Infrared Spectroscopy for Pollution Monitoring

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Lecture-03
Techniques of Elemental Analysis

Introduction about the analytical science and environmental pollution controls, now today I want to discuss a little bit about the spectrophotometry and other techniques which we have already completed in our previous courses and then I will give you a very brief introduction regarding the infrared spectroscopy. Afterwards we will proceed on the structure of the atom, so we will spend about 1 or 2 hours on the structure of the atoms and electrons protons, neutrons etc.

And then go on to the electromagnetic radiation, so yesterday I was trying to tell you that the earliest form of spectroscopy application was the spectrophotometry. So spectrophotometry is you know practiced quite a lot all over the world even now and the earliest applications where somewhere around 1930s when the first type of calorimeters where introduced into the market.

And now a days the total spectrometric determinations all over the world exceed more than 100000 compounds and more than 30 million estimations all over the world. We can imagine the popularity of these techniques in day today life, so another advantage a spectrophotometry is that the procedures can be easily automated now which is with little or no manual intervention.

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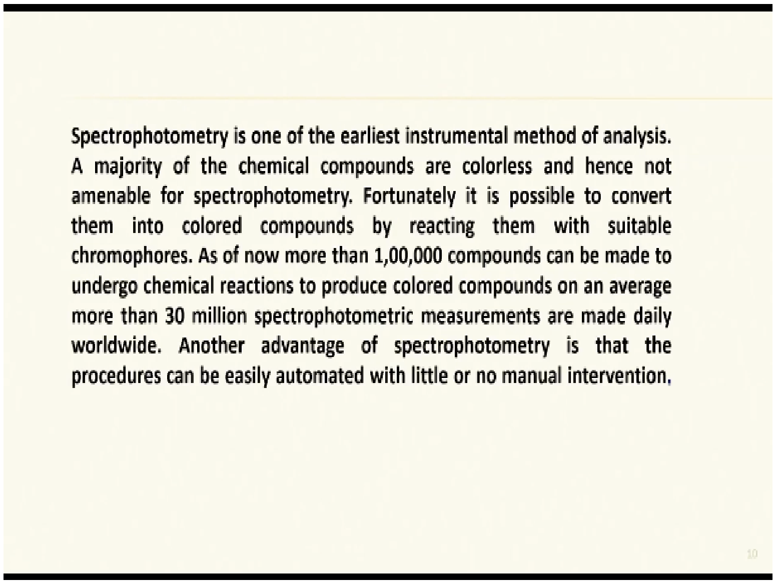

Spectrophotometry is one of the earliest instrumental method of analysis. A majority of the chemical compounds are colorless and hence not amenable for spectrophotometry. Fortunately it is possible to convert them into colored compounds by reacting them with suitable chromophores. As of now more than 1,00,000 compounds can be made to undergo chemical reactions to produce colored compounds on an average more than 30 million spectrophotometric measurements are made daily worldwide. Another advantage of spectrophotometry is that the procedures can be easily automated with little or no manual intervention.

So, all these things considered make way for the determination has lot of organic compounds, inorganic compounds, metals, non-metals, biochemical compounds, and radioactive compounds. So many of them are determined by spectrophotometry is one of the best instrumental techniques, one of the cheapest very cost effective etc. okay. Now what is spectrophotometry based on I will give brief of very brief introduction, it is based on the measurement of color of the chemicals.

Heterocyclic chemistry and analytical chemistry are rapidly changing subjects which almost where almost frenetic activities are attested by the complex research papers all over the world most of the time. And new journals are there with the proliferation of monographs, reviews, conferences, symposiums, seminars and so many other ways of dissemination of the information. And they cover all aspects of the signs that is spectrophotometry.

That is including the instrumentation including the new methods, including standardization several other aspects of the day today applications of the technique. So, that interdependence of these 2 major branches that is analytical science that is heterocyclic chemistry and analytical chemistry, how does it make a difference. Normally if I have to measure any color as their basis of it is identification and quantification the material should be colored.

If the material is not colored then I must have a reagent which when added to the compound which I want to analyze should form a color, that is where heterocyclic chemistry comes in okay, all chemists are known all over the world even for to the general Layman as the man chemist is a man who plays with the chemicals produces different colors and exciting colors in the laboratory, in the test tube etc., which is very very true in some aspects but exceedingly true with respect to spectrophotometry.

So, the most of the new reactions, new methods are all based on finding a chromophoric reagent for a compound of interest. So the interdependence of these 2 chemicals, these 2 scientific fields rather that is heterocyclic chemistry and analytical chemistry, it has resulted in the resurgence of UV visible spectrophotometer. That is due to the enhanced selectivity and sensitivity, yesterday I talked a little bit about sensitivity, selectivity and then specificity also of the method, analytical methods.

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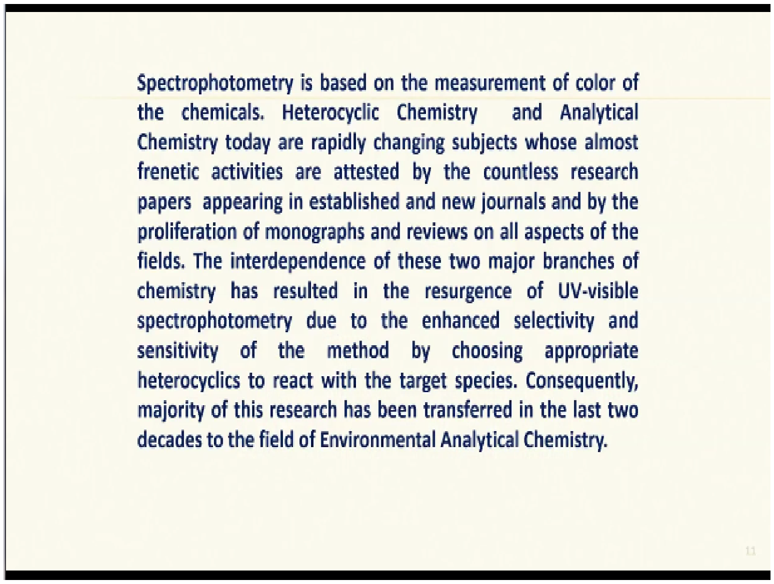

Spectrophotometry is based on the measurement of color of the chemicals. Heterocyclic Chemistry and Analytical Chemistry today are rapidly changing subjects whose almost frenetic activities are attested by the countless research papers appearing in established and new journals and by the proliferation of monographs and reviews on all aspects of the fields. The interdependence of these two major branches of chemistry has resulted in the resurgence of UV-visible spectrophotometry due to the enhanced selectivity and sensitivity of the method by choosing appropriate heterocyclics to react with the target species. Consequently, majority of this research has been transferred in the last two decades to the field of Environmental Analytical Chemistry.

We can make them by choosing appropriate heterocyclic's to react with the target species consequently majority of this research has been transferred in the last 2 decades to the field of environmental analytical chemistry which itself has grown into big science now. So, environmental analytical chemistry is that field of science wherein a sample collected from a matrix is reacted with the chromophoric reagent to produce a color which is characteristic of the compound.

And once they characteristic compound is formed it is molecular spectrum in the UV and visible region provides reasonable identification as well as quantification possibilities for the analysis okay. So while spectrophotometry addresses molecular absorption of the colored compounds, atomic absorption spectrometry has taken over as far as inorganic metallic elements are concerned okay.

Basically atomic absorption spectrometry was also initially sort of a competitor to the spectrophotometry. In spectrophotometry the principle is to convert the molecular compound or any compound into another molecular compound to obtain the molecular spectrum okay. So in atomic absorption spectrometry mainly aimed at producing the atoms in the electromagnetic environment.

So the electromagnetic environment was produced by introducing the metal sample into a flame which produced about 2300 degree centigrade and wherein most of the metals could get converted into their atoms. And these atoms produced in the flame, when they interact with the electromagnetic radiation of specific wavelength.

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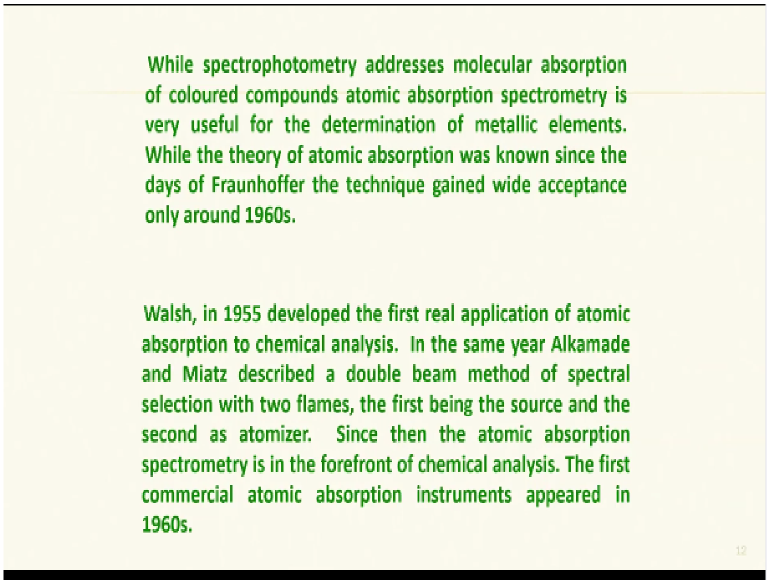

While spectrophotometry addresses molecular absorption of coloured compounds atomic absorption spectrometry is very useful for the determination of metallic elements. While the theory of atomic absorption was known since the days of Fraunhoffer the technique gained wide acceptance only around 1960s.

Walsh, in 1955 developed the first real application of atomic absorption to chemical analysis. In the same year Alkamade and Miatz described a double beam method of spectral selection with two flames, the first being the source and the second as atomizer. Since then the atomic absorption spectrometry is in the forefront of chemical analysis. The first commercial atomic absorption instruments appeared in 1960s.

Then what happens the atoms get excited to next higher energy level and when the atoms come back to the ground state the absorbed radiation is returned back to the environment and which is a characteristic of the concentration of the substance. And the theory of atomic absorption even though it was known since quite longtime somewhere around 1700s by Fraunhoffer and several other scientists who measured the spectrum of solar energy.

And found some dark lines in the solar energy spectrum, at that time it was postulated that the dark lines presently seen in the solar energy spectrum are the absorption lines of the atoms elements present in the solar atmosphere. So, the principle was known about 200 years before but the technique was brought to the laboratory only in somewhere around 1955 that is align by a scientist called as Alan Walsh and he is an Australian scientist.

And what he did was he said to the electromagnetic radiation required for the absorption of the metal should be produced by the same element. Then the resonance between the atoms and the radiation would be absolutely matching and perfect and then atomic absorption can take place is there is a sample in the form of atoms. So, there were 2 requirements, one is production of the atoms that was number 1 in an environment of electromagnetic radiation, second is absorption of the radiation.

So, what he said is you make the electromagnetic radiation of the atoms by making a lamp of the atom. We all know that tungsten lamps we know, then if you want to determine copper use copper lamp, make a filament out of copper and take that radiation through a flame where atoms are being produced. We know how to produce radiation from tungsten, tungsten lamps are there since 1930s right maybe much much earlier.

Since the time of Thomas Alva Edison okay, now the subsequently instrumentation experiments, instrumentation advances have made truly double beams spectrophotometers etc. and with 2 flames, single flame, background correction and all that. And atomic absorption today is one of the most advanced techniques for the determination of metallic elements okay. So the metallic elements if you want to determine in the environment, the best thing we know about and is the atomic absorption.

But why atomic absorption because it is specific, if you have the metal atoms in the sample, if you do atomic absorption you must get a signal. So if is not there, it is not there in the sample, it is pass, fail test as well as the contradiction. So, that is where the atomic absorption is actually is in the forefront of chemical analysis because of this property. So, the first commercial absorption, atomic absorption appears somewhere in the 1960s.

Now a days there are fantastic instruments in the market available and we can also make. So, the spectacular in advances in instrumentation, electronics, automation and computers so over the years have made atomic absorption, spectrometry.

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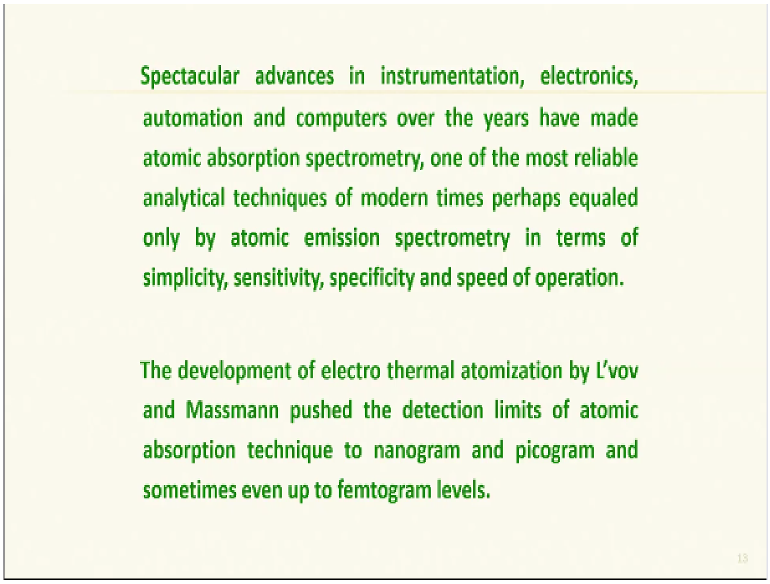

Spectacular advances in instrumentation, electronics, automation and computers over the years have made atomic absorption spectrometry, one of the most reliable analytical techniques of modern times perhaps equaled only by atomic emission spectrometry in terms of simplicity, sensitivity, specificity and speed of operation.

The development of electro thermal atomization by L'vov and Massmann pushed the detection limits of atomic absorption technique to nanogram and picogram and sometimes even up to femtogram levels.

One of the most reliable techniques of modern times perhaps equaled only by atomic emissions spectrometry that 2 only in the last decade okay. That atomic emission spectrometry we have I will discuss within a minute but in terms of simplicity, sensitivities, specificity and speed of operation both are comparable that is atomic absorption as well as atomic emission. Now there was an exciting development of in the atomic absorption region.

That is I have written in the last paragraph in this slide by L'vov, he is the Russian scientist and another scientist Massmann, he is an American. They push the detection limits of atomic absorption technique to nanogram and picogram levels, that is 10 raise to -9 and 10 raise to -10 grams okay. And sometimes even up to femtogram levels, that is 10 raise to -15grams, now you can imagine we cannot even weigh 10 raise to -6 grams but we can determine 10 up to 10 raise to -15 gram levels of the metals okay.

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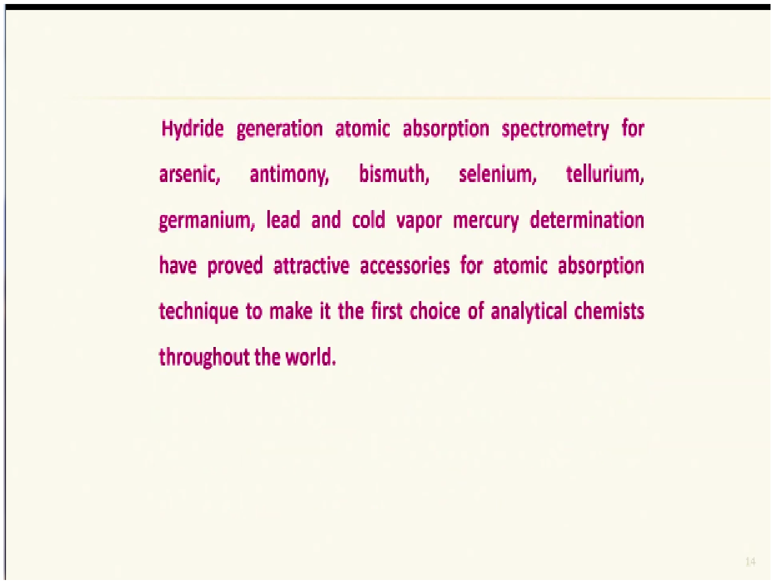

Hydride generation atomic absorption spectrometry for arsenic, antimony, bismuth, selenium, tellurium, germanium, lead and cold vapor mercury determination have proved attractive accessories for atomic absorption technique to make it the first choice of analytical chemists throughout the world.

Now the another exciting development was the hydride generation atomic absorption and this one hydride generation technique is meant only for the few elements which produce hydride. And the hydrides have got a property that you just pass some amount of nitrogen in the sample. If there is a metal hydride it will be pushed out of the liquid and that pushed out liquid can be convert can be taken into a flame or something like that environment of high temperature where even around 1000 degree centigrade.

The hydrides decompose to give you a metal and hydrogen, a hydrogen will laid in the maintenance of the temperature of the atomic absorption and hydride metal can be determined. But this technique is useful only for few elements, those elements include Arsenic, antimony, Bismuth, Selenium, Tellurium, Germanium, Lead that is all only these 6 or 7 elements are amenable to the determination as hydrides.

But the beauty is most of these elements Arsenic, antimony, Bismuth, Selenium, Tellurium, Germanium and Lead. They are all environmental pollutants. And the laws are very strict where the determination of these elements is required in not parts per million but parts per trillion 10 raise to -9 or 10 raise to -12 gram levels in the environment okay. That is one of the important aspects where atomic absorption meets the legal requirements or rather.

The other way around legal requirements have taken note of the advance of these techniques and push the limits of exposure for the man to nanogram and femtogram not femto yet and picogram levels nanogram and picogram levels okay. So, that is the that is why atomic absorption hydride generation is the first choice of analytical chemist throughout the world as far as these elements are concerned okay.

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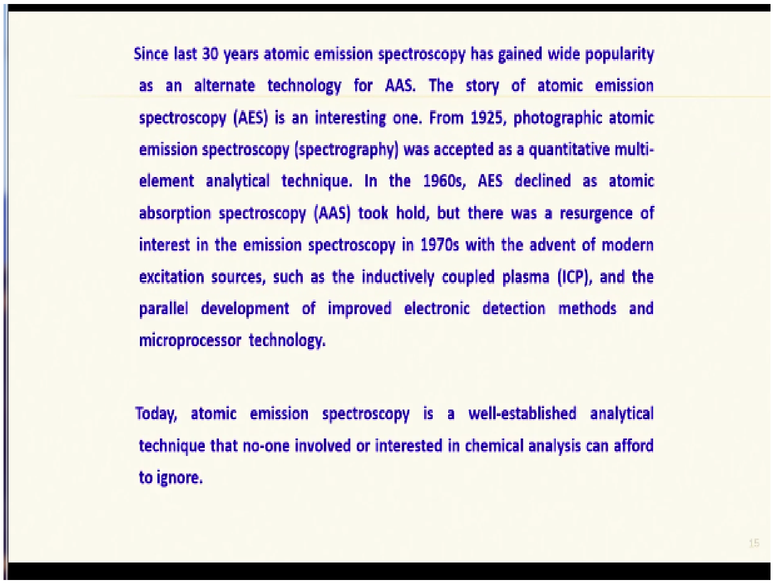

Since last 30 years atomic emission spectroscopy has gained wide popularity as an alternate technology for AAS. The story of atomic emission spectroscopy (AES) is an interesting one. From 1925, photographic atomic emission spectroscopy (spectrography) was accepted as a quantitative multi-element analytical technique. In the 1960s, AES declined as atomic absorption spectroscopy (AAS) took hold, but there was a resurgence of interest in the emission spectroscopy in 1970s with the advent of modern excitation sources, such as the inductively coupled plasma (ICP), and the parallel development of improved electronic detection methods and microprocessor technology.

Today, atomic emission spectroscopy is a well-established analytical technique that no-one involved or interested in chemical analysis can afford to ignore.

Now since last 30 years I have been people are talking about atomic emission, so what is atomic emission. Atomic emission spectroscopy has gained wide popularity as an analytical alternate technology for AAS atomic absorption okay. So the story of atomic emissions spectroscopy is also an interesting one from 1925 onwards people have been using atomic emissions spectroscopy, it is probably comparable to spectrophotometry in it is historical practice right from 1925, 30s etc. people have been using atomic emissions spectroscopy.

That was known as spectrography at that time okay. Now spectrography was expectant as a quantitative multi element technique even at that time. But with applications only in the foundry where very high temperatures could be obtained from the melt of the metals when they were have been processed and metals where being produced. So, the technique is not new but the development since 1960s the atomic absorption atomic emission declined where somewhere around 1955 to 60s when Alan Walsh developed atomic absorption.

Because the determination of atomic emission was somewhere around in the % level at that time but atomic absorption push the limits to ppm level microgram level, so little bit setback for atomic emissions spectrometry as a technique. But with the advent of modern excitation source such as inductively couple plasma and the parallel development of improved electronic detections, detection methods and microprocessor technology etc.

Again brought back the atomic emission spectrometry to the table where we work. Now the beauty is the earlier atomic emissions spectrometry was restricted only to the foundries. But and that to only the minerals, metals okay, metals which have being produced as for general use. Now the atomic emission spectroscopy is applicable to all elements not as a produced metal but even as ion.

So, the detection limit has been push to the equivalence of atomic absorption, that is why today atomic emissions spectroscopy is a well established analytical technique that no one involved or interested in chemical analysis can afford to ignore. So, that means if you want to do metal analysis you have to first compare which one would be best for you that is atomic absorption or atomic emission. Because the sensitivities are comparable and then techniques are available, instrumentation is available.

And the only thing you will have to look for is the speed of operation, complicity of the sample and application time, both are equally fast also. There is no specific advantage in terms of time as for as both these techniques are concern okay, now look at the next slide.

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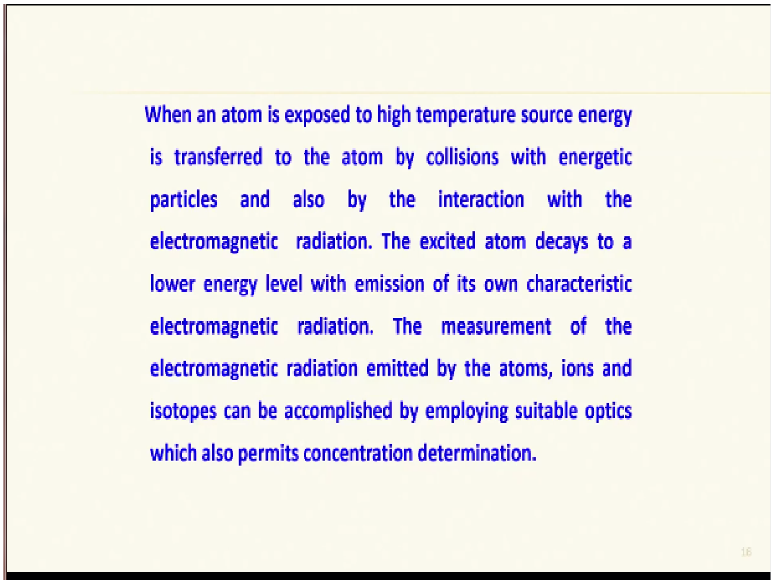

When an atom is exposed to high temperature source energy is transferred to the atom by collisions with energetic particles and also by the interaction with the electromagnetic radiation. The excited atom decays to a lower energy level with emission of its own characteristic electromagnetic radiation. The measurement of the electromagnetic radiation emitted by the atoms, ions and isotopes can be accomplished by employing suitable optics which also permits concentration determination.

The idea of atomic emission is very simple, so when an atomic atom is expose to high temperature source energies transferred to the atoms by collisions with energetic particles. This is all very well known and also the energy is transferred by interaction with the electromagnetic radiation. This point to have been stressing since quite longtime and later on we will spend some more time this also.

So, the excited atom normally decays to a lower energy level with the emission of it is own characteristic electromagnetic radiation. This also, this is the principle I am talking about, this whole slide tells you about the principle of atomic emission. So the measurement of the electromagnetic radiation emitted by the atoms ions, isotopes etc. can be accomplished by suitable optics which also permits concentration determination.

Now the point is atomic absorption can give you only the concentration of the metals as far as the metal is concern. Here what we are talking it is the ions, atoms and isotopes also, so see the advance of the science towards different applications in specific instances. So the atomic emission has got it is own advantages and it has also got it is own disadvantages which I have already covered in my earlier NPTEL demo as a courses. Now I want to talk to you about the organic compounds, so when the energy of the atomic electromagnetic radiation is not very high.

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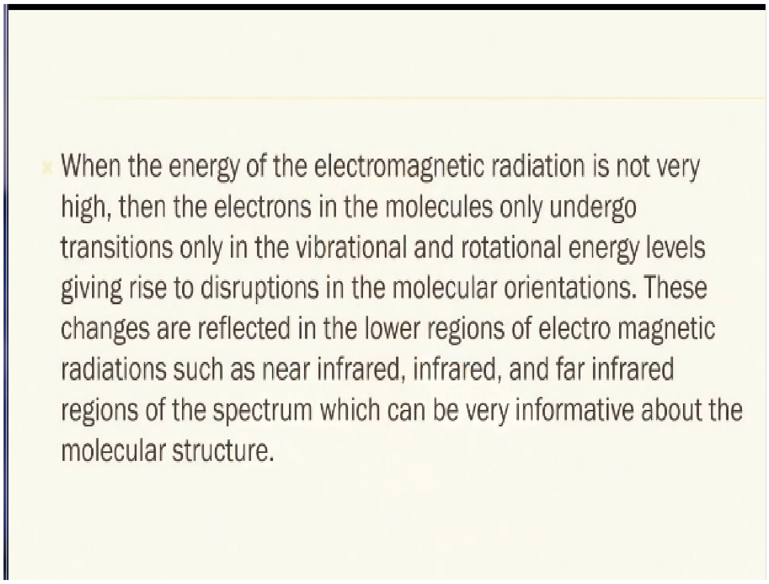

- When the energy of the electromagnetic radiation is not very high, then the electrons in the molecules only undergo transitions only in the vibrational and rotational energy levels giving rise to disruptions in the molecular orientations. These changes are reflected in the lower regions of electro magnetic radiations such as near infrared, infrared, and far infrared regions of the spectrum which can be very informative about the molecular structure.

Look at the slide now what I had written here when the energy of the electromagnetic radiation is not very high. Then the atoms are not produced then what happens, the electrons are excited but they cannot escape, that means the atoms are not produced and the electrons in the molecules only undergo transitions in the vibrational and rotational energy levels. So that gives rise to disruption in the molecular orientation, so this you must understand.

So what happens now, the energy is focused on an organic molecule or organic moiety, now the energy is not sufficient to excite the electrons okay. So, the molecule instead of becoming, it can become like this the molecule may twist or the molecule may elongate or it may bend so many other possibilities are there. And these changes occur because of the changes in the vibrational and rotational energy levels.

I will explain to you what are the vibrational and rotational energy levels later also but if you are already familiar there should not be any confusion of what I am talking about. So these changes are reflected in the lower regions of electromagnetic radiations such as near infrared, infrared and far infrared regions of the spectrum. So, if you want to take a make sense out of this sentence you should understand that an electromagnetic radiation is a combination of the radiations of different frequency, different energy.

So, that contains cosmic rays, gamma rays and then beta rays, alpha rays, X-rays, hard X-rays, soft X-rays and then ultraviolet, far ultraviolet rays, vacuum ultraviolet, far ultraviolet, ultraviolet, visible region, near and far infrared, far infrared and far infrared, microwaves, radio waves etc. It is a big combination of all the elements of the electromagnetic radiation.

So these changes molecular disruptions when expose to electromagnetic radiation appear in the infrared, far infrared and near infrared regions of the spectrum which can be very very informative about the molecular structure of how they get distorted. And what happens when they these radiations fall. So what are the types of frequencies and what are the types of transitions that occur that will be studying in this course okay.

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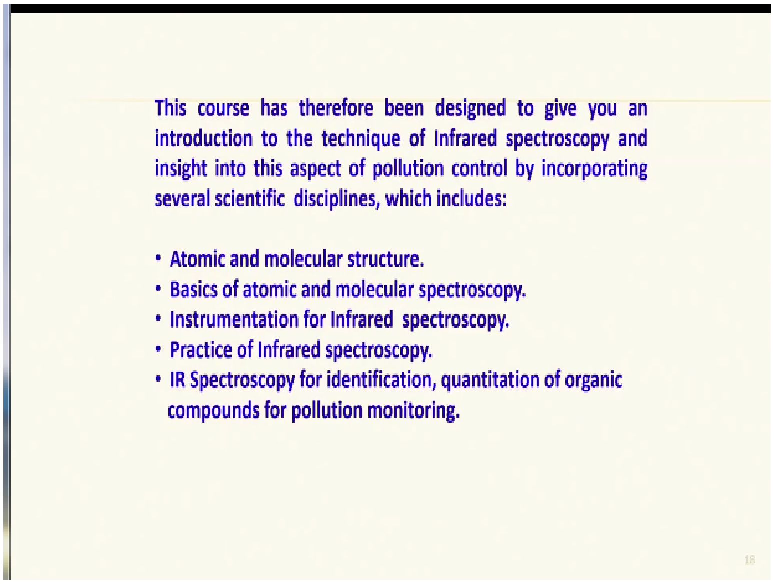

This course has therefore been designed to give you an introduction to the technique of Infrared spectroscopy and insight into this aspect of pollution control by incorporating several scientific disciplines, which includes:

- Atomic and molecular structure.
- Basics of atomic and molecular spectroscopy.
- Instrumentation for Infrared spectroscopy.
- Practice of Infrared spectroscopy.
- IR Spectroscopy for identification, quantitation of organic compounds for pollution monitoring.

Now this course has been therefore designed to give you an introduction to the technique of infrared spectroscopy and insight into this aspect of pollution control by incorporating several scientific disciplines. I am telling about the course now, that is we will be studying atomic and molecular structure, will be studying basics of atomic and molecular spectroscopy and then instrumentation for infrared spectroscopy.

Practice of infrared spectroscopy, infrared spectroscopy for identification and quantification of the organic compounds for pollution monitoring. So we will continue our discussion in the next session okay, so our next session will start on the atomic and molecular structure with maybe little bit of repetition for you if you know the subject but if you do not know the subject it will be a revelation to you, thank you very much.