Environmental Quality:
Monitoring and Analysis
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Lecture No. 32
Vapour – Part 3

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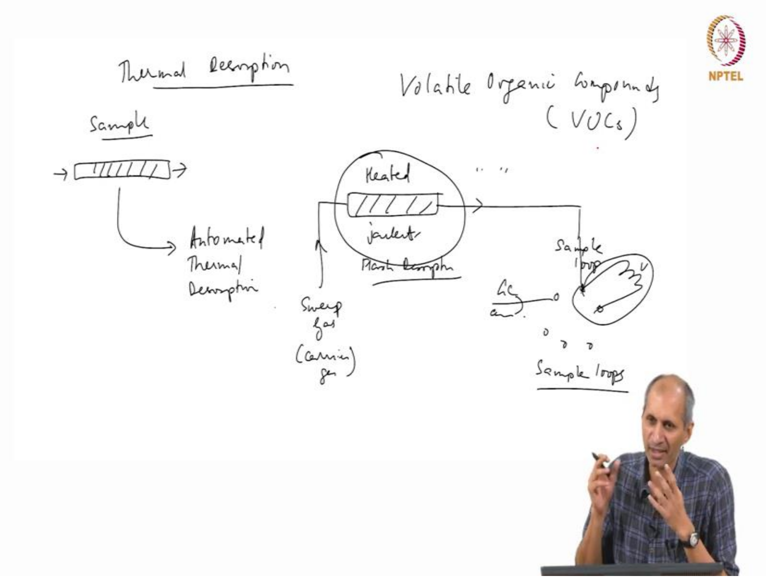

So, while coming back to our thermal desorption what is done is the following. So, you take you sample, your sample in a tube, wherever in the usual way you attach it to a pump and then bring the sample this tube is brought to what is called now it is called as an automated thermal desorption unit. It is an accessory to a GC a step before a GC. You can it does not have to be a GC it can be anything. Any analytical instrument it is an accessory before analytical instrument the processing accessory.

And so, this thermal desorption tube is placed in this in a heated in chamber or jacket or whatever and it needs to go to an analytical instrument. So, let us say it needs to go to a GC for example, assume that it is going to a GC. So, this tube when you heat it you heat it to very high temperature what will happen is it will all come out the desorption will happen, but it desorption cannot say that it has to be taken out quickly. So, what we do this is we do flash desorption.

Flash desorption means it is very quick happens very quickly the temperature that shoots up very fast. Everything comes of in one shot. If you are doing slow temperature increase little by little it will come the absorption as of changing slowly but you want all of you to come at once. Why do you want all of it to come at once because when you are sending gas here to sweep everything out, you want the volume of the sample to be as small as possible?

Because now you are going to inject it into GC you know, if you recall the GC or injection is very quick, we are injecting a pulse there. So, we want it to be as close as possible to a pulse. Otherwise, separations is other problem in sample injection, your sample chromatography, retention time will change and all that so, it is very difficult to manage it to the extent possible they try to do this as quickly as possible. It is a very interesting system.

A lot of chemical engineering concepts go into this and how quickly you can convert this into a pulse sample. So there is a usually a sweep gas. Essentially that what it does, it sweeps it, whatever is now these are just takes it flushes it out, is usually the carrier Gas that is used in the GC, you do not want something else mixing whether you are using argon or helium or nitrogen, you use the same thing here. So it is usually the carrier gas in the GC and it goes in into the GC, how can it go into the GC.

GC has what is called as you can have an accessory there when you are doing gas sampling, I will discuss this there. When you do gas sampling, you can have what is called a sample loop. The sample loop is the holding place for the sample, you are sending in certain concentration. And you would like the sample loop to hold all the sample that you are bringing. So this is important, because what you measure in the GC depends on what you are injecting and what you are desorbing, it has to be in a finite well defined volume.

So that you know what that volume is, you know what the sample volume is, otherwise you do not know what you are injecting what is coming out and all this is a big mess. So, this is all carefully calibrated and done. So the sample loop will allow you to keep this in place, it is not getting into a sample loop at you can go and read about it, you can type GC sample loops and the schematics for that becomes very, neat system where the sample there is a 6.

There are 6 ports and a sample loop essentially will go in and there is a small loop, this is a loop, this is a certain volume of this loop depending on this is the injection volume, you can have it as big as you want 100 micrometers to 1 ml or whatever. And the other part of the system, there is a GC gas coming in and it goes to this is a carrier gas coming in from another cylinder and it goes to the GC somewhere.

What happens is when you switch is a certain configuration of this where it is called as a loading cycle when you switch, the DC gas will take the sample loop and go to DC. So that is what will happen. I am not drawing it here but there is called as the rotary this thing. So, there is I will not draw it here, we will just leave it like this, go and read about sample loops. I will put it up out of the context here. So, it is possible to do it and people do it and calibration now has to be done on this basis.

When you are doing 80D, you have to calibrate like this, which means that I have to inject a known concentration of guessing calibration that becomes very, difficult. Because now we are calibrating a concentration, you have to do it on the context of this 1 and also you have to do some adjustments to your calibration. If you want to use an older calibration you have to make sure that it corresponds to smaller so separate.

But the idea here is you are now eliminating, 1 processing step manual processing step you are automating everything, so that your hope is that things are this is especially good for what is called as volatile organic compounds or your VOCs basically which compounds which have high Henry's high volatility high vapor pressure high very low KOW there are likely things like benzene calling all those things which classify under VOCs.

There is another application of this kind of system using what is called when you are doing analysis of VOCs in water. Suppose you want to analyze benzene in water the Henry's constant of benzene in water is very high. So, when you are doing all that extraction, the moment you take sample. Sample is constantly going out, so one of the things people do is when you are extracting again there is a chance of losses are quite high so people do not do liquid extraction for VOCs.

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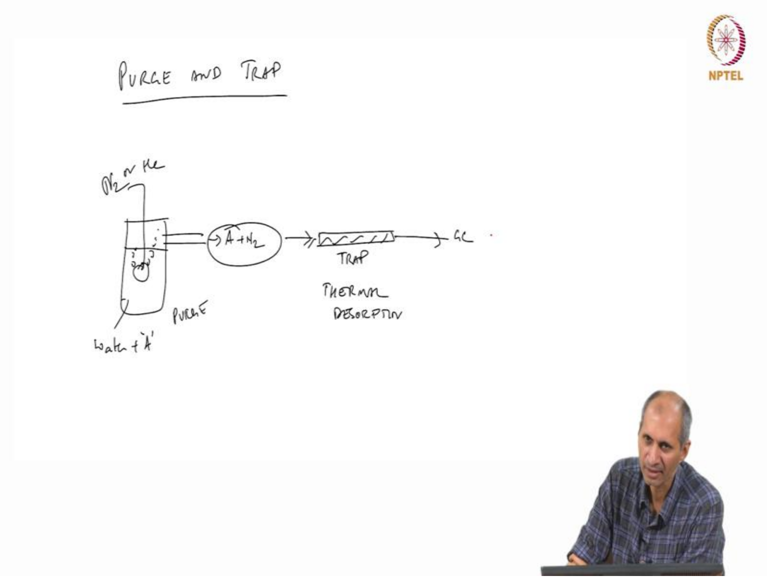

They use another technique called as purge and trap you will see this in the methods that you are using. This is a sample processing accessory. What this does is it takes the water sample directly and it purges it you purge with nitrogen. Nitrogen gas is released. When nitrogen gas is flushing out all the volatiles in the system you are stripping the water. This is the water sample water + analyte and analyte + nitrogen both of them are coming out. Again nitrogen or anything helium or argon whatever you are using.

This comes out you are basically you are extracting but you are not extracting using solid you are extracting using the gas vapor phase because that is favorable is a volatile component anyways, coming out. No at this point this becomes like a vapor sample air sample now, what do you do automated you put a small thermal desorption tube here, we are doing the absorption here, it goes in and sits here this is trap, this is the purge we trap it until all of it is purged you project it for 15 minutes, 20 minutes, half an hour whatever time you determine that this is a mass transfer problem.

You know how long you need to purge it depends on what is the concentration, what is the flow rate of the bubbles and what is the size of bubbles and all that we just purge everything all sets and then you go and trap it you trap it. Once you trap it trapping see cycle is done then you do what we did in the thermal desorption you do thermal desorption after that and then it goes to a

GC or GCNS or whatever through a sampling loop again, has to go through a sample loop to do this to the accessories which are very useful in analyzing.

So all of these are directed towards only one thing, all the accessories as we are trying to increase our confidence in our analysis, quality control and quality analysis is the focus in most of these methodologies that are developed for these kind of things. So, we will just go over quickly.

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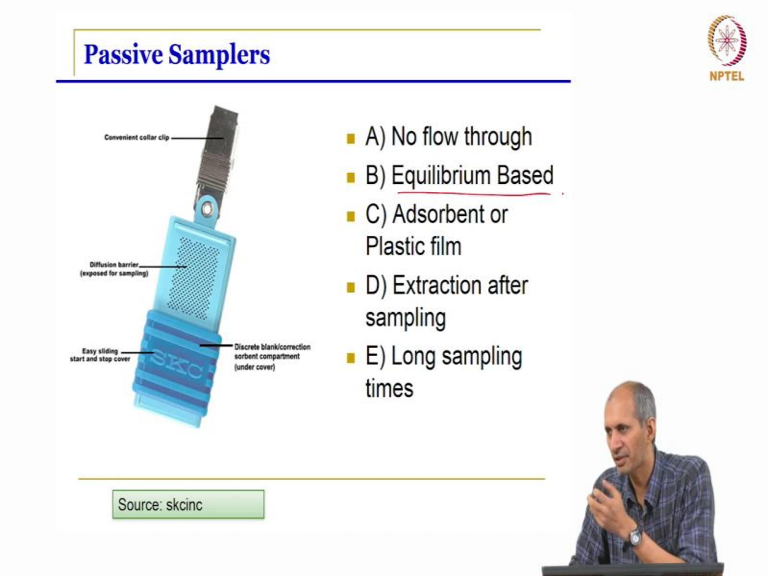

Passive Samplers

- A) No flow through
- B) Equilibrium Based
- C) Adsorbent or Plastic film
- D) Extraction after sampling
- E) Long sampling times

Source: skcinc

So, this is the other type of samples is something called as passive sampler, this is a new thing, and not a standard method is still under development. So, this is an equilibrium based sampler, which means that in all the other things what we have done is we take a sample of air, we know what the volume of air and we extract whatever is there and that we exactly get concentration mass by volume.

Here some cases for example, if you want to take ambient air samples in the way we described just now, what is called us active sampling. Active sampling is where I have actively I am pulling in a certain volume of air. But the problem is I need a pump, sometimes I need electricity, sometimes I need somebody there and some things may be stolen and all that sort of the logistical problems are there.

So, what people have come up with is what is called a passive sampler, you put 100 of this passive sampler, which means it is just a matrix, some substrate and it comes to equilibrium with the ambient air or ambient water, wherever you put it in water, you put it in air. And this is one such thing. So, it again works on it is an equilibrium based method means, at the end of some period, you take it out.

You assume you find out if it is in equilibrium with something else with the ambient air and you extract all the work is in, in, in a laboratory in a processing facility. But there is nothing else in the field you can have 100 of these things, bring it back to the lab when you find out what is the concentration on the so, essentially what we are doing is in this case.

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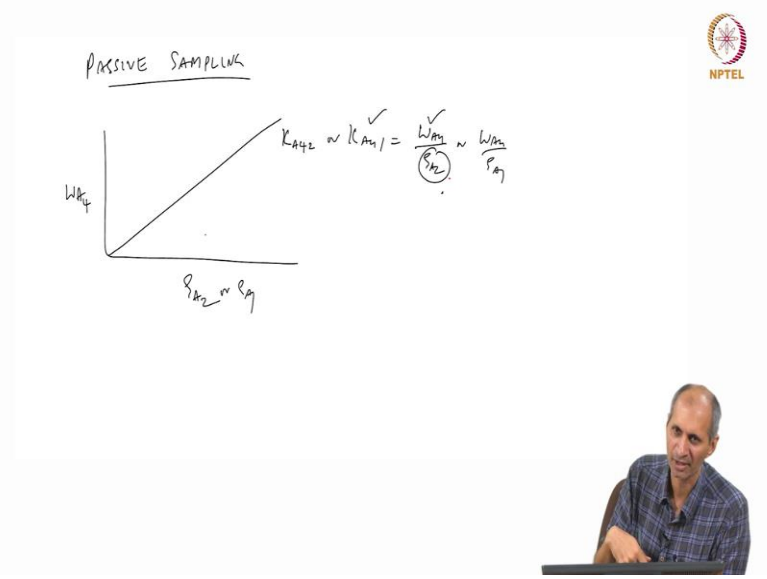

We are using a partition constant we are using some other material we are using some substrate, some solid. So we have a partition constant here, just KA42 or KA41 if we know this number this equals WA4 divided by rho A2 or WA4 divided by rho A1, we measure this we know this we can calculate this number. This is very useful for getting long term, average concentrations of materials. And it is also cheap when it is easier for people to find.

So, people use this to find out especially when the flow is all not very difficult to manage it and all that. It is equilibrium so it is long term average, so you cannot use it like a daily average and all like that. It is a long term average there is it is useful for processes which are the interpretation of this is that say for example, you have a lake or a river or an ocean. It is there for a long time and things are not going to change over 2 days or 3 days.

This is a long term process. Similarly, with atmosphere also for atmosphere your long term average exposure average we are talking about 30 years, 40 years, 50 years and all that. So, things do not change very rapidly what we are talking about is something pollutant is entering mixing. And this pattern stays for a while until you make a drastic change. Suppose I all of a sudden if I say I am removing all vehicles today, it will take about a month for everything to reset to go to some other value.

Because there is already some concentration that might get for it to get flushed out. So, this is an this is good for those kind of you cannot use this to suggest that, is the other end right we are on one hand we are saying we do not we are not happy with 24 hour averages. We want to go real time. This is the other extreme, but this is sometimes useful because it is very cheap to do outside. You know, logistically, it is very difficult to go and install something, especially in a place like this people will come and steal components and go away.

So, finding electricity is a problem. You need batteries, which means battery operated things are again expensive, you have to charge them you have to bring it back all these issues are there, and this one does not have that. But as a rule generally with all these things. The more money you spend, the less information you get, if you can use less information and smartly, then you can you have to find where your objective is based on it. So this is so one other thing I will just finish up in a minute.

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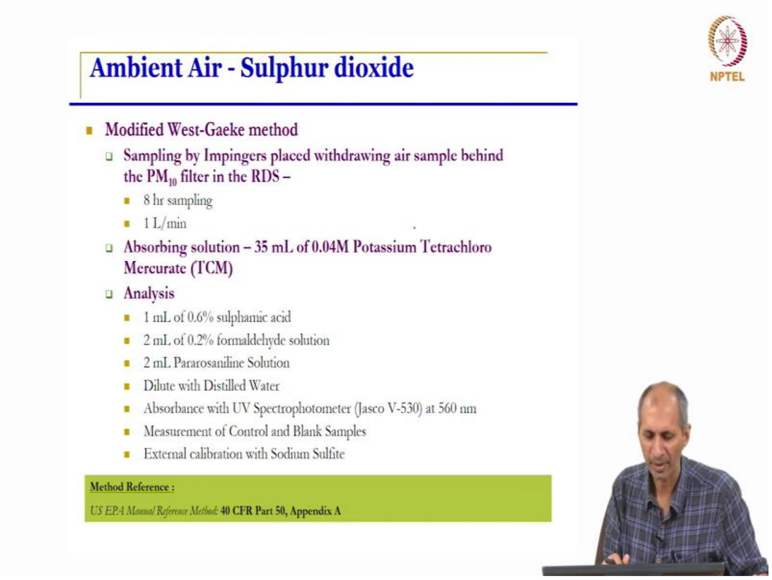

Ambient Air - Sulphur dioxide

- Modified West-Gaeke method
  - Sampling by Impingers placed withdrawing air sample behind the PM_{10} filter in the RDS –
    - 8 hr sampling
    - 1 L/min
  - Absorbing solution – 35 mL of 0.04M Potassium Tetrachloro Mercurate (TCM)
  - Analysis
    - 1 mL of 0.6% sulphamic acid
    - 2 mL of 0.2% formaldehyde solution
    - 2 mL Pararosaniline Solution
    - Dilute with Distilled Water
    - Absorbance with UV Spectrophotometer (Jasco V-530) at 560 nm
    - Measurement of Control and Blank Samples
    - External calibration with Sodium Sulfite

Method Reference :

US EPA Manual Reference Method: **40 CFR Part 50, Appendix A**

Now, there are various kinds of passive sampling devices people have worked with a lot of things. This is used in indoor air pollution a lot people use it to find out what is passive, passive smoking people in restaurants and bars and all that. So, they have this thing sitting here and there are some standard methods for measurement of the pollutants like Sulphur dioxide and nitrogen oxides.

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Impinger Technique for Gases

So normally the technique that is used for the priority gases, SO2, NO2 you have, you can impinge it you can collect it in a solution and measure it as a chemical method for doing it. It is all there in the standard methods. The other option is you have some coupon which does that equipments which use UV fluorescence and things like that so, it is all there in this go and read it, I think there is nothing extra that I can.

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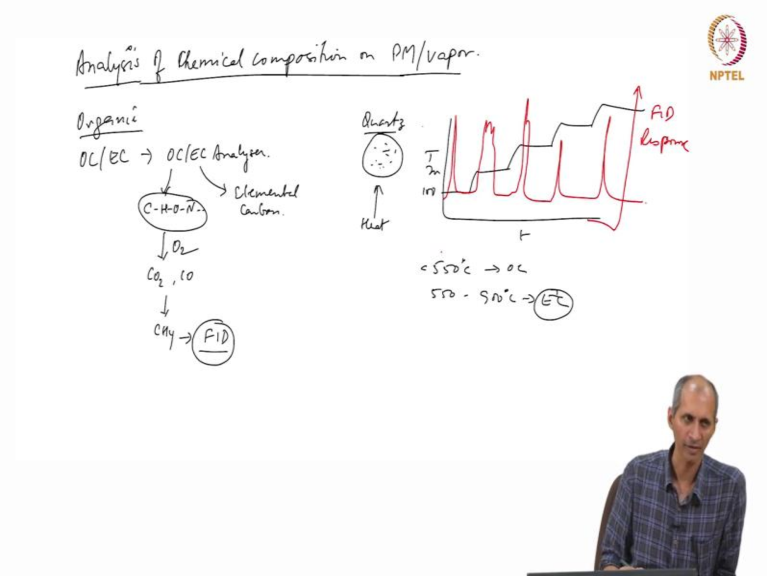

So, we have a little bit of balance material remaining in the analysis. So, we are looking at analysis of different species we summarize as PM and vapor. So, the organic analysis this summarizes this we have something called OC you see organic carbon elemental carbon this is done using an instrument just call as the OC/EC analyzer. What they do here is this similar to the GC for 1 section of this thing.

So, as I mentioned earlier the OC/EC instrument itself works in terms of the OC component is all organic components which have some structure from C-H-O-N, the EC component is what is called as elemental carbon. So, this portion can be combusted you can oxidize it like the Organic Carbon Analyzer, we talked about long back when we what is called as total organic carbon. So, you combust it and then whatever comes out you measure the CO2 or CO using infrared instead here what they do is they oxidize it you get carbon dioxide or carbon monoxide.

This is converted back to methane using a reduction reaction. So, this methane can be detected using a flame ionization detector flame as industry has is very sensitive so, and you can use a GC kind of system to without the chromatography. Chromatography but what it does is, this is a detector using the GC so, they take the sample of the particulate matter on the filter directly so, you collect a sample on a filter paper.

Take a small amount of the filter paper small part of the thing and you heat it so you heat it to different things you heat it temperature sustain you heat it at some 100 degrees then you increase it to 200 then you increase it to 300 and increase it to 400 and increase it to 500. Each temperature you keep it for some time, every time you do this corresponding to this you get a signal in the this thing. So, 100 you will get a signal and then you will get some signal in the 200 then you will get some signal in the 300 then you will get some signal in the 400, 500 what this corresponds is the amount.

So, the amount of this red signal indicates the amount of material organic carbon which will come out which will volatilize at that particular temperature. So, you are taking fractions like you have, we do not have any idea of what this chemical specifically is, but we know that this is all constitutes what is constitutes organic carbon 500 degrees it will burn off it will combust is a car there is just burning off with oxygen.

And it will coming out and then it is converted to methane and methane is measured. So, we can calibrate it by adding a known amount of organic carbon and it is measured in terms of signal for methane then so, the calibration is done like that beyond 500 degrees, it is used an optical method is used along at higher temperature goes up 900 degrees centigrade, from 500 to the, up to less than about 550 degrees centigrade is the organic carbon somewhere around this 550 to about 900 degrees centigrade is the elemental carbon.

Because this does this carbon it will not become carbon dioxide or anything it will stay as it is a soot and this is measured since it is not going to form anything else, it is just another method of measurement which is optical at the high temperature. So, what is reported as the as different fractions of organic carbon and different fractions of elemental carbon, all elemental carbon can be clubbed in one group?

And so, people use this data OC/EC ratio of organic or elemental carbon to look at where the source could be. So, if the elemental carbon is high the source is very likely to be from combustion, diesel combustion and all that which form soot carbon elemental carbon, some commercial sources are very specifically they form soot. So, you know that the if the OCC ratio is different in different places you will know that possibly the source contributing to air pollution and that area is coming from this source.

So, now based on profiles of various sources you can get information regarding or you see source contribution which sources contributing to air pollution in that given area. This is one instrument which is a very specialized instrument. So, here because this filter paper is directly put into the instrument and condensed to withstand temperatures of up to 1000 degrees, this filter use quartz filter paper. In the so, we had mentioned in the previous class that we use quartz, teflon, nylon and different materials. The quartz is specifically used for organic carbon elemental carbon analysis.