Environmental Quality:
Monitoring and Analysis
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Lecture No. 26
Analysis Methods – Gas Chromatography
(Mass Spectrometry)

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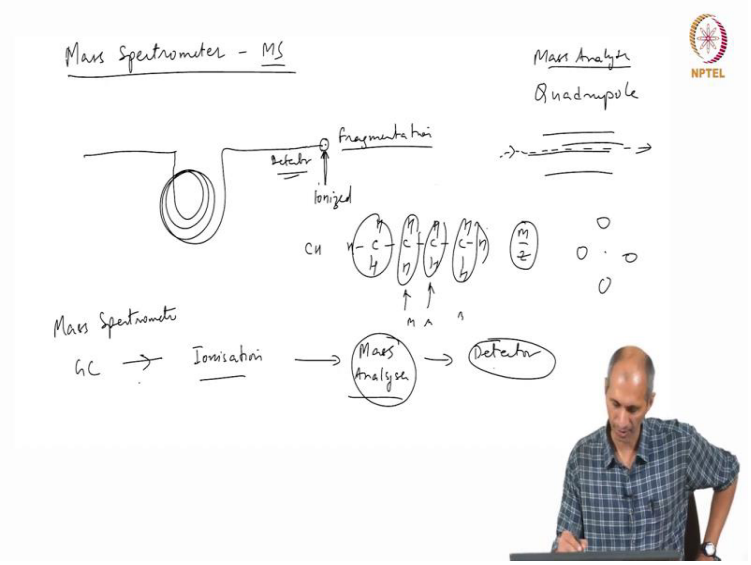

Okay, so we are continuing our discussion on chromatography. So, we will discuss a little bit about mass spectrometer for organic analysis. So, in mass spectrometer detector, what happens is it is so similar to the regular GCV that has a GC column that goes out and you have the FID or something that comes here. The detectors here in the mass spectrometer is a big detector.

It is not a small device like the FID or GCV what happens in the mass detector is that everything that comes into the detector were essentially ionized and fragmented into small segments. And in this trivializing theory, mass spectrometry is a very complex field and involves the interaction with energy of different forms. In this case, energy is in the form of high energy electrons. Its not very high energy also, but is fairly moderate.

There are other devices where you can ionize it to a much larger extent and do further things. But what essentially happens here is that there is a fragmentation that happens to organic molecules that is coming. And each time when it fragments, the instrument has the capacity to measure the intensity of each fragment. So for example, if you have a compound that looks like C-C-H what this can do is it will fragment in terms of CH2, CH2, CH2, CH3 and so on.

Each of these fragments has a certain mass and there is also a charge because it is already ionized. Based on this mass and mass by charge ratio you can separate each fragment, and analyze for each fragment similarly as we did yesterday for chromatography. We analyze each fragment and then measure the amount that is contained in each fragment. I will show you an example in a minute.

So, this mass spectrometer instrument has a device called as a mass analyzer. So, If the sample is coming from the GC, flowing and goes into ionization then it is a mass analyzer. And then there is a detector, which analyzes everything including the mass. The detector is put before the GC if you are analyzing even without separating components. If we are putting after the GC we are separating components and analyzing it. But you do not have any information about the qualitative part of the detector at the end of it. Different types of mass analyzer exists but 1 of the common mass analyzer is called as a quadrupole. Very simply it is a channel which has about 4 magnets. If you look at it in such a way that it has 4 magnets and there is a path, this is the pathway of the analyzer.

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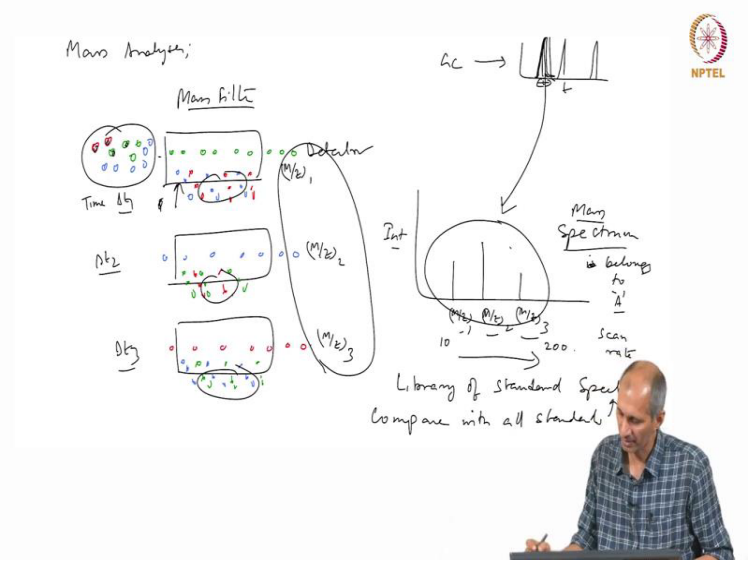

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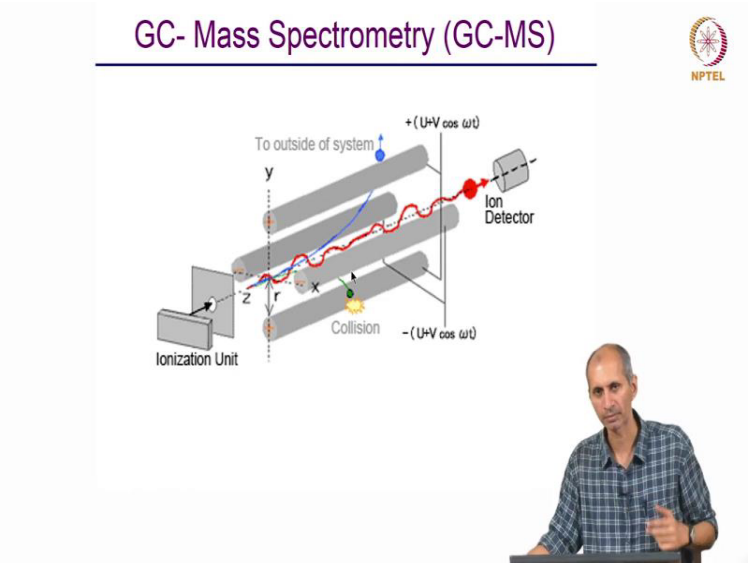

This is a mass analyzer so, this is coming from the GC. And right here, this is the place where ionization happens, large amount of energy is given and the compound that is coming in it bombards, and fragments are going through this. These 4 rods you see are the analyzers, these rods essentially act like a magnet. Very simple terminology is like a magnet really, it is some sort of an electromagnetic device. What it does this it pulls as there is a trajectory.

Some of the things that have a certain mass is programmed to allow 1 mass to go through and the rest of it is pulled out. It is also called as the mass filter. Let us assume that it is like a mass filter,

do not worry about the details of it. What it allows is, there are several m by z things. Let us give different colors: this is some reds, some green fragments and some blue fragments these are all going in like what it does for a particular setting of the mask filter.

It can pull out all the blues, all the reds and only the greens go through the detectors. So this happens, which means that it is separating the fragments of a component itself. 1 compound is broken into fragments and 1 of these fragments is being analyzed. And then it switches to the next one. So this is, say from time t1 to t2 we will call it as some delta t1 and the next delta t t2 the same thing happens but now it will allow all the green ones. The red ones are pulled out so that it only allows the blue ones to go through and so on.

And the third time segment it allows the red ones to go through, this is done very rapidly. So, from time delta t1 times time intervals delta t2, delta t3 it is trying to analyze M by Z 1, M by Z 2 and M by Z 3 corresponding to 3 different fractions of the thing. So, the detector is really allowing 1 of these fragments to go through and then all this information is then re constructed.

So, the signal that now looks like this at one particular time as the compound is going through the chromatograph GC system and MS, you will get M by Z 1, M by Z2, M by Z 3. This is the intensity of the signal. All these 3 intensities together represent the compound that is getting out. So, in other words in the GC system you are getting peaks that are coming out.
This is a flow system which is coming out as a function of time. So, each 1 of these things is going through the detector. There is a mass analyzer and at every point if you are able to quickly scan all the mass by charges, for example if I want to get mass by charges from say 10 to about 200, the maximum mass by charge is the molecular weight of a compound beyond that you cannot have anything.

So, if the molecule does not fragment it will come in as it is so, then the molecular weight will be the mass of that fragment. So, it does not have anything to fragment and requires higher energy to fragment, we are not able to provide that much energy in the GC. There are some things which are fragmentable in the GC energy, if you need to fragment more, you need to go to really high energies and you do not have that in the instrument here.

So, in the range that you are looking at, the beginning of a peak to the end of the peak is the speed at which the compound is going. In this time, it has to go and scan everything, all the fragments, it has to scan from 10 to 200 as many times as possible it keeps going. So, what it will do is it has a certain rate what is called as a scan rate.

So, you can imagine that if something is flowing at a certain speed, and everything is flowing right, you have a mixture of these things which is flowing through this mass analyzer. While it goes through this mass analyzer you have to scan through all the mass that is of interest to you. And therefore, you will get intensities assuming that this is all well mixed. What we mean by will mixed is that at time say 1 second and 1.2 seconds the composition is the same, either 1 of this fragment does not get ahead of the others which means there will be a problem that time. So we assume that they are all well mixed and then you pull out all of them except one and then measure that. This is recreated when the compound comes out like this in the exit, this is the mass spectrum of whatever has come out. How do you identify now, if this is compound X? we have to check if this is compound, say everything corresponding to this peak has now come out. So the intensity of all these 3 peaks will add up together, that is the general idea. There may be losses because it is not the entire thing, you have lost some of them and now you are only collecting the signal for a fraction of it because you are losing all of it here, here, here and here.

You are, not analyzing it really. This is another important point to remember. But nevertheless you get signal corresponding to the fragments of this and this is how you use this to identify the compound. You have a mass spectrum, which is like a signature of this particular compound. What this says is, there is a certain fraction of M Z 1 there is a certain fraction of M Z 2 and a certain fraction of MZ 3.

You can reconstruct the structure of the compound using this, but that is a longer method, there is an easier way of checking if this is a spectrum, the spectrum corresponds to a particular compound. So, this is the signature of the compound, is there is a way in which you can verify or cross check if this mass spectrum belongs to a particular compound A? How will you verify if this is a spectrum corresponding to 1 particular compound? Easy method?

This is a signature spectrum, how will you verify this is this belongs to a particular compound. You have to identify since now you have got a lot of data now and this data is a spectrum. So, spectral information is like a signature. How do you know that this signature belongs to a compound? There is no wavelength here, you are talking about different spectrum too. We will come to that also at the end of this discussion.

If you do not know what it is, one option is, whenever we are stuck like this we make use of a standard. So, what standard will you check it against? You do not know so, you will compare this with a library of standard spectra. For all known chemicals that are being manufactured and you think it is there in this compound there is a library of standard mass spectra. Every time somebody manufactures a chemical, they will measure properties and one of the properties is mass spectrum.

There are other spectra information that you also get like infrared, UV, visible absorption fluorescence spectrum and all that, it's the information that pertains to the signature of that particular compound. So, you compare the reference with all standard spectrum which is a very painful process.

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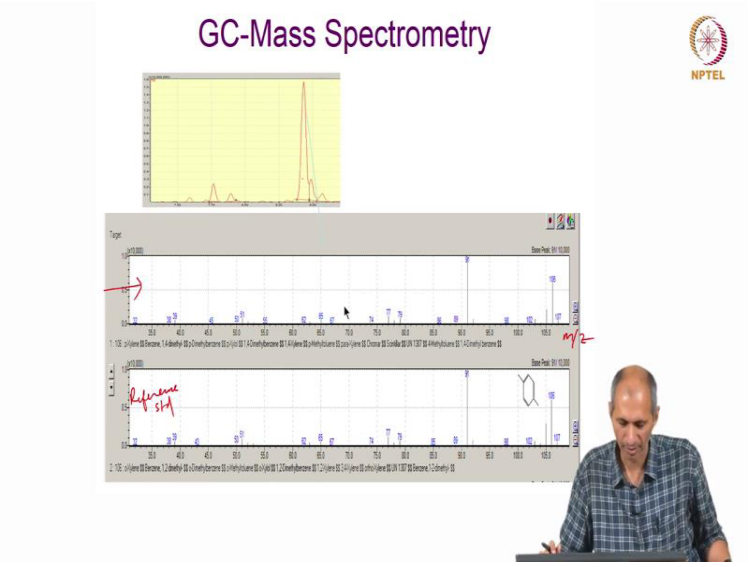

For example, suppose I take this peak, this is a chromatogram from a GC and we have said that now, this is a 2 dimensional thing. So, here this is the time axis and this is the intensity, this is a signal intensity this is time and you can see these numbers here are 7.5, 10, 12 this time is in minutes. Now, if I take this one particular peak expanded it in the software, the mass spectrum of this peak corresponds to this.

So, the first one here is the mass spectrum corresponding to this peak. What I'm doing is, I am taking the mass spectrum for the entire thing. So first in this peak the mass spectrum of this corresponds to this. So you can see that on the X axis here is M by Z and the Y axis is some intensity. Again, you can see small lines and you can see some numbers that's the mass by charge and there is one big number big peak at 91 and another one big peak at 106.

Now I have a library of such spectra if I do not have a library, I can say, this is benzene. Can I go and see this? This is benzene really, I know benzene maybe in a sample and they supposed to come around this time from the retention time analysis, I want to confirm this is really benzene. So I inject benzene and I compare the spectra with a reference spectra in it. So this 1 is a reference standard of benzene, the second peak.

So what it does really is you see that some of the peaks which are there in the first one or not, they are in second and some peaks are there here are probably are not there in the first one. So, we do a match.

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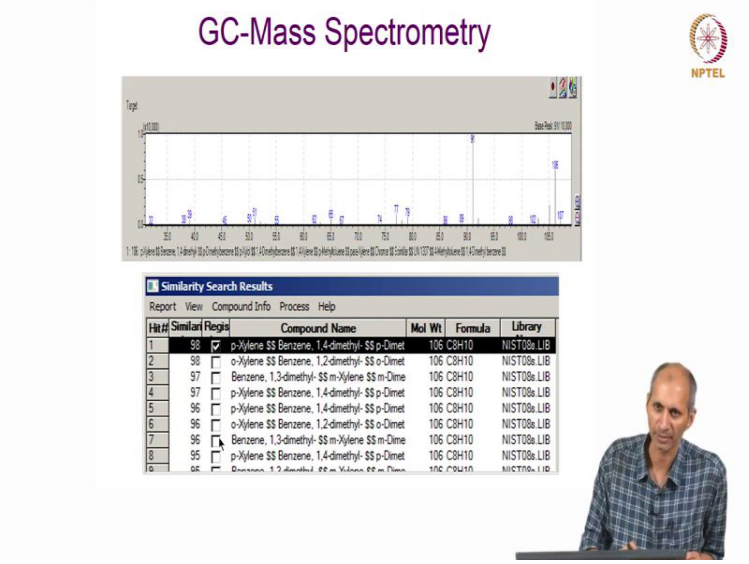

So, the instrument will allow you when you do the match then this what you get is called a similarity search. In the olden time it used to be done manually, but now software does it very quickly. So, it will give you say 98% match to benzene, which are all isomers, you know if you have compounds have same molecular formula it will look the same, you have to figure out based on some other thing whether which one of the isomers is this.

So, this is why it does not give you 100% again, it only gives you a very high probability of the compound. So, this is xylene in this case, the 1, 4 dimethyl benzene, 1, 2 dimethyl benzene is para xylene, ortho xylene all these are possible. So, that information is not available here. You have to go to some other way of finding out but that at least you know it is xylene. So this is the way mass spectral GCMS is used. So, if you have a new compound, you need the spectra for that and you will compare most of the times.

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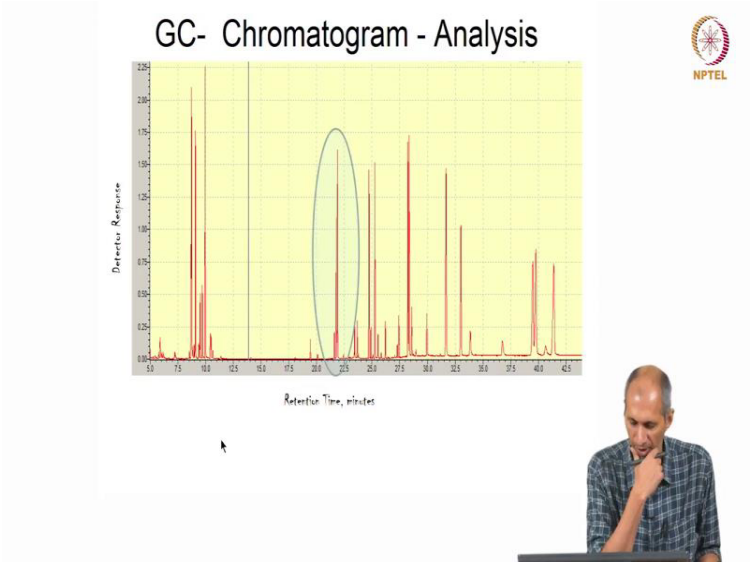

So, yesterday's lecture, we have talked about quantification, and we will look at that a little bit. So this is how the chromatogram looks at detention time in minutes at detector response. Then in current modern software, you can do all these things, you can expand and go and look into a peak and all that.

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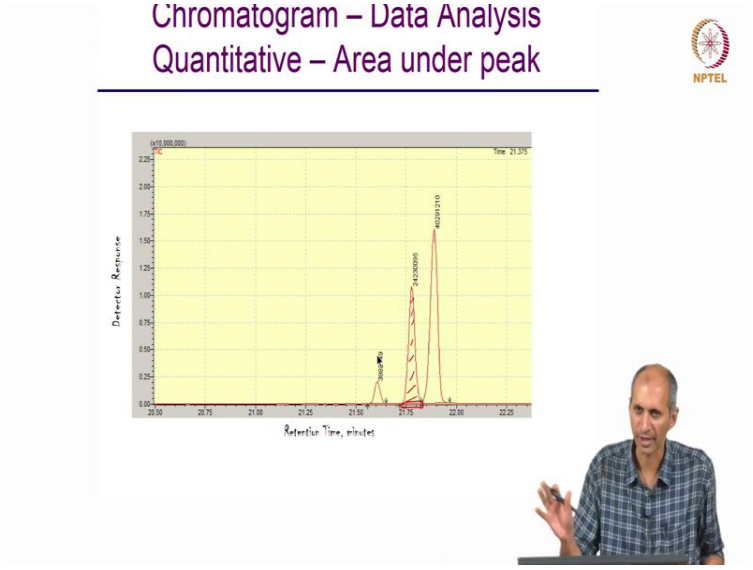

So if I am expanding that particular section of the chromatogram it looks like this. You can see peak shapes. They look very nice scene. But you can also see that sometimes if you notice this point, there is a particular you know it is not going back to baseline. It is stopping short, which means that it is separated and not exactly nice. But you see by in laws there are 2 peaks so it is