Environmental Quality: Monitoring and Analysis
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Lecture – 12
Environmental Sampling

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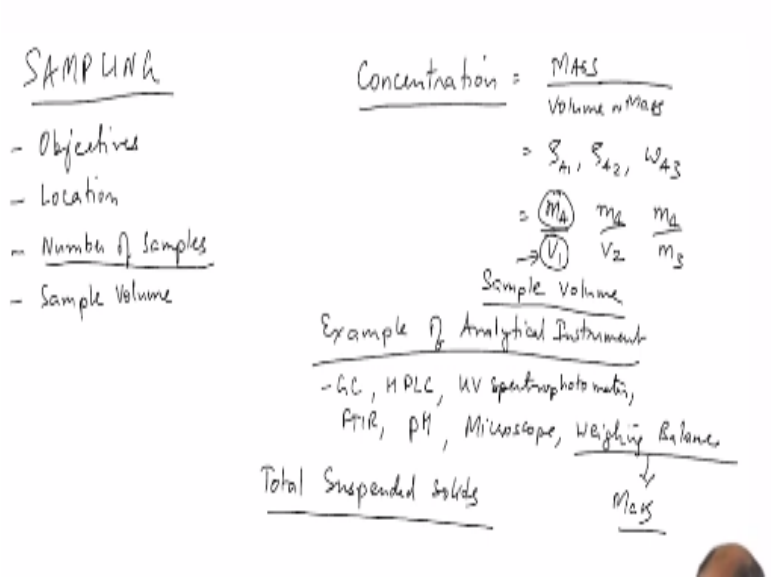

So, we will continue with our discussion on sampling. So, last class we talked about sampling and the objectives of sampling, different objectives that we can think of. So, one of the things we had discussed is in terms of location is the sampling objectives. You need sampling objectives and this objectives based on objectives, we can do a sample location, where do you want to sample, what do you want to sample, okay, right, ok So, the next question that you will have and there's also number of samples and all that. So, number of samples.

So what is the definition of sample? So we discussed that definition of a sample is a quantity, it is amount. So what is our goal of sampling? So, our goal of sampling is eventually we would like to get some measure of concentration. This is our goal, concentration. Concentration means concentration is mass by volume or mass. It is a mass fraction or a mass concentration. So, it is either you are talking about rho A1, you are talking about rho A 2 two or you are talking about WA3. These are the things that we are interested in measuring eventually.

So, you are interested in getting mass over some volume of air, this is mass over some volume of water, and this is mass over some volume of solid, yeah. So, if we want to get this, this is the information we want, we need this and this. So, this brings us, this denominator here is what we would call as the sampling volume, the sample volume, we will come back to this in a minute after this discussion. We will come back to number of samples a little later because it relates to something else. Sample volume, yeah.

Let me take an example of one of the analysis methods. So I have to give you an example of one of the analysis method before we go on with this. So, what we mean by sample volume, ok. What is the analytical instrument you are all familiar with? You can just name some and I will pick, what is the most commonly known analytical instrument? Example of an analytical instrument. GC. GC How many of you know what a GC is here, please raise your hands, okay.

Next. HPLC. How many of you know what an HPLC is? Okay, less than half, how many, anything more? From high school you have done lot of analytical instruments. UV, UV what UV? UV spectrometer. How many of you know what a UV spectrometer is? More number of people, but not all, okay. Turbidity meter, ah? turbidity meter. How many of you have seen turbidity meter? Six people. Next, anything? FTIR. Start from high school? Start from high school? Ah? FTIR, How many of you have heard of FTIR? Six people?

Anything you have used from high school, what is the uh? pH meter Okay. Then, something more. Burette and pipette. Burette and pipette is not analytical instrument; it is a handling instrument. Microscope, microscope, okay. Weighing balance weighing balance. How many of you have used a weighing balance? How many of you have used weighing balance? please honestly raise your hands, then if you do not raise your hands, we will ask you to go back. All of you have used weighing balance, hopefully somewhere, weighing balance.

So, we will start with weighing balance, okay. It measures mass. Weighing balance measures mass, okay. Now, let us say that we will do a simple measurement of total suspended solids. So, I have to I will describe you what the total suspended solids method is and then based on this example, I will explain what we mean by, what we are trying to discuss here okay. So, we will go to the next page next page.

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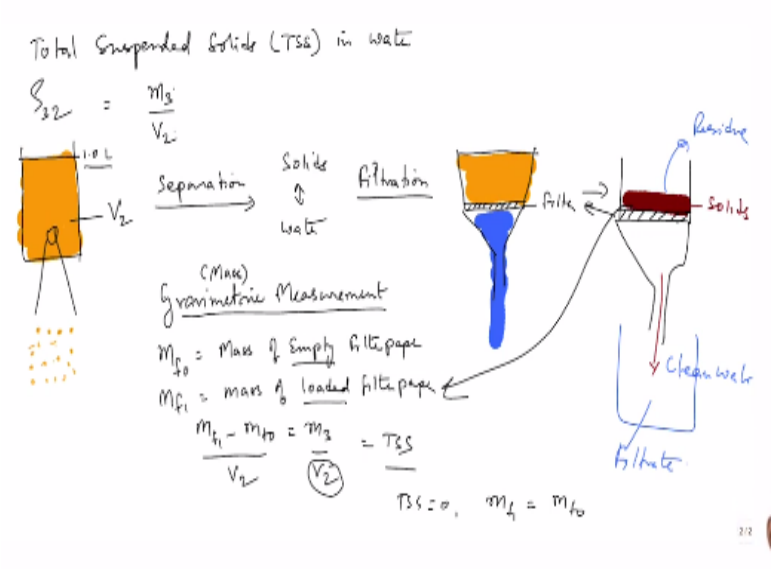

We will do total suspended solids in water. So what we are measuring really is Rho 32. We are measuring solids in water, we are not measuring chemical concentration, we are measuring solids concentration in water. So it is like this. You take a water sample. The water sample looks muddy, okay. It looks muddy, then you know that something is there in the water sample, yeah. So, in order to measure the amount of this thing, so what we are actually measuring is m3 by volume of 2, this is our measurement.

So we would like to measure the solids that are suspended in this water sample, yeah. So, what is the simplest way to do this? You simply want to measure mass over volume. So what are 2 measurements we need? One is the volume of this water. So, I can take a water sample, I can measure. If this says 1 liter, let us say 1 liter, I can fill up this water to 1 liter and I know that this is 1 liter, I know the volume, right. Let us assume that we know it is 1 liter okay, and then how do I measure the mass that is contained in this 1 liter?

This is suspended, which means that, you know, if you take a snapshot of this, it will look like this, it will look like this. The mass is all suspended in the water. So, what do I need to do in order to measure the solids, suspended solids? Yeah, I need to filter filter. What am I doing when I am filtering? Separating the sollids from the liquids. So I am separating, this is the separation of the solids from the water. I'm separating solid from water, I can do it in different ways, okay. The simplest way in which is done is by filtration.

What we do by filtration is I take a filter, I need to trap these particles physically, I need to contain them physically using a filter, some kind of a device straining and here I put the water

and what I get here will be clean water. So, which means that at this point when the filtration is done, what will happen is on top of the filter, I will see some thick layer of some thick layer of solids that are trapped and the clean water that is collected. So, this is what we call as a residue and this is the filtrate, yeah. Now, how do I measure the amount of solids here.

I have separated it and the solids that are collected on the filter paper, I can I have to measure it. Now, I measure it using weighing balance. I do what is called as a gravimetric measurement. When we say gravimetric measurement, it is mass measurement. We use a physical we use a balance, weighing balance to do it. So, here what we do is there is a filter paper, the filter paper that is on the thing. So, the mass m3, we will write as m0 is mass of an empty filter paper. So, this is the empty filter paper.

Before we start the filtration, the filter paper has a weight, is empty filter paper, and once we finish, so this is a loaded filter paper. So, mf1 - mf0 should give you m3 that is there divided by the volume of water will give you the total suspended solids. This is simple a very simple assessment of it. Now, how is this related to sample volume because there is a certain amount of suspended solids concentration in this in the water. If I take a water sample that does not look brown, that not look even like yellow, can I say that there are no suspended solids in it by this method, I mean I cannot say it unless I do this method, okay.

So, if I take 1 liter of water okay, what is the condition under which I can make this measurement using this method I have described? There is a condition. There is an assumption or condition under which this will work. Is it possible that I get a value of total suspended solids as 0? Yeah. When? Pure water sample. No, no, when? Based on experiment when? Pure water and all you don't know it's pure. When? So, when the TSS is 0 when mf1 is the same as mf0, but when this happens, can I absolutely be sure, can I say with 100% certainty that there are no solids in the water. Not sure.

Why? Dissolved within, it is lighter. No we are not talking about it, we are only talking about suspended solids. Sir, there can be particles which are smaller to the diameter of the filter. That is one. One possibility is that the filter is not trapped all the particles that it has gone through. Let us relax that assumption, let us say filter is the best filter you can get for all particles that you can think of and it will stop it but that's a one of the points. What other

reason can there be when you get a 0 reading but you are not really sure that its actually TSS is 0. Initial measurement is wrong or error.

Let us assume that's all not true, no errors, no errors in measurement. The filter is nice. What do you know about balances? This has to do with balance, the weighing balance.

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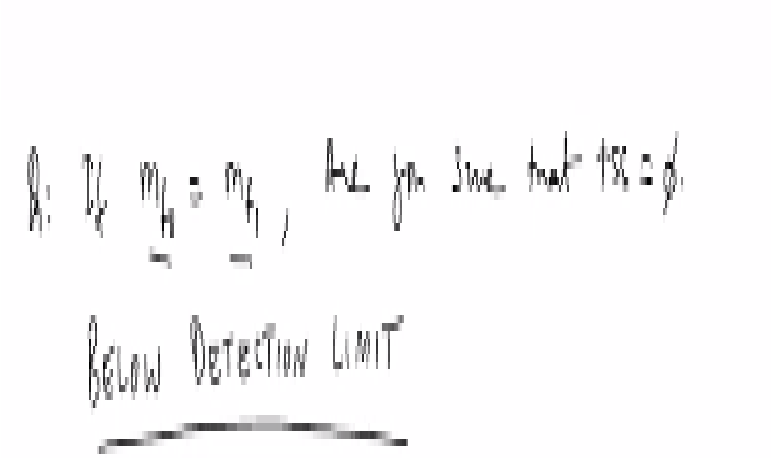

The question that we are posing is if mf0 is the same as mf1, are you sure that TSS is 0, This mf0 and mf1 being equal, which means there is no there is no change in weight that is registered that is the true statement, yeah. What does that mean? I am giving you another example. You look here. Are you seeing, you see this room? You are able to see the screen here. Do you see anything in between? No, does it mean there is nothing in between? How do you know there is something in between?

Are there any particles in between there? How do you know? Can you see it now? You cannot see it. You cannot prove it, but how do you know it is there. So, what is the meaning of that? Below detectable range. You cannot detect with whatever you are doing right now, but you can detect it with another method. So, what this means is that it is it is not 0, it is below detection limit, this is the accurate term for analysis, chemical analysis, any analysis, you are not allowed to use the word zero, it's a very philosophical things sometimes but you cannot see it, that is all.

It does not mean that it is not there, which is true for a lot of measurements people make. It is true for this PM10, PM2.5 and all that. People did not know there is something called PM10,

PM2.5 or nanoparticles until they had the tools to see it, okay. So it is the accurate statement is below detection limit, maybe it is there, maybe it is not there that we don't know. It's not there. So it is below detection limit. So coming back to this below detection limit, how many of you have, what kind of balances have you used? Weighing balance? Have you used this digital balance, a four digit balance?

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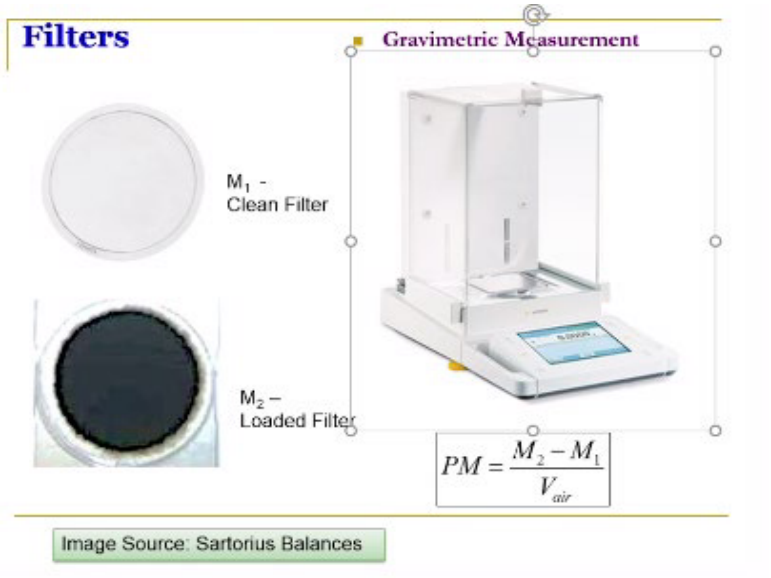

This is a four digit balance, okay. This is what a filter looks when it is clean and when it is dirty. This four digit balance if you look at it here, I don't know if you can see it clearly and we will try to expand it. So you can see something here, 0.0000 grams, it says 0.0000 grams. So this is 0.1. The last digit is 0.1 milligrams, yeah. On top here, somewhere you will see something written. What you will see is the range of this instrument it says 50 grams to 0.00001 grams, 0.1 milligrams.

So if anything is there below 0.1 milligrams, you will not see it, it will register as 0, okay. So, that is similar to what we would call as close to detection limits, it is not it is not necessarily the detection limit, what they write there is not a detection limit, what they write there is what they are able to register. Detection limit has a bigger meaning, we will come to that in a minute, but the instrument has a range in which it can operate okay, if it is below that range, you cannot see it.

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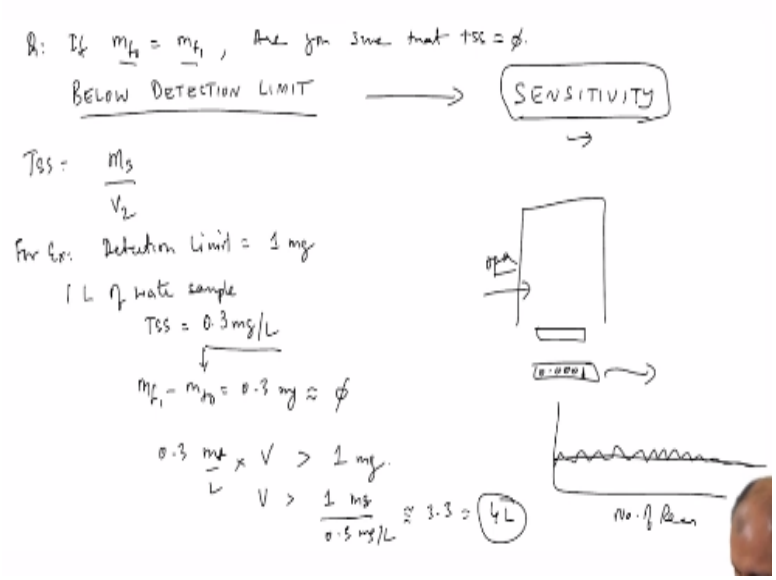

So, what do we do in our example, coming back to our example, if you are not able to see a difference, what can you do to check if there is a difference. So, our TSS is m3 by V2, yeah. Let us say for example, let us say that the detection limit for a gravimetric balance, for a weighing balance is 1 milligram, this is below it, it cannot measure. The minimum it can measure is 1 milligram, right. Now I take 1 liter of water sample with a TSS of 0.5 milligram per liter. I am not going to see anything in the balance.

My balance, let me say to be very clear, I will put it as 0.3. Sometimes this 0.5 will fluctuate and show up as 1, that we do not want that, we'll use 0.3. I know this through some other methods, I have analyzed it, but if I put this I filter 1 liter in a filter paper and I put the filter paper, I am going to register a weight difference mf1 minus mf0 is going to be 0.3 milligrams because I am using 1 liter of water sample. So in the instrument, I am going to be seeing 0, instrument will say 0, it is below the detection limit of the instrument.

If I want to be if I don't have any other instrument to measure this, what can I do? what can I do? Increase the volume. So, I can increase this volume, this 0.3. If I want to increase say 0.3 milligrams per liter multiplied by volume, it must be greater than the detection limit, in this case it is 1 milligram. So, I can say my volume must be greater than 1 milligram divided by 0.3 milligrams per liter. So, it is at least around 3.3 liters or something. So, I will use I have to use at least 4 liters in order to see something in this.

So, the sample volume that you collect is related to the concentration that you expect to see in the sample and the detection limit of the instrument you have at your disposal. Is there

another word, is there another word for detection limit? detection limit, there is something called this is detection limit, what is the commonly used term to represent the capacity or capability of an instrument to detect. So, what would you like in an instrument, a good instrument you would like to have higher detection limit or low detection limit?

Lower. Lower, you must be able to go as low as possible, yeah. So, what is that feature of an instrument called? Least count. Ah? Precision. No. Accuracy. No. Sensitivity. It is called sensitivity. The instrument is very sensitive means small changes it can be grab, the more sensitive it is, it will respond to a very small changes in whatever is the stimulus you put on it okay. It does not matter how the instrument works.

Most physical balances do not measure actual mass, they measure some pressure and that pressure is converted some voltage or something, all of them are like that okay, except the balance that you have in old vegetable shop, they will put one weight one standard weight on one side, the other one other side, they will balance and then they will see, even there the sensitivity is the middle thing where it is moving, it has to be in the middle somewhere, all that is there. So, all digital balances are based on pressure transducer where it measure the pressure.

The more sensitive that pressure devices, the more sensitive the weight measurement can be, so which means that it will also, we will come to that in a minute. This feature of sensitivity when you see sensitivity, when you look at instruments listing characteristics, specifications, you will see sensitivity and it is listed as a lowest concentration. The lowest theoretical concentration that the instrument can measure will be listed there. So, in the case of the balance is 0.00001 grams. It can detect 0.00001 grams okay.

Whether it is useful to you or not is a different question, okay, but somebody has tested and say this is the minimum it can actually give you a sensitive reading, some reading, okay. How many of you have used a digital balance for your properly for your work? Few of you have used it, yeah. What is other thing that you observe in balance like this? When you put a sample, what do you do? What is the procedure that you follow? You make it 0, then you put your sample, and then how long does it take for you to get a reading. Hmm.

Many of you said you close this thing. So, there is a door here okay. This is a sample. This part here what we are talking about, here is the sample plate, okay. So there is a door here. Why do you close the door? You have seen lot of balances right. Outside we have this big large, in railway stations or someplace you have a big weighing balance, people take 50 kilos of this thing and put it on it, it is not closed balance, it is open, so what is the reason, why are you closing it? More sensitivity?

More sensitivity, no, sensitivity is sensitivity right. I put a gram or piece of dust it will also it is supposed to weight, it will weight, but what is the problem? What do you observe if you do not keep the door closed? So this is the balance, right? This is your weighing plate, yeah. If the door is open if the door is open, what do you observe in the reading? Fluctuations. It fluctuates yeah, it fluctuates. How will it fluctuate? Where will it fluctuate? Last digit. Most of the times it will fluctuate in the last digit.

So it will be 0.0001234 210 213 1234. What do you do? You close the door. If still fluctuating, then what do you do? This last digit is useless because it is fluctuating. So if I track the signal, if I take if I connect this to say to a computer or if I have some student who is sitting there and who has photographic memory and who keeps reading out the numbers as they are appearing and somebody is writing them down and they are plotting, they plotted the number of readings, it will keep going like this, yeah.

From this kind of reading, what will you, how can you infer anything? What will be the number that is useful to you? Average. The average. Yeah, that is enough. Suppose I do not put, before you are going to 0, you said you will zero the instrument right? Yeah. You have not even put your sample, you have just let the thing instrument on and it is fluctuating. If you put it as 0, it will go to -1.1, 2, -2, -2, +2, -2, +2, it will fluctuate there also, yeah.

So, I put a sample, it is still fluctuating. How do I know that I have put the sample? Whether it is actually showing the signal or not? You are understanding my question? It is fluctuating and then I put a sample, it is still fluctuate, I am unable to determine.

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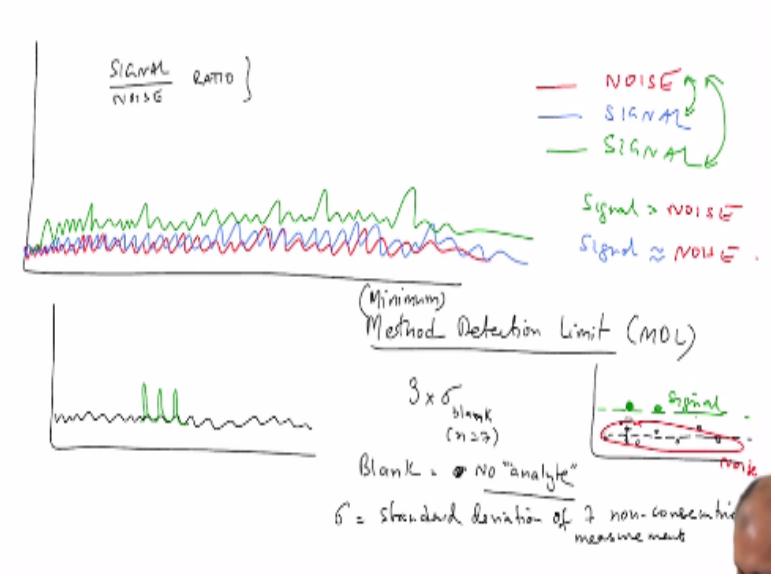

So let me give you, I have nothing on my sample. I am getting this reading. This is the kind of signal I am getting, right. Now I put my sample, yeah. Suppose I get a signal like this, reading like this. Can I make any sense out of this? Just looking at it, you know that you have put a sample, you know there is something on it, I can see something, but I am not able to see any reading. I know that it has. What is the problem? In the calibration, no we are not there yet. That is the next question, but here, what is the problem here? Can I make any sense out of this?

No. Delay in measurement. No delay in measurement. It has to do with the measurement itself, the magnitude of the measurement, still related to detection limit only okay. Now, when will you consider, suppose I have I I have another sample which looks like this, which let me write it in green color. Is there a difference between this green one and the red one and the blue one? The blue and red you cannot differentiate very clearly this is we are not able to find out whether if it is, what is the red? what is the red? What you call the red? Is there a term for this red signal?

There is no sample, instrument is fluctuating, giving you some reading. It is not zero line, it is called as, the red part the red is called as noise. The blue is a signal, the green is also a signal, but in the red and this two, I cannot differentiate between the signal and the noise, it is very close to each other. In this case, I am able to differentiate between the signal and noise. This signal in the green is much significantly greater than the noise. This signal in the blue I am not sure, but almost the same as the noise.

This is where we have this term called as the signal to noise ratio. So what this means is that is the following. So if you take a simple signal, if you have if this is a noise, if there is some signal that goes well above that, I am distinctly I'm able to verify that it is greater than. So, there is a statistical method to find this out. So, what is this? When you have signal like this, it is a distribution, you have a large distribution of signals, large number, and you have another distribution of noise.

The statistical question that you asked here is you do what is called as the hypothesis test. How many of you have done statistics? Statistical hypothesis testing, you have heard of hypothesis testing? No, you will not do it in depth, but go and read about it. We will verify if this distribution, signal numbers that you are getting is different significantly different than the noise. So, statistically when you do this, it turns out that people consider, you can make your own choice, you can decide that if the signal and noise are this much 10% apart.

I will consider it as signal, but your uncertainty is very high. People ask you is there really a signal, you cannot really say yes, surely. So, your certainty about the separation of noise signal must be really good, okay, that you are reasonably confident that this is the signal and this is not the noise. What we mean is that we are actually seeing some value of the mass and we are not just seeing noise, okay. Otherwise what will happen? You will get a wrong reading, maybe it is below detection limit, but you are assuming that it is near detection limit, you will report a higher mass or something like that, that's that's a problem.

So, the signal to noise ratio, the general assumption this this gives you rise to a term which is called as a method detection limit. This is called as method detection limit because it is not specific to the instrument, it is specific to the way you are doing your measurement. For example, if I keep a filter paper which is empty, that is my base measurement and if I keep a filter paper which is loaded that is also that's a signal measurement, right? The noise measurement and signal measurement, the difference between these two is what I am interested in.

So, it is related to my method, the way I am doing it. It is not the instrument supposed to give me 0.1 milligrams that is what is called an instrument detection limit, but the instrument detection limit is useless in many cases because we are not going to go there, we are always doing something else. We are doing we are not working there, what we are now, we are not

saying that it is the difference, what we are saying is the actual measurement itself, what we are saying is it is related to this noise some fluctuation is happening and that is a different thing than what is the lowest or the least count.

So the method detection limit is is defined as 3, this 3 number is is a statistical test, test statistics, it is a T test, I don't want to give you details now, it's a T test with 95% certainty or something. So it is 3 multiplied by sigma, which is the standard deviation of what is called as a blank, which is n equal 7. What it means is it is the standard deviation of 7 nonconsecutive blank values, blank means there is nothing, no sample is there. This comes to our definition of what is a blank, okay. A blank, as a name suggests, is something there is no analyte.

The term analyte is a reserved keyword for whatever you are measuring. In this case, you are measuring the solid that is the analyte, yeah that is the analyte. So the no analyte is a keyword. So a blank is something which does not have the analyte. There are different kinds of blanks, we will talk about that in a minute. So it is a blank. In this case, the blank here will be an empty filter paper. You are taking a filter paper out of a box, it is not exposed to air, you keep, it will show some reading yeah.

You take it out, after some time switch on the balance again, put it again, it will show some reading. You do it 7 times. Nonconsecutive times means the instrument may not give you the same reading each time, that is the other reason why we are doing it. This is also the fluctuation of the instrument, so it is a noise that is generated by the instrument for various reasons. The reasons could be all kinds of things, voltage fluctuations or the instrument is not working properly anything.

So, the this is sigma is the standard deviation of 7 nonconsecutive measurements of a blank. What this means is that when you do 7 nonconsecutive measurements, you are probably getting something like this. You will get one reading, second reading, third reading, fourth reading, fifth reading, sixth readings, seventh readings, you are getting a fluctuation. The standard deviation, this is the average approximately, the standard deviation is some measure of the spread. Now, we are going 3 times above this spread. So we are taking if this is a spread, second, third.

Only if you have a signal that is somewhere here, around here we are taking that as the signal, this is a significantly away from the noise. This is all the noise. These are these measurements are all the noise and this we consider as the signal, okay, clear. So, you have to measure the method detection limit for every instrument and every analyte. Whenever you are you set out to do an analysis method, the first information you need to know is the minimum detection limit or this is method detection or minimum detection all of them you can use both of these minimum detection limit, but it is it is strictly speaking the method detection limit because minimum does not mean anything, it is it's an undefined, it is a very vaguely defined term. Method detection limit is more specific. So as we are going to be doing a lot of methods, each one of them will have a different detection limit, so what is relevant to your measurement that's all, okay. Because we are not going to be sometimes we are going to be putting it on a filter paper, sometimes we will be putting it on something else, sometimes we may doing you know there is various ways of doing it.

And all of these have different ways of manifesting themselves in the in the instrument. So, the method detection limit or based on this kind of analysis must be done, the signal to noise ratio has to be done in order to do this. So, 2 things we have summarized here. If we go back to our original thing. Yeah, now, the sample volume is based on the detection limit, the method detection limit of your measurement, yeah. So, how much volume you need to take depends on what is the instrument you are using first of all. So, the instrument selection has to come upfront at this point, the sample volumes we will go back to will go to a new page.

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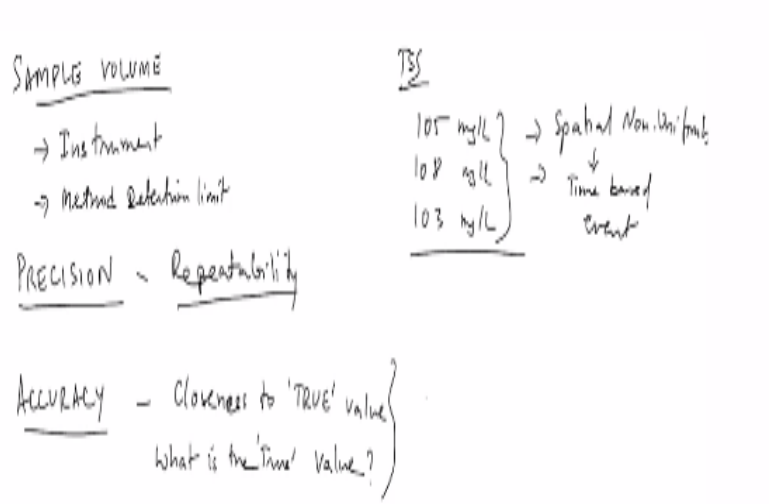

So will the factors determining you have to choose the instrument, you have to select the instrument, then you select sample volume, yeah. So, when we do different analytical methods, you will see the simple example we talked about, TSS applies there in all. The instrument we are using is not a gravimetry, it is not balance, but it would be other things, but the same thing applies for that also okay. So, the sample volume is determined by these these kinds of things, instrument, you have to select the instrument first upfront.

Which means you must know what are the instruments capable of doing it? Okay. So we come to the next question. We have about five minutes left, we will start this question. There is another term, some of you already mentioned it in today's class called as precision. What is precision? There is another term used in conjunction with this precision. So when you take a measurement, there are 2 things people are always talking about. One is precision, other one is accuracy. Accuracy. What is the difference between these 2, precision and accuracy?

What is precision? What is precision? What is accuracy? We will go to the easier answer, accuracy. How close to actual value. Yeah, accuracy is closeness to what we call as true value. Is this an easy question to answer? What is a true value? Your next question is what is the true value? Why are we worried about this this closeness to true values is I think the crux of all measurements is a value that you are giving. The people are asking always asking is it true or not, no?

So, then how will you prove it, you have to prove it. You have to prove that your value is as close as possible to, the reason I use the word as close as possible to true value is for the reason we discussed in the previous slide is that you cannot get a single value, you are always going to get a range of values based on the what of the instrument? Precision. Precision of the instrument. The instrument will not give you the same reading every time you go. It will give you a range of values.

So every time you open a balance you keep, it will give you one value, you open and keep it again, it will give you another value, ideally 0. Precision should be very good, it’s the same, but precision is not, if instrument is not very precise it will give you a range of values for various reasons, okay. It relates to the instrument range instrument works, okay. So precision is what we call as repeatability, repeatability of a sample. For example, if I am taking a water sample, I measure TSS. I do once, I do it again, what is the value I get? Maybe different.

Third time I do I get a different value. So I make TSS measurements, I sent 3 of you to make TSS measurements, right. One of you get some measurement of 105 milligrams per liter, the other one gets 108 milligrams per liter, the other one gets 103 milligrams per liter. What is the meaning of this? Somebody is all reporting 3 different values from, this is not an easy question to answer. This is where I think you have to take the entire system into account. I have a lake. All of you are taking samples from that. Lake is a big thing, let us say well let us say well. I have a well.

You go dip, put a bucket down, get some water, or put a pump, get some water. First sample 105, second sample 108, third sample 103. What does it mean? Is something wrong with the instrument? You don't know. What could be wrong? What could be the reason for this kind of measurements? Different samples. We have different samples. What does it mean by different samples? The amount of, you are right, yeah. The amount. What does it mean when different samples? What do you mean by different samples? You have same well I am taking water from. So there is another piece of information that is missing. May be location or timescale. Timescale. How far is the time and location? Both are important, okay. So I chose well because well is small.

If I say a river, river definitely it is moving. If I take sample every 5 minutes, I am not sampling the same thing, I am sampling something which is coming from upstream, I do not know what happened upstream, somebody just threw a bucket of mud in that 5 minutes between 2 samples. So, one of them is larger than the other, all these are possible. It is not 100% uniform. It is not uniform, spatial variability is there for some reason and you have only partial information here, you only have this thing.

Third reason could be, what could be the third reason? You have spatial non-uniformity, this is one because of some time based event happening, something is happening in the timescale you are taking samples. Suppose I take 3 samples simultaneously. 3 of you are standing there, all 3 of you dip free your sampler into it and take it at the same time. There is no time based event. It just it just represents spatial this thing.

It could represent spatial non-uniformity or it could represent that the instrument the method you are doing, the instrument itself is like that where it does not measure, there is this much

of fluctuation always there. How can you check if that fluctuation is really from the instrument or from the sample? This is a matter of precision, repeatability of a particular sample. So, how do you establish that this is not coming from the system and it is coming from the analytical instrument?

Get the same sample. Now, how do you get the same sample? This is ostensibly the same sample right, but you are not sure. By taking from the well, I am not sure that it is the same sample, we have all the reasons you have mentioned. So, what we will you do now? Blank, no, we do not need a blank, we need a sample. We need something in the analyte. Take more volume and divide it into three. So, that is where this comes into question, the accuracy.