Environmental Quality: Monitoring and Analysis
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Lecture No. 31
Vapour - Part 2

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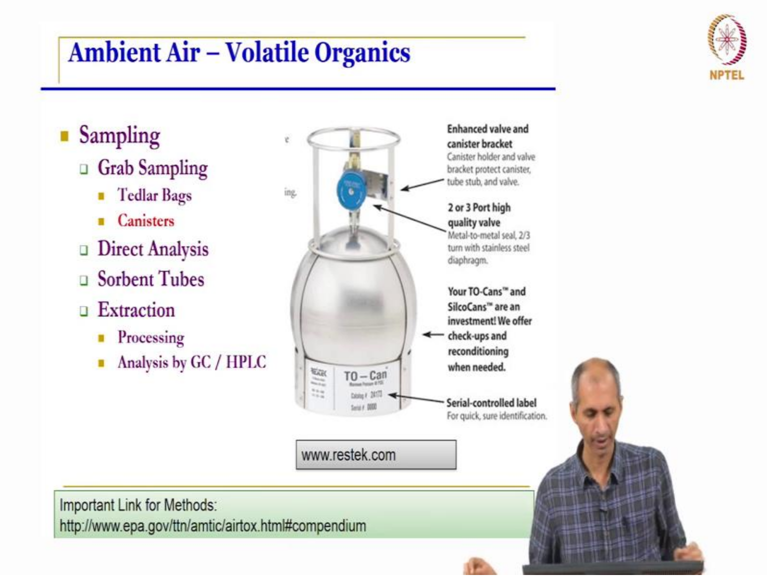

Ambient Air – Volatile Organics

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So yesterday's class, we had stopped around this point, looking at just show you some pictures of what the canister looks like before grab sampling of ambient air.

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So here, this is the other one this is the Tedlar bag that I was talking about this bag and this is kept inside a vacuum and then sampling is done into the bag using a pump.

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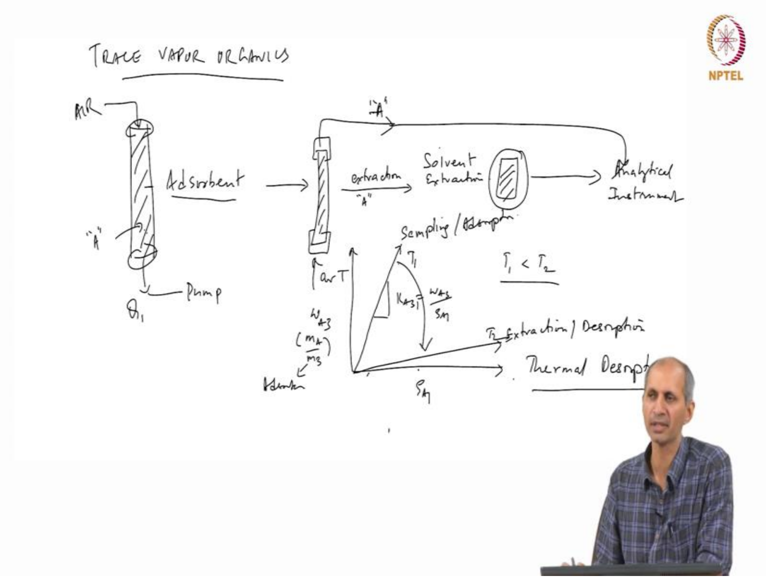

The alternative for grab sampling is typically the alternative for grab sampling is when then for trace vapor organics you have to accumulate this is not enough material for you to directly analyze from a grab sample. So, you have to collect enough material and then go to this thing. So, what is generally done is the more generally done is the vapor sample is drawn just like the way we do for PM 10 sampling.

We collect on a filter paper we do have a filter and this filter is an absorbent. And different materials are dropping materials are available that you can use to trap. So, the air goes through this there is a PM filter before this. So that is only the vapor is allowed to go in. And the analyte A gets trapped on the absorbent so you need a pump, when pump is pumping at some flow rate Q1 of A and for a certain period of time if you are sampling you get a volume of air that you have processed through this absorbent.

Now after the absorbent, once you have finished it this tub absorbent e is taken out and capped is close the ends are closed because you do not want absorbent to leave the system you want it to stay there so that you at least want to isolate it, and then the A is the analyte is extracted. So typically when you want to extract it, you use the same kind of procedures we have been using for extraction for solids and other things water use solvent.

One option is to use a solvent what you are doing in extraction is this. So, we go back to our partitioning this thing this we are calling as rho A1 and this is WA3, here the WA3 here we are talking about the absorption. This is the mass of A3 in this case, this is the absorbent. We want to select a material for the absorbent from air which has something like this, the slope is very high which means that the slope of this is what we call as KA31 the ratio WA3 divided by rho A1.

So, higher the slope, which means the higher absorption capacity, so, it will take a lot more equilibrium is towards the solid. So, when you do when you have a concentration in air you bring it in contact absorbent like this absorption is towards the mass transfer is towards favorable towards the solid. And therefore, you will end up transferring most of the material from the gas phase into the solid phase but that is in the sampling. This is in the sampling.

When you want to dissolve when you want to do the extraction, you want to do the reverse you want to do something like this. You want to have the extraction is lengthen it is where you want to get everything off the solid and so, you want to change condition in such a way that this is what you want. So, which means that now you have to bring it in contact with something else and you can not do extraction in air obviously.

Because this that is sampling absorption happens here and this is disruption is happening here in this case. So, how do you change it from this to this 2 possible things one is using a different solvent, one way is to use a solvent where the solvent the partition constant of this, now, we are moving this we are taking it away from this it is not rho A1 anymore. We will, in this case we are using a solvent we will use another concentration in the solvent is what we are looking at. One way is to use the solvent.

As we have already seen the case of water and soil and other thing. But the Second way, if you do not want to bring another solvent into question, because once you bring a solvent, you have to look at solvent concentration and evaporation of solvent and all those issues are there sample processing losses are more. So, in order to prevent this, one of the things people do is to do what is called us in any other way in which you can change the absorption term.

From this point to this point, the absorption can you switch it from here to here is there any other thing that you can do to switch it to make it favorable towards the vapor side which means pressure and pressure or temperature 1 is temperature so, there is T1 and T2. So, which temperature? What is the relation between T1 and T2 which is so, typically T2 is higher temperature. So, when you do that you can also do with pressure is not in the what we are operating in pretty much are constraints are much more difficult.

To do pressure kind of things, you have to apply a vacuum and amount of vacuum or applies energy intensive. So, temperature is an easier way of doing it. So, this is called as thermal disruption when you do this which means when you do thermal disruption, you are increasing temperature. So, somehow you are increasing temperature. So, what happens when you increase temperature? Whatever is there in the system will go out. Where will it go? You have to let it go somewhere.

So, your idea is in solvent extraction, you are extracting, you have a solvent, small bottle that contains the liquid, you can store it and you can take it to a GC or an HPLC and inject it. In the case of thermal disruption your idea is not even a solid, which means you are still using some gas or air itself, but where is it going? So, what do you want what ideally what would you like to for it to happen? You understand my question.

So, there is an intermediate stage here, before it goes to the analytical instrument in the solvent extraction process, where they are holding you are holding the sample inside an extract for some time till you get. In thermal disruption, what we are doing is we are sending in air at a higher temperature. What will happen when you send high temperature? What is coming out, will contain all the analyte. Do you want to hold it anywhere in between? You want to hold it how will you hold it?

Again, you have to use a solvent or you have to use another absorbent trap which is again the same problem. So, we do not do anything we directly go to the instrument and that is the that is what is the analysis method where we in fact they did not even transfer anything they the same tube that is used here is now taken to a thermal disruption unit and temperature is increased and whatever A that is coming out directly sent to the analytical instrument. So, the instrumentation is a little more sophisticated, more, we have not discussed that in the case of.

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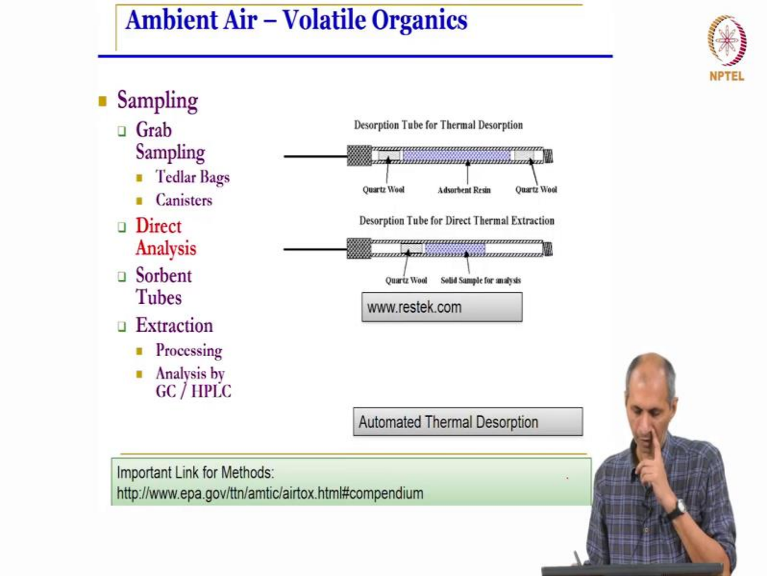

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Automated Thermal Desorption

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This is the automatic thermal disruption tube. So, here direct extraction there is direct analysis is done.

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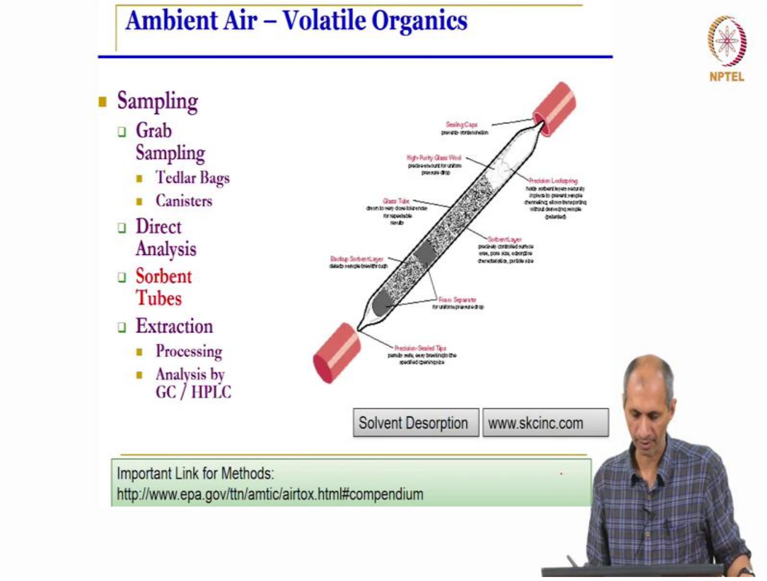

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And this is an example of some of this tubes that are available commercially there are different types of tubes they have a material. So, these are for both thermal extraction. Thermal extraction tubes are very different because they are they have to be heated so they are made of some material, stainless steel usually. We can also use glass but glass is not easy to take and fit into something else.

And so they use stainless steel is easy for us to fit it into a GC system and all that. This is generally the tube used for glass for fallen extraction and carbon tube commercially, there are a lot of solvent material driven materials that are available, you can have very small, this is the size of about 3 quarters of an inch or 6 mm in diameter or less than that and about this much this height, this length.

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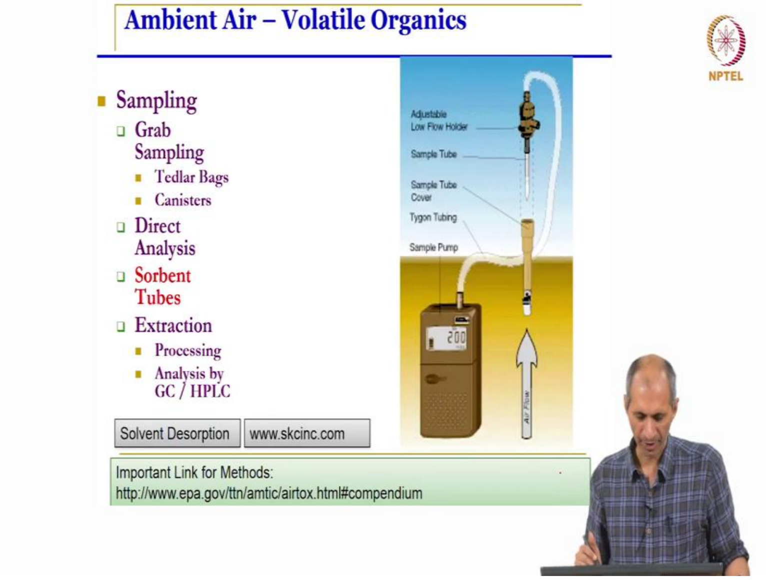

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And the methodology of sampling is usually something like this. We call as low volume sampling, low volume sampling, and the reasons are not very obvious but intuitive. You have a solvent tube and you place a pump behind it. And in front of the solvent tube, there is nothing ambient there, except that you do not want particulate matter to fall into it. So you keep some kind of device there.

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So typically, there is when you typically when you place a solvent tube like this, is a pump and the tube is placed here, if you leave it open up, stuff will fall into it material will fall into it. So, usually they there is a small tube that is down and you can even have a sampler if you want, you can have a filter there all that. So, the solvent tube themselves have a small filter and right in the beginning there is a glass will or some kind of material which you do not extract, you can extract it if you want.

Basically we will take all the particles, but that does not have interest to us. So, commercially they do that. So it is inverted, so that nothing accidentally falls into it which is not part of the vapor phase. And this is a pump. This is a low volume pump. This is a low volume sampling. The reason it is low volume sampling is you will see that on this sorbent tube there is a flow rate that will be return when you cannot sample more than that for it.

And this has to do with the efficiency of sampling here. So let us say this is the absorbent tube. Flow is happening from here and it is going out there is a certain lengths and there is a maximum flow rate that is allowed. I will just very briefly mention why this is this is to do with your goal of sampling is the following. When you sample for Q into some time, you are sampling a sample for 8 hours. Your hope is that whatever your chemical is going into the tube, in this 8 hour period stays in the tube.

What it means is that all the A is contained in this region. When will it go out when can you get this question doubt that whatever I am measuring inside the sorbent tube is what is corresponding to what has gone in. So, when is it not possible when this is not true? You understand my question? Suppose I extract this and I get some concentration rho A1 say some concentration MA corresponding to this to this tube whatever is there in this tube, I also know the volume multiplied by rho T.

Now, what if under what conditions is this less than the true value? Losses how? In this case the loss would mean this, trap, whatever this sorbent, absorbent tube is not capturing everything that is actually sent in there are losses due to extraction and all that that is a different issue. But here fundamentally what we are also saying is that whatever is being sent in is not retained in the column. So, you will say, so, the amount you are expecting is Q into delta t into rho A1 this is the ambient air concentration, this is the concentration ambient air.

This is what you would expect this is the total amount of MA1 is this. But whatever you are measuring if you are measuring MA1 measured is less than MA1 through ambient, under what conditions is this possible? There are 2 conditions in under which this is possible one of them is very straightforward. So, I put it to you and I forget about it and go for 25 days and come back after 25 days what could have happen? It would not leave out. See absorption is there towards the gas if you want these are what else can happen.

Clues are all there exhaustion is capacity is full it is full, we have reached the capacity of the absorbent is so what will happen is it will fill up, then it is no, it is already at equilibrium for when this happens when the entire thing is that equilibrium and what is coming in which means it has reached capacity and it will not absorb anymore, it will just go through. So, it exceeded the capacity is exceeded. This is one reason why.

So, how do you make sure that this is not true? This does not happen. How do you know that it is not happened in your sample? How can you check it does not happen? So, you do not know whether you do not know the concentration of the material in the atmosphere so you do not know what value to use here. So you do not even know when whether it has exceeded or not. So, how can you check experimentally in the design?

So, that is part of the design, if you notice the notice this one you notice this tube, what do you notice about this absorbent tube design? This is the flow occur from here flow starts from here anything you notice this is absorbent material, this is absorbent material. Why are there 2 sections? This is airflow is occurring from here this is in there this is a big glass wall filter and all that which will take out particulate matter but there are 2 sections here.

Why not have just one long single section and be done with why are they why do they have 2 sections? Usually the 2 sections are same, but there 1 smaller section in the back for 2 reasons. 1 is you measure whatever is here. And whatever is here separately, you do not mix it. If these 2, the corresponding WA3 here and the WA3 here are the same, which means that it is saturated. If this is higher when this WA3 is higher than this, which means that it is not saturated, second one is still not reached capacity.

So you know that it is good value is good that is one second reason is the other reason that we are talking about what is the other reason where if capacity is not reached, you still not you are losing material, it is going through the column that is related to the flow rate. Because there is something called as breakthrough curve and all these things packed with absorption.

The breakthrough curve looks like this. When you are measuring you are sending something into a column at some Concentration, this is a rho A1 in this is Q into time the volume of air at the exit this is x, the y axis is the exit concentration rho A1 at exit what you would expect normally is that there is nothing coming out the exit. Because everything is being trapped at some point it will go up and it will do this so this means it is exhausted done.

When the inlet concentrate when the exit concentration equals to the inlet concentration, so this is y axis is exit concentration, but this number here is rho A1 in when the inlet concentration is same as exit which means that we have now reached exhaustion. The bed is exhausted. This point is called as the breakthrough. Normally what you would expect ideally is something like this, you would expect breakthrough to happen like this, it completely gets filled and it suddenly jumps up.

But in reality does not happen, you will see this kind of breakthrough. The reason we see this kind of breakthrough is no there are there is a rate in which absorption happens in the column and this rate it is based on the design of pack but mass transfer systems if I increase the flow rate, so, very simply it is like this. This is absorbent and the material is going in the gas it has to absorb, there is a rate at which it has to absorb, but if the flow rate the velocity is very fast, it does not have enough time to absorb.

So, it will not absorb fully it will not come to equilibrium here this will not come to equilibrium with this solid here. Before it comes to equilibrium, it moves on. It is now in contact with the next one. So, it absorbs little bit here a next one. If I reduce the flow rate to such an extent that it is spending almost infinite amount of time at each point it will come to equilibrium everywhere and then move on.

So, as the as it progresses, it finishes equilibrium in each point and then progresses forward. But if it does not happen if you increase the flow rate, what did happen? What happens is it is partial equilibrium here, partial equilibrium next stage and so on. So, there is a band there is a region in which the mass transfer is happening. So, in terms of fragment adoption, we call this you have the senior, the beginning of the backward say or somewhere in the middle of the process. There is a region this is the flow rate.

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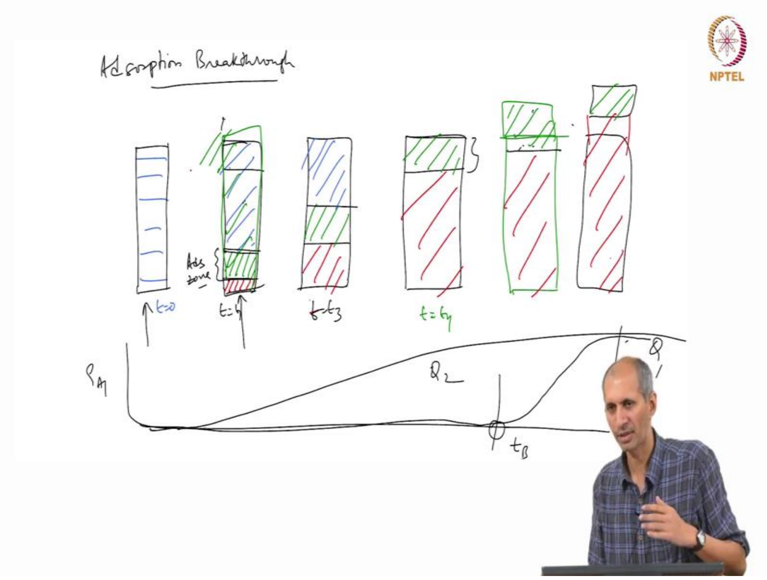

I will put it in a new slide it is easier to do it this way. This is also applicable in other processes for this thing. So, let us say that air is going in from here a time and initially this entire bed is clean will indicated by the blue color, it cleans fresh nothing as absorb, this time t = 0. At time t = t1, some absorption has already taken place. What you would find is there is this zone which is saturated completely exhausted.

But there is a zone in which absorption is happening and there is a zone in which is still clear. This zone is called as the absorption zone or the mass transfer zone, this is where the active absorption is happening. The region below this, it is already saturated the region above this the blue region is not touched at all so it is clean because by the time it comes here they, the all the A is absorbed already. It is so small and this is very insignificant amount of absorption taking place.

But as you go in time, what happens is this zone moves. So you keep on going they are doing this when it reaches the end of the column, you will reach there is a stage where you will see that this is entirely done. So, when you go further the next one this is the end of the column. This is done the column is over here, but you see that this zone is got scraped out this come out now, which means that right here, the breakthrough is here we are here.

So, if I do the breakthrough curve along with this, what is happening is a concentration of rho A in the exit is here. Nothing is happening around this point starts coming out. It is going up when this thing entirely goes out. Here you have another section here where it is completely, the entire thing is out the green section is here and this is all the red section. So at that point, you will see that starts creeping up and by this time it is gone to the exhaustion.

So this distance is represented in terms of this curvature here. So when you design for this kind of system for a sampling system, you do not want the concentration to cross this value. This is at the time of breakthrough. You want when breakthrough happen, it means that the sampling is now ineffective because it is gone through the column. So, your goal is to keep every all the analyte in the column in the time of sampling. So the moment this starts happening, you have to stop sampling.

So, we need to know; what is the time of breakthrough this depends on the flow rate. So, what may happen is the flow rate if you increase the flow rate this is Q1, let us say something happens like this. If this happens if the breakthrough curve looks like this at a different flow rate, what do you expect is relationship between Q2 and Q1? What this means is that, when I am doing for Q2, it means that the breakthrough curve is big. It is already come out.

At this point it has come out, which means that the absorption zone is huge. This green zone now looks like this. The Green Zone is this big. When can that happen? Q2 is very, high. So you just shooting it has no time to absorb it just going through. Which is the reason why these columns have a flow rate return on it so you cannot operate it above that flow rate. Basically the velocity flow rate is depending on the velocity.

And all that we calculate velocity at the back calculate because that is what you are measuring. For this column, there is a flow rate specification that is given. And this is true even for when you are doing wastewater treatment or waste absorption for purification, this breakthrough curve is important but for water treatment, and all that the flow rates are very small, you cannot send it very quickly because pressure drop is very high. But for gas systems, usually you are pumping the gas at very high flow rates and some this becomes critical, you will lose waste.

There is a problem is both in terms of managing water quality or air quality as well as the amount that you are spending for absorbent and you are wasting a lot of absorbent and when you are doing this, you are not utilizing the capacity of the absorbent in this case. So this is just an aside from that. So when you look at this, there is a lot of design that goes on into this small tubes that you are doing.