Environmental Soil Chemistry
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Lecture – 60
Analytical Techniques for Assessing Soil Pollution Continued

Welcome friends to this last lecture of week 12 or module 12 of this NPTEL online certification course of environmental soil chemistry, and in this week, we are talking about different analytical methods for measurement of soil pollution. In this last lecture, we will be talking about some methods for inorganic pollutants and also we will be talking about the analytical methods for major organic pollutants.

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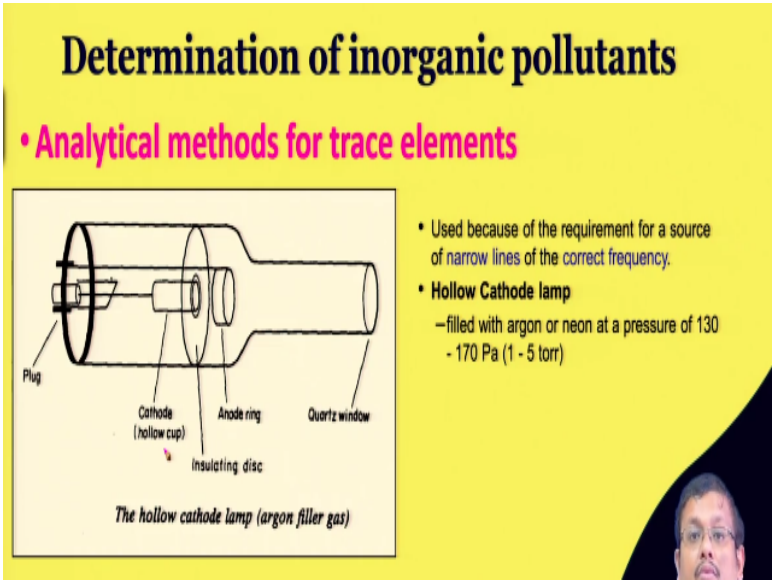

So in the last lecture, we are talking about the working principle of atomic absorption spectroscopy and I showed you the schematic diagram of the atomic absorption spectrometer and then we talked about the hollow cathode lamp. So, this is the picture of the hollow cathode lamp. You can see here, it has different components. It has a quartz window, it has an anode ring, and there is an insulation disc and cathode also present here and also there is a plug.

So the hollow cathode lamp has a particular element, the cathode is made up of that particular element and this is why we use the hollow cathode lamp. We use the hollow cathode lamp because the requirement for a source of narrow lines of the correct frequency and this hollow cathode lamp is basically filed with, why we call it hollow, because it is filled with argon or

neon which are inert gases at a pressure of 130 to 170 pascal or 1 to 5 torr. So this is how we call it hollow cathode lamp.

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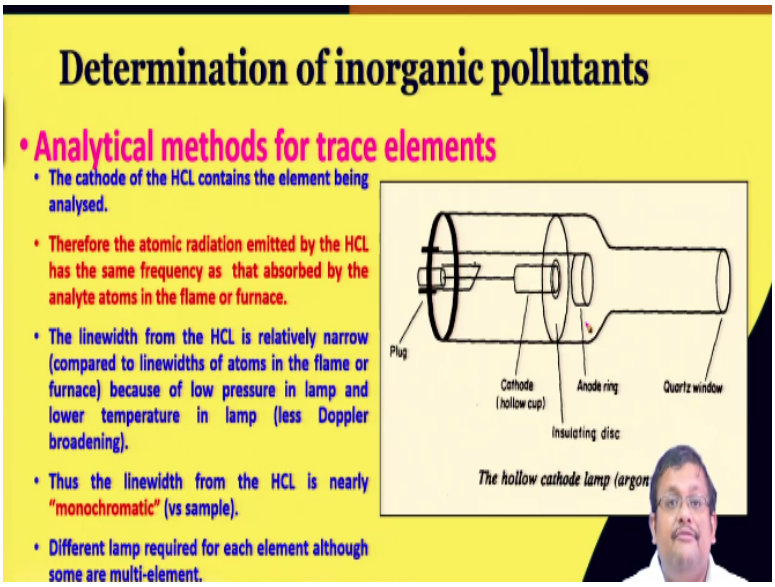

Now, the cathode at this hollow cathode lamp as I told you contains the elements being analyzed. So therefore, the atomic radiation emitted by the HCL or hollow cathode lamp has the same frequency as that absorbed by the analyte atoms in the flame of furnace. So basically it says that since the cathode of a hollow cathode lamp is made of a particular element, which is suitable for measurement of a particular element.

Therefore, the atomic radiation which is produced by this hollow cathode lamp or emitted by this hollow cathode lamp has the same frequency, which will be absorbed by that element under consideration which is in the flame or furnace. Now the linewidth from this hollow cathode lamp is relatively narrow, which is compared to the linewidth of atoms in the flame or furnace.

Because of the low pressure in lamp and lower temperatures in the lamp that is creating less Doppler broadening. So the linewidth from the HCL is monochromatic versus the sample. So basically that is why I am telling you we are producing the monochromatic radiation, which has the wavelength which perfectly coincide with the wavelength which is being absorbed by the particular element or it is basically the same wavelength.

So different lamps are required for each element, although some are multielement. So, this is a characteristic feature of this AS that you need to use individual hollow cathode lamp for individual element okay.

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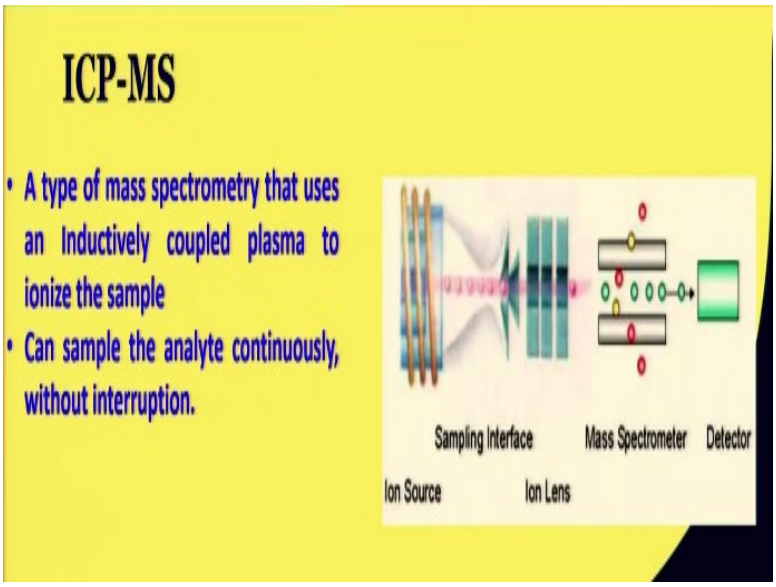

So, we have covered the AS. Another important instruments which we are going to talk about this is called ICP-MS. Now you know what is ICP that is inductively coupled argon plasma, so basically the same. So the ICP-MS is a type of mass spectrometry that uses an inductively coupled plasma to ionize the samples and this is very, very precise and very, very sophisticated instrument.

And this instrument is basically used by the laboratories as a gold standard for measurement of different elements. So this can measure a wide range of elements and the precision level is quite accurate and also the level of detection or limit of detection is very, very low. We can go up to ppb to ppt sometimes. So, the basic principle is it has an ICP, inductively coupled plasma for ionizing the sample.

Which is attached to a mass spectrometer for measurement of those individual ions. So one of the major benefit of this instrument is it can sample the analyte continuously without any interruption.

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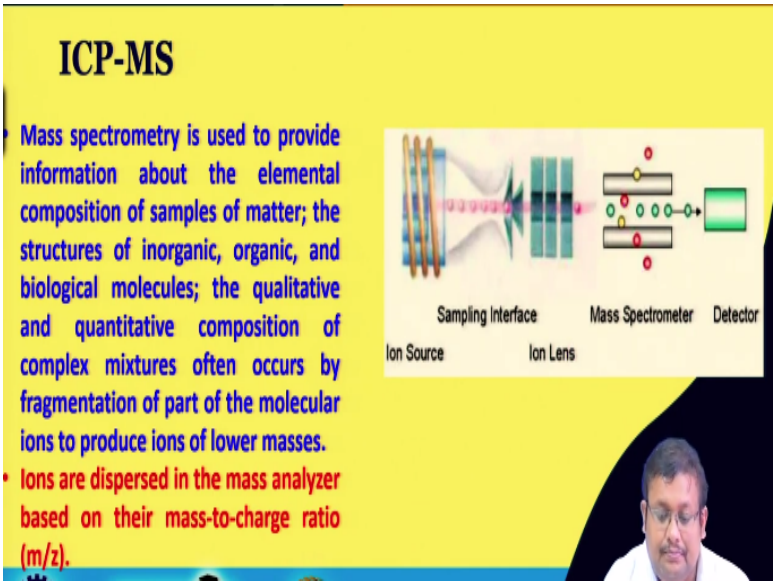

Now, mass spectrometry, what is the benefit? You have already seen ICP-AES, atomic emission spectroscopy. Now we are talking about ICP-MS which is more sophisticated. What is it you can ask me, now mass spectrometry, remember this MS stands for the mass spectrometry. Now mass spectrometry is basically used to provide the information about the elemental composition of the sample of matter.

And the structure of the inorganic, organic and biological molecules and the qualitative and quantitative composition of the complex mixture often occurs by fragmentation part of the molecular ions to produce the ions of lower masses. So, you can see it has a wide range of application. If you want to go to the more detailed level, you have to go with this ICP-MS. Now remember that in this ICP-MS, the ICP part helps in the proper ionization of the samples.

And in these ions that dispersed in the mass analyzer when it goes as you can see these ion source or sampling interface is there. So this is an ICP, so from this ICP, the ions goes to the mass spectrometer. These ions are dispersed in the mass analyzer based on their mass-to-charge ratio, we denote by this m by z. So based on these, their dispersion, according to their mass-to-charge ratio they are being separated and further they are being detected.

So that is why ICP-MS is more sophisticated. If you want to go for measurement of a particular species of ion, for example if you want to measure the harmful species of arsenic in the soil or water like arsenic 3+ or arsenic 5+ you have to go with this ICP-MS.

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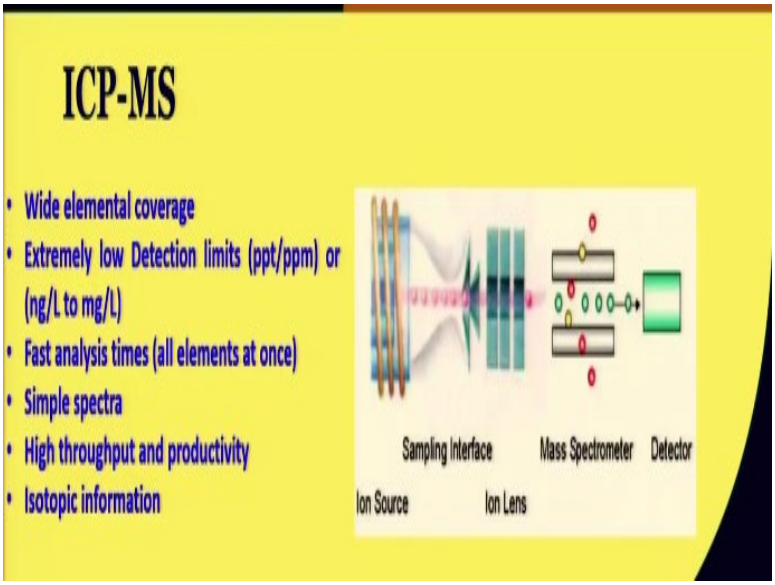

Now, what are the benefits of ICP-MS. The benefits of ICP-MS is first it has wide elemental coverage, it can measure a wide range of elements, I will show you in the next slide. It has extremely low detection limits. It can go up to ppt or ppm sometime to or basically nanogram per liter to milligram per liter. So you can see it can go up to parts per trillion levels. So it has fast analysis time, all elements at once.

Simple spectra, the spectra is simple, high throughput and productivity. It can measure wide range of elements in a single go and it can give you the isotopic information also. So you can see these are the benefits of using the ICP-MS.

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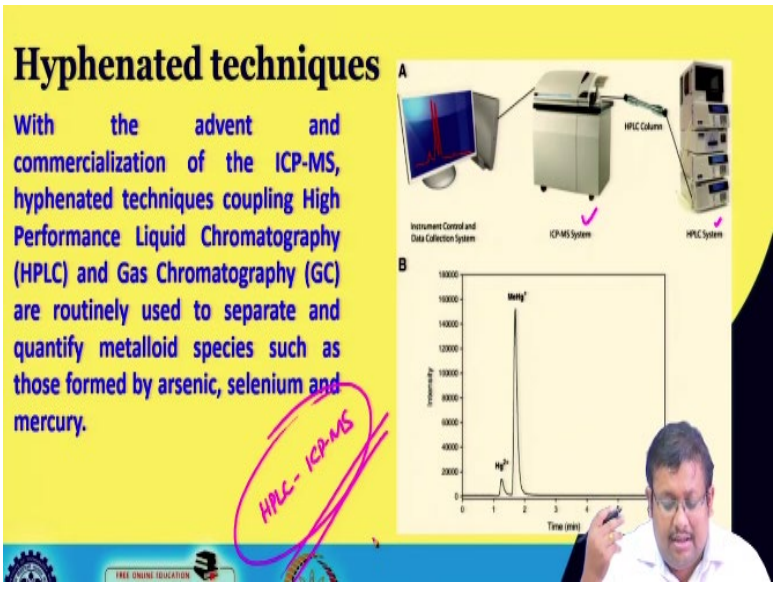

Now there are certain advancement of these different types of analytical techniques nowadays, also help for development of different hyphenated techniques. What are these

hyphenated techniques? Now with the advent of commercialization of the ICP-MS, hyphenated techniques coupling high-performance liquid chromatography and gas chromatography are routinely used to separate and quantify the metalloid species such as those formed by arsenic, selenium, and mercury.

As you can see here, these are hyphenated techniques where we are basically combining these HPLC system to ICP-MS system. So we call it HPLC-ICP-MS. So basically these type of things will be useful for separating and quantify metalloid species and their analysis like metalloids like arsenic, selenium mercury. As you can see here the mercury species are measured through this hyphenated technique.

So sometimes instead of HPLC, we are also attaching the gas chromatography, so GC-ICP-MS. So these are hyphenated techniques that are used for more advanced and more sophisticated analysis and more accurate analysis of the desired species, which are creating the pollution in the soil.

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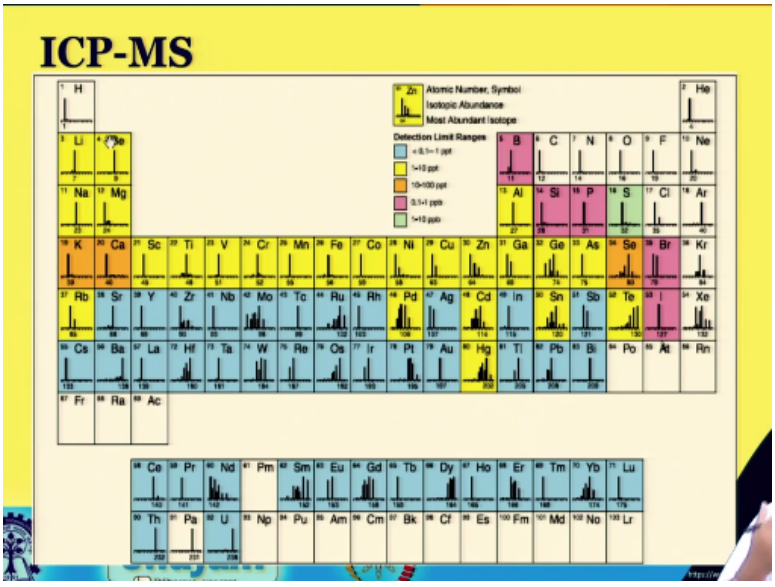

So this chart shows the different elements, which are being measured by this ICP-MS and you can see the detection limiting range. You can see that this light blue are basically showing less than 0.1 to 1 ppt. So you can see these are high. These elements can be measured if they are present in very, very less quantity in the soil. So 1 to 10 ppt, then 10 to 100 ppt, 0.1 to 1 ppt, 1 to 10 ppt.

You can see the detection limit for this instrument is exceptional and very few instruments an match with this level of detection limit. So, this is why ICP-MS is widely used for these different types of analytical laboratories and also different types of environmental pollution analysis projects.

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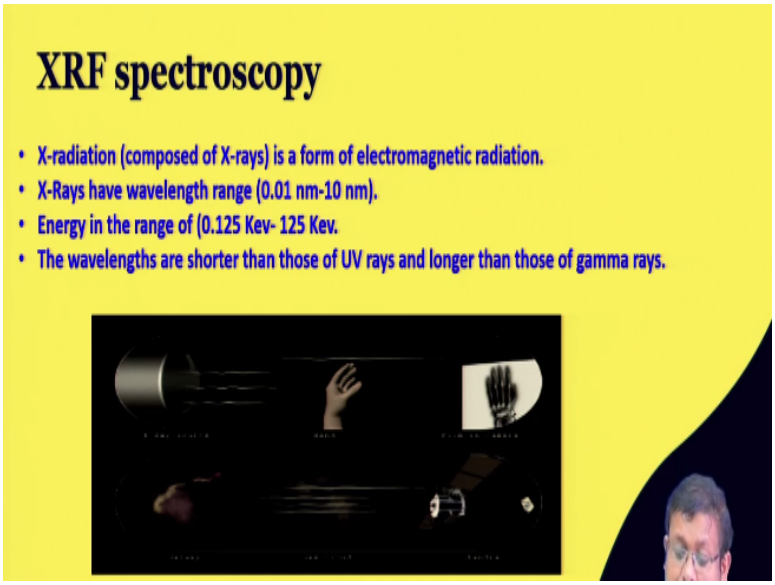

Now regarding the total elemental analysis, let us talk about another important spectroscopic method that is called extra fluorescent spectroscopy or XRF. Now before going to the XRF, let us little bit talk about the x-ray radiation. Now, you know that X-radiation composed x-rays is a form of electromagnetic radiation, and these x-rays were accidentally invented by the scientist Roentgen.

And you can see here this is the first ray of his wedding ring, which he took and so it was accidentally invented. And these x-rays have wavelength range from 0.01 to 10 nanometer, and it has the energy range from 0.125 kilo electron volt to 125 kilo electron volt, so wide range, and the wavelengths are shorter than those of UV rays and longer than those of gamma rays. So, this is about the x-ray.

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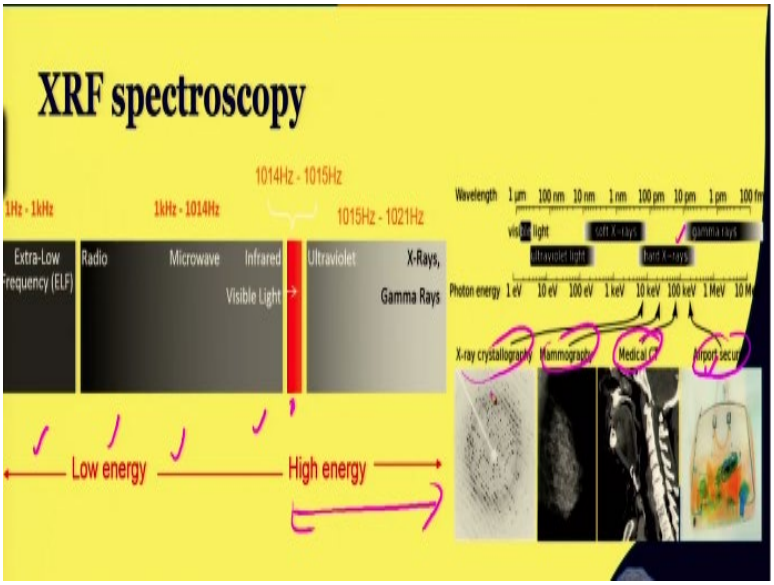

Now, if you see the electromagnetic radiation and different types of x-rays, so these are the gamma rays and you can see x-rays and ultraviolet rays and after that this portion is the visible light, and from there we are getting the infrared, microwave, radio wave, extra low frequency and so on and so forth. So, these ultraviolet, x-rays and gamma rays come under these high energy radiation.

Then infrared, microwaves go towards the low energy radiation. Now different types of x-ryas are there, we can see. After the gamma rays, you can see the next week get the hard x-rays and hard x-rays you can frequently see in the airport security scanner. So, airport security scanners use the hard x-rays, which are having the higher energy and the soft and also the relatively low energy x-rays are used for medical computed tomography, mammography, and x-ray crystallography.

So hard x-rays are basically used for airport security, whereas comparatively lower hardness x rays, which are showing the low hardness are used for medical computed tomography and then mammography and x-ray crystallography as you can see in this picture.

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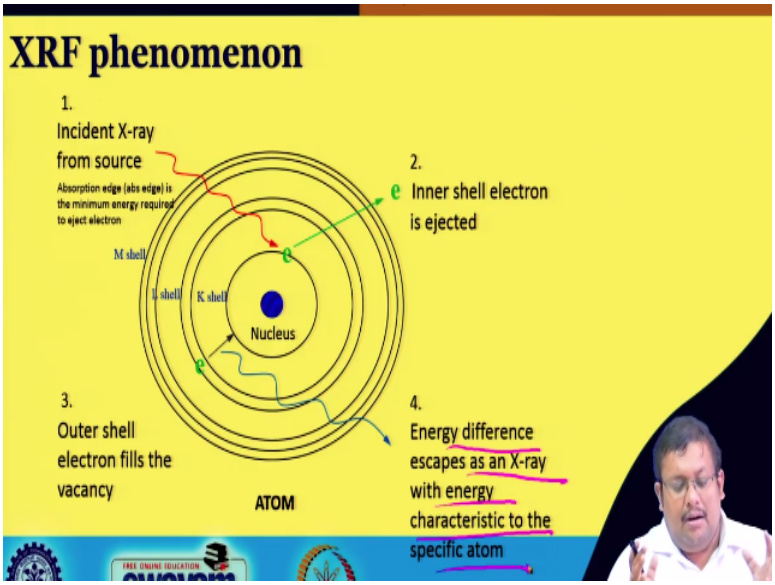

Now this x-ray fluorescence phenomena. What is x-ray fluorescence phenomena? Now, if we incident an x-ray from a source, let us consider there is an x-ray source. Now in this x-ray source, if we generate this x-ray and this x-ray basically goes towards an atom and ejects electrons from the inner shell. There will be a void and as a result of this void, the outer shell electron fills this vacancy.

So there will be vacancy when these initial electrons will go up and this vacancy will be filled by this outer shell and you know that there are different shells like K shell, L shell, M shell and so on and so forth and when these outer shell electrons fills the vacancy, there is an energy difference because when it moves from the higher energy levels to the lower ground state, they will release some energy.

So this energy difference escape as an x-ray with energy characteristic to the specific atom. So, this is the phenomenon of x-ray fluorescence. So we are basically pointing an x-ray to eject inner shell electrons. These electrons when they are ejecting from the ground state, it is producing a vacancy and this vacancy is filled up by the outer shell electrons.

When it is coming to fill the vacancy, it is releasing some energy in the form of fluorescence and that is the principle of x-ray fluorescence.

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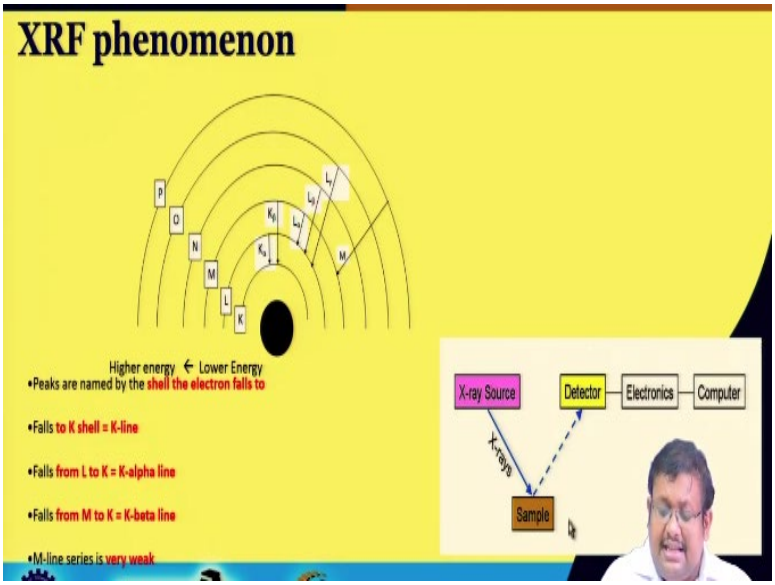

So, you can see there are different types of orbitals like K, L, M, N, O and P. Depending on from where these outer shell electrons is moving, we have, different types of peaks are named. For example, if some outer shell electron falls to this K shell, then we call it a K-line and if the falls from L to K, then we call it K-alpha. If they fall from M two K, then we call it K-beta and so on and so forth and M-line series is very weak.

So, this is basically the direct excitation method you can see here. There is an x-ray source which are producing these rays to the samples and this fluorescence is being basically detected by a detector, which is basically further operated by electronics and the computer. So, this is how this x-ray phenomena basically operates.

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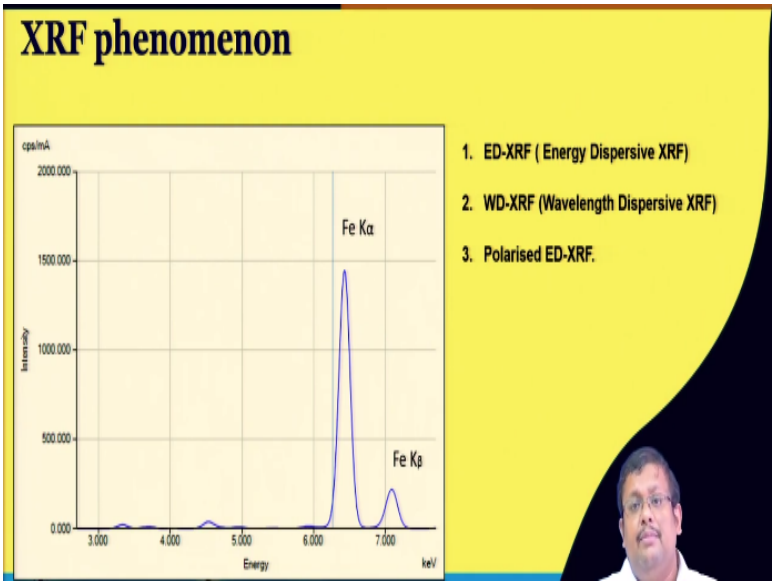

This you can see that K-alpha line and K-beta line of iron just for an example. There are different types of x-ray fluorescence spectroscopy, 3 types mainly. One is called the energy dispersive x-ray fluorescence. The second one is called the WD-XRF that is wavelength dispersive x-ray fluorescence and the third one is called polarized ED-XRF.

So we do not have enough time to discuss all these, but these are very sophisticated and very accurate method for total elemental analysis.

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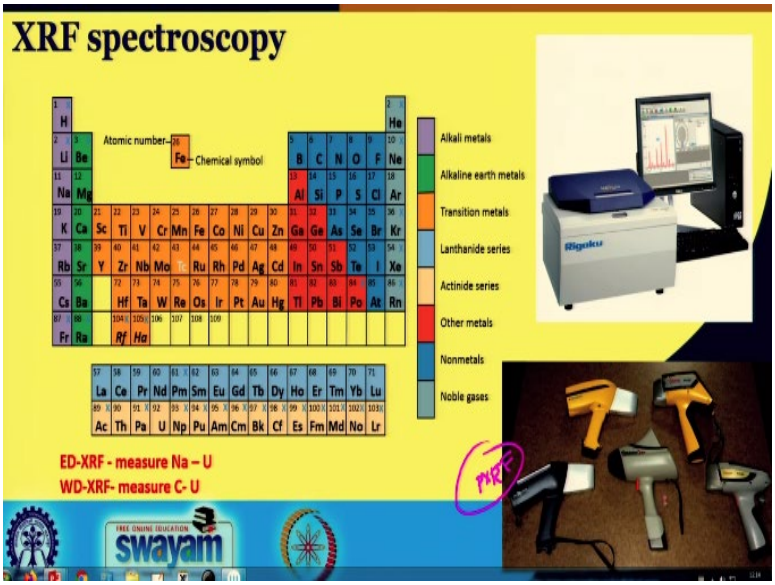

Now, what are the elements which you can measure to this x-ray spectroscopy? Now, if you consider the ED-XRF, obviously this is a periodic table, you can see the ED-XRF can measure the elements from sodium to uranium. So you can see a wide range of elements it can measure. However, these WD-XRF has wider range of application. It can measure from carbon to uranium.

So obviously wavelength dispersed XRF is more sophisticated and more costly than ED-XRF. So, this is an example. This is a picture of this ED-XRF, a benchtop ED-XRF and now scientists have developed this handheld ED-XRF instruments. We call it portable XRF or PXRF. So, these are called the portable XRF or PXRF instruments, which basically are using the same ED-XRF principle, but they are portable in nature.

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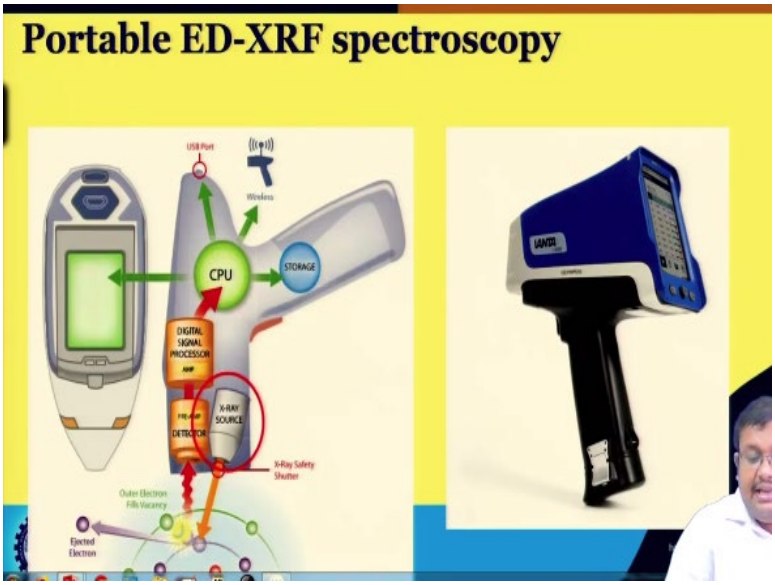

So this portable XRF spectroscopy or portable x-ray fluorescence spectrometer, basically this is the construction. So, there is an x-ray source which generate the x-rays, which ejects the electron, and when the outer shell electrons goes to fill up the vacancy, it will release the fluorescence which are being detected and digital signal processor is there. Ultimately it goes to the CPO or central processing unit, which basically stored it and or transmit through wireless.

So, this is basically this is the working principle of portable XRF. This is an example of portable XRF from Olympus. There are several companies which develop this instrument. These are very portable technology and they are very easy to use. They are operated through batteries. You can literally carry it in any field and you can measure the elemental concentration directly in the field.

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So why XRF is so popular. There are several reasons the XRF is popular. First of all, it helps us for elemental analysis. It is fast. The handle XRF can give you the results of total elemental concentration in only 60 to 90 seconds. It requires minimum sample preparation. It can deal with the powdered samples like soil. It can deal with the liquid samples also. Now non-destructive in nature. It is flexible.

It can analyze the solids, liquids and powders. It is very precise. It has got low cost of analysis and it can be operated by experts and non-technical operators, and it is simple to operate. You can see here the scientists are using directly this handle XRF or handle EDXRF in the field for measurement of elemental concentration in the soil.

So instead of bringing the samples into the lab and going for the cumbersome methods, you can directly go to the field and you can directly measure the elemental concentration in the field itself.

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Now, we have covered these inorganic pollutants, let us focus on the organic pollutants and what are the methods. So, let us start with the pesticides. Remember that in the field experiments, soil solution can be recovered with inert porous cup lysimetric equipment, which will help us for this pesticide residue analysis in the field.

Among the laboratory techniques, water extraction by pressure or centrifugation is basically used to extract the pesticide residue. And also remember that mixtures with nonpolar solvents are also used with the most lipophilic pesticides.

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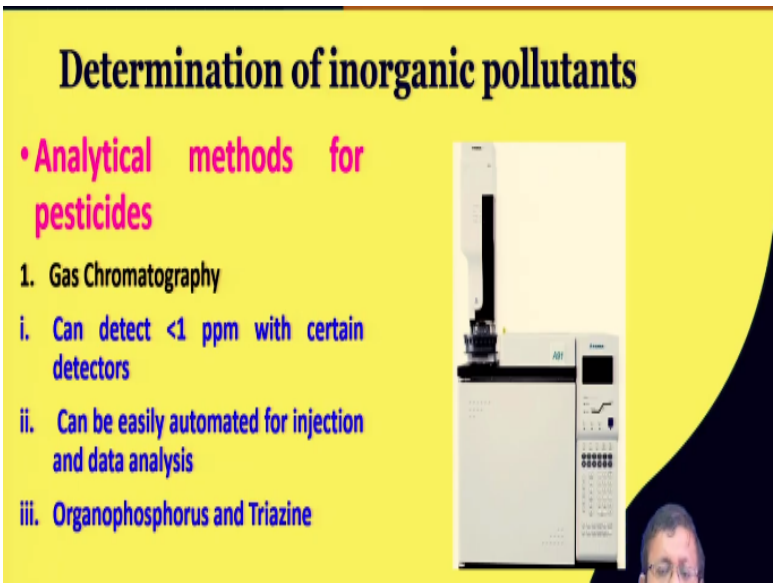

Now, what are the analytical methods for pesticide analysis? The most important analytical methods used for the pesticide analysis is gas chromatography method. Now this gas chromatography method can detect less than 1 ppm with certain detectors, it has got different

types of detectors like TCD detector, like ECD detector, like FID detector, we will discuss. Now this gas chromatography can detect less than 1 ppm with certain detectors.

And it can be easily automated for the injection and data analysis, and which has been used for measurement of different pesticides like organophosphorus and triazine, etc.

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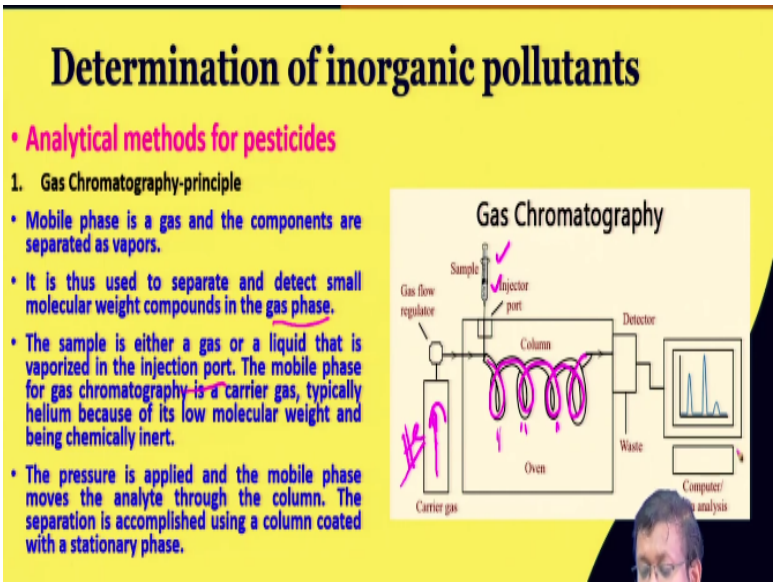

So let us see the principle of gas chromatography. Now, this shows the schematic of the different parts or different components of the gas chromatography. So, in the gas chromatography, mobile phase is a gas and the components are separated as vapors. So, it is thus used to separate and detect small molecular weight compounds in the gaseous phase. The sample is either a gas or a liquid that is vaporized in the injection port.

So you can see there is a carrier gas which used to carry the sample. So sample could be either gas or liquid, which are basically introduced through these injection ports and the mobile phase for this gas chromatography is this carrier gas which I have already told. Typically, it is helium because of his low molecular weight and being chemically inert. So, this pressure is applied and the mobile phase moves.

So this mobile phase basically moves through this columns with the sample and the separation is accomplished using a column coated with a stationary phase. So, these columns are basically a coated with the stationary phase. So we are injecting the sample. We are flowing this a carrier gas or the mobile phase, which is basically helium. So, this helium mixed with the sample is moving to the column.

This column is basically coated with the stationary phase and based on the interaction of the sample with the stationary phase, it will be detected and ultimately we will be seeing different peaks of different components of our analyte.

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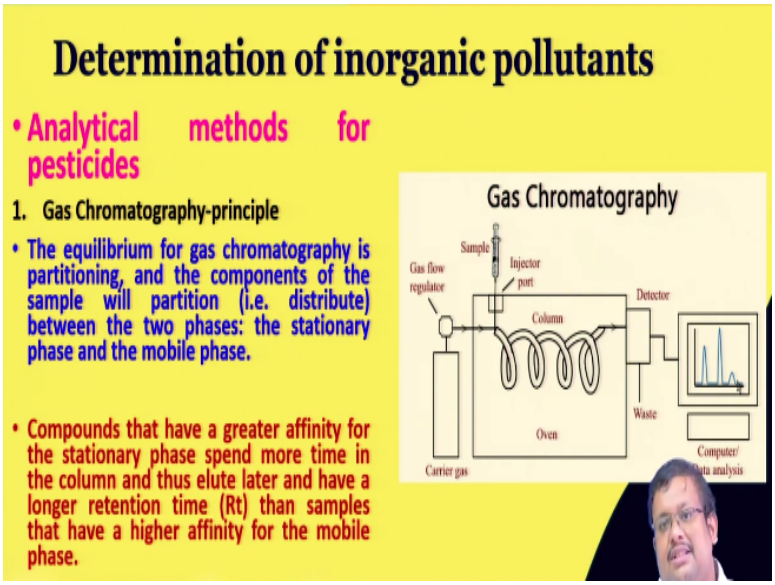

Now the equilibrium for gas chromatography is partitioning and the components of the sample will partition or distribute between the two phases that is stationary phase and mobile phase. So, this component, this sample when we are moving through this mobile phase, through this stationary phase, which is present in this column, these samples will differentiate themselves. They will separate out.

So components that have a greater affinity for the stationary phase will spend more time in the column and thus they will elute later and have a longer retention time, and based on this retention time, we will get different peaks as you can see in this picture. So, longer retention time than the samples that have higher affinity for the mobile phase.

So those samples which have got higher affinity for the mobile phase will elute more easily as compared to those compounds, which are having lower affinity for the mobile phase and higher affinity for the stationary phase. So the components which are having higher affinity for the stationary phase will be eluting later, and therefore they will give the different peaks. So based on this peak analysis, you can get the idea about the different components of the analyte mixture.

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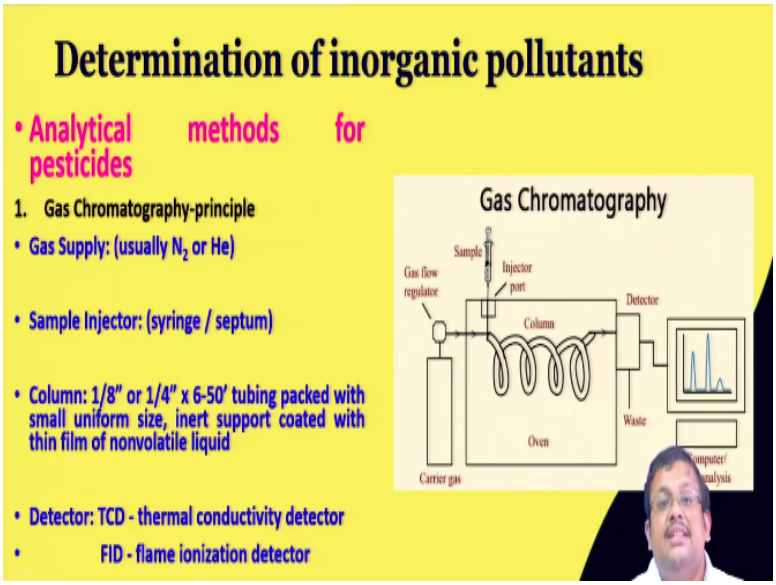

Now in the gas, usually we use the nitrogen or helium as the carrier gas. Sample injector is either syringe or septum and columns are basically different types of tubing packed with a small uniform size, inert support coated with the thin film of non-volatile liquids. There are different types of detectors, either TCD detector or FID detector. TCD stands for the thermal conductivity detector and FID stands for flame ionization detector. They are used for the specific purpose. So this is gas chromatography.

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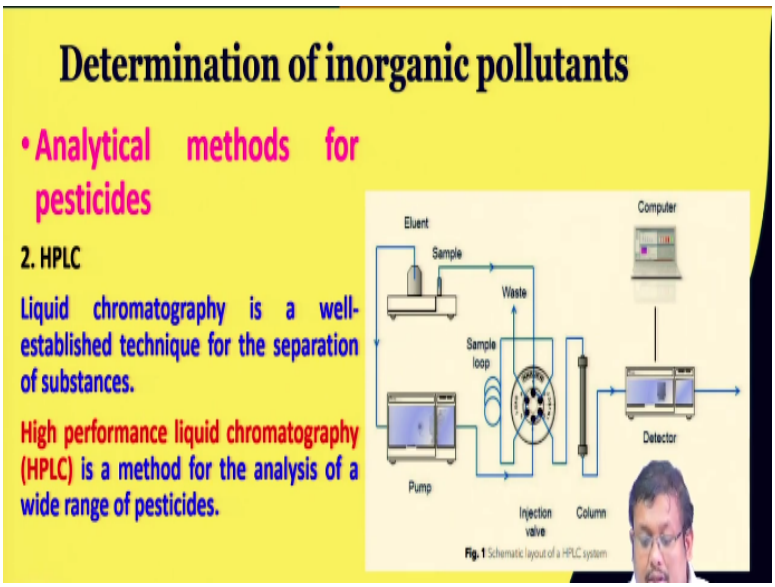

The second one is HPLC. HPLC stands for the high performance liquid chromatography, is a kind of liquid chromatography and it is a method which is widely used for wide range of pesticides.

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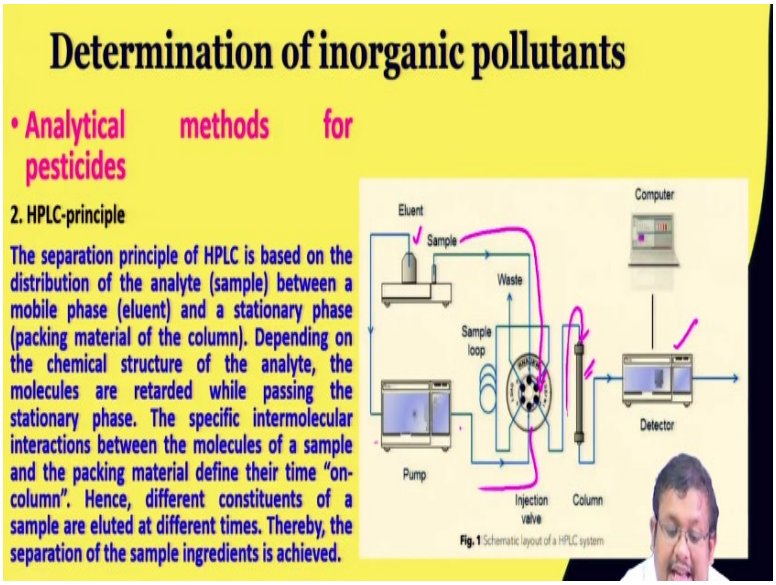

So if you see the principle of HPLC, it is also same. So basically the separation principle based on the separation chromatography is a separation basic principle. So you can see the separation principle of HPLC is based on the distribution of the analyte or the sample between a mobile phase that is eluent and the stationary phase that is the packing material in the column.

So basically, you can see in this picture, there is a sample which we are injecting in this injecting valve and also there is an eluent which is a mobile phase. So, we are moving this eluent through a peristaltic pump through high pressure and this eluent is moving with the sample through a column, which is packed with a stationary phase. So based on the sample interaction with the stationary phase, they will have either higher affinity to the stationary phase or lower affinity.

So based on that, they will produce, they will elute at different times and therefore they will be detected just like as gas chromatography. So basically, the separation principle of HPLC is based on the distribution of the analyte or sample between a mobile phase that is an eluent and a stationary phase that is packing materials of the column. Depending on the chemical structure of the analyte, the molecules are retarded while passing the stationary phase.

And the specific intermolecular interaction between the molecules of the sample and the packing material defines their time on the column, so retention time in the column since different constituents of a sample are eluted at different times, thereby the separation of the sample ingredients is achieved. So, this is basically the working principle of HPLC.

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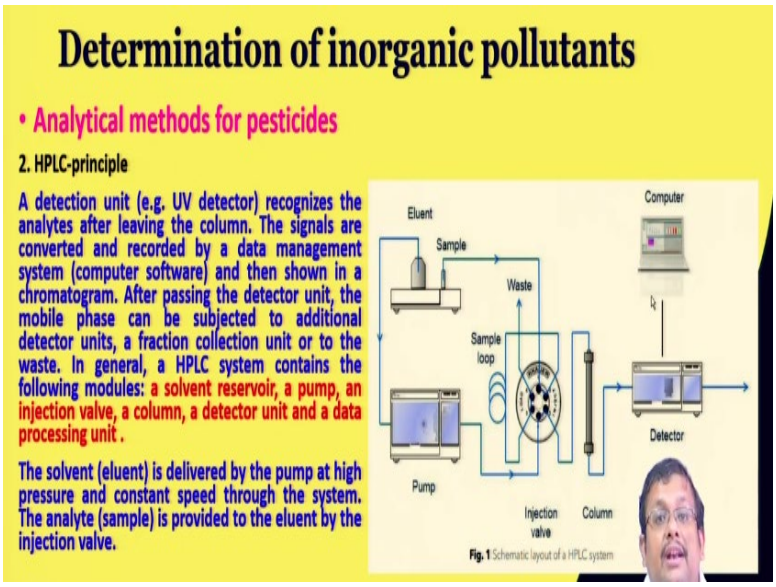

A detection unit is there, UV detector recognizes this analyte after leaving the columns and the signals are converted or recorded by a data management system and then shown in a chromatogram just like in case of GC we are getting a chromatogram, in case of HPLC we also get the chromatogram. After passing the detector unit, the mobile phase can be subjected to additional detected unit, a fraction collection unit to the waste.

In general, HPLC system contains the following models, what are these? A solvent reservoir as you can see it is an eluent reservoir, a pump, an injection valve, a column, a detector unit and a data processing unit. Now the solvent eluent is delivered by this pump at high pressure and the constant speed through the system and the analyte or sample is provided to the eluent by the injection valve as we have already seen.

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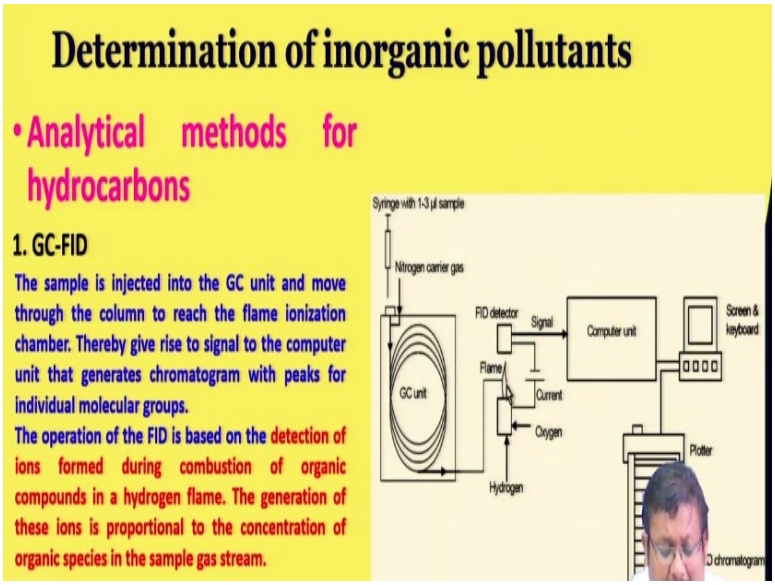

Okay, let us talk about the hydrocarbons. Now in the hydrocarbon basically it is measured through FID detectors. So this FID detector stands for the flame ionization detector. So the sample is basically injected into the GC unit and it moves through the column to reach the flame ionization chamber. So this is the flame ionization chamber.

Flame ionization chamber thereby give rise to signal to the computer unit that generates chromatogram with the peaks of individual molecular group. The operation of the FID is based on the detection of ions. So this is an FID detector. So this FID detector operation is based on the detection of ions formed during the combustion of organic compounds in a hydrogen flame. So you can see this is a hydrogen flame.

So detection ions forms. Due to the flame, there will be the formation of ions and this flame is produced by the hydrogen gas and the generation of these irons are proportional to the concentration of the organic species in this sample gas stream. So, this is how this GC-FID basically works.

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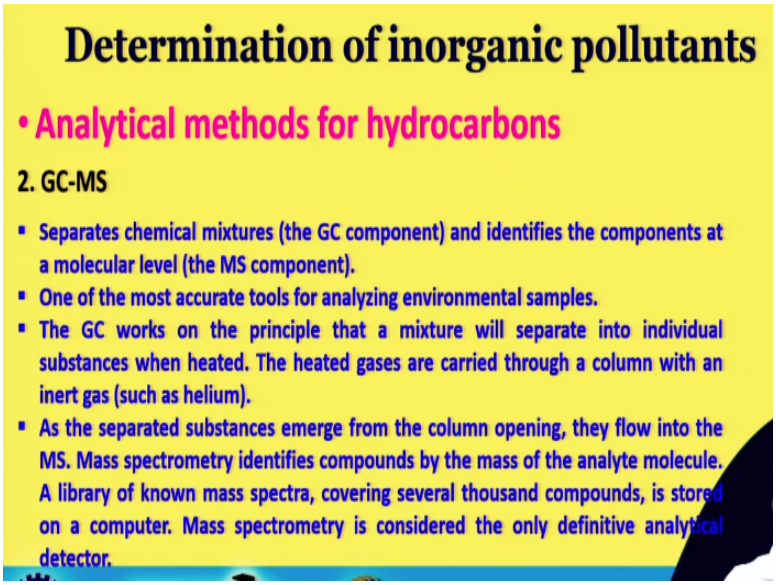

Another instrument is there that is called GC-MS, which we generally use. So basically, it is another mass spectrometry attached to the GC system. So this GC-MS separates the chemical mixture and identifies the components at a molecular level and remember that it is a most accurate tools for analyzing environmental sample just like we have discussed in case of ICP-MS.

GC works on the principle that a mixture will separate the individual substance when heated and the heated gas are carried through the column with an inert gas such as helium. As the separated substance emerges to the column opening, they flow into the mass spectrometry and this mass spectrometry basically detects the different components of this gas mixture. So, this is how this GC-MS basically works.

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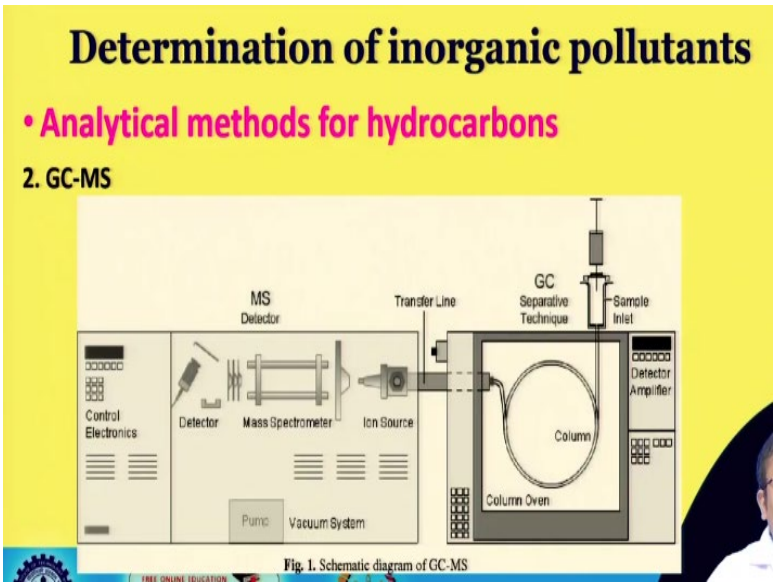

So this is the schematic of GC-MS. You can see here this is the sample inlet, then GC column. Ultimately, there is a transfer line, it goes to the ion source and then it moves to the mass spectrometer and finally to the detector and control systems. So this is the schematic diagram of GC-MS, which is a very sophisticated instrument.

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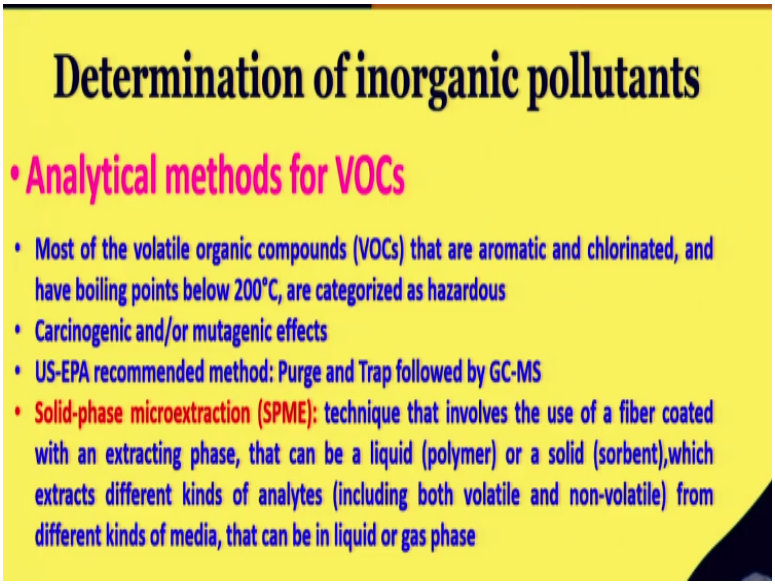

Analytical instruments for volatile organic compounds. These volatile organic compounds, they are both aromatic and chlorinated and have boiling points below 200 degrees centigrade, they are categorized as hazardous. There are different methods for analyzing them. They are carcinogenic. US-EPA recommended methods are purge and trap followed by GC-MS technique.

And another technique is known as a solid-phase microextraction or SPME, which is a technique that involves the use of a fiber coated with an extracting phase that can be liquid or polymer or a solid or sorbent which extracts different kinds of analytes including both volatile and non-volatile from different kinds of media that can be liquid or gas phase. So, these volatile organic compounds are also being analyzed in different types of environmental chemistry laboratory for detecting the pollutants.

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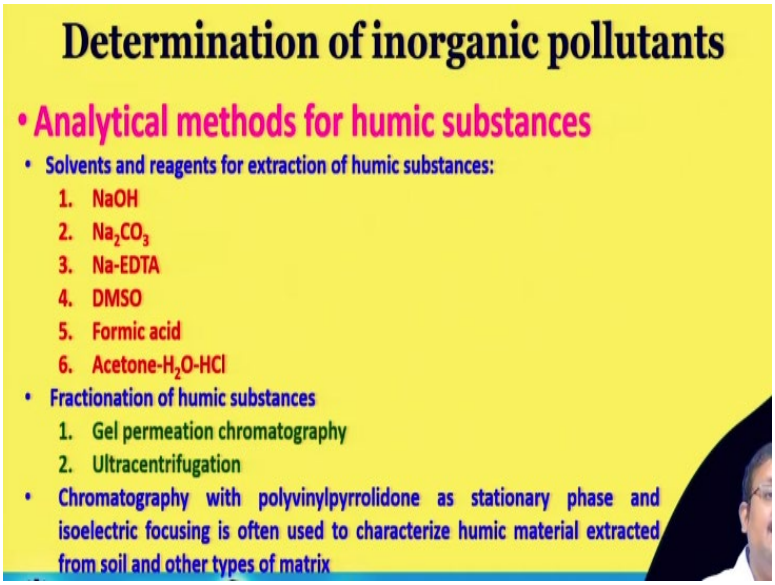

And finally, we are going to talk about the analytical methods for humic substances. So there are different types of solvents and reagents for extracting the humic substances like sodium hydroxide, sodium carbonate, sodium EDTA, dimethyl sulfoxide, formic acid, acetone water HCL mixture. Fractionation of this humic substances can be done by gel permeation chromatography or ultracentrifugation.

Chromatography with this polyvinylpyrrolidone as stationary phase and isoelectric focusing is often used to characterize the humic material extracted from soil and other types of matrices.

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So guys, this brings the end of this week's lecture and end of this course, and in this week, we tried to cover as much as analytical methods as you can cover. However, remember that there

are more methods, sophisticated methods, which are available in the environmental science domain. It is not possible for us to discuss all of them, but I would recommend you to please go through different advanced analytical chemistry books and see what are the advanced option for measurement of the environmental pollutants, which are present in the soil.

These are the references which are used for this module and you can consult these sources for more comprehensive information of a pollutant analytical methods for soil pollutant measurement. So friends, we have completed almost.

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We have completed, we have wrapped up this course, and I would like to specially acknowledge the contribution from my two Ph.D. students, Ms. Swetha RK and Ms. Swagata Mukhopadhyay who helped me for developing the contents for this course and also helping me for the creating the assignments and managing it. So, I hope that in this course you have learned something which is really useful to you.

And I am hopeful that all these things will be useful in the longer run in your future endeavors and also in future research. I wish you all the best. And again, if you have any queries, please feel free to email me and feel free to ask your questions and I will be more than happy to answer your queries. Thank you very much and I wish you all the best in your career. Thank you.