Basic Environmental Engineering and Pollution Abatement
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Lecture 14
Instrumental Techniques for Environmental Analysis - 2

Hello everyone. Now, we will discuss on the topic Instrumental Techniques for Environmental Analysis Part two.

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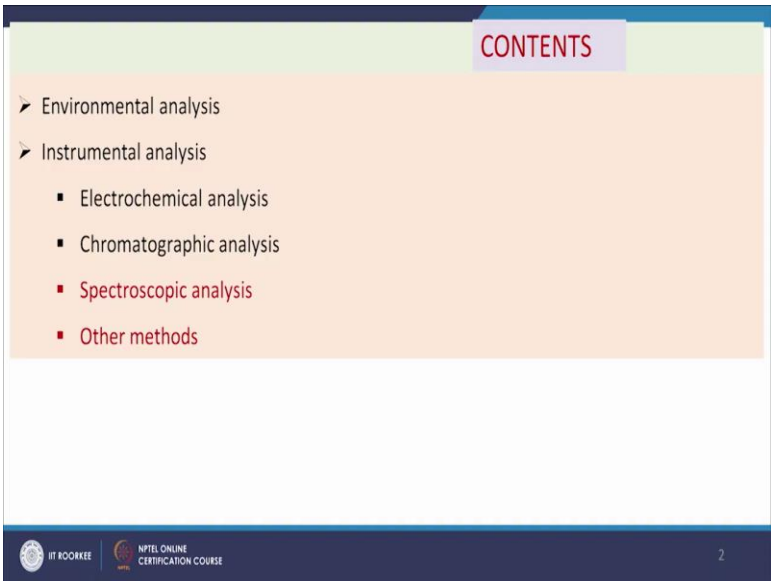

In the part one of this topic, we have discussed on gas chromatography and liquid chromatography and this class we will discuss on the spectroscopic analysis, that is UV spectrophotometer and FTIR.

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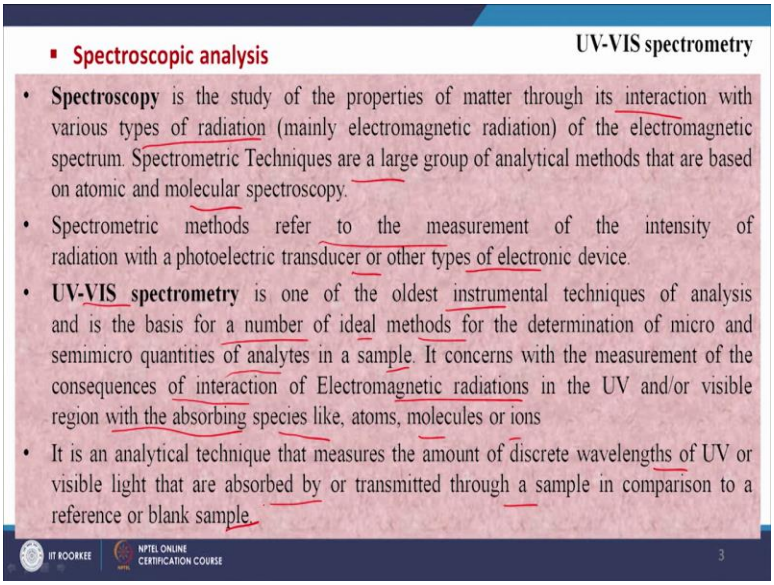

Now, we will see first UV visible spectrometry. So, spectroscopy is the study of the properties of matter through its interaction with various types of radiation, normally, electromagnetic radiation of the electromagnetic spectrum and spectrometry techniques are a large group of analytical methods that are based on atomic and molecular spectroscopy.

Spectrometric methods refer to the measurement of the intensity of radiation with a photoelectric transducer or other types of electronic device and UV visible spectrometry is one of the oldest instrumental techniques of analysis and is the basis for a number of ideal methods for determination of micro and semi micro quantities of analytes in a sample, it concerns with the measurement of the consequences of interactions of electromagnetic radiation in the UV and or visible region with the absorbing species like atoms molecules or ions.

That means, if we have one sample and then if we radiate some electromagnetic radiation, let us say light so, then it will be capturing some part of it and different elements will be capturing different light or radiation of different wavelength and intensity of the radiation will also be reduced when it will pass through the sample. So, by decreasing the intensity we can quantify and by knowing the wavelength of the radiations that is being absorbed by the molecules or the element, we can know what type of molecule it is or the element it is.

So, it is an analytical technique that measures the atom, the amount of discrete wavelengths of UV or visible light that are absorbed by or transmitted through a sample in comparison to a reference or blank sample.

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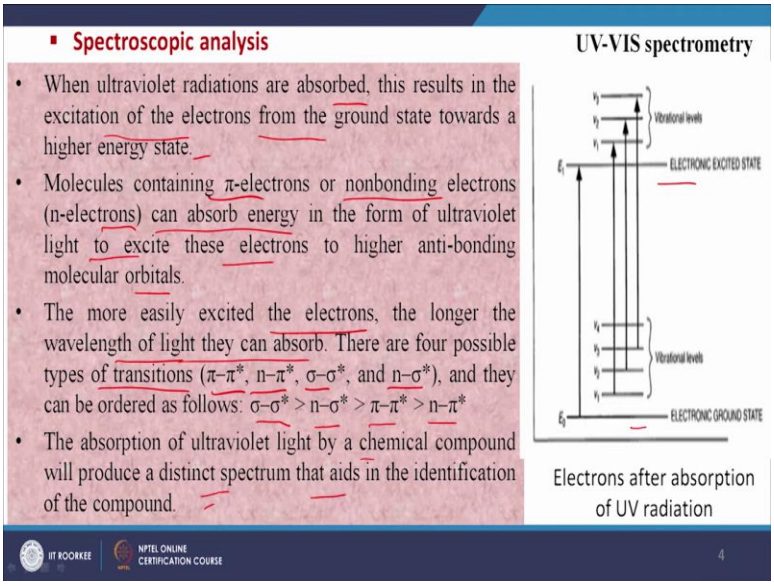

When ultraviolet radiation are absorbed, this results in the excitations of the electrons from the ground state towards a higher energy state. So, when we are sending some radiation, let us say UV radiation are visible also UV and visible UV is more powerful than the visible, then both are having some capacity to excite the external electron from their base to the excited state for example, here you see these are base position and these are excited position.

So, electrons may transfer from waste to excited state and different types of electron can be available, let us say pi-electron or nonbonding electrons or n-electrons so they can absorb energy in the form of ultraviolet light to excite these electrons to higher antibonding molecular orbitals. The more easily excited the electrons, the longer the wavelength of the light, the longer wavelength means less powerful, they can observe. There are four possible types of transmission that is pi-pi transmission, n-pi transmission, sigma-sigma and n-sigma transmission.

That means there are four types of electron that can be shifted to four other positions and they can be ordered as follows that is this is greater than n-σ and π- π and n- π, so these are there and absorption of ultraviolet light by a chemical compound will produce a distinct spectrum that aids in the identifications of the compound.

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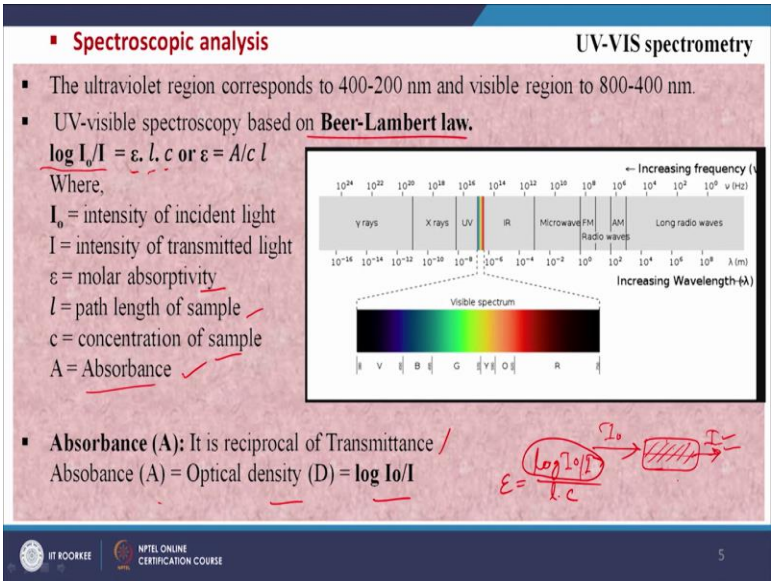

So, how does UV visible spectroscopy spectrometry works? It works on the principle of Beer-Lambert law, what is that principle? So, if we pass some radiation or UV light through a sample which is present here. So, when it will be passing through it, the some part of light or electromagnetic radiation will be absorbed and particularly in this case of UV, UV light will be absorbed and the intensity will be reduced.

So, here we are having more intensity, here we will be having less intensity and that

$\log I_o/I = \acute{\varepsilon} * L * C$

where έ is equal to nothing but the molar absorptivity and C is the concentration of sample and L is the path length of the sample and this molar objectivity e is equal

έ = A/CL, where A is the absorbance.

So, this is a relationship so, we can get it here

$\acute{E} = (\log I_o/I)/LC$

Now, this is nothing but absorbance A. So, absorbance it is reciprocal of the transmittance also. So, we will see in the reciprocal of the transmissions, we say absorbance A is the optical density and the log Io/I. So, absorbance is also called as optical density. So, now you see, so, what will happen, more the concentration, so, this value will be more because I value will be less than the

Io so, this ratio will be more so, this absorbance value will also be more. So, more the concentration we will be getting more absorbance value and less intensity of the transmitted light.

So, now, if we can have some detector, so, that will detect the quantity of light which is being transmitted. So, that can give us some idea the how much each light is absorbed and which is proportional to the concentration present in it and we can get the value of the concentration of the element.

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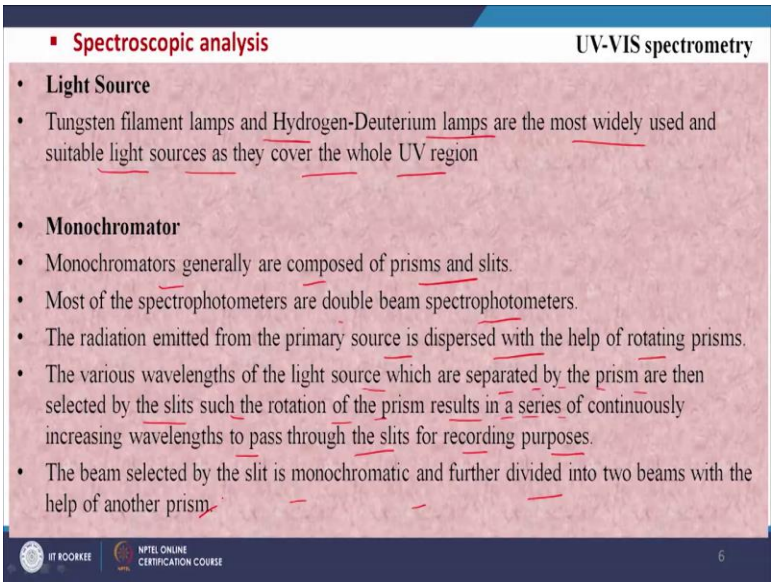

Now, if we see the different parts of the UV visible then one is that we have to send some light UV light. So, light source is needed, so tungsten filament lamps and hydrogen deuterium lamps are the most widely used and we have to send a monochromator. So, monochromator generally are composed of prisms and slits, we have to send one type of ray or wavelength we have to send. So, most of the spectrophotometers are double beams spectrophotometers.

And the radiation emitted from the primary source is dispersed with the help of rotating prisms. The various wavelengths of the light source which are separated by the prism are then selected by the slits such the rotation of the prism results in a series of continuously increasing wavelengths to pass through the slits for recording purposes. The beam selected by the slate is monochromatic and further divided into two beams with the help of another prism.

So, this is the how the monochromatic light is generated by the use of this monochromator. Then, we will be using one sample and another reference. So, through both the light will be passed, and we will be measuring how much light is being absorbed.

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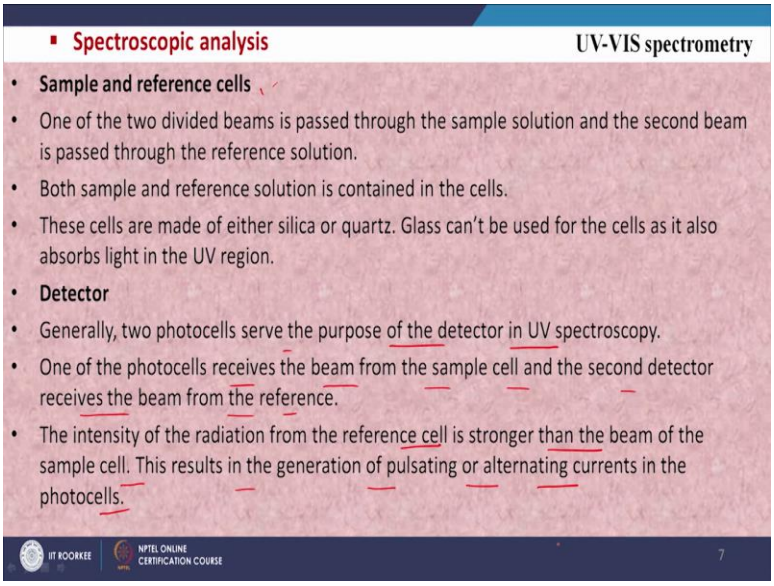

So, that will be your sample and reference cells two cells are needed. And if it is a double beam, then simultaneously the light two beams will be sent one through the sample and another to the reference and if it is a single beam, so, it will be sent once it will be sent to the sample and after that, it will be sent to the reference, not simultaneously. So, that way two different arrangements are there and then after that, we will detect, detector is necessary.

So, generally two photo cells serve the purpose of the detector in UV spectroscopy, one of the photo cells receives the beam from the sample cell and the second detector receives the beam from the reference, the intensity of the radiation from the reference cell is stronger than the beam of the sample cell. This results in the generations of pulsating or alternating currents in the photo cells.

So, photo cells the intensity is changing and the intensity of light which is emitted from the which is transmitted from the sample is lower than that of the reference. So, there will be some variations and pulsating or alternating currents will be generated.

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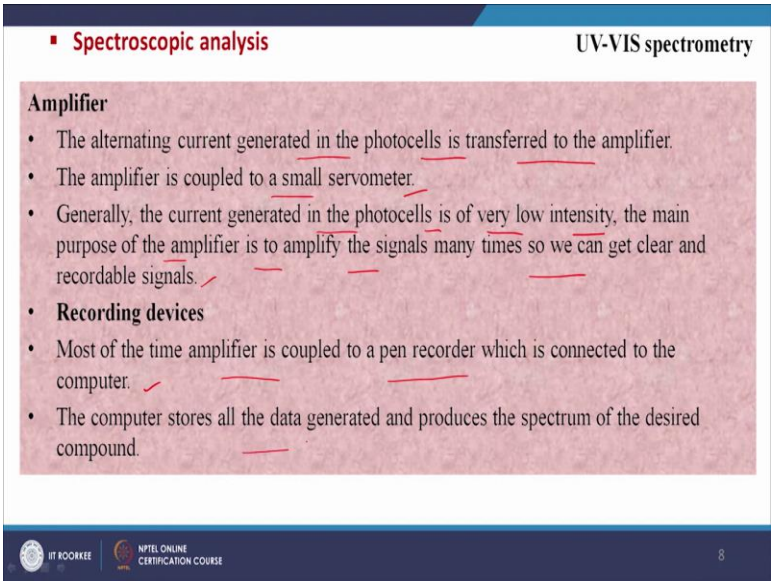

And then that amount of current which is generated that is not very high. So that has to be amplified, so amplifiers are used, the alternating current generated in the photo cells is transferred to the amplifier, the amplifier is coupled to a small servometer and generally the current degenerated in the photo cells is a very low intensity, the main purpose of the amplifier is to amplify the signals many times so we can get clear and recordable signal.

So, record link devices are also needed and most of the time amplifier is coupled to a pen recorder which is connected to the computer and the computer stores all that data generated and produces the spectrum of the desired compound.

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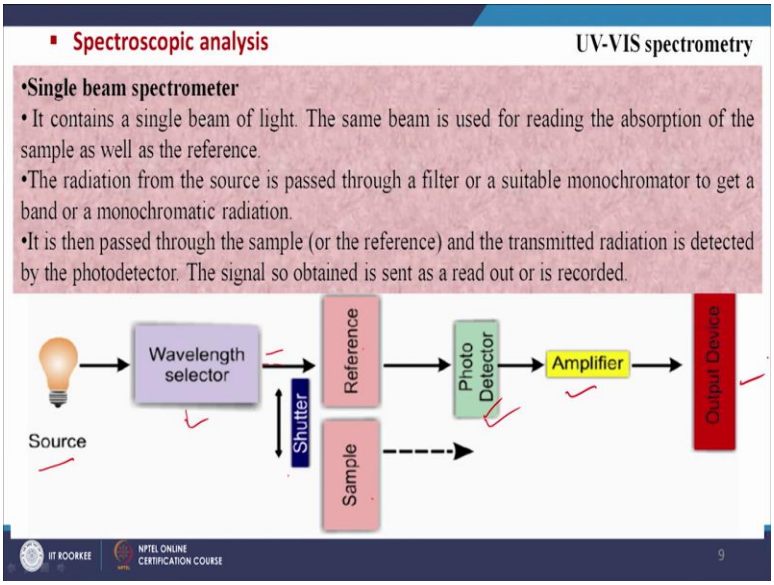

So, this is the working of the UV spectrometry. So, here is the light source, wavelength selectors that we are having monochromator, that is monochromatic light we need to produce then shutters are there so these shutters will allow the passage of this light. So, here it is going there so this is reference other time it will be passing through the sample not in the same time because it is single beam because from this we are getting one beam only. So, then it will be going to the photo detector and for bottom photodetector the signal will be formed and that will be amplified and then it will be going for output device.

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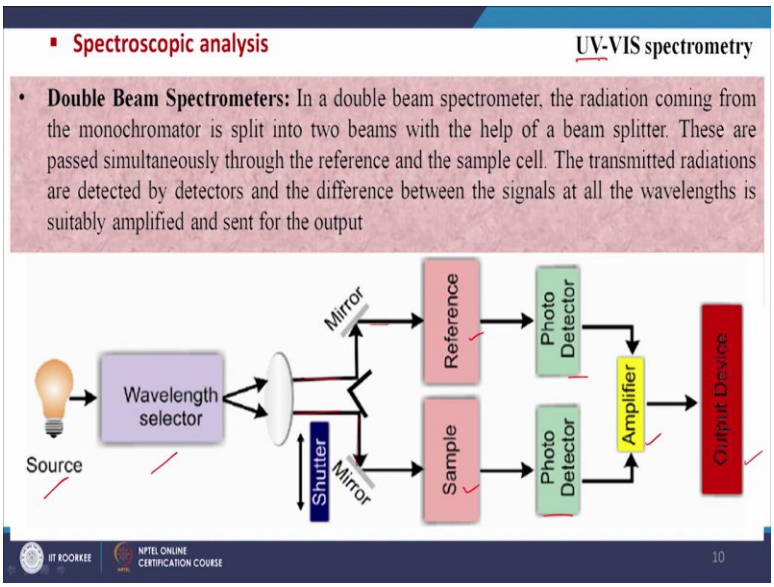

And this is for a double beam spectrometers. So, in this case, source wavelength selector wavelength selector is giving us two beam these two beams. So, these two beams are simultaneously it is one beam is going to the reference and another is going to the sample then this is we have photodetector here also photodetector so, then the difference is giving some signal and that is amplified and again it is going to output device.

So, this way the UV works, UV visible spectrometry works and double beam or single beam spectrophotometers are available.

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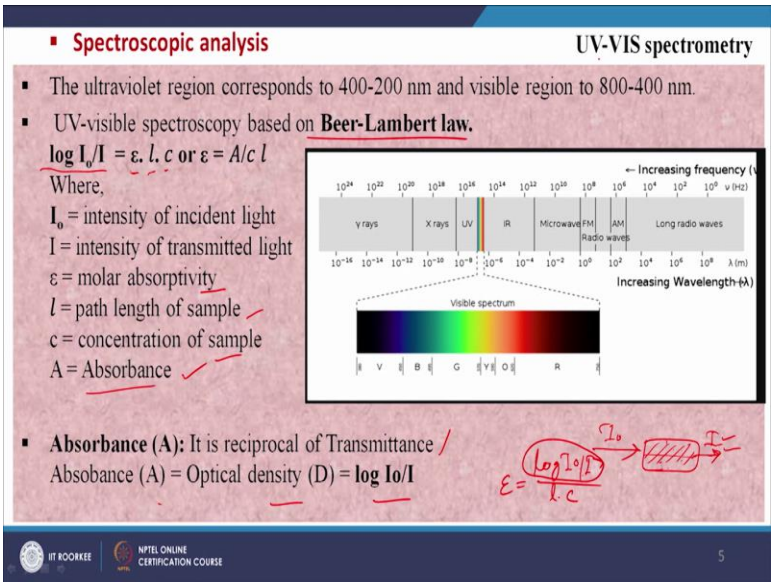

So, UV and visible the main difference is their wavelength, the monochromatic light which we are generating that wavelength the visible is high having more wavelength, as you mentioned here so the ultraviolet region corresponds to 400 to 500 nm and visible region. So, 400 to 800 nm is your wavelength.

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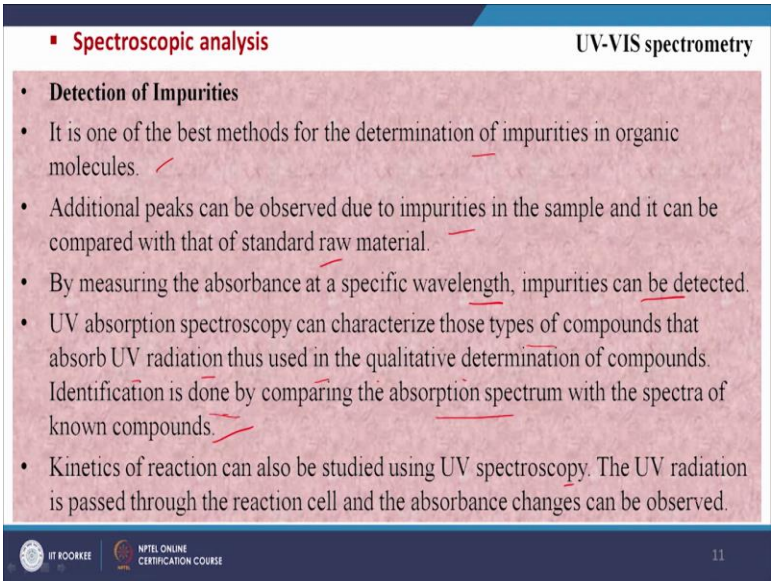

Now, detection of impurities, it is one of the best methods for the determination of impurities in organic molecules. And additional peaks can be absorbed due to impurities in the sample and it can be compared with that of the standard raw material and by measuring the absorbance at a specific wavelength impurities can be detected. So, a particular type of compound or element those will be able to capture or absorb light of that particular wavelength or monochromatic light of a specific wavelength.

So, if we see our major light intensity we are getting for a particular wavelength, but minor absorptions we are getting in other wavelength, that means, that minor is basically because of the impurities and UV absorption spectroscopy can characterize those types of compounds that absorbs UV radiation thus used in the quantitative determination of compounds identification is done by comparing the absorption spectrum with the spectra of known compounds like other methods here also we need some standard molecules and kinetics of reactions can also be studied using UV spectroscopy, the UV radiation each pass through the reaction cell and the absorbance changes can be observed.

So, that way we can measure how with time the concentration of the element or the pollutant changed.

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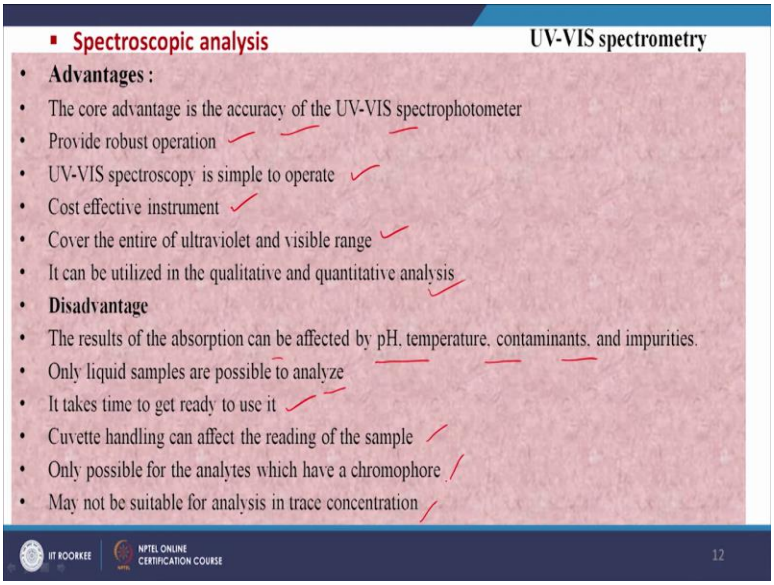

So, UV visible has some advantages as well as disadvantage. So, the core advantage is the accuracy of the UV visible spectrophotometer provide robust operation UV visible spectroscopy is simple to operate and cost effective instrument and cover the entire of ultraviolet and visible range. So, wide range of wavelength they can handle and it can be utilized in the quantitative and qualitative analysis.

And it has disadvantages as well, the results of the absorption can be affected by pH, temperature, contaminants and impurities and only liquid samples are possible to analyze and it takes time to get ready to use it and cuvette handling can affect the reading of the sample and may not be suitable for analysis in trace concentrations. The instrument has some detection limit so detection limit for UV visible may not be less, with this ppb then it may not be able to give us.

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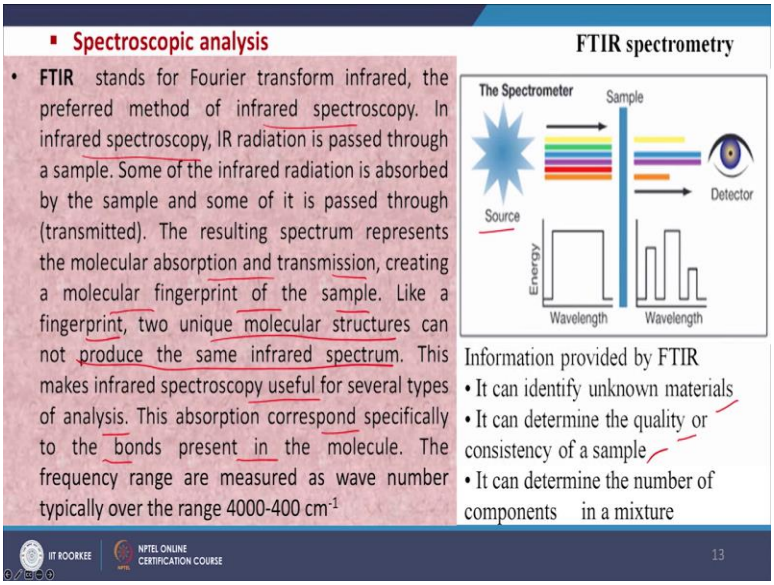

Then next is FTIR spectrometry that is Fourier transform infrared spectrometry and FTIR stands for Fourier transform infrared, the preferred method of infrared spectroscopy. In infrared spectroscopy IR radiation is passed through the sample unlike UV visible, in case of UV visible we pass UV visual range of monochromatic light, but here in FTIR we will be processing IR light.

So, IR we know the wavelength is more than that of the UV visible and so, less powerful. So, the IR will not be able to shift the outer cell electrons from its base to an excited state, but it can give some vibrations or rotations of different bonds. So, FTIR gives us more idea about the functional groups present in the molecules etc. So, the resulting spectrum represents the molecular objections and transmission creating a molecular fingerprint of the sample like a fingerprint two unique molecular structures cannot produce the same infrared spectrum.

So, this makes infrared spectroscopy useful for several types of analysis. These absorptions corresponds specifically to the bonds present in the molecule, the frequency range are measured as wave number typically over the range 4000 to 400 cm^{-1}. So, you see here, this is the FTIR spectrometry, we have one IR source, then we have the sample. So, when the light will pass through it, then some will be absorbed and rest will be going out and then we will be detected and we will see at which wavelength the light is available here.

So, information provided by FTIR, it can identify unknown materials, it can determine the quality or consistency of a sample, it can determine the number of components in a mixture.

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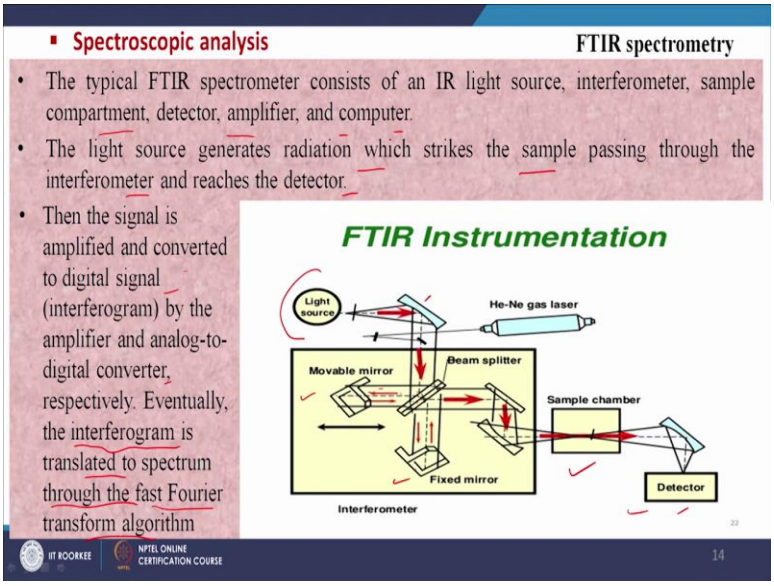

And in this case, so we have a light source, so this light is coming to this mirror, there is a number of combination of mirrors. So, that is called interferometer. So, interferometer is the most important part of the FTIR spectrometry. So, here it is coming to this mirror and then from the parallel beams are coming, it is through this one that is your beam splitter and then through the beam splitter, it some light passes through it and some is reflected and there is one movable mirror and another is your fixed mirror.

So, again these two mirrors reflects the light this direction. So, one it is coming and again it is coming to this and again it is one part is coming here the dust part is another is after reflection is going there also. So, in these two part, two beams are marching here and going as a single beam. So, this single beam is passed through this sample chamber. So, here we will put the sample and then it will be detected, what type of our detector will be able to detect this one.

So, from the sample, this ray will be going out and it will be coming to the detector, so that way. So, the typical FTIR spectrometer consists of an IR light source, interferometer, sample compartment, detector amplifier and computer and the light source generates radiation switch strikes the sample passing through the interferometer and reaches the detector, then the signal is

amplified and converted to digital signal by the amplifier and analogue to digital converter respectively.

And eventually, the interferogram is translated to spectrum through the fast Fourier transform algorithm, so that is it is called FTIR.

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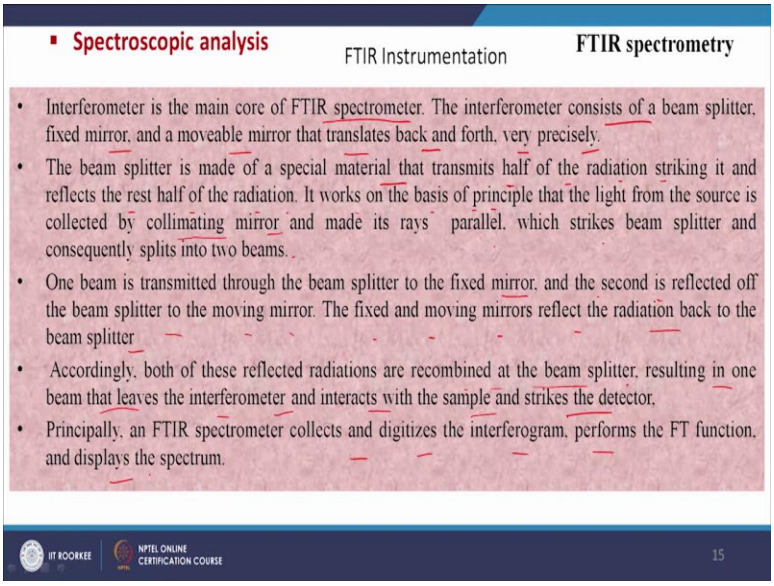

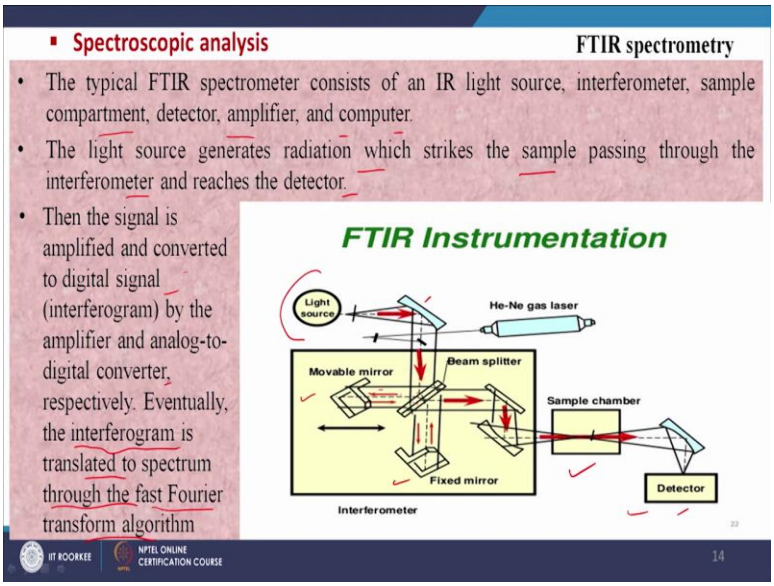

And the interferometer is the main core of FTIR spectrophotometer. A spectrometer the interferometer consists of a beam splitter, fixed mirror and a moveable mirror that translates back and forth very precisely that just we have discussed. The beam splitter is made of a special

material that transmits half of the radiation striking it and replace the rest half of the radiation. It works on the basis of the principle that the light from the source is collected by collimating mirror just like this collimating mirror, we have discussed and made its rays parallel which strikes beam splitter and consequently splits into two beams.

So, this is the mechanism. One beam is transmitted through the beam splitter to the fixed mirror and the second is deflected off and the beam splitter to the moving mirror and the fixed and the moving mirrors replaced the radiation back to the beam splitter. And accordingly both of these reflected radiations are recombined at the beam splitter resulting in one beam that leaves the interferometer and interacts with the sample and strikes the detector.

So, principally the FTIR spectrometer collects and digitizes the interferogram performs the FT function and that displays the spectrum.

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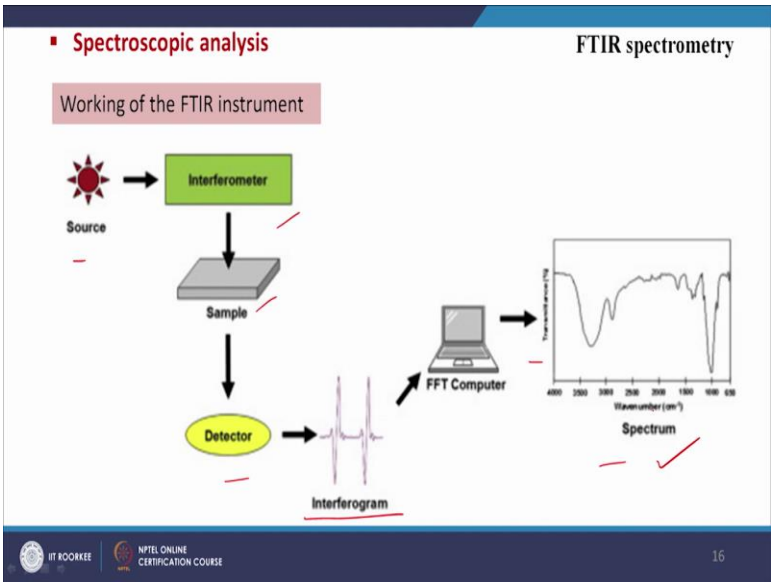

So, this is the role of the FTIR just like the source, then interferometer, then it is going through the sample the single beam and then detector then interferogram which we are getting that is converted to this spectrum. So, that is why FTIR. So, here we have a transmissions and then transmittance and this is our wave number.

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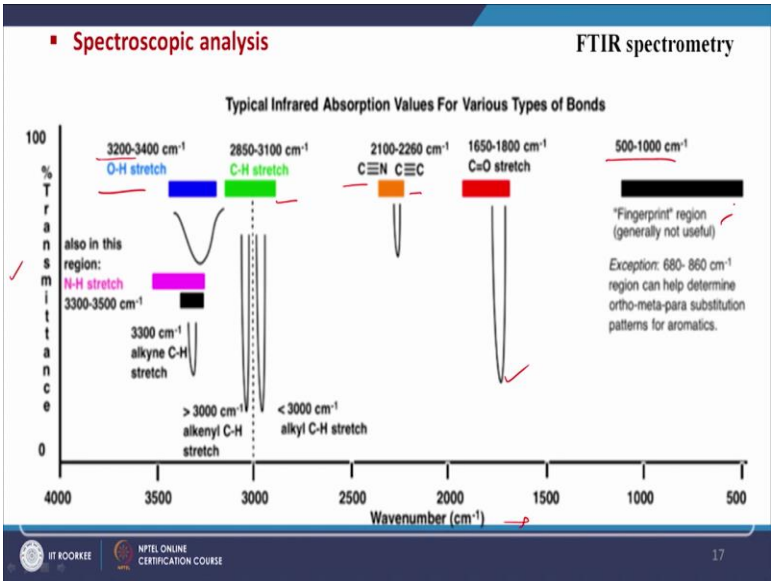

So, if we see this type of spectra we will get, so this is your percentage transmittance and this is our wave number. So, in this wave number we see we get different peak here due to transmittance. So, these two this range, it is CH stretch, OH stretching this to this is 3200 to 3400. Similarly, 2100 to 260 CN or C, triple C, CC triple bond. So, these are the different functional group as we were talking about. So, now if C double bond strength is responsible for these peak again.

So, and in these range say 500 to 1000 this is basically fingerprint region and this is not that useful for organic compounds.

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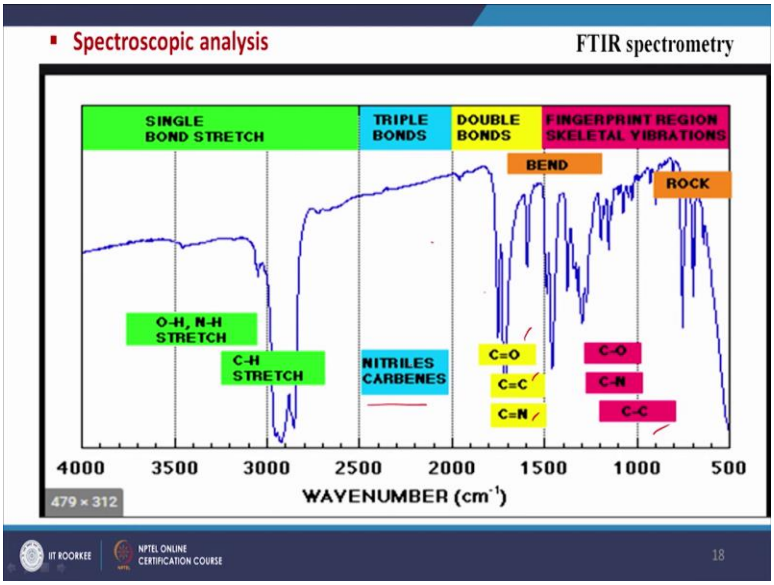

This is another example here also single bonds stretching triple bonds, double bond. So, the IR has low energy, so as I have mentioned it is absorbed by the molecules as for the different vibrations and rotations of the double and triple bond, so that way the different peaks are generated. So, this peak is CO, CC, CN, CO, CN, CC like this. So, nitrile if it is nitriles or carbons so, within this range we can get some peak.

So, there are some library also so that gives that which at which wavenumber what type of compounds or what type of functional groups can be responsible or can be available. Now, how to put the sample in case of FTIR, so we will see the FTIR can analyze solid, liquid and gas samples and if it is a solid sample, so there are some defined method which has to be followed to use it for analysis.

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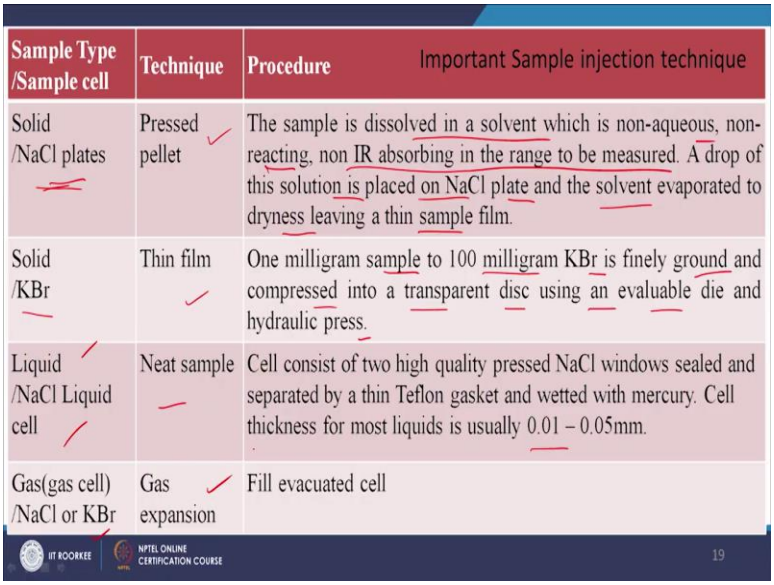

Like say, NaCl plates can be used or potassium bromide can be used for solid samples. So, if NaCl plates are used in that case, so the technique is called pressed pellets and one KBr the technique is thin film. So, in this in this in the first case for NaCl plates, the sample is dissolved in a solvent, which is non-aqueous and non-reacting, non IR absorbing in the range to be measured.

So, this is the property of the adsorbent and a drop off this solution is placed on NaCl plate and the solvent evaporated to dryness, leaving a thin sample film. So, this is one prescribed method we need to follow for the analysis and when you will go for KBr method so, then one mg sample to 100 mg of KBr is finely ground and compressed into a transparent disk using an evaluable dye and hydraulic press.

So, the solid sample may have some color also and it may not be that transparent. So, to increase its transparency this KBr is used and the sample is liquid then NaCl liquid cell can be used and this method is need sample and the cell consists of two high quality pressed NaCl windows sealed and separated by a thin teflon gasket and wetted with mercury. Cell thickness for most liquid is usually 0.01 to 0.5 mm. Similarly, for gas samples NaCl or KBr can be used and gas expansion is the method.

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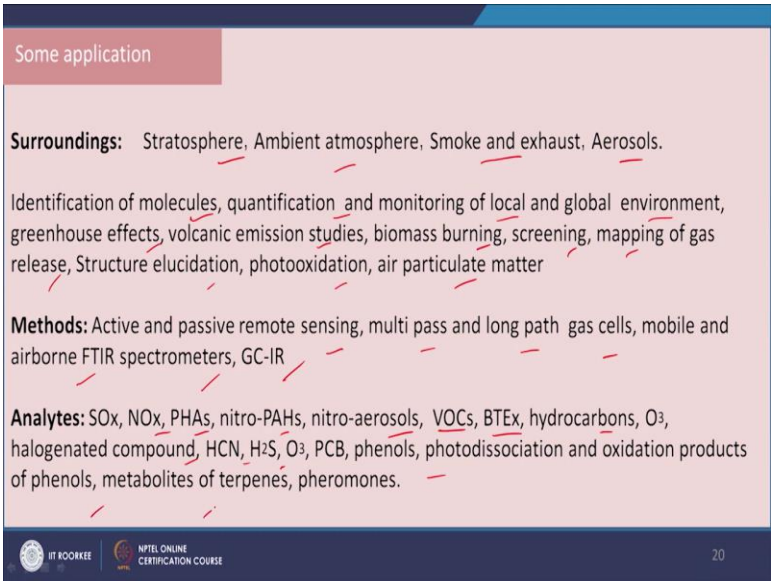

And now some applications we will see. So, these FTIR can be used for different applications, like the analysis of pollutants in the stratosphere, ambient atmosphere, smoke and exhaust and aerosols like say identifications or molecules quantifications and monitoring of local and global environment and greenhouse effects, volcanic emission, studies, biomass burning, screening, mapping of gas release, structure elucidation, photooxidation, air particulate matter.

So, these can also be analyzed and methods active and passive remote sensing, multi pass and long path gas cells, mobile and airborne FTIR spectrometers and gas chromatography, infrared spectroscopy these are also some methods which are used and analytes like say SOx, NOx, PHAs, nitro-PAHs and nitro-aerosols, volatile organic carbons and BTEx and hydrocarbons ozone, hydrogenated compound, HCN, H_2S, O_3, PCB, phenols, photodissociation and oxidation products of phenols, metabolites of terpenes and pheromones.

So, these are different application and I will give you some applications which is reported in this literature.

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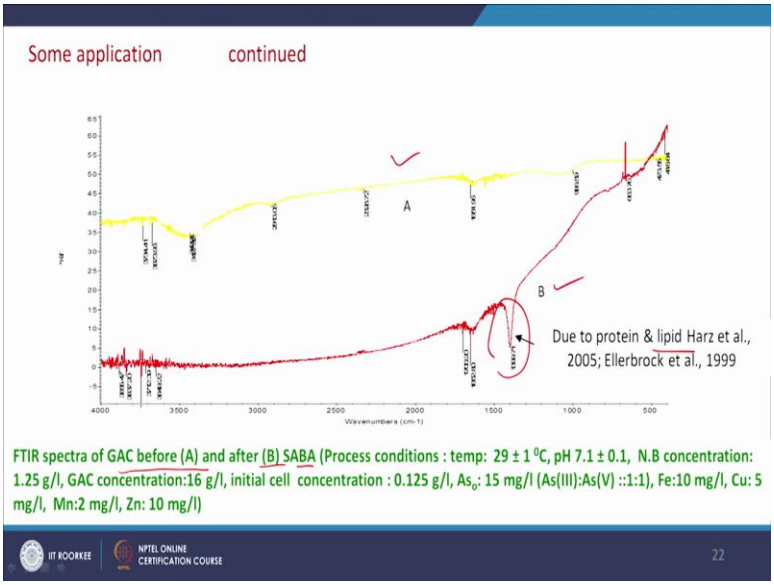

So, here it is, it is giving us two, this is A and this is B. So, A is nothing but FTIR spectra of GAC before and after SABA, that is simultaneously adsorption and bioaccumulation method. So, if we take say scale water samples and adsorption, then that will be only adsorption if we use microbes and the pollutants then also there will be biodegradations or in case of conservative pollutants like say arsenic though arsenic will not be degraded by the microorganisms it will be captured and stored.

So, that is by accumulation and if we use simultaneously the adsorbents and microbes in the beaker, so simultaneously adsorptions and bioaccumulation will take place. Now, whether the bio layer is formed or not that can also be confirmed by the FTIR study as shown here FTIR for GAC we are seeing here but when we are taking the GAC sample after the simultaneous adsorption by accumulation or SABA, so then we see the some new peaks have arised here. So, this peak is because of the protein and lipid so that protein and lipid is associated with the microbial biomass so that way also we can correlate.

So, this type of environmental applications we will find in many cases where FTIR or any other instrumental analysis can give us some insurance that, yes this phenomena is available in that particular case. So, now we will see the advantage of this FTIR spectrometry, so and its disadvantage as well.

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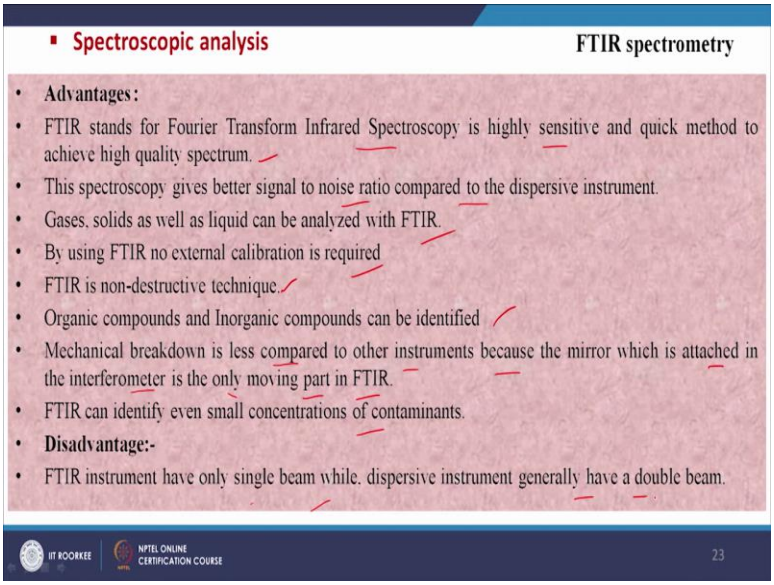

So, FTIR stands for Fourier transform infrared spectrometry is highly sensitive and quick method to achieve high quality spectrum and this spectroscopy gives better signal to noise ratio compared to dispersive instrument and gaseous solids as well as liquid can be analyzed by FTIR and by using FTIR no external calibration is required and FTIR is non destructive technique organic compounds and inorganic compounds can be identified and mechanical breakdown is less compared to other instruments because the mirror which is attached in the interferometer is the only moving point in FTIR.

And FTIR can identify even small concentrations of contaminants and it has some disadvantage that FTIR instrument have only single beam while dispersive instrument generally have a double beam. So, these are some advantage and disadvantage, after that we have seen that the GC, HPLC, FTIR, UV visible we have discussed, apart from that many other instruments are also used as I have mentioned in the previous class.

So, those instruments are not that important particularly for the analysis of water quality parameters or any environmental quality parameters but those will be very very useful for the studying different aspect of environmental pollution and develop technologies for the treatment of wastewater or cleaning air. So, after this in this class, thank you very much for your patience.