Environmental Quality: Monitoring and Analysis
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Lecture – 18
Tutorial Continued

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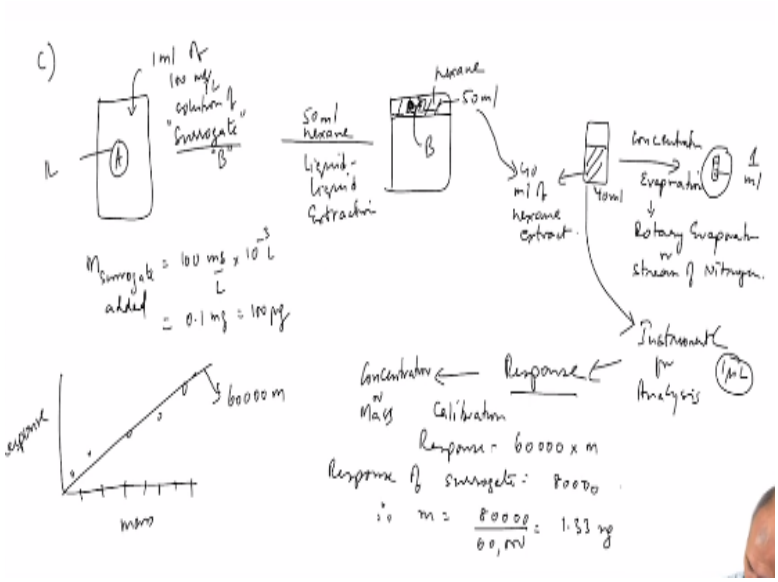

So problem C relates to, you have a sample, 1 liter. To this, we are adding 1 ml of 100 milligram solution of a surrogate. So, on Friday's class we discussed what a surrogate is? The surrogate is a compound that likely to behave like the analyte of interest. So A is analyte of interest that we are interested in finding concentration of. We are calculating the recovery of A in the process of analysis, so the surrogate is expected to behave like the main compound and we calculate the efficiency of recovery of A by using the efficiency of recovery of the surrogate.

So in this problem we add 1 ml of 100 milligrams per liter. So how much what we are adding? The mass of surrogate that we are adding, added is 100 milligrams per liter into 1 ml that is 10 raised to -3 liters that is 0.1 milligram, this is what you are adding. We find the recovery by finding out how much of this is recovered in the end by the instrument eventually and based on that we figure out how much is lost.

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answer using algebraic expressions. If possible, calculate the concentration of pure aqueous phase.

c) In the measurement of the concentration of A in the leachate water, 1mL of 100 mg/L solution of a surrogate B was added to 1L sample before extraction procedures. The sample was extracted with 50 mL hexane and 40 mL of this extract was concentrated to 1 mL and 1µl of it was injected into an analytical instrument. The response of B obtained was 80,000 units. Calibration of B in the analytical instrument provided was Response = 60000m, where m is the mass of the analyte in ng and Response was in arbitrary units. Estimate the extraction efficiency based on the surrogate analysis.

2. Estimate the minimum water sample that is required for the measurement of total suspended solids (TSS) in the range of 10 – 30 mg/L using a method of filtration followed by gravimetric analysis of the filters. A 4-digit balance (least count of 0.1mg) is being used to weigh the filters to obtain gravimetric measurements of the filter paper. Standard deviation of random measurements of the filter paper was obtained as 5.4 mg.

3. Soil with moisture content of 10% (wet basis and considered as wet) is measured to have a contamination of chemical A with a loading of 100 mg/kg. What is the expected concentration of A in the pore vapor. Assuming no evaporation is taking place from the soil, what is the fraction of chemical on the solid phase and the vapor phase. Assume any other properties relevant to the calculation.

So the problem gives you the extraction procedure. The sample was extracted with 50 ml of hexane okay. So 50 ml of hexane was added okay. So right now we are not looking at A, we are only looking at a surrogate. We are using the surrogate analysis only in this, but we can also be looking at A in this process, so the calculation is the same if we are doing. So we have all the surrogate and let us call the surrogate as B, we will call the surrogate as B, so all B is getting into 50 ml.

So idea is whatever is extracted, it gets into this 50 ml. There is 50% of B that is there of 100%, all of it is supposed to go to B, in the hexane, this is a hexane layer. Now out of which we take 40 ml of the hexane into a smaller volume, this is extract. So out of this 50, we only take 40 out. There are practical reasons for this. So when you add hexane on top of water and you shake it, we shake it for extraction, so when we are doing this, we do some extraction, we do liquid-liquid extraction.

We will shake it so that there is transfer of the chemical from the water to the hexane and we do it for some amount of time half an hour, 1 hour, 2 hours whatever, 1 day depending on what it is and then we have to now separate this. We are separating the hexane from the water for further analysis. When we are removing it, sometimes we find that we are unable to remove everything because some part of the hexane will not separate out cleanly from the water, it will stay near the water interface, so you cannot take out everything.

When you try to take it out with a pipette, you will take out some water also, so we do not want that. So clearly we take out some fraction of it, let us say fill this level and let us say we

extract we take out about 40 ml of the hexane of the 50 we had it okay. So now this, we further process it. So in the example what we have seen is this extract was further concentrated to 1 ml. So we do a concentration of this. So typically concentration of this 2 was very small volume.

We are concentrating 40 ml to 1 ml. We usually typically concentrate a solvent by evaporation. There are various equipments that are used, different types of evaporators that are used. If we have very large volumes of extract, we use what is called as a rotary evaporator. We will go over it again when we talk about the methods itself or just stream of nitrogen or some inert gas. We gently flow air over it and so it evaporates, so we give it conditions for evaporation.

The purpose of our concentration step, what is the objective of this concentration step? So we are now taking this 1 ml sample, 1 microliter of this sample is injected into an instrument for analysis. The instrument gives a response. Now why are we doing this concentration step? Can we directly go from the 40 ml extract through the instrument? **"Professor – student conversation starts."** The amount of it being very less to do it. You can do it, the only reason we are going from 40 ml to 1 ml is you are concentrating it. **"Professor – student conversation ends."**

The concentration is 40 times larger here, so therefore your chances of seeing it, you do not know what the concentration is in the sample So if you are expecting it to be trace levels, you want it to be as high as possible and so therefore we are reducing it to as low volume as possible. So 1 ml is just a notional number, you can go to very small volumes if you want, it takes more effort and it is a little bit you have to be careful, you can go all the way up to 50 microliters if you want, there are instruments to do it.

We will go over it when we are discussing the methods. So this concentration step sometimes is necessary and just to make sure that you are getting enough response. So once you get a response, you need a number you need a concentration number, so that to get that number we use a calibration. We use the calibration to get concentration or mass whatever that is that you are looking at. Typically in some instrumentation, the calibration is in terms of concentration of this sample that is injected into the instrument, but sometimes people will just do it for any loss, to prevent any confusion, they will calibrate in terms of mass directly.

So in the problem what is given is the calibration, this is a calibration response okay. The response here says calibration and its response = 60,000 into m, m is mass of the analyte in nanograms and the instrument response was obtained to be 80,000 units. This is a calibration, calibration is response = 60,000 into mass, yeah this is the equation that is used in a calibration chart. So the calibration chart is made by injecting different amounts of standards, mass and response and we get different.

So, what we are saying is this equation of the fit that we are getting is 60,000 m. This is the closest equation I am getting. So, for an unknown sample, my response of the unknown sample in this case the surrogate is 80,000, yeah this one. Therefore, the mass that corresponds to this is 80,000 divided by 60,000 is 1.3 nanograms, okay. What this says is 1.3 nanograms is what it injected, so 1 microliter of your sample is injected into the GC and that gives you a response of this much, because your calibration is in terms of mass we have to do this.

If it is in terms of concentration, there is a different interpretation to this okay. So here directly 1 microliter of this extract okay contains 1.33 nanograms. So what is a backward calculation that we need to do now in order to calculate how much of B is there in the original in the extract? Okay. How much of it extracted? So we are interested in finding out how much of it is that being extracted into this particular level?

So you are back calculating until this point and then we will then compare it with whatever we added okay. We have added 100 nanograms here, so this is 1.33 nanograms. So we will go to the next page.

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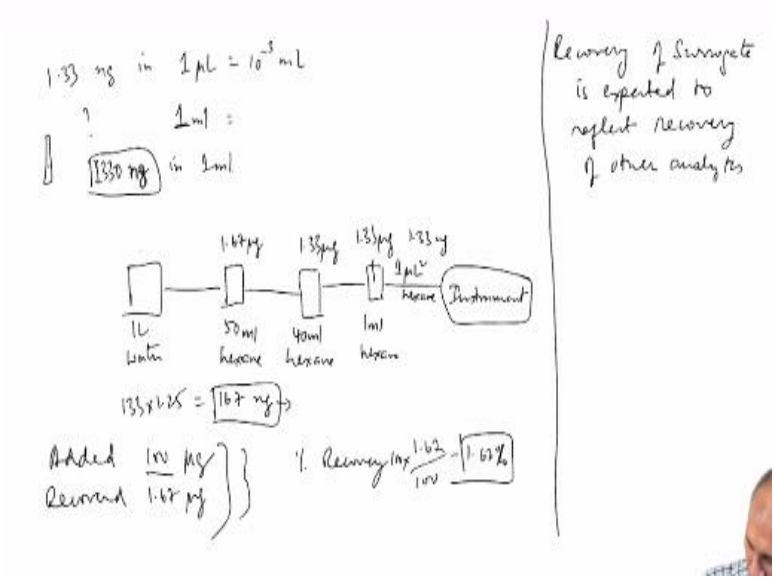

The 1.33 nanograms in 1 microliter, 10 raised to 3 - 3 ml yeah, I think we are already you know bit of a problem, the number is not correct. Let me change the number, let me put this as instead of 80,000, let me put it as 8,000, this will make it 0.133 nanogram in 1 microliter. So, we are taking 1 microliter, the mass calibration, how much of it is there in 1 ml? This is 1000 times this, so 1 ml you expect 133 nanograms in 1 microlitre okay. This is an illustration calculation just to show you what it is in 1 ml.

So we are in this 1 ml, so what we have determined now is at this point it is 0.133 nanograms, what is obtained from the instrument that is contained in this one. So 1 ml will contain 133 nanograms, how much will this 40 ml hexane contain? **"Professor – student conversation starts."** The same. How much will 50 ml contain? Into 5 by 4. So it is 1. 133 into 5 by 4. **"Professor – student conversation ends."** How much will this contain? It should contain the same.

We will now know what is extract, so this is what is being extracted, so 133 into what is it 1.25. We calculate that roughly about 30, 40, 75, 65 about 200, 200 one-fourth of 125, that is 30, 160, about 170, 167 nanograms okay. Here extracted 167 nanograms, is that correct? Still we are still off, we have only added 100 nanograms, so that is very off okay. So this is a calculation. So this is also a good illustration. So you have added 100 nanograms, you have recovered 167 nanograms. So there is a mistake somewhere.

So normally you would see if there are only losses occurring, you will see this number is usually lower than this number okay, but since we are doing this, something is wrong

somewhere, either the calibration is wrong or the mass that we have calculated is wrong, one of these mistakes will occur okay. So we will check where there is a mistake there. So all these possibilities exist, in the sense, see if you have done any mistake in the unit, 1 ml of this. **"Professor –student conversation starts."** Sir 0.1 mg is not 100 nanograms. That is true, the original problem is itself correct. **"Professor – student conversation ends."**

This is 100 micrograms, not 100 nanograms okay, and then we can go back to our 8,000 and it will make everything a little more better. Now this is 1.33 nanograms, this becomes 1.33 micrograms. So we only have 1.67 micrograms according to this calculation, it is very small okay. So the percentage recovery is 1.67 by 100 is 1.67%, 100 into 1.67. So, then you have to apply, so this recovery of the surrogate generally is expected to reflect recovery of other analytes that the surrogate represents okay. So this is the calculation, you have to be careful when you are doing this, because a lot of unit conversions and all that.

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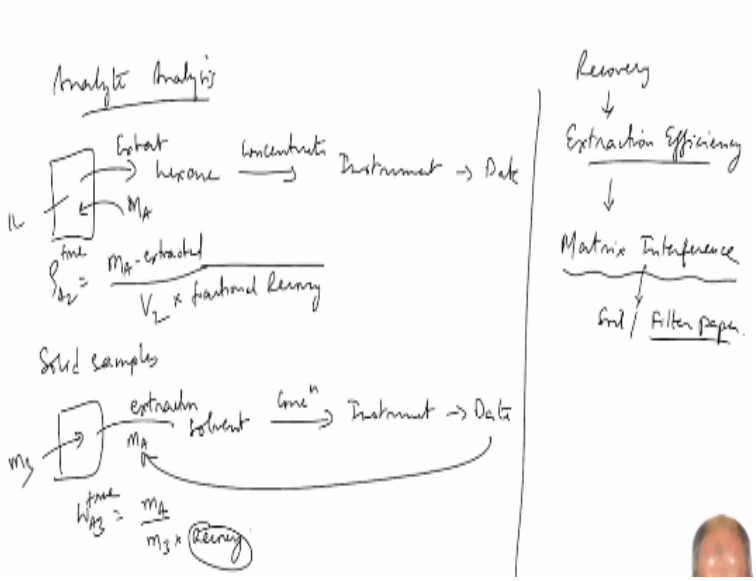

So the same kind of surrogate recovery analysis is also, see right now we have done this for water samples, so when we do here for example if we were to do the same calculation for analyte, analyte analysis we take say 1 litre of the analyte, we transfer, we extract to hexane, we concentrate, and we take it to the instrument and we get data using the calibration. So, we get to some point, we get some number here okay, we get a concentration of rho A2. We get a mass, so we get mass of A at this point.

This mass of A now has to be divided by this volume to get rho A2. This mass of A extracted divided by the volume of the water sample multiplied by fractional recovery will give you the

true concentration. So in the case if you are doing solid samples is also the same, we are still doing the same thing. Solid samples also we are pulling out or extracting. Solid samples we will take a mass, certain mass of the solid sample, then we are doing all the extraction okay into a solvent, then we do concentration, and we do instrument, you get data.

So right here and from here we get back we get some mass of A. Then this WA3 will be mA by the m3 multiplied by recovery again true value. So again there you have to do the recovery. Recovery of chemicals from solid it is a little more tricky for various reasons, say it is if you want to add a surrogate, one of the things that determines the recovery is the extraction efficiency. So recovery is also called as extraction efficiency, the main part of it. Now you know you are pulling out some chemical from water or from soil or sediment or some such thing.

You are extracting or you are doing mass transfer from there. Sometimes, it is difficult for mass transfer to happen. So, water is very straightforward, you are mixing water with another solvent, you have easy access to water, everything is nice, but solid depending on the nature of the solid, there is a large porosity of solid, very small pores, chemical does not want to come out it, resistance of mass transfer is very high. It will take a long time, it may not even come out okay.

So the extraction efficiency is sometimes very low for solids, so people try to use different kind of extraction methods to do it, okay. One of them being ultrasonication or high-temperature extraction in order to shift the equilibrium or do something about it in this process. So, the extraction efficiency in solid sample is a little more tricky than just water analysis. The other matrix that people extract from is filter paper. If you are doing air sampling, we do filter papers, we extract from filter papers.

If you want to know what is the composition of some dust collected in the atmosphere, so you are collecting it on filter papers and you extract the filter paper directly. So we talked about something called as matrix interference last week. Matrix interference is, that is the reason we add the surrogate. Matrix interference is 2 things, here matrix interference is whatever is there in the sample, water sample that you are collecting there or the soil that you are collecting there or the air samples.

The interference of other chemicals present in that to the analyte of interest one is that. Second is the matrix itself. So you have soil or filter paper, the filter paper now becomes a matrix, the solid sample. It has something that will also be extracted. Soil is very simple, its natural environment, there is a lot of other stuff there which naturally belongs there, but when you are doing air sampling for example, you are collecting the air on a filter paper. The filter paper is not an inert material, sometimes filter paper has different compositions and that some of the filter paper may also come into your extraction.

So your extraction must be designed in such a way and the filter paper itself must be chosen such that the interference that you are getting from the filter paper is minimized. These are all things that one has to take care of. So, we will go over this when we are doing the analysis methods after this section, any questions on this? The calculation itself how to, it is very straightforward, mass balance calculation, there is nothing great about it. It is only you have to read the method that is given. So you have to write a small flowsheet kind of thing to understand what is it, most of you I think have some idea of it.

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Response was in arbitrary units. Estimate the extraction efficiency based on the surrogate analysis.

2. Estimate the minimum water sample that is required for the measurement of total suspended solids (TSS) in the range of 10 – 30 mg/L using a method of filtration followed by gravimetric analysis of the filters. A 4-digit balance (least count of 0.1mg) is being used to weigh the filters to obtain gravimetric measurements of the filter paper. Standard deviation of random measurements of the filter paper was obtained as 5.4 mg.

3. Soil with moisture content of 10% (wet basis and considered as wet) is measured to have a contamination of chemical A with a loading of 100 mg/kg. What is the expected concentration of A in the pore vapor. Assuming no evaporation is taking place from the soil, what is the fraction of chemical on the solid phase and the vapor phase. Assume any other properties relevant to the calculation.

Estimate the minimum water sample that is required for the measurement of TSS in the range 10-30 milligram per liter using a method of filtration followed by gravimetric analysis. A 4-digit balance is being used to weigh.

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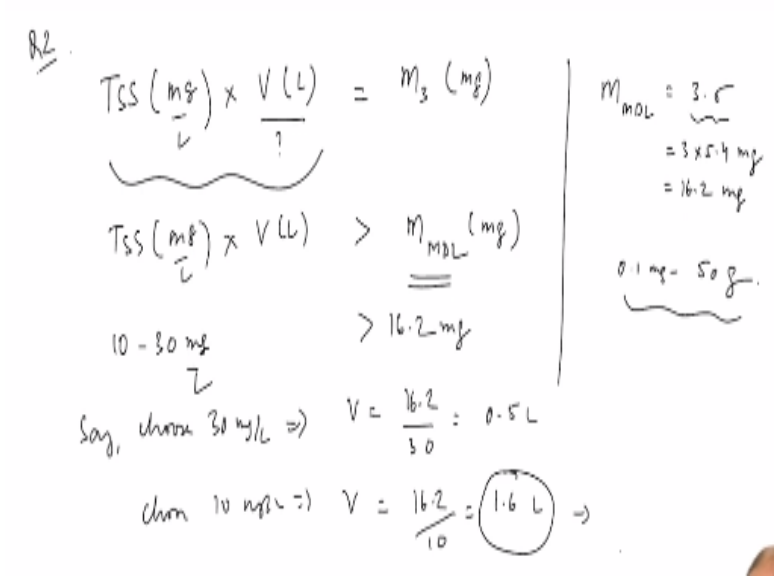

So here priori I know, so what I am asking is TSS is milligram per liter multiplied by volumes in liter will give you a mass m3 suspended solid in milligrams, yeah. What they are asking is how much is this? What is the minimum volume that is required okay? So for this entire thing must be greater than, instead of this thing we will write this here. For this TSS of milligrams per liter multiplied by volume must be greater than m, what is this value here, what should I write here? Minimum detection limit, the MDL in milligrams.

This MDL is given in the calculation as mass MDL. It is a 4-digit balance, least count of 0.1. What is also given is standard deviation of random measurements of filter paper obtained as 5.4 milligrams. So here it is written down that it is 3 into Sigma of random measurement, I have not given, this 3 into sigma applies only if there are at least 7 random measurements that is the t-test statistics about 2.99 something, So this is the general equation that is given. So we have 3 into 5.4 milligrams.

Standard deviation is 5.4 milligrams for that balance for whatever reason. So we have this is 15, 16.2 milligrams is the minimum, yeah. Now the value of this TSS I am telling you is between 10 and 30, so it could be 10 milligrams per liter or it could be 30 milligrams per liter. Sometimes we are given this kind of things, a concentration in this range, so what will be your minimum? if I choose 30 milligram per liter, let us say I choose 30 milligrams per liter, the volume will be 16.2 by 30, some value.

If I choose 10 milligrams per liter, the volume is 16.2 by 10. This is about 1.62 liters, this is 0.5 liters, which one will you choose? 1.62 because it has still has a better chance of you

finding whatever you want to analyze. So you choose the lowest possible concentration and then get the highest possible volume that you need. So if I work with 1.6 liter, I have a better chance of finding out anything above 10 okay.

Now if the concentration becomes too high, suppose this here we are looking at, based on this statistic, you go and collect 1.62 liters of a wastewater sample that is coming from say after in the first stage of a water treatment, sewage treatment plant or something, very heavy, lot of solids in it okay. You are on the other end, you have now crossed the limit of the balance, what will you do then? Say the balance now, the balance is 0.1 milligrams to say 50 grams. Your sample is so full of solid in a filter it is crossing 50 grams, what will you do then?

That is the easy part, there is no problem there, what will you do? If you are expecting that the concentration is going to cross the limit of the measurement, this one measurement, what we usually do? We dilute. Dilution to bring it in the range of the measurement, that is very easy to do. You dilute right at the beginning, you go back dilute the sample and measure. You keep diluting until the measurement comes into this range. The dilution is not a problem because you can do it, you can get a measurement if you do dilution.

Concentration is the problem because you cannot measure it. If it is below the detection limit, there is nothing you can do about it unless you collect a very large volume of water and then you have to worry about whether it is uniform, non-uniform, you may not even get a reading. So the standard methods of analysis take this into account. So there is no limit to it, I can take 1 liter, I can take 45 liters, 50 liters for a water sample, but it does not make sense sometimes.

So people define water quality on the basis of sampling volumes, they will say 1 liter, I am fixing this as 1 liter based on whatever instrument you are going to use. If it is not there in 1 liter, do not worry about it. So you can expect that the concentration is going to be below some value and that value is okay, safe, then do not worry about it, but in some instances where the concentration even if it is below your direction limit can still be dangerous, then you have to expand the scope.

You have to go back and say, I will collect larger volume and if it is not there. So for **for** example if I am taking 1.6 liters and still my amount of mass that I am seeing is below the detection limit that corresponds to a concentration of TSS, which is less than 10 milligrams

per liter. In my risk analysis if I say 10 milligrams per liter is my minimum amount, below 10 milligrams per liter it is okay, it does not pose a significant threat to health or anything it is fine, we will leave it there, so we do not worry about it.

So the methods are all depending on what your objective is, your method specifications can change which is include volume of sample you are taking and all that. So there are standard methods, but the standard methods have a particular objective, when you read the standard method, you will see.

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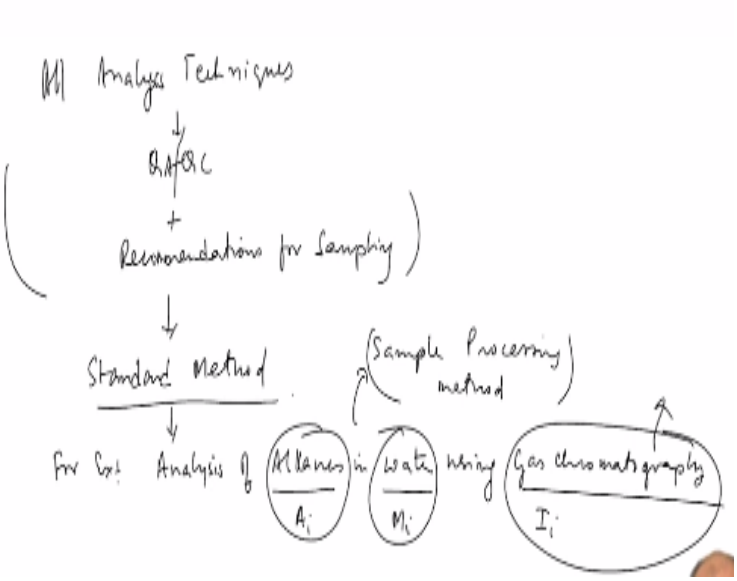

So all analysis techniques QA/QC and recommendations, sampling, etc. they are all combined to form what is called as a standard method. There are different standard methods you will get. For example the standard method is analysis of alkanes in water using gas chromatography. So there are 3 key words in this. There is chemical, there is a matrix, and there is an instrument. The 3 things that are specified I can change, I can say chemical, I can give index, I can give matrix index, and I can give an instrument index.

I can mix and there are multiple combinations of this possible. I can analyze alkanes in soil using a different technique, I can analyze alkanes in air using a different technique in particulate matter and the method will be different because the sample preparation, the sample extraction, processing, everything will change when I am changing any of these things okay. So, you have a very large number of standard methods very specifically for each combination of these things.

So I cannot go over all of these with you obviously, so we will go over some general principles and how you can mix and match and how you adapt. For example, I can use gas chromatography for the analysis for alkanes in all the 3 matrices, what will change is the sample processing, but the instrument part will not change okay. From the instrument everything is the same, but before it comes to the instrument it will be different. So along with attached to a standard method, there will also be a processing method, sample processing.

So sometimes, analysis the standard method includes the sampling as well as processing and instrument all of them, but sometimes they will only have instrument, you can do everything pre-processing you do and bring it to the instrument and this is the process you have to follow, so depending on how you want it, these are all different arrangements can be done okay. So, we will start this next week, next week we have a bunch of holidays, I think Monday is working day, Tuesday and Wednesday are holidays, Thursday. So we will meet.

If you are okay with it, we will meet this Friday, so we can start right away and then we will do next week Thursday and Friday, so up to it, we can meet this Friday evening, otherwise if you all taking off a long break, we will skip this Friday also. So I will start the analysis methods, it is all there in the PPT's. Okay, we will stop here. **"Professor – student conversation starts."** Sir, in the previous problem, what is the importance of that 4-digit accuracy that thing. It is just sometimes it is additional information that is all.

It gives you some idea that what is the, see the standard deviation has to be above that number, you cannot have it below that. So somebody is giving you 0.1 and standard deviation is 0.05 which means this is mistake, you cannot have that. That is all. Lot of these problems will have additional information, so you have to know which one to use okay. This is the information given to you based on what is the available system. Sir, tomorrow exam is **(( )) (37:57)**? Exam tomorrow, you are asking where?

Exam is in you come to 355 in the same corridor MSB 355. Exam is in both 355 and 356, but I think depending on other 2 exams how many show up. You start sitting in 355, it gets full we will come to 356, but you come to 355. There is no particular seating order, so you come sit wherever you want. We will first sit in 355. If you come late, you will go to 356

depending on how many are there, I am not sure how many are there in the other course. So 1 A4 sheet, A4 sheet is, can you show me one of your books?

That is a little bigger than A4 sheet, but approximately it is fine. Do not bring A3 and all that, I will check, I will just come around and check. Usually you have no problem, but sometimes the people have a long sheet. You can write however small you want, even write on both sides that is up to you. No printed matter and no xerox copies, no photocopies of somebody's hand sheet. I cannot write it and then give it to my classmate and then they go use it.

Idea is for you to go through the notes yourself and write whatever you want to write, but somebody might take an easy road, take a photocopy of whatever somebody else has done. I do not see a point in that because your sheet is yours because you remember certain things, you cannot remember certain things, you want to write those down and all that, so you cannot have a generalized cheat sheet okay. **"Professor – student conversations ends."**