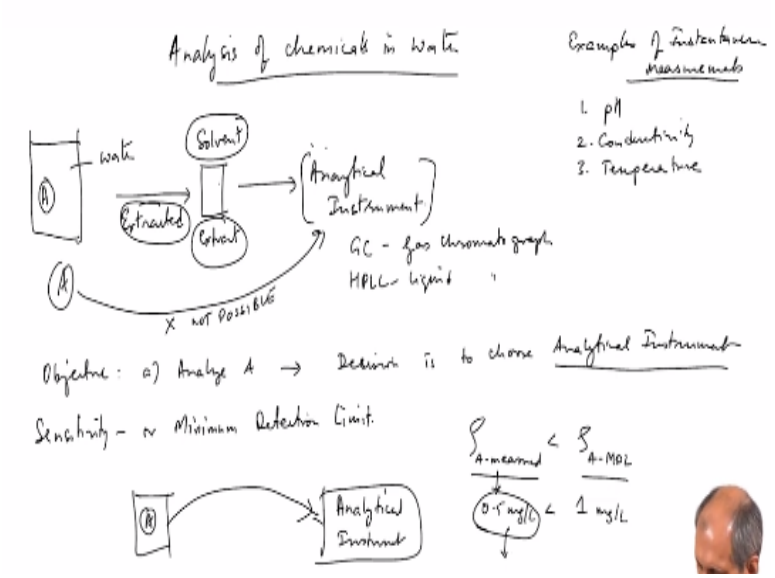
Environmental Quality: Monitoring and Analysis
Prof. Ravi Krishna
Department of Chemical Engineering
Indian Institute of Technology – Madras

Lecture – 15
Environmental Analysis of Organics in Water

In this lecture, we are going to talk a little bit about the analysis methods for organic and inorganic chemicals there are in water, sediment, and other matrices. This is the general pre-analysis method. Analysis method, we just have an overview of the analysis method again.

(Refer Slide Time: 00:34)



We will start with water and the same kind of principles are applicable for the other matrices as well. So, let us say we have a sample of water which has some analyte. When we say an analyte here, we are looking at multiple analytes, but our representation will be this A which is one analyte. So, for the analysis the general flow of the information is as follows. This A needs to be extracted from the water or any matrix into an extract and then from here it needs to be transferred to an analytical instrument.

The reason we have to do this is very often you cannot take the analyte A directly to the analytical instrument, this is not possible. For example, there are sensors and the reason we do it is there are not enough sensors in order to do all this in an instantaneous manner. For example, if you want to measure temperature of air or relative humidity of air or some few chemicals in air, you have a probe that is available commercially and you can just show it in the atmosphere, in the air or water and it will give you things like this.

So examples of instantaneous measurements, things like pH, the pH in water, you have pH meter that can be dipped into water and it can give you the pH, conductivity is such, temperature. These are all probes that will give you direct analysis of whatever you are measuring by a simple probe. There is no need of processing of the sample, nothing is required, directly it gives you a direct readout. This case some of the chemicals that we have discussed you cannot read out directly and the instrument cannot take a water sample directly into it.

Therefore, it is possible, sometimes it is only possible for us to do it via an extraction into some other medium into some other solvent. Typically, what we are doing is this solvent can be input into the analytical instrument. This is true for a variety of instruments such as the gas chromatography or to some extent the limited extent the HPLC liquid chromatography. So, in this context, the first thing that one has to do is if your objective is to analyze A, the first decision you have to make is to choose the analytical instrument.

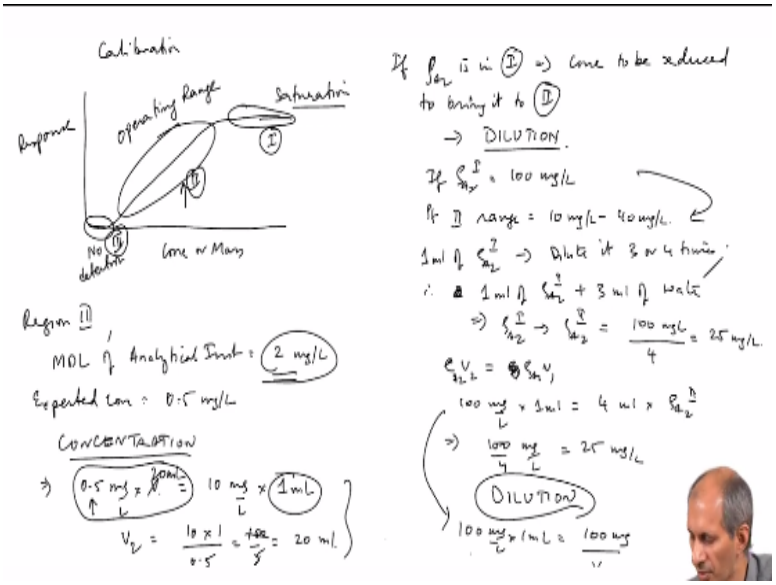
Then from there you work backwards and what is the suitable solvent or a form in which the analytical instrument can receive the sample, you know the analyte in and therefore how do you bring it to that form from the water. So, the sequence of water to an extraction of chemical from the water to solvent, solvent to analytical instrument depends on the instrument and one has to do that survey before coming to this. So, the most general methods for GC and even HPLC to some extent, this is the sequence.

The other reason why we would like to extract something from water into a solvent and then take it to an analytical instrument is also for purposes is that we have discussed something called the sensitivity or the minimum detection limit. So, if the concentration, if I take water directly, let us say that there is an instrument that I can directly inject water into this instrument and the instrument is capable of doing that I can measure A.

However, if the measured concentration, it is whatever I am measuring, the rho A measured is less than the rho A minimum detection limit, then I would not be able to see anything, I cannot use that reading essentially. So, my only way in which I can measure A, let us say for example, the concentration, the minimum detection limit to say is 1 milligram per liter, and the concentration that I expect in the water sample is 0.5 milligrams per liter, it is less than the minimum detection limit and therefore I cannot use this instrument to do this.

However, if I can increase this concentration, to a region which is well above the minimum detection limit, then it is possible for me to measure it.

(Refer Slide Time: 06:59)



So in a different view of this if I look at the calibration, let us say that I do not have any signal and then I have a linear signal and then I have a saturated signal like this, this is the response and this is the concentration or mass. This is a typical calibration curve. So here, we are talking about this range where there is no detection and this range here which is saturation. So, when you do an analysis, it has to lay in this, this is the operating range of a calibration. Therefore, we are always looking to bring the concentration of the analyte in this operating range.

So if the concentration is very high, so it is beyond the saturation of the detection, if the concentration is in point this region 1 and we needed to bring it region 2. This we call this a region 3. If rho A2 is in 1, it needs to be reduced, concentration has to be reduced to bring it to region 2 and this we do by dilution. For example, if you have the concentration, if rho A2 in region 1 is 100 milligrams per liter and if region 2 range is between 10 milligrams per liter and 40 milligrams per liter.

Then to bring this to this range, I can take 1 ml of rho A2 at 1 and dilute maybe 3 or 4 times, for this maybe I can take 1 ml of rho A2 in 1 and add 3 ml of water. The concentration of 1 to region 2 will become 100 milligrams per liter divided by 4, this is 25 milligrams per liter. In other words what we are doing is applying this formula rho A2 v2 equals rho A1 v1. All we

are doing is doing 100 milligrams per liter in to 1 ml equals 4 ml into some concentration and this is 100 divided by 4 milligrams per liter is 25 milligrams per litre.

$$\rho_{A2}V_2 = \rho_{A1}V_1$$

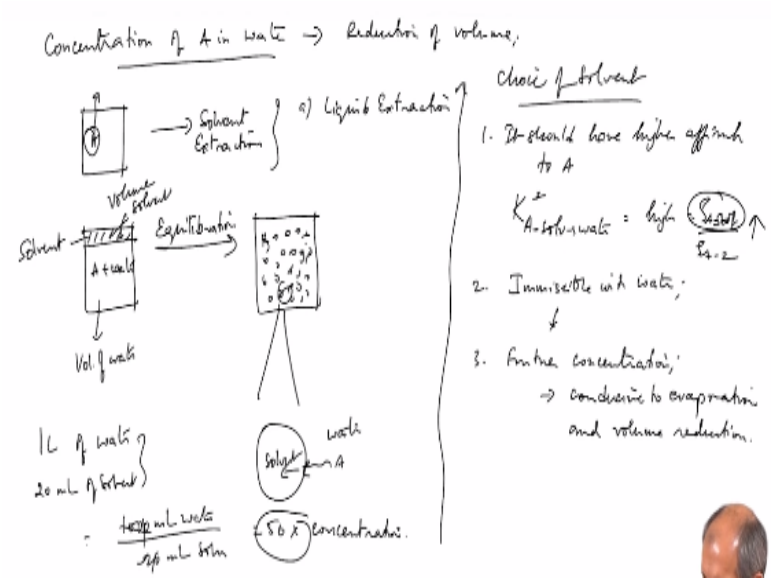
This is called as a dilution. So we do the dilution to bring the concentration from region 1 to 2. What if the concentration is in regions 3? If region 3 concentration, let us say the MDL minimum detection limit of this instrument let us say that it is 2 milligrams per liter and the expected concentration is 0.5 milligrams per liter. So how do I bring it into region 2, is by concentration, I can do concentration. It is the opposite of dilution, which means that what I am doing in dilution is I am taking the same mass.

I am taking here in this in this example, what I am doing is I am taking 100 milligrams per liter into 1 ml, this is essentially 100 milligrams. I am dividing by a volume. So this volume instead of having this 100 milligrams, instead of being present in 1 ml, it is now present in a larger volumes, means diluted, so we are increasing the volume to reduce the concentration. Likewise here if you want to increase the concentration, you have to reduce the volume, we are increasing the volume here, we are reducing the volume here.

So therefore we take 100 milligrams. So here in this case, we would like to increase concentration. So we have 0.5 milligrams into some volume. Yeah, just some volume. Equals we want to bring it well above the minimum production. Let us say that I would like to bring it to 10 mg per liter and I would need at least 1 ml, I am looking at 1 ml of this. The volume that I need here initially is 10 into 1 divided by 0.5 and that becomes 100 by 5 is 20 ml okay.

So what I am doing essentially is I am taking 20 ml of a sample, which has a concentration of 0.5, and I am and reducing the volume from 20 ml to 1 ml. So, how do you reduce the volume?

(Refer Slide Time: 12:47)



So, concentration of A in water requires reduction of volume. It is very difficult to reduce the volume of water because the only way to reduce volume of water is to evaporate it, but in the process of evaporation, some A will also go out and to evaporate at room temperature, to keep the rate of evaporation very low, it takes a long time and a lot more energy to evaporate water. So, therefore, it is convenient for people to do instead of doing evaporation, they do what is called as an extraction, solvent extraction, that is one way.

They would transfer the A from water to another medium which has a greater affinity for A. So the solubility of A in that or the partitioning of A into the solvent has to be much greater. So, solvent extraction, one of the methods available is called as a liquid-liquid extraction, in which we choose a solvent, we add to A plus water, we have some small amount of solvent and then we shake I, we equilibrate it. So, when we are doing an equilibration, what we get is the solvent now breaks up into small bubbles droplets and forms an emulsion and there is extraction happening.

So, from the water then transferred to this. So if you look at this here, what happening is this is the solvent and this is the water. Since the driving force is in this direction, thermodynamic equilibrium of the material is towards the solvent, they are not in equilibrium. So, therefore tries to go towards equilibrium and tries to get into the solvent. So, we will choose a solvent and our goal here is to also reduce the concentration which means that the volume of water and the volume of the solvent, the ratio of the volume of water to volume of solvent will give you essentially the concentration ratio.

How much you want the concentration. For example, if you take 1 liter of water and extract with the 20 ml of solvent, what you are essentially getting is 1000 ml of water divided by 20 ml solvent. You are getting a 50 times concentration theoretically. If all the amount of A that is present in the water gets into this thing you are getting 60 times. So, in order to do this, the selection of the solvent is such that the solvent has greater affinity for this chemical into A. So, the choice of solvent depends on that.

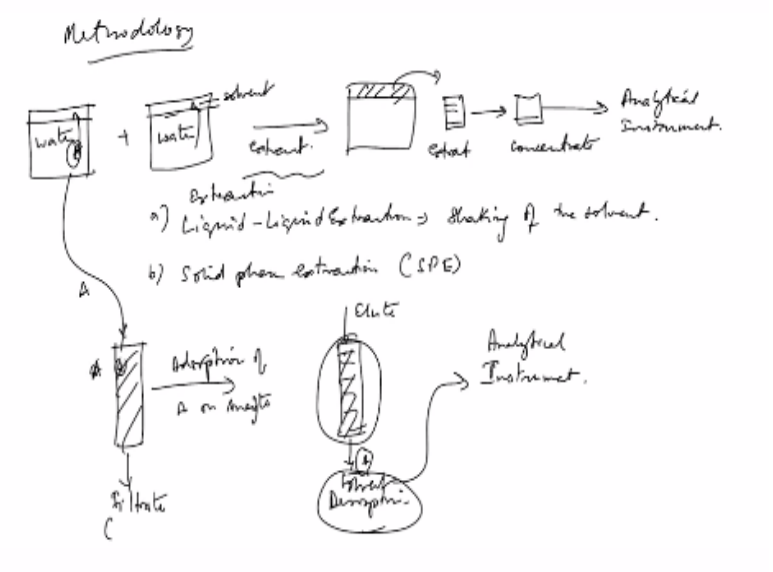
So, there are a large number of solvents. Also one of the main prerequisite of choice of solvent is the first prerequisite is that it should be, in other words, the partitioning constant of A from solvent water should be high, which means the concentration of A in a solvent to concentration of A in water should be high. So, at equilibriums, the A will prefer to go into the solvent more than just to remain in the water. So, that is one prerequisite. Second this they should be immiscible, should be immiscible with water largely.

We know that the immiscibility is a concept that is not in this context of solubility, immiscibility is not a good concept because there is always going to be some solubility of A, of the solvent in the water itself, but now we are looking at the bulk phase of the solvent to retrieve a lot of A that is present in the water. So, little bit of solution in 20 ml if 0.01 ml is dissolved in the water that does not matter, so we still have bulk of the solvent still as a solvent phase so immiscible in water.

The reason we wanted to be immiscible is that we want to separate it from the water that is the whole point. So once we separate it, we able to have concentrated this thing okay, that is one. The second thing that we should be able to do is already we are achieving a 50x concentration here. If you want to further concentrate it, I can, this should be amenable for further concentration. In order to do this, the solvent that is chosen you must be able to evaporate it slowly at least you know and volume reduction very easily.

So, this is the general idea behind bringing, when you are doing extraction you have to work backwards. You have to first start with the analytical instrument and find out what is the detection limit and find out if the instrument directly can handle the water, cannot handle it you have to extract it with the solvent and then figure out if after extraction if can still go directly, that cannot go directly it needs to be concentrated further and then introduced into the extraction. So, the methodology is the follows.

(Refer Slide Time: 19:01)



So you have a water sample. Now you add a solvent. You extract, then you transfer the extract into another bottle and then you concentrate it further and the analytical instrument. So these extraction methodology you can have various ways of doing it. One method of extraction is called as a liquid-liquid extraction where you add a solvent and then shake it and then you keep shaking it.

So, once you do this liquid-liquid extraction will depending on what is the analyte of interest, your solvents can change, and this information is available in the standard method. So, which analysts are you interested in therefore which kind of solvent should you use? The other kind of more recent one is called as solid phase extraction or solid phase the other variants of it. This is called SPE. Here, what is primarily done is the water sample is sent through an adsorbent bed.

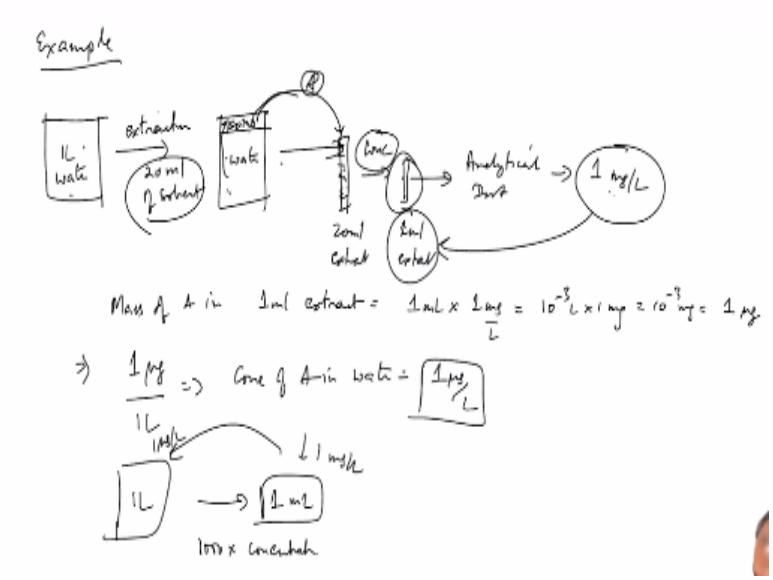
So, here the analyte A that is present in the water will now adsorb. The adsorption analyte and once the adsorption analyte is done all A that was originally present in the water has now moved to the analyte. So, it is similar to all the A that is present here as it is moving towards the solvent here, the same thing happens here. All the A that is present in the water is now present in the adsorbent small tube, adsorbent tube, but this adsorbent tube the only thing that has accomplished is that you are dealing with a large volume of water.

Now you have reduced the volume for a very small tube, but you cannot introduce this directly into analytical instrument. For that, you have to again elute the A from the column by a suitable

solvent and this solvent is doing desorption here and thus this solvent can now go to an instrument and in the process you can take this extract and concentrated further. So, it allows you the processing of very small volumes in the SPE and this is less messy than the liquid-liquid extract.

Liquid-liquid extract involves the physical operation between 2 liquids and separation of that can result in loss of sample. The SPE is a little more easy to handle. However, SPE requires you to buy this, the infrastructure is higher you need to buy this tube which are usually non-reusable. Then you have to buy a pump and the associated setup to do all these things. and

(Refer Slide Time: 23:20)



So, I will do a small example here in terms of what we are looking at and what this means here. So let us say that I have one liter of water. I am extracting using 20 ml of solvent and so I get 20 ml. So I remove all the 20 ml, assuming I remove all 20 ml. So let us assume that for the time being. Sometimes it is not possible to get all the time 20 ml okay. So, I remove all the 20 ml and then reduce it further to 1 ml. So, this is 20 ml of extract and this is 1 ml of extract and this 1 ml I introduce into analytical instrument and I get a concentration of 1 milligram per liter.

The analytical instrument gives out a concentration based on the calibration and all that. It gives a value of this. Now, this one is not the concentration of A in the water sample, it is the concentration of A in this sample. So, what we have done is we have done a concentration step here and an extraction step here okay. The 2 things have happened to analyte. All the analyte

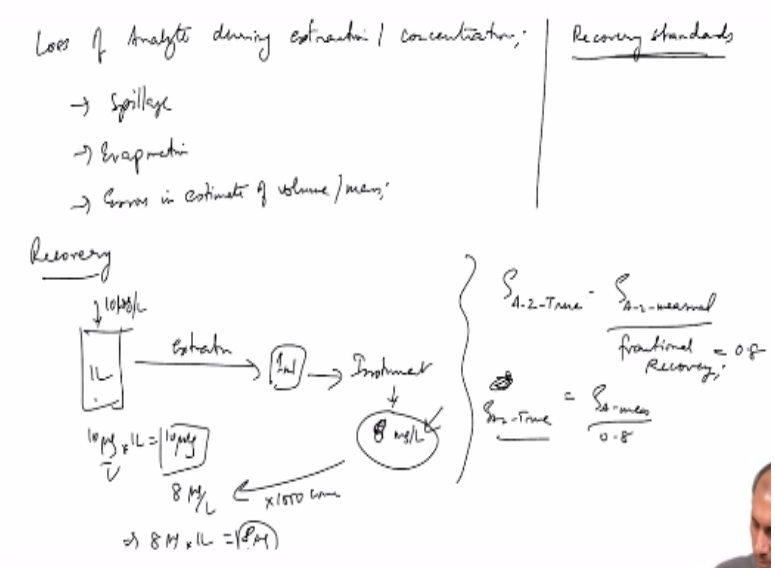
that was present in the water has now gone through this solvent and is now present in 20 ml. This 20 ml is further concentrated into 1 ml okay.

So, this 1 milligram per liter corresponds to this one okay, which means this concentration, so the mass of A in 1 ml extract is 1 ml into 1 milligram per liter. This 1 ml is 10 raised to -3 liters into 1 milligram, so 10 raised to -3 milligram, which is 1 microgram. So what this means is that I have extracted and analyzed and the total extract that I have here is 1 microgram, so this 1 microgram is what is present here also. So we are taking the 1 microgram and transferring it everywhere.

So, there is no change in this 1 microgram. So, this 1 microgram is what we have extracted. So, this 1 microgram is present here, which means the same amount is present here, same amount is present here, and the same amount is present here. So, effectively what we are saying is you have 1 microgram present in 1 liter of water. So the concentration of A in water is 1 microgram per liter. So, it is very clear right, 1 microgram per liter because this is a calculation we do.

What we have essentially done is we have taken whatever A is present in 1 liter and we have transferred it to 1 ml, this is 1000 times concentration, which means if I get a value of 1 milligram per liter here, we have to divide it by 1000 times, so which makes it 1 microgram per liter. So, this is an illustration of the calculation that we do in order to measure the concentration of chemical in water due to extraction.

(Refer Slide Time: 27:31)



One of the things you have to understand that during the extraction, there are so many of these steps that are present here that there is always a possibility of loss of analyte during different processes, during extraction, during concentration and these losses mainly occur because of either say things like spillage, it can occur because of evaporation or errors in estimate of volume, mass etc. So, in order to do this, we need to do what is called as a recovery.

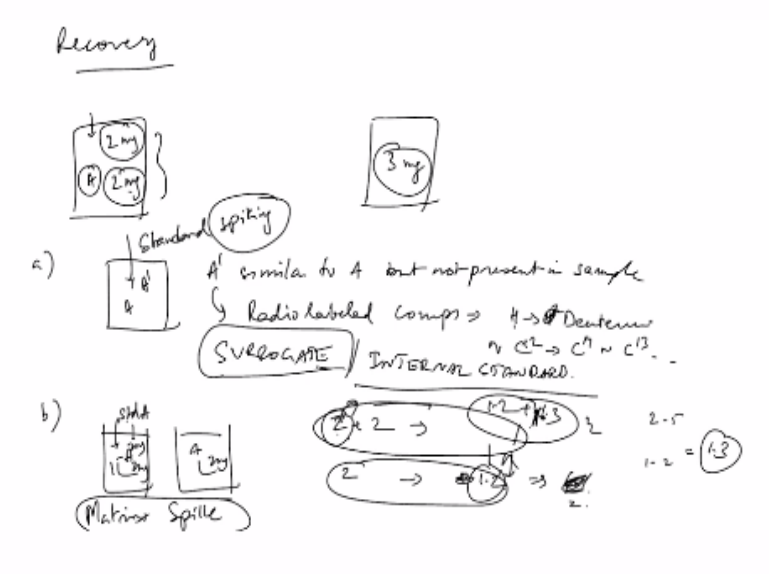
So recovery is usually done by taking a known analyte and putting it into a sample and taking it through the entire process and finding out how much you have recovered. So, for example, if I take 1 liter and if I add 10 micrograms per liter here, which means that I have added 10 micrograms, 10 micrograms per liter into 1 liter is 10 micrograms, and I go through the extraction and finally I get 1 ml and this 1 ml I analyze it into the instrument and I get 8 milligrams per liter or 8 ppm.

So from the previous example what we have done is it is an 8 milligram per liter in the instrument corresponds to a factor of 1000, this is concentration. So we have to divide by 1000. So here it becomes 8 micrograms per liter, which means that 8 micrograms per liter into 1 liter is 8 micrograms. What it means? You have added 10 micrograms, I only recovering 8 micrograms, so it means 2 micrograms has lost somewhere. So this number that you are getting is smaller than the actual concentration that would have existed here.

Therefore, the true is A2 measured divided by fractional recovery. Fractional recovery in this case or in other words, the fractional recovery is found out from adding a standard from a known amount. The fraction recovery in this case is 0.8. So therefore, the true A measured divided by 0.8 will give you the rho A true value. So, the standards that we use for recovery you can either use an analytical standard in water and run it.

You can make an analytical standard yourself and run it or you can buy the standard, its known concentrations and add a certain constant volume of that in order to get this. So essentially, one must know what is the mass that you' are adding into the system, but the problem is sometimes when we are doing this recovery, we can do it with clean water.

(Refer Slide Time: 31:16)



So one of the problems in doing this recovery is that if you do it in the lab, I am doing a recovery for a particular analyte, which means that it would be useful if I use that analyte for the recovery estimation. So I can use an analyte, but I cannot use it in the water sample that I am actually bringing commercially because I do not know how much of A is there in that sample. So I need to do this you know clean sample, but one of the problems in doing in clean water sample is what is called as matrix interference.

In the process of the extraction and analysis, sometimes the matrix, the water sample that I am bringing from a lake or a river, they have certain characteristics that will influence the analysis and then analysis may be different from if you are doing the same recovery using distilled water or some clean water sample. So in order to do this, they would like to use a recovery, they would like to make the recovery from the actual field sample okay, but there is a problem. In actual field sample, there is some amount of A already there.

So if you add standard of A again, you do not know how much original A was there and you do not know how much you are going to be recovering, okay. So let us say that there is already 2 milligrams sitting in the water and you are adding 2 more milligrams and what you are getting. Let us say you get 3 milligrams. I know only about this 2 milligrams and I get 3 milligrams here, which means there is a problem. I do not know what this is, this 3 milligram where is it coming from? I do not know how much of that is coming from here and how much of it is coming from here, okay.

So, there is a problem here. In order to circumvent this, one approach, the first approach is we add something which is not A. You add some other chemical called A prime which is very similar to A but is not present in water okay. So, A prime is similar to A, but not present in water. So, typically these are radiolabeled compounds, where in the compound one H is replaced by deuterium or C12 is replaced by C14 or C13 or some such thing. It is radiolabeled isotope, it is not present in the in the actual sample but it will show up in the this thing

So, you can calculate the recoveries based on this compound similar, so this is called as a surrogate, sometimes is also called as an internal standard. There is a subtle difference between the two, but if you are doing calibration with this, then you can use it as internal standard. In some sense yeah it is an internal standard because this is something that is known, anything that is known can be given the label of a standard as long as it is provable, traceable. So the surrogate is added to the system and then tries to mimic the behavior of your actual analyte of interest okay.

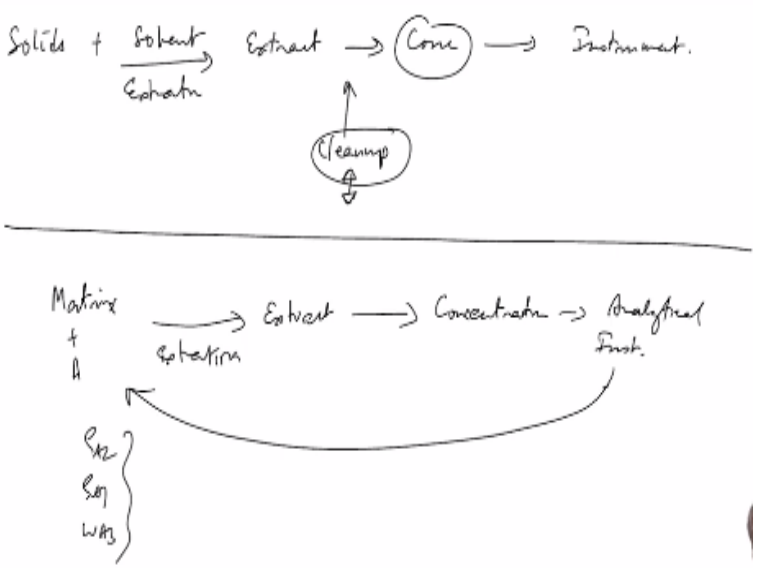
The second thing is the surrogates are very expensive to buy. What people also do is they take two samples instead of one. They take one liter sample, another liter sample into this, it has already has some A, they add some standard of A and in which in the second one they do not add anything, okay. So let us say that there is 2 mg here already and they add 2 mg here, there is 2 mg here and they do not add anything. They extract both of them, and the first one, this is 2 + 2 gives you 3, this is 2 it gives you 1.2 okay, let us say 3.5 and this gives 1.2 or some such value.

So, from here I can guess that, so this is giving only 1.2 which means that there is 60% efficiency of this. S what they will do is the difference between these two, so the first one also should be 1.2, the second one should give me, it cannot be 3.5, it has to be less than this. This is giving 1.2, then the other one should be less than some 4 value, a value of 4. So, say it is 1.3 okay. So they use the difference between these two, the difference between these 2.5 -1.2 is 1.3. This 1.3 is what is out of 2 that you are added externally, 1.3 is recoverable.

So, it means that there is 70% recovery on the basis of this. So, this process is called as a standard spiking. This is called as a matrix spike. The split matrix spike, you split the matrix and you spike one of them in order to do this. So, in implicit all of this you see is the use of

standards. The standards are very important in this kind of behavior, in this kind of analysis tool. So, the same thing applies to solids also.

(Refer Slide Time: 37:04)



When you are extracting solids plus solvent in extraction method and then you do a concentration. You have an extract and then you will do a concentration and the instrument. Typically, in solid for example, you are using soil, there is a lot of other things that will come when you extract using a solvent. Therefore, before you go to the step of concentration, there is another step here that is called as Cleanup. It is to remove any material that can act as an interference in the analysis, predominantly this includes colloidal particles, they are not concerned with the chemical at all.

Sometimes they may adsorb a lot of this chemical here, so that is one thing, but you are interested in a solid, so it should have extracted everything from the soil, but it does cause some damage to the instruments. Therefore, they try to remove it before, so this is cleanup. The procedure for cleanup that are available in the standard methods that will be discussed in the course work. So this is the summary of this thing. So, in all of these, some of this will be reiterated again and again in the methods again.

So it is you have a matrix, you extract, this is a process and then analysis for the calculation you go back in this manner, reverse direction to find out how much mass is that you have recovered and analyzed divided by the total volume of the matrix or mass of matrix to get the concentration number to get, either rho A2 or rho A1 or WA3 three. So the mechanics are different, but the principle behind this is all the same. Thank you.