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

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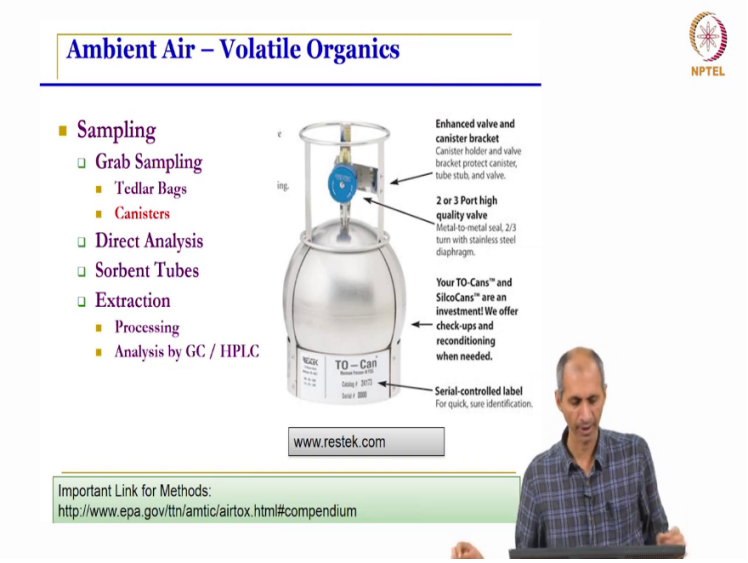

So, yesterday's class, we had stopped around this point, I'll show you some pictures of what the canister looks like before grab sampling of ambient air.

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

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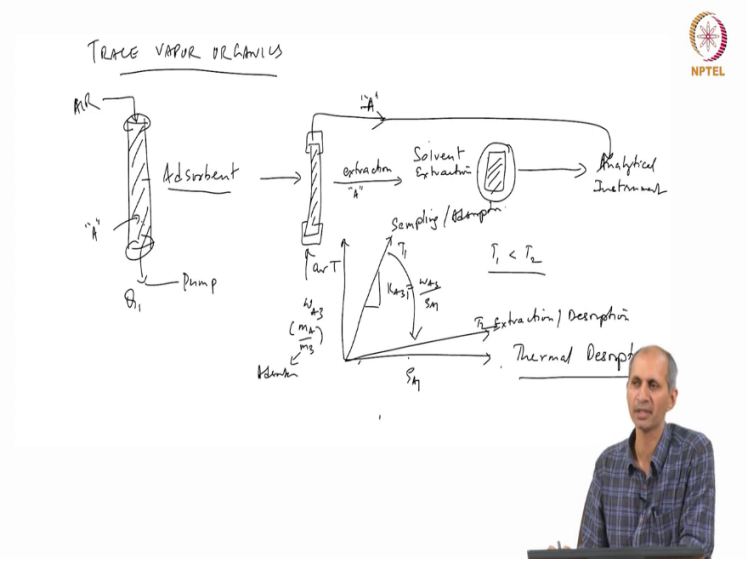
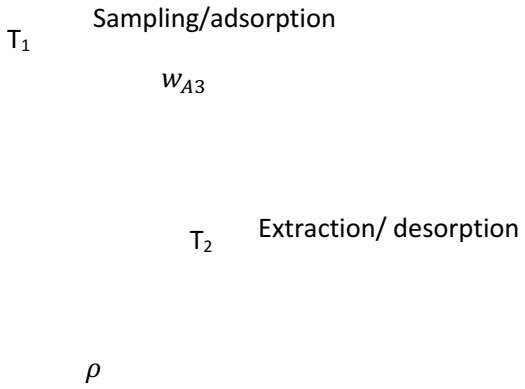


For trace vapor organics, you have to accumulate, this is not enough material for you to directly analyze from a grab sample. So, you have to collect enough material and then go to this thing. So, what is generally done is the vapor sample is drawn just like the way we do for PM 10 sampling, we collect on a filter paper, we do have a filter and this filter is an adsorbent. And different adsorbent materials are available that you can use to trap. So, the air goes through this adsorbent, there is a PM filter before this. So that only the vapor is allowed to go in. And the analyte A gets trapped on this absorbent. So, you need a pump, so 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 adsorbent.

Once you have finished this, the absorbent tube is taken out and capped, the ends are closed because you don't want the adsorbent to leave the system you want it to stay there so that you at least want to isolate it, and then 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 as 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.



Here we are talking about the adsorption. W_{A3} is the $\frac{m_A}{m_3}$. In this case, m3 is the adsorbent. We want to select a material for the adsorbent from air which has something as shown in the graph, the slope is very high. The slope of this is what we call as K_{A31} is the ratio $\frac{WA3}{\rho_{A1}}$. So, higher the slope, which means the higher adsorption capacity, so, it will take a lot more, equilibrium is towards the solid. So, when you have a concentration in air you bring it in contact with the adsorbent like this, adsorption or mass transfer is 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. But when you want to desorb, 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 something like this 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, ok. So, which means that now you have to bring it in contact with something else and you can't do extraction in air obviously. Because that sampling adsorption happens here and this is desorption is happening here in this case. So, how do you change it from that to this, 2 possible things one is we are using a different solvent, one way is to use a solvent. Now, we are taking it (adsorbate) away from this adsorbent, so the X axis of the graph is not ρ_{A1} anymore. The partition constant of this new solvent will be completely different. So, we will in this case, use a solvent as we have already seen

in 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 these 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 as in any other way in which you can change the adsorption isotherm from this point (adsorption) to this point (desorption), 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? We can do that by changing Pressure or Temperature. Temperature one is temperature so, there is T_1 and T_2. So, what is the relation between T1 and T2, typically T2 is higher temperature. So, when you do that you can also do with pressure but it is much more difficult to do pressure kind of things, we have to apply a vacuum and amount of vacuum we have to apply is energy intensive. So, temperature is an easier way of doing it. So, this is called as thermal desorption when you do this, which means when you do thermal desorption, you are increasing temperature. So, what happens when you increase temperature? Whatever is there in the system will go out, yeah. 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, yeah. In the case of thermal disruption your idea is not to use a solvent, which means you are still using some gas or air itself, but where is it going? So, ideally what would you like to for it to happen? So, there is an intermediate stage here, before it goes to the analytical instrument in the solvent extraction process, where you are holding the sample inside an extract for some time till you get. In thermal desorption, 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 adsorbent trap which is again the same problem. So, we don't do anything, we directly go to the instrument and that is what is the analysis method. In fact they don't even transfer anything the same tube that is used here is now taken to a thermal desorption 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, we have not discussed that.

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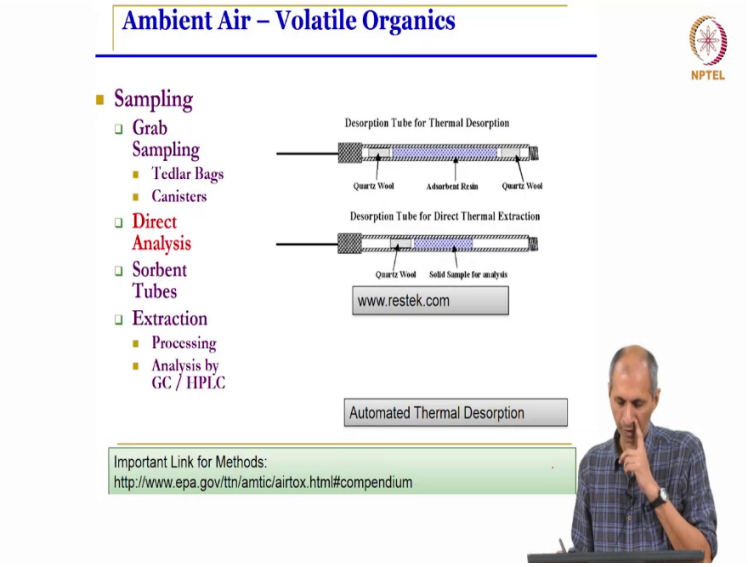

This is the automatic thermal desorption tube. So, here direct extraction there is direct analysis is done.

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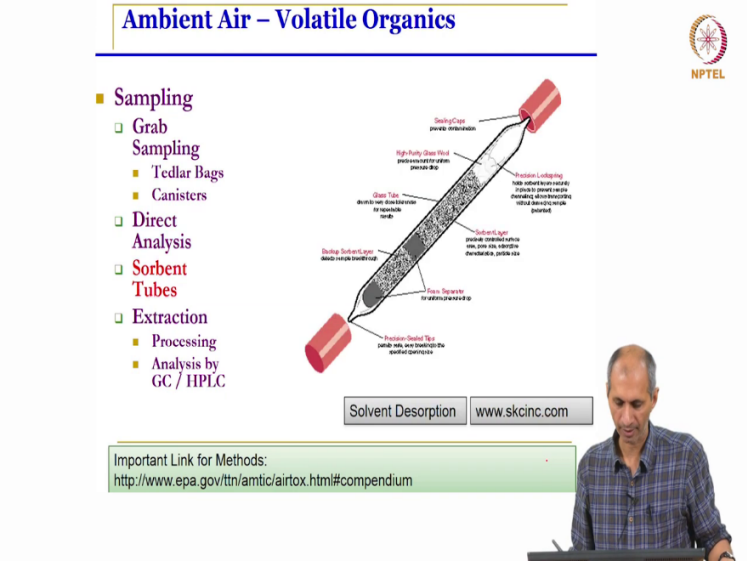

This is an example of some of this tubes that are available commercially, there are different types of tubes they have a material. Thermal extraction tubes are very different because they have to be heated so they are made of some material, stainless steel usually. We can also use glass but glass is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

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

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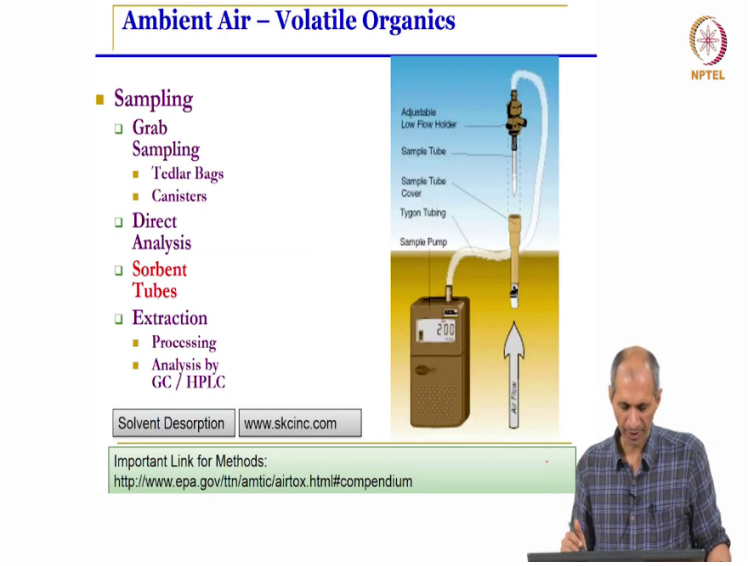

And the methodology of sampling is usually something like this. If you call as low volume sampling, and the reasons are not very obvious but intuitive. You have a solvent tube and you place a pump behind it. And in front of the solvent tube, there is nothing just ambient air except that you don't want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

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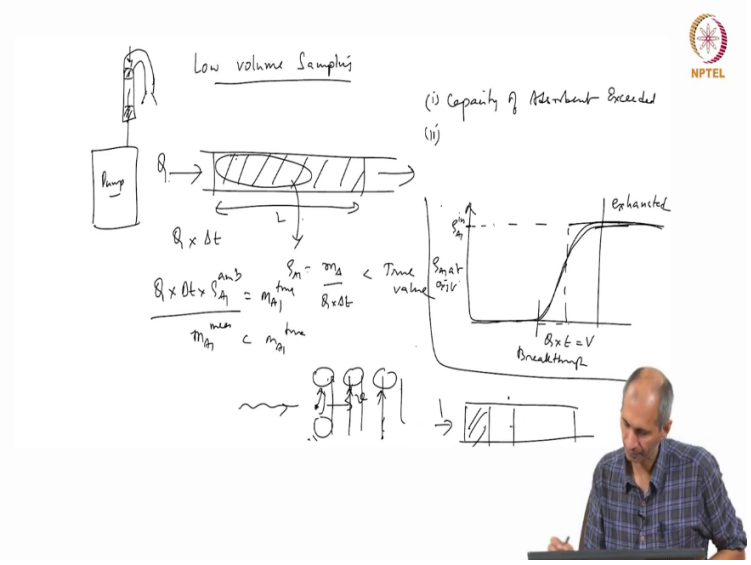

So typically, when you place a sorbent tube like this, this is a pump and the tube is placed here, if you leave it open up, stuff will fall into it, material will fall into it. So, usually they there is a small tube that is down and you can even have a sampler if you want, you can have a filter there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

Basically, it will take all the particles, but that's not of 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 written that you cannot sample more than that flow rate, ok. And this has to do with the efficiency of sampling here. So, let us say this is the adsorbent tube. Flow is happening from here and it is going out and there is a maximum flow rate that is allowed. I will just very briefly mention why this is. See, your goal of sampling is the following, when you sample for Q for 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, right.

What it means is that all the A is contained in this region. When will it go out? When can you get this 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 is this not true? You understand my question? Suppose I extract this and I get some concentration ρ_{A1} corresponding to this tube whatever there in this tube, I also know the volume (Q×Δt). Now, under what conditions is this ($\frac{m_A}{Q \times \Delta t}$) less than the true value? If there are any losses. Losses how? In this case the loss would mean this trap, whatever this carbon adsorbent tube is not capturing everything that is actually sent in, yeah, 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, the amount you are expecting is $[Q \times \Delta t \times \rho_{A1}]$, ρ_{A1}this is the ambient air concentration.

This is what you would expect this is the total amount of m_{A1} is this $[Q \times \Delta t \times \rho_{A1}]$, ok. But if whatever you are measuring m_{A1} is less than m_{A1} through ambient,

$m_{A1}^{measured} < m_{A1}^{true}$, under what conditions is this possible? There are 2 conditions 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? Desorb? It won't desorb. See adsorption isotherm is there towards the gas it won't desorb, what else can happen? So, capacity exhaustion. Yeah, exhaustion, this capacity is full, we have reached the capacity of the adsorbent. So, what will happen is it will fill up, then it is already at equilibrium so when this happens, when the entire thing is at equilibrium and which means it has reached capacity and it will not adsorb anymore, it will just go through. So, it exceeded, the capacity is exceeded. This is one reason why it happens.

So, how do you make sure that this doesn't happen. How do you know that it is not happened in your sample? How can you check if this is not happened? So, you don't know the concentration of the material in the atmosphere so you don't know what value to use here. So, you don't even know when whether it has exceeded or not. So, how can you check experimentally in the design? So, that is the part of the design, if you notice this tube, what do you notice about this adsorbent tube, the design? This is the way, the flow occurs from top, anything you notice? Why are there two sections? This airflow is occurring from here this is the in, but this is a big glass wool filter and all that which will take out particulate matter but there are two sections here.

Why not have just one long single section and be done with, why do they have two sections? Usually the two sections are same, but there is one smaller section in the back for two reasons. One is you measure whatever is here and whatever is here separately, you don't mix it. If these two, the corresponding w_{A3} here and the w_{A3} here are the same, which means that it is saturated. If this is higher when this this w_{A3} is higher than this, which means that it is not saturated, second one is still not reached capacity. So, you know that it's good, value is good, that is one. Second reason is that we are talking about. If the capacity is not reached, still you are losing material, it is going through the column that is related to the flow rate. Because there is something called as breakthrough, there is something called as breakthrough curve in all these things pack bed adsorption.

The breakthrough curve looks like this. When you are measuring you are sending something into a column at some concentration, if we draw a graph of Volume of air Verses the exit concentration, what you would normally expect 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 exit concentration equals to the inlet concentration, see this is y axis is exit concentration, but this number here is ρA1 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.

So, but in reality, it doesn't happen, you will see this kind of breakthrough. The reason we see this kind of breakthrough is there is a rate in which adsorption happens in the column and it is based on the design of pack bed mass transfer systems, if I increase the flow rate, so, very simply it is like this. This is adsorbent and the material is going in the gas, right it has to adsorb, there is a rate at which it has to adsorb, but if the flow rate the velocity is very fast, it does not have enough time to adsorb. So, it will not adsorb 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 it is now in contact with the next one. So, it adsorbs little bit here and 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 it progresses, it finishes equilibrium in each point and then progresses forward. But if it doesn't happen if you increase the flow rate, 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 packed bed adsorption, we call this you have this here, the beginning of the packed bed say at somewhere in the middle of the process. There is a region this is the flow rate.

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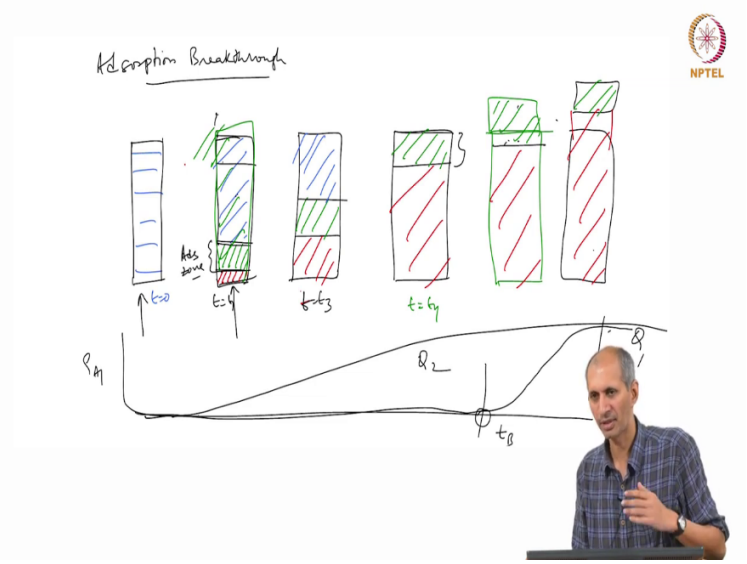

This is also applicable in other processes for this thing. So, let's say that air is going in from here at time initially this entire bed is clean will indicated by the blue color, it's clean, fresh nothing has adsorbed, this time t = 0. At time t equals to say t1, some adsorption has already taken place. What you would find is there is this zone which is saturated completely exhausted.

But there is this zone in which absorption is happening and there is this zone in which it is still clear. This zone is called as the adsorption 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, the all the A is absorbed already. It is so small and this is very insignificant amount of adsorption taking place.

But as you go in time, what happens is this zone moves. So, you keep on going they doing this when it reaches the end of the column, you will reach this, 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, it has 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 this is a concentration of rho A in the exit is here. Nothing is happening right 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 into the exhaustion.

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

So, you 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's already come out, right 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 adsorb it just going through. Which is the reason why these columns have a flow rate written on it so you cannot operate it above that flow rate. It's basically the velocity flow rate based depending on the velocity porosity and all that they calculate velocity and they back calculate because that is what you are measuring. So, 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 adsorption 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 the problem is both in terms of managing water quality or air quality as well as the amount that you are spending for adsorbent so you are wasting a lot of adsorbent when you are doing this, you are not utilizing the capacity of the adsorbent 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 these small tubes that you are doing.