have to push, you have to have a vacuum pump to pull the water across a filter, there is a pressure drop that is acting here. So, you have to push it across at using the filter. So, even with the vacuum pump you would not be able to filter it sometimes with 0.7 micron filter.

So, between 1 and 0.7 micron if there is this much difference, I would rather use a 1 micron filter what will be my loss of information if I use a 1 micron filter versus 0.7. let us say that some small particles will get through from 1 microns pore size, 1 micron does not mean all particles below 1 micron will not get filtered. That is not true there is filtration theory. It is not the pore size, it is much more complicated. So you will get retention of particles much lower than 1 micron.

But there may be other particles which will still going on, that is one of the basis for which we use 1 micron filters instead of 0.7 filters and 0.7 is not really needed and 1 micron is probably good enough to do whatever collide removal you want. But still there is this question one has to draw a line somewhere and the basis for that is one of this is if filtration was very easy people would use 0.5 but filtration is not easy.

And so 1 micron filter is used. What is the difference between 1 and 0.7 in terms of information lost? What is TSS? How is analysis done? How do you get m_3? By weighing it's a gravimetry measurement. So, if I take particles that are 1 micron versus particles that are 2 microns versus

particles that are 0.7 microns or 0.5 microns. And let us say there are 10 raise to 6 particles. You calculate what is the mass contribution of all these.

You can calculate, take the density of the particle as they say 2000 kilograms, or 2 grams per centimeter cube, it will turn out that the even if you have a million particles, the contribution to mass is very very small. You would not even probably see it in the balance that you are using the 4 digit balance that you use, you may not even see it in terms of contribution to mass. So, while it gives you a little more separation, 0.7 and below these filters will give you a lot more separation than 1 micron filter.

The information that you get from terms of mass gravimetry is decreasing it is almost negligible. You can do the calculation, for yourself convince yourself how much is the loss. So, since the total suspended solids methodology is based on gravimetry. It does not really matter, below 1 micron, you are not going to get any additional information and you are also going to get you are going to waste your time by trying to push it through this thing and you are not getting any additional information.

So, 1 micron is set as standard filter size for TSS because it is TSS standard filter size. When you do water analysis use general TSS analysis which means you are filtering the sample and that filtered sample is what we usually take for analysis of water. Now, it does not mean that the water that is filtered through 1 meter does may contain collide which have organic and for that you have to measure the TOC and then correct that value. That is a separate issue.

And nothing you can do about it in terms of separating, but you can at least calculate the TOC and say, I know the total concentration. Now I know that TOC, I want to find out what is the actual aqueous phase concentration based on the calculations we did last week.