Basic Environmental Engineering and Pollution Abatement
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Lecture 13
Instrumental Techniques of Environmental Analysis - 1

Hello everyone. Now, we will discuss on the topic Instrumental Techniques for Environmental Analysis, Part 1. We have already discussed that different types of pollutants enter into the environment, in water, in air, in soil and they create different types of health impacts, if they are present above certain limit, in the water or in the environment.

Now, in this class, we will discuss how to analyze the concentrations of different pollutants in the environment. As you know that for the analysis of any chemical component there are many methods available including qualitative and quantitative analysis. So, qualitative analysis gives us some idea about the presence of particular elements or pollutants and quantitative analysis gives us the quantifications of the pollutants or elements present in the system or in the environment or in any solution, whatever may be the case.

And we also know that with the advancement of the technology, new and sophisticated instruments have been developed which can analyze the concentration of the pollutants in environment, in water or air or in a gas sample with more accuracy and even very trace amount or very small amount or smallest concentration is also possible to be detected by the instrument.

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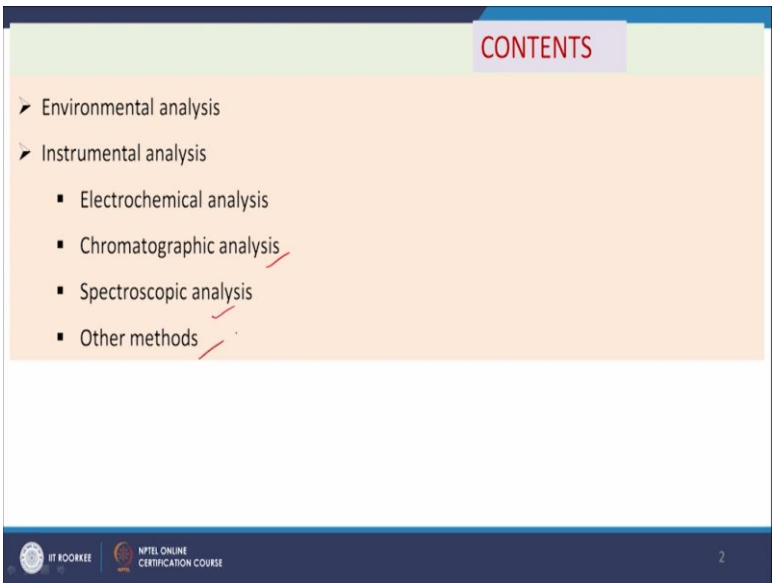

So, in this class, we will discuss about the environmental analysis that is instrumental analysis, electrochemical analysis, chromatographic analysis and spectroscopic analysis and other methods.

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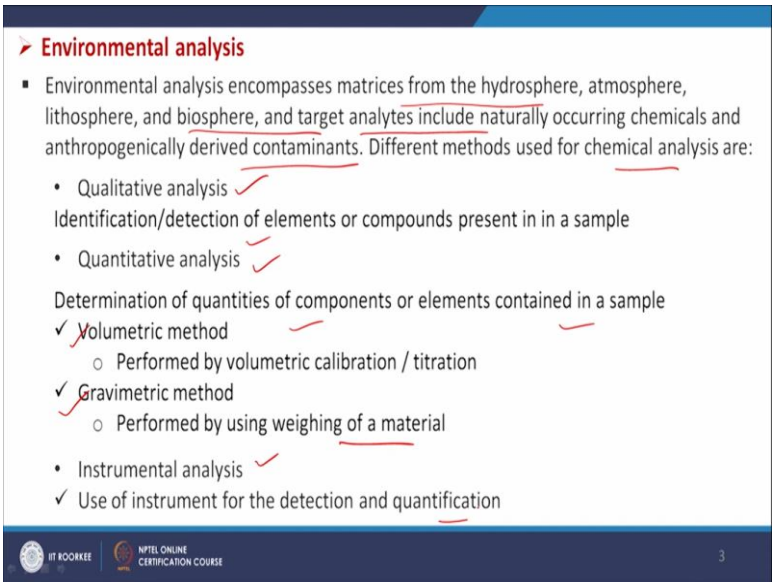

Now, as I have discussed that environmental analysis encompasses matrices from the hydrosphere, atmosphere, lithosphere and biosphere and target analyzed include naturally occurring chemicals and anthropogenically derived contaminants. And different methods used for chemical analysis are qualitative analysis quantitative analysis.

And the advancement is your instrumental analysis. By Instrumental analysis, we can perform both qualitative as well as quantitative analysis. We have mentioned that qualitative is to identify or detect the elements or compounds present in the sample. And quantitative analysis, determination of quantities of components or elements contained in a sample.

And in our laboratory normally, we do volumetric titration or volumetric method to know the concentration of the any elements in a solution. And then we also do gravimetric method that is performed by using weighing of a material. So, these are normally used in the lab apart from this instrumental analysis that use of instrument for the detections and quantifications that is the another attractive area.

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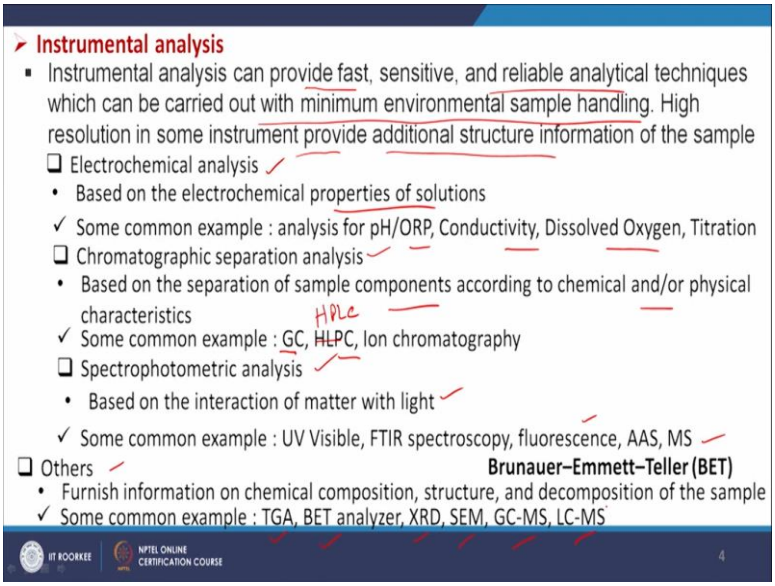

And nowadays particularly when the concentration are very very small, we are talking about like say arsenic, fluoride in the water or nitrate or NOx, SOx in the air. So, those concentrations are very less. So, detection of those by using instrumental analysis is very very appropriate.

Now, the instrumental analysis can provide fast, sensitive, and reliable analytical techniques which can be carried out with minimum environmental sample handling. High resolutions in some instrument provide additional structural information of the sample. So, another advantage for using instrument it is that the sample volume required is lesser with respect to lab tested without instrument or chemical tested.

Then these instrumental analysis methods may be based on the electrochemical analysis or chromatographic separation analysis or spectrometric analysis or some other techniques as well. So, in case of electrochemical analysis, this is based on the electrochemical properties of solutions for example say analysis of pH, oxidation-reduction potential conductivity, dissolved oxygen and titration.

And chromatographic separation analysis, this is based on the separation of sample components according to chemical and or physical characteristics of the element in the sample and some example are GC and HPLC, gas chromatography, high performance liquid chromatography and ion chromatography.

And spectrophotometric analysis, this is based on the interactions of matter with light, like say UV and FTIR. And fluorescence spectroscopy, Atomic Absorption Spectroscopy and Mass Spectroscopy. Other methods which are also used for the analysis of environmental parameters those are say TGA, BET analyzer, XRD, SEM, GC-MS and LC-MS. We will be making some discussion on these instrumental methods.

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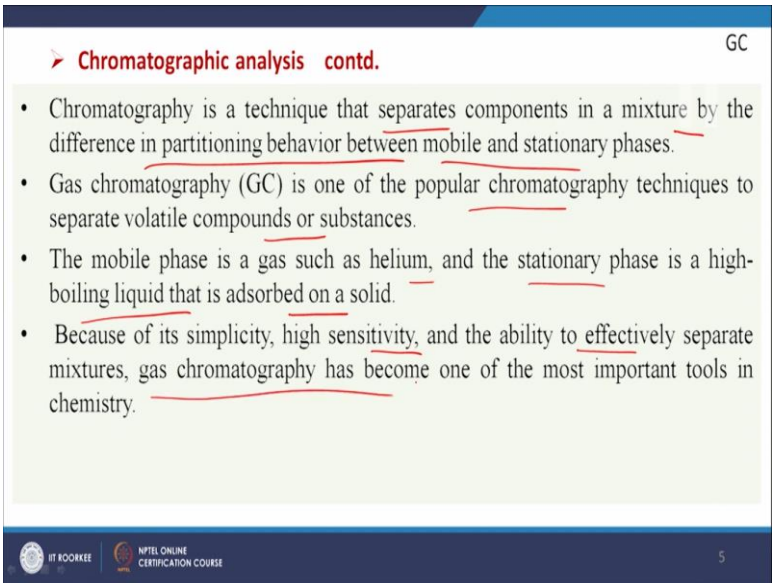

The first is chromatography. So, gas chromatography and liquid chromatography, both we will discuss. And chromatography is a technique that separates components in a mixer by the difference in partitioning behavior between mobile and stationary phase.

So, if we have one mobile phase and another stationary phase, the mobile phase may carry the pollutants of the element which need to be separated from it and the stationary phase may help to capture that selectively or capture that preferably. So, when the mobile phase will pass through a column where the stationary phase is available then depending upon the interaction or affinity of the elements with the stationary phase, compounds' or components' the retention time will vary.

And we will be exploiting this property so, more the interactions, the retention time will be more and less the interaction, retention time will be less. So, if we have some known samples, so, we will be able to know for known sample, what is the retention time and in our case, what is the retention time, by comparing we can ensure that this type of compound or the element is present in our sample. And then it can be the mobile phase can be in gas phase or maybe in liquid.

So, when it is a gas phase then it is called gas chromatography. And this gas chromatography is one of the popular chromatography techniques to separate volatile compounds or substances and the mobile phase is a gas phase, gas such as helium and the stationary phase is a high boiling liquid that is adsorbed on a solid. And because of its simplicity, high sensitivity and the ability to effectively separate mixers, gas chromatography has become one of the most important tools in chemistry.

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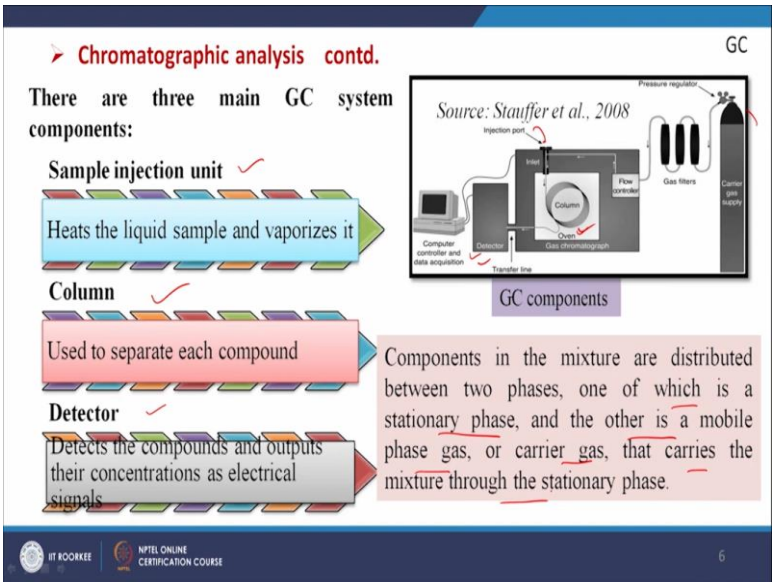

And here we will see the working of this, the working of the GC and its components. So, here different components are there. One sample injection unit, we need to inject the sample and like say here, we need one column. So, this is our column, this is sample injection and one will be our carrier gas and then detector and sample injection unit that hits the liquid sample and vaporizes it.

Column, this is our column and that is used to separate each compound, our element and then detector. This is our detector which detects this and so, this is our carrier gas which acts as a mobile phase. And then we are putting our injecting the sample here. It is going through this column and then it is going out and then at the detector it is detected and a signal is created and which is recorded in the computer.

So, this is a functioning of the GC and components in the mixer are distributed between two phases, one of which is a stationary phase and the other is a mobile phase. Gas or carrier gas that carries the mixer through the stationary phase.

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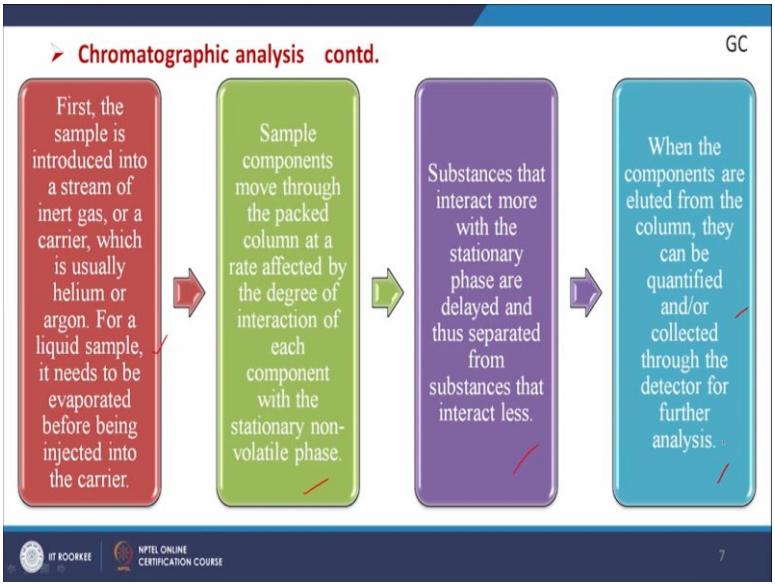

So, this slide also explains the process once again. So, first the sample is introduced into a stream of inert gas or a carrier which is usually helium or organ. For a liquid sample it needs to be evaporated before being injected into the carrier. And then sample components move through the packed column at a rate affected by the degree of interactions of each component with the stationary non-volatile phase.

And then substrates that interact more with the stationary phase are delayed and thus separated from substances that interact less. And when the compounds are eluted from the column, they can be quantified and or collected through the detector for further analysis. So, these are the different steps.

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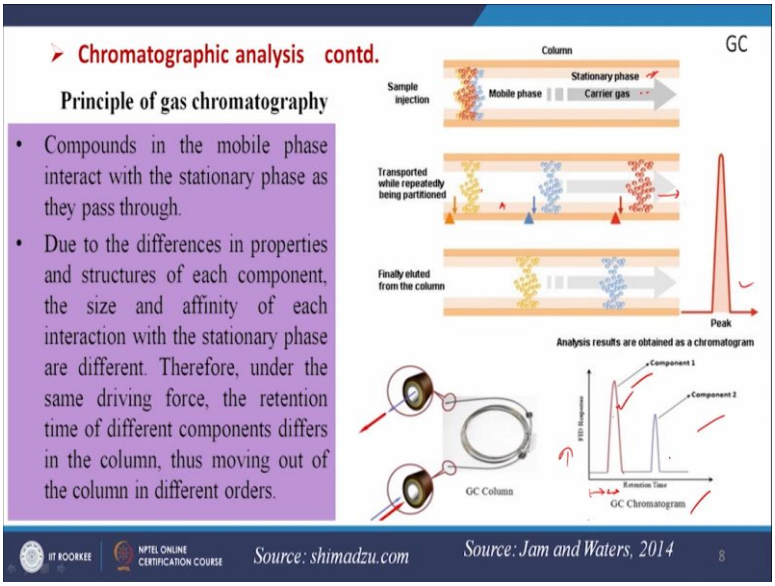

And here also the same thing is shown here. So, you see this is our mobile phase and sample is injected here and will be passing through. And this is our stationary phase here and this is our carrier gas. So, there will be interactions of this molecule, you see here different types of molecules are present here or elements are present here.

So, those are having different affinity. So, after a certain time, the location of these molecules or elements from the entry point are varying with time. So, which are having less interactions, these are coming fast. Those are having more interactions, those are remaining here. So, gradually with time interval, if we have number of pollutants present here in the sample, so, depending upon the affinity, some will come first and then followed by the next ones which are having relatively more affinity towards this stationary phase.

So, as once this is coming here, so, then our detector will be able to detect it and one peak we will get. So, this one peak we will get. So, this is the methods for the analysis of elements using GC. And here this is GC chromatogram. This is a component 1 and component 2. So, this component peak we are getting first. So, at lesser time, this is time and this is our response. So, if it is with less time it is coming out that means retention time is less. So, this compound has less interactions with the stationary phase.

Now, if we use some standard samples here, then if we can measure what are the time required to get the peak and you can match this time interval or if you can the residence time you can match then we can identify the possibility of the component present here with this, with the known value. Similarly, if multiple components are present, we can also identify the

multiple components. So, this is qualitative analysis. We can also do quantitative analysis by measuring the area of this peak.

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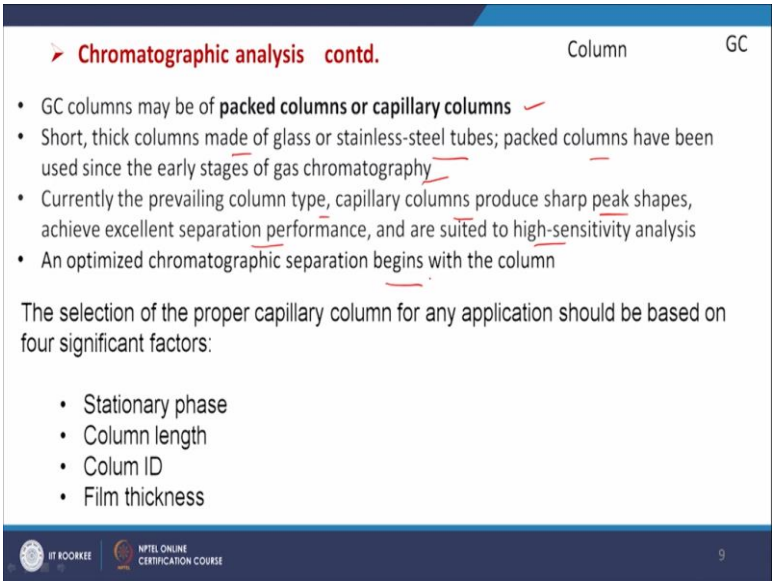

Now, what are the different parts of GC? We have seen that it contains column, it contains detector and these are the two major component. And in this column, we see that GC columns may be of packed weight or capillary columns. It may be packed weight or capillary column. If it is a packed weight then relatively it is shorter and it is thick columns made of glass or stainless steel tubes.

Packed columns have been used since the early stages of gas chromatography but with the advancement of the technology, nowadays, capillary tubes are being used. So, currently, the prevailing column type that is capillary columns produce sharp peak shapes and achieve excellent separation performance and are suited to high sensitive analysis and optimized chromatographic separation begins with the column.

Actually, column is very very important for the efficient separations of the pollutants or elements and as a result the performance of the instrument for analysis purpose. And how can we select the column? We can select the column; we can consider different parameters of it or varying properties like say stationary phase, what is the stationary phase, what is the column length, what is the column ID and what is the film thickness. So, now, we will see.

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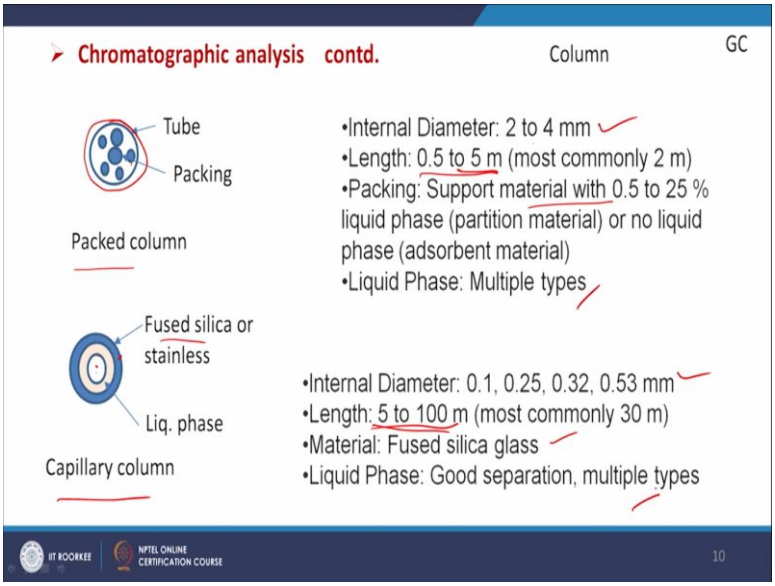

So, this is our packed weight column. Say if it is a packed weight, so, this is our tube, outside is our tube and then inside is we are having say these are packing materials. And in this case, the internal diameter of the tube is 2 to 4 mm and length is 0.5 to 5 m. Support material with 0.5 to 25% liquid phase. And liquid phase may be of multiple types.

So, this is for packed weight column. And for a capillary column, you see, this is our fused silica stainless steel that is the outside of it and then we are having one liquid layer and liquid layer and which are associated with this fused silica or silica. And from this inner part the the carrier gas or mobile phase will flow and there will be interaction between the components and the liquid phase here.

So, in this case, we will see that internal diameter is very very smaller with respect to this. This is obvious because we need more interactions with the liquid. So, that is what this diameter, this diameter is very less and length is 5 to 100 m. If you had it as 0.5 to 5 m but here we are having 5 to 100 m. So, more longer coil is made and then material fuse silica glass and it gives good separations and the liquid may be of multiple types depending upon the nature of the elements present in the system.

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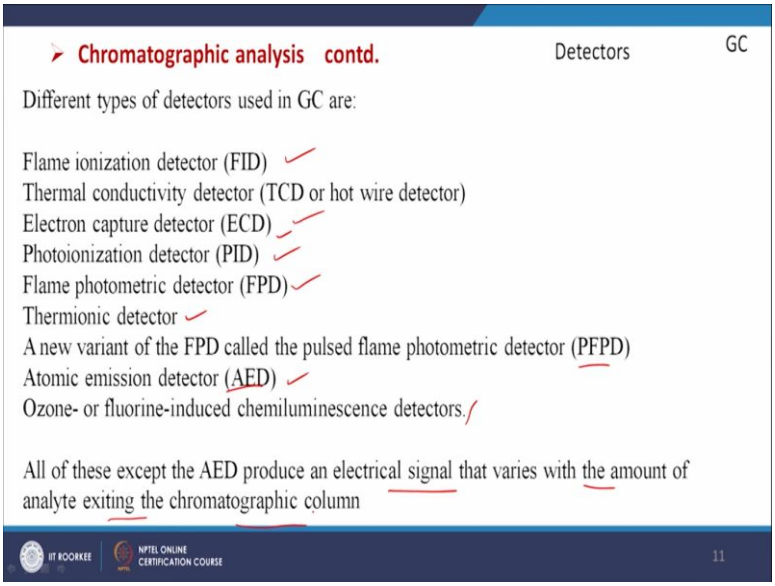

Then next but important part of GC is your detectors. So, detectors the main job is to detect the element present in it and also to quantify it. So, different types of detectors used in GC are flame ionization detector then thermal conductivity detector that is TCD and electron capture detector, ECD and photo ionization detector, PID, flame photometric detector, FPD and thermionic detector.

And a new variant of FPD that is flame photometric detector is called as the pulsed flame photometric detector, PFPD and atomic emission detector, AED, ozone or fluorine induced chemiluminescence detectors. So, out of all those detectors except AED, all production electrical signal that varies with the amount of analyte exiting the chromatographic column. So, they create some electrical signal and that is proportional to the concentration and the peak also we get and that area of the peak gives us the concentration of the element. Now, we will see how the chromatogram we get.

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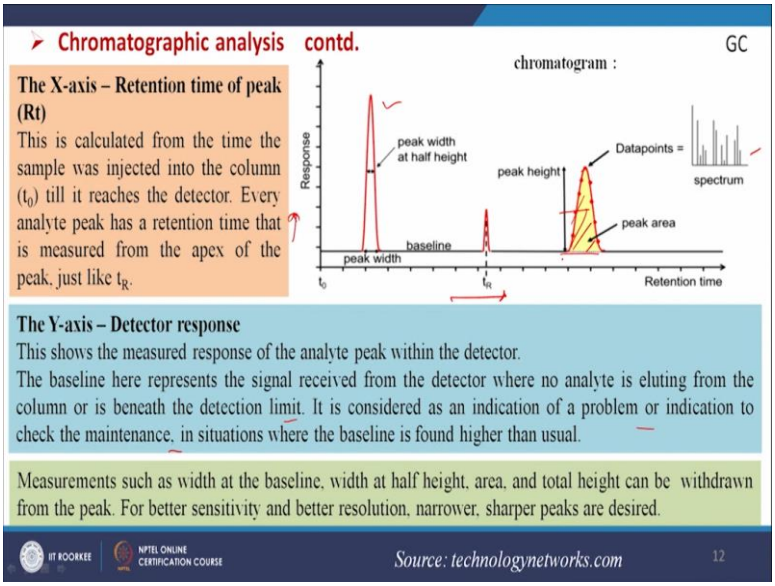

So, this is an example of the chromatogram. So, here we see the x-axis, where it indicates the retention time and y-axis is the detector response. Now, we see. So, up to certain time there is no peak but and one baseline is there. This Baseline indicates that no pollutants is present then or any element is present. So, this indicates one element is present that means it is coming out.

So, only carrier gas is coming the baseline. So, this is coming means this one is coming, this peak is coming means one element is coming out from the column with the carrier gas. That is another, this peak, another component is also present. It is coming after certain time, residence time more than this further another one. So, likewise more the elements present will get the more the peaks.

So, measurements such as width at the baseline with a half height that means this is our baseline width and of a half height width we can measure and at the peak height also we can measure this is our peak height, maximum height. So, we can get from this. And we can also get the area. So, this area is the concentrations of the particular element present in the sample.

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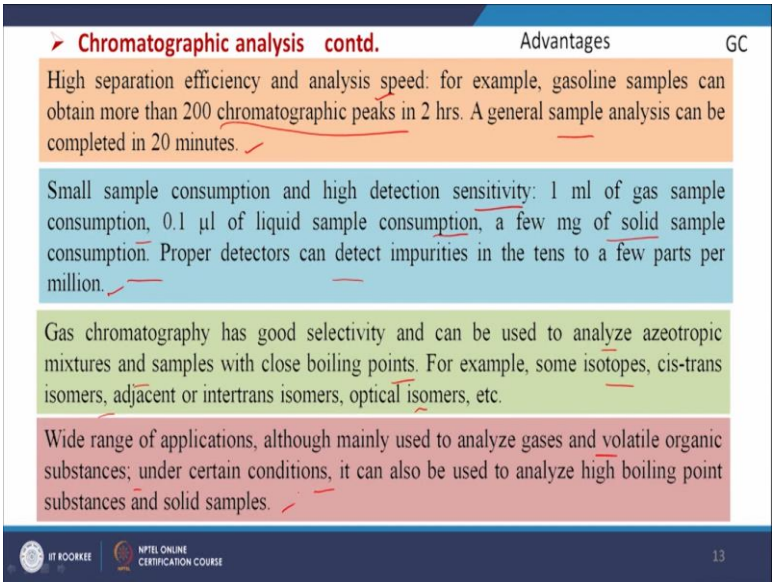

And this GC has some advantage. So, high separation efficiency and analysis speed, for example, gasoline samples can obtained more than 200 chromatographic peaks in two hours. A general sample analysis can be completed in 20 minutes. And small sample consumptions and high detection sensitivity 1 mL of gas sample consumption 0.1 µL of liquid sample consumption.

A few mg of solid sample consumption. So, proper detectors can detect impurities in the tens to few parts per million that is PPM or even PPB level we can measure. And gas chromatography has good selectivity and can be used to analyze azeotropic mixers and samples with close boiling points.

For example, some isotopes, cis-trans, isomers, adjacents or intertrans isomers, optical isomers, etcetera and wide range of applications, although, mainly used to analyze gases and volatile organic substances, under certain conditions it can also be used to analyze high boiling point substances and solid samples.

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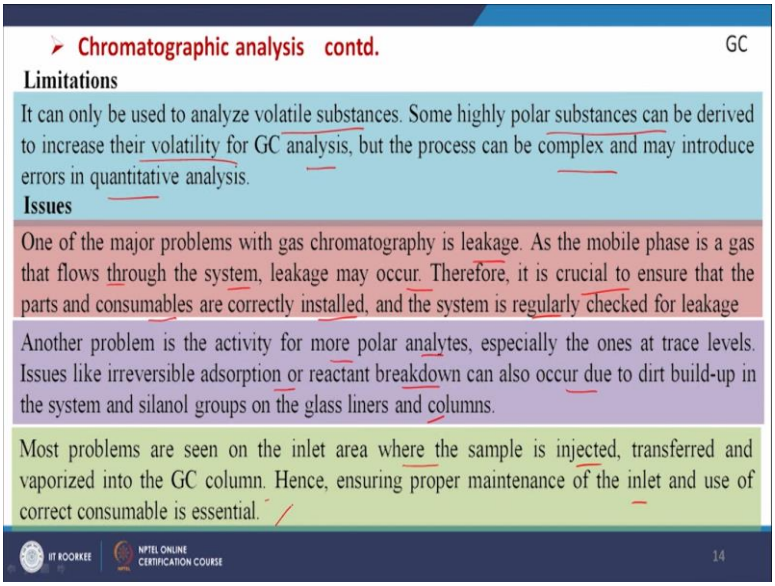

And GC has some limitation also. What are those limitations? It can only be used to analyze volatile substances. Some highly polar substances can be derived to increase their volatility for GC analysis but the process can be complex and may introduce errors in the quantitative analysis. And some issues are there.

One of the major problems with gas chromatography is leakage. As the mobile phase is a gas that flows through the system, leakage may occur. Therefore it is crucial to ensure that the parts and consumables are correctly installed and the system is regularly checked for leakage. Another problem is the activity for more polar analytes. Especially the ones that trace levels.

Issues like irreversible adsorptions or reactant breakdown can also occur due to dirt buildup in the system and silanol groups on the glass liners and columns. So, these are the some negative points. And most problems are seen on the inlet area where the sample is injected. So, transferred and vaporized into the GC column, hence ensuring proper maintenance of the inlet and use of correct consumable is essential.

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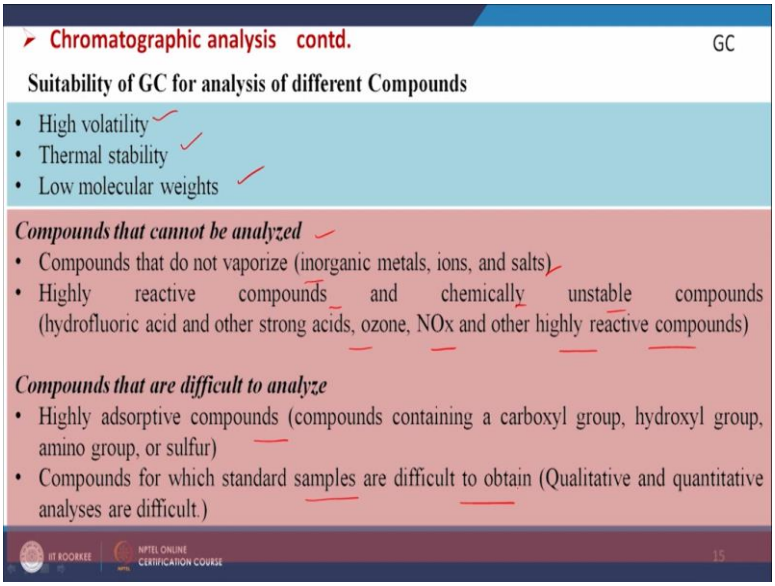

And suitability of GC for analysis of different compounds. It is suitable for analyzing compounds with high volatility, thermal stability, low molecular rates. So, compounds that cannot be analyzed. Let us say compounds are do not vaporize inorganic metals, ions, salts, etc, those cannot be analyzed.

Highly reactive compounds and chemically unstable compounds. So, those are also not be able to analyzed by this GC. So, hydrofluoric acid and other strong acids, ozone, NOx and other highly reactive compounds, for example. And then compounds that are difficult to analyze like say highly adsorptive compounds and compounds for which standard samples are difficult to obtain. Because without standard we cannot determine this.

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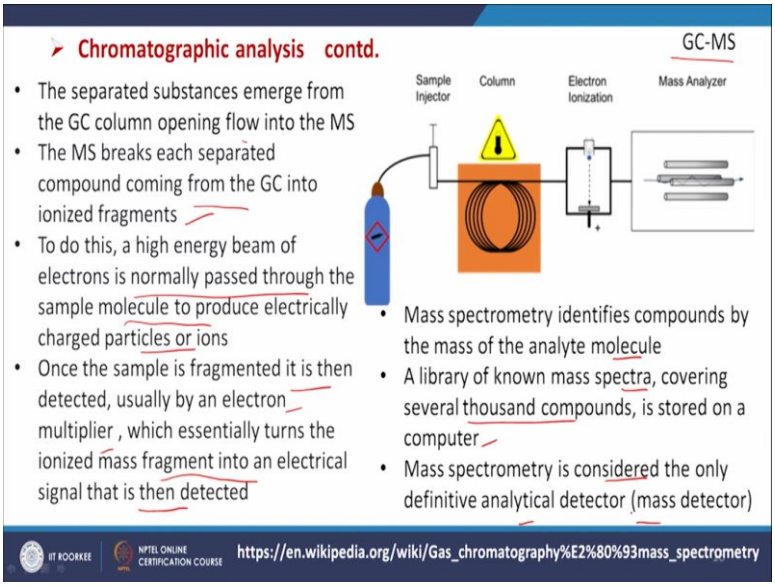

Then another advance instrument is GC-MS, Gas Chromatography Mass Spectroscopy. So, in this case, from the outlet of the GC when we will be getting some element which is coming out from the GC column, so, that will be coming into the mass spectrometer and this will be converted into ions. Then the MS mass spectrometer or spectroscopy will detect the compound as per their molecular weight or mass.

So, the separated substances emerge from the GC column opening flow into the MS. The MS breaks each separated compound coming from the GC into ionized fragments and to do this a high energy beam of electrons is normally passed through the sample molecule to produce electrically charged particles or ions.

Once the sample is fragmented, it is then detected usually by an electron multiplier which essentially turns the ionized mass fragment into an electrical signal that is then detected. And mass spectrometry identifies compounds by the mass of the analyte molecule. The library of known mass spectra covering several thousand compounds is stored on a computer and mass spectrometry is considered the only definitive analytical detector or we can say the mass detector.

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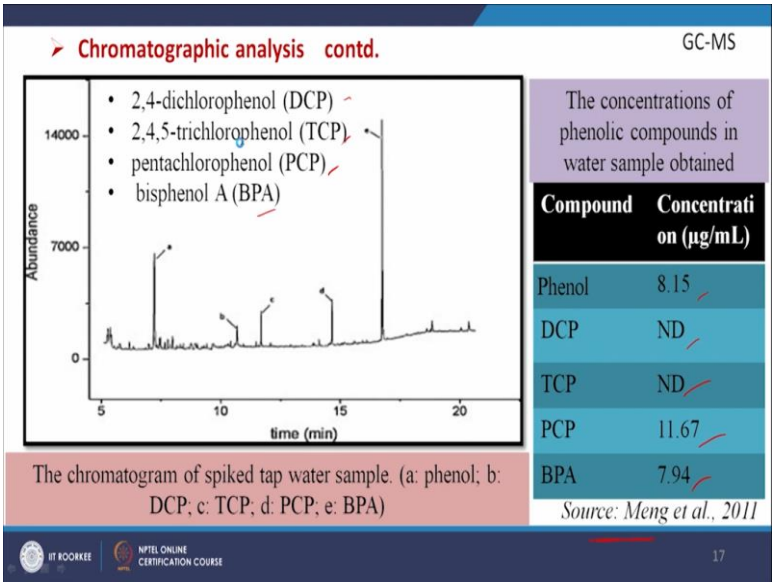

And this is one example. As per this reference, they have detected different types of phenolic compounds in water. And you see the peaks at different intervals and analyzing with standard samples or from the library, the peak area is compared with the concentration and then the concentration sensor measured like say phenol 8.15 DCP that is ND, this is ND non detectable and then PCP 11.65 and BPA equal to 7.94. So, DCP, TCP, PCP and BPA are mentioned here. So, that way GCMS is used.

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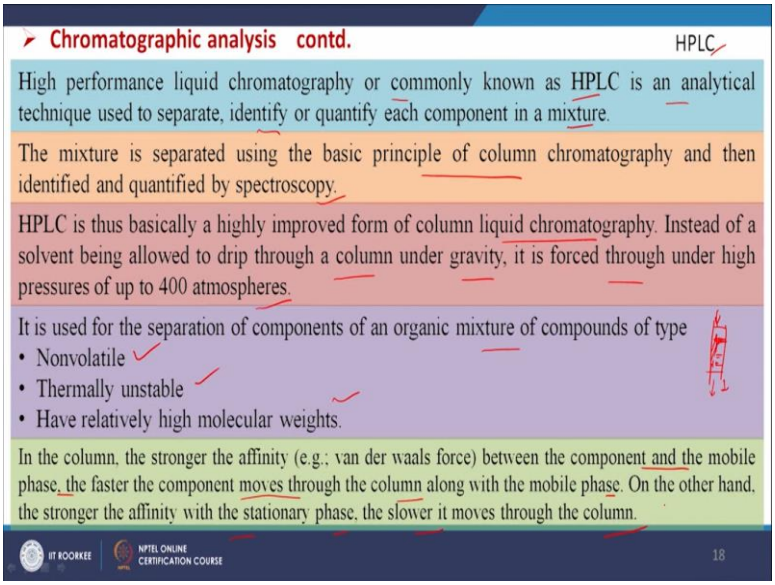

And now, we will start discussion on the liquid chromatography and high performance liquid chromatography that is HPLC. So, what is this in case of HPLC? Our mobile phase will be

liquid, not gas. And so, one will be stationary phase. So, one column will be there HPLC column will be there and then mobile phase will be liquid.

And then the high performance liquid chromatography are commonly known, as HPLC is an analytical technique used to separate identify or quantify each component in a mixer. So, what will be happening? If we have say column, we are packed with some material and from the top we are putting the liquid containing the element.

So, depending upon the affinity the different elements will be captured here at different locations. And after certain time interval it will be coming out. So, some element will come out first and then followed by other and followed by other, depending upon the affinity. So, that way that is under gravity the liquid can fall.

But in that case we may not get very first separation and we may not get the more precision. So, in HPLC, a column is used through which the carrier liquid or say mobile phase is passed at high pressure. So, if to create the pressure, a pump is used and this pass through and when it is passes through the high pressure, so, the separations becomes more effective.

So, the mixer is separated using the basic principles of a column chromatography and then identified and quantified by spectroscopy. The HPLC is thus basically a highly improved form of column liquid chromatography. Instead of a solvent being allowed to drip through a column under gravity, it is forced through under high pressure of up to 400 atmospheres.

It is used for the separation of components of an organic mixture of compounds of types A non-volatile compounds and then thermally unstable and have relatively high molecular weights. And in the column, the stronger the affinity between the compound and the mobile phase, the first are the component moves through the column along the mobile phase. On the other hand, the stronger affinity with the stationary phase, the slower it moves through the column.

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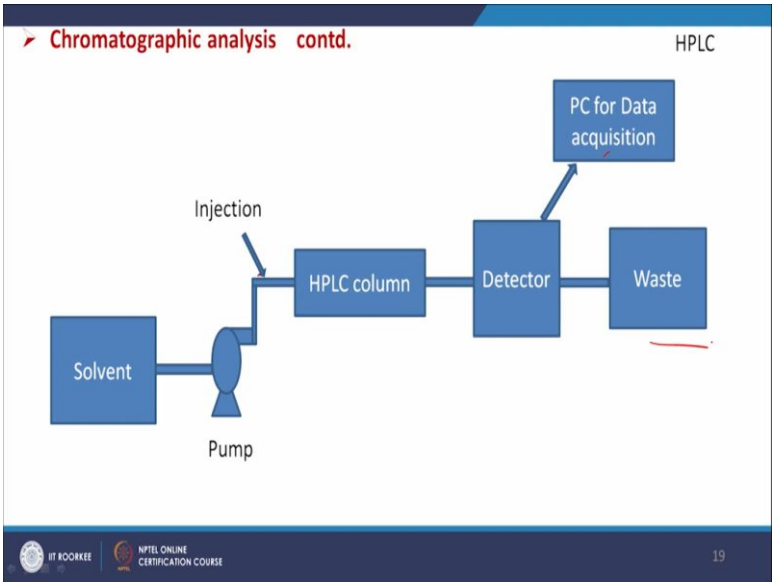

And here say this is a solvent. From this pump we are giving high pressure here and then injection the sample is injected here. And it is going through the HPLC column. Depending upon the residence time, elements will be coming out after different time intervals. And then here the detector will be used to detect that. So, the signal will go to the PC and it will be recorded there and the carrier solvent will be wasted. So, this is the flow sheet of the HPLC or analysis.

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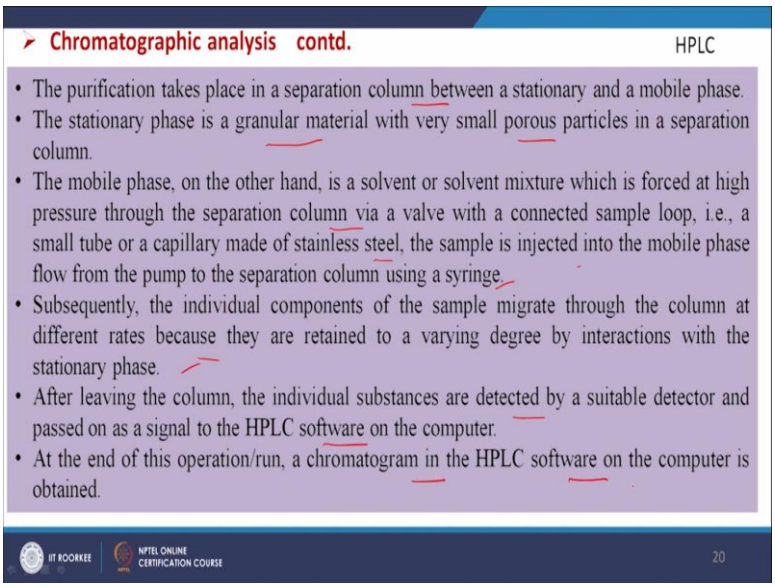

Now, the purification takes place in a separation column between a stationary and a mobile phase. The stationary phase is a granular material with very small porous particles in a

separation column. The mobile phase, on the other hand, is a solvent or solvent mixture which is forced at high pressure through the separation column via a valve with a connected sample loop, that is a small tube or a capillary made of stainless steel.

The sample is injected into the mobile phase flow from the pump to the separation column using a syringe. So, here also the capillary column is used. And subsequently, the individual components of the sample migrate through the column at different rates because they are retained to a varying degree by interactions with the stationary phase. And after leaving the column, the individual substances are detected by a suitable detector and passed on as a signal to the HPLC software on the computer. And at the end of this operation, run a chromatogram in the HPLC software on the computer is obtained.

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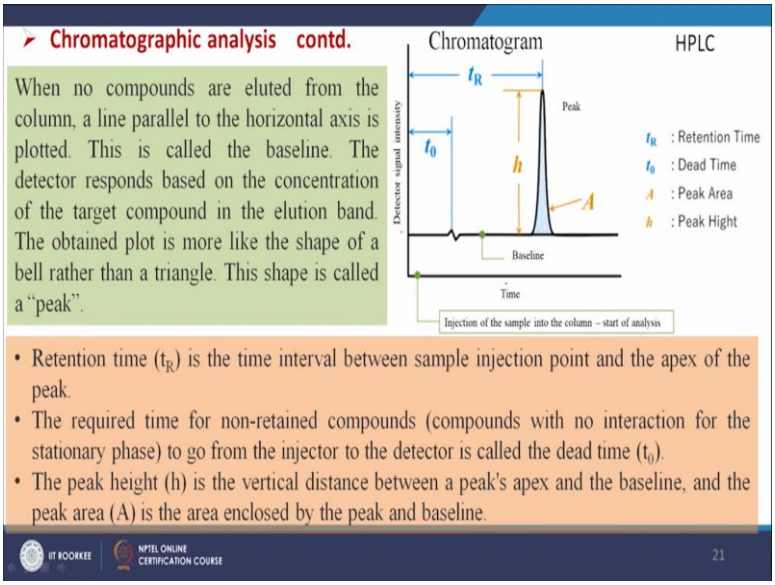

So, this is the chromatogram just like your GC, similar way. So, here also this is a baseline is there. That means no element is coming out, only the carrier liquid is coming or the mobile phase is coming. And then first time, some signal we get, some peak we are getting. And this is our t_R that is the retention time, from this to this. And this is our height. In the similar way to that of GC process, we can get the peak also.

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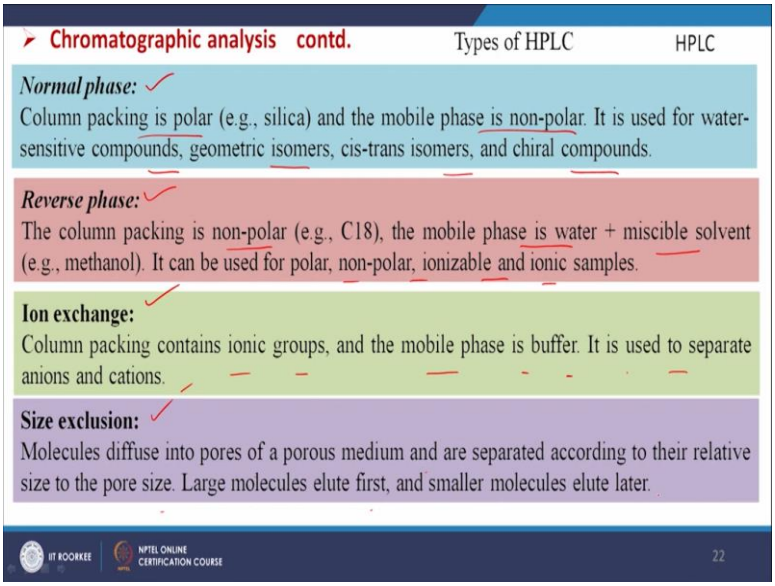

Now, types of HPLC. HPLC may be operated in normal phase, in may be reverse phase, in ion exchange or size exclusion. That means how the separation is taking place, what is the principle of separation that is most important. Say in normal phase, column packing is polar, that is a silica.

And the mobile phase is non-polar. It is used for water sensitive compounds, geometric isomers, cis-trans isomers and chiral compounds. Reverse phase, the column packing is nonpolar; the mobile phase is water plus miscible solvent. It can be used for polar, nonpolar, ionizable and ionic samples.

So, apart from ion exchange can also take place. So, column packing contains ionic groups and the mobile phase is a buffer. It is used to separate anions and cations. Apart from that size exclusion is also possible. So, what is the size of the element and what is the pore size that way the bigger size elements are arrested. So, molecules diffuse into pores of a porous medium and are separated according to their relative size to the pore size. So, large molecules elute first and smaller molecules elute later.

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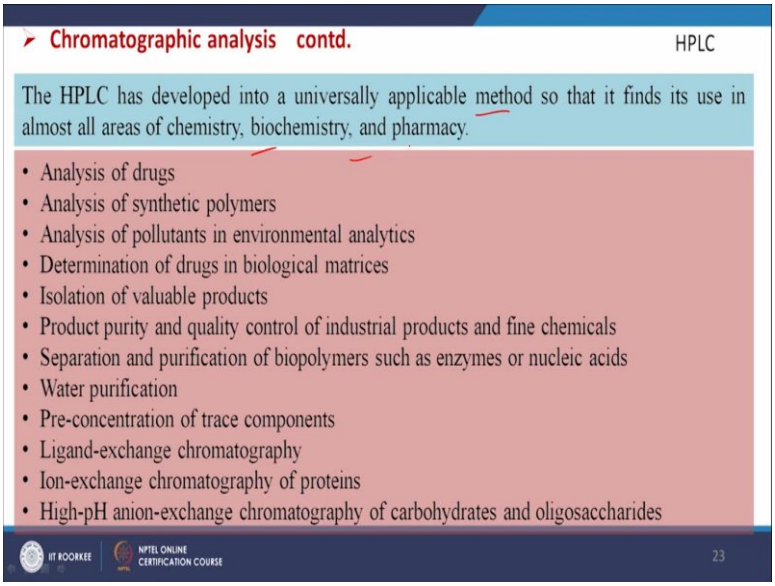

The HPLC has developed into a universally acceptable method. So, that it finds its use in almost all areas of chemistry, biochemistry and pharmacy, even in environmental area also. So, these are the different HPLC applications.

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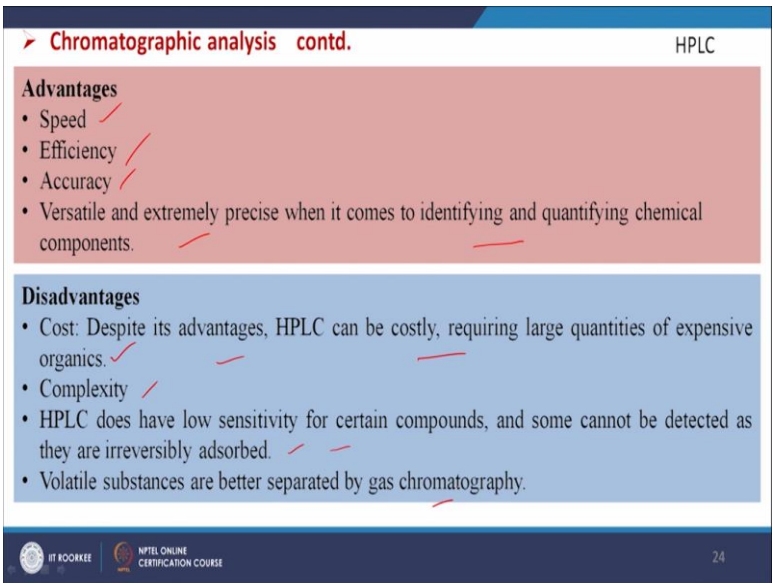

And it has some advantage like say a very fast process, a high efficiency, accuracy and versatile and extremely precise when it comes to identifying and quantifying chemical components. And it has some disadvantage also. Its cost, despite its advantage HPLC can be costly requiring large quantities of expensive organics and complexity, as also high pressure has to be created. HPLC does have low sensitivity for certain compounds and some cannot be

detected as they are irreversibly absorbed. And volatile substances are better separated by gas chromatography.

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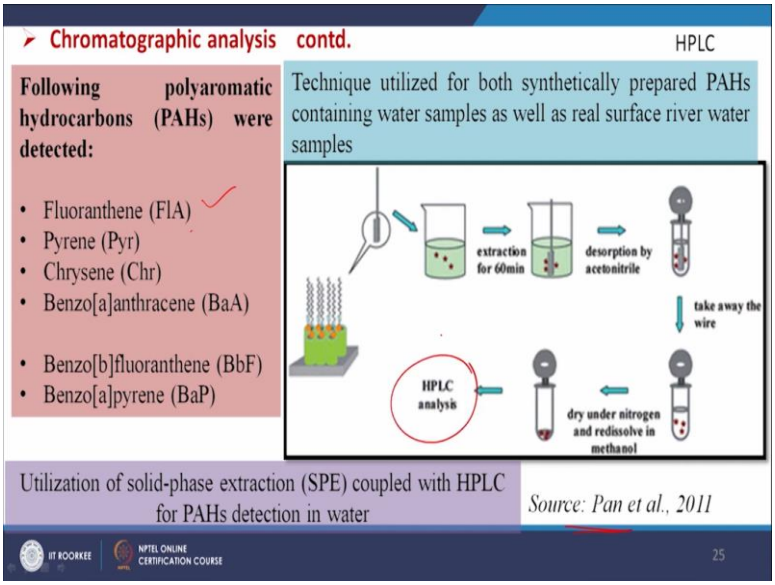

And this is an example of analysis of water samples containing different PAH's that is Poly Aromatic Hydrocarbons. So, these are the different PAH and they have, these researchers have identified it. And this is the method, this is not important but this is HPLC analysis is there.

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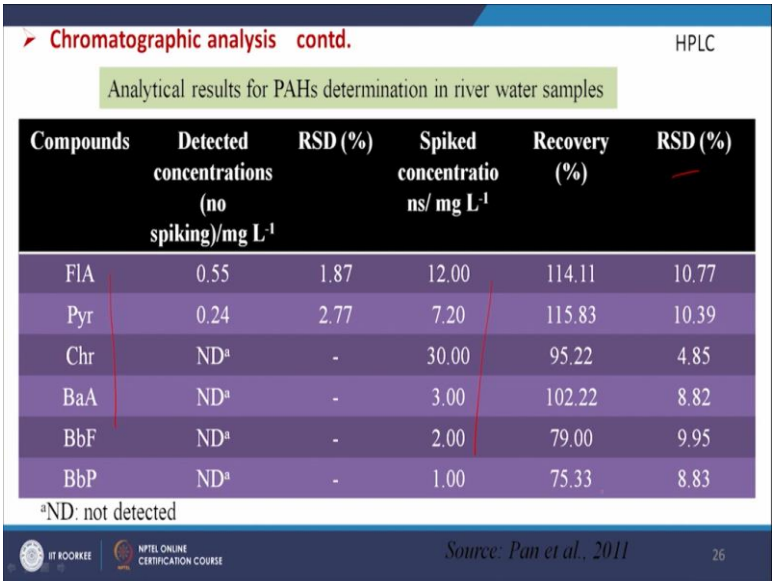

And by this analysis, they have quantified like this. So, this is some example of the use of HPLC. So, these are the detection concentrations of different types of PAH's and this is a

spikes concentration and these are the detection concentration. There are some detection limit basically and these are the recovery and this is your relative standard deviation. So, these are some example of HPLC, basically. So, after this in this class, thank you very much for your patience.