Characterization of Construction Materials
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Lecture – 55
Spectroscopy Techniques – UV and IR Spectroscopy – Part 2

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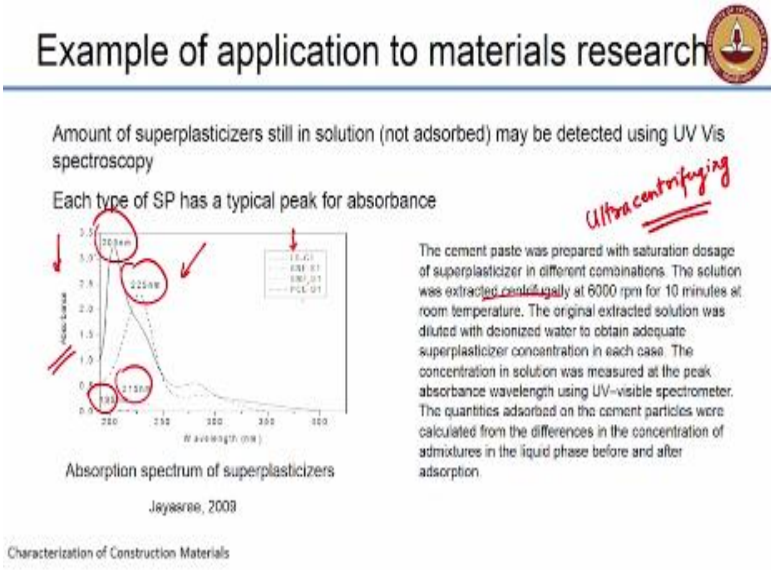

Example of application to materials research

Amount of superplasticizers still in solution (not adsorbed) may be detected using UV Vis spectroscopy

Each type of SP has a typical peak for absorbance

The cement paste was prepared with saturation dosage of superplasticizer in different combinations. The solution was extracted centrifugally at 6000 rpm for 10 minutes at room temperature. The original extracted solution was diluted with deionized water to obtain adequate superplasticizer concentration in each case. The concentration in solution was measured at the peak absorbance wavelength using UV–visible spectrometer. The quantities adsorbed on the cement particles were calculated from the differences in the concentration of admixtures in the liquid phase before and after adsorption.

Absorption spectrum of superplasticizers

Jayasree, 2009

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Now, this is an example of how this was applied in construction materials research. So, the idea was here to determine how much of the superplasticizer that you add to the cementitious system in the beginning stays on with respect to time. So, we know that one of the primary means of mechanism of action of superplasticizer is to adsorb on the surfaces of the cement particles. Now, if all the superplasticizer that you add into the concrete gets adsorbed on the cement particles' surface in the beginning itself, then there will be a rapid drop in the tendency of the superplasticizer to disperse the particles. So, what we want ideally is a system where some portion gets adsorbed in the beginning while a part of the superplasticizer remains in the solution and gets adsorbed at later stages. So, here we wanted to find out based on the chemical species of the superplasticizer, what was the tendency of these superplasticizer molecules to get adsorbed in the beginning or with respect to time or how much superplasticizer was still remaining in the solution.

Now, the problem here is we need to extract the superplasticizer from the cementitious paste. So, one way of extraction is by ultra centrifuging. We do ultra centrifuging; what is the principle of centrifuging? You rotate at very high speeds, so that you can separate the solid and liquid phases. So, right after cement paste is mixed with the superplasticizer and the water, you do this ultra centrifuging to remove the solution which will essentially contain water mixed with your superplasticizer. So, you repeat this experiment after 1 hour of mixing water and superplasticizer into the cement, the solution that you separate will have water and some part of the SP which did not get adsorbed onto the cement.

So that is what essentially was being done in this case, and you can see here the UV absorbance spectra for the different chemical species. In this case, there were 4 different chemical species that were used. One was lignosulfonate, one was sulphonated naphthalene formaldehyde, one was sulphonated melamine formaldehyde, and the final one was polycarboxylic ether. So, these are 4 different chemical families of superplasticizers and you can see for the plain molecules, for the plain superplasticizers, the absorption spectra are quite different. For instance, for lignosulfonates, the primary absorbance happens at a wavelength of 205 nm. So, is that in the visible range or ultraviolet range? It is in ultraviolet range. In fact, all of these 4 compounds are in the ultraviolet range, but they have very specific wavelengths at which absorption actually happens. So, if you are taking the solution which is removed by ultra centrifuging and subjecting it to ultraviolet-visible light spectroscopy, you can detect the presence of these species and by calculating the relative heights of the absorbance spectra, you can determine how much of it is actually remaining in solution from one time to the next.

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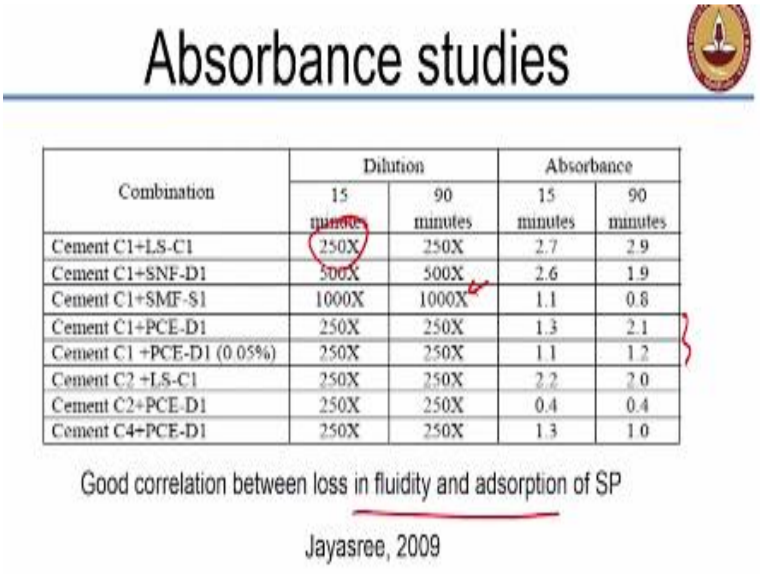

Absorbance studies

Combination	Dilution		Absorbance	
	15 minutes	90 minutes	15 minutes	90 minutes
Cement C1+LS-C1	250X	250X	2.7	2.9
Cement C1+SNF-D1	500X	500X	2.6	1.9
Cement C1+SMF-S1	1000X	1000X	1.1	0.8
Cement C1+PCE-D1	250X	250X	1.3	2.1
Cement C1 +PCE-D1 (0.05%)	250X	250X	1.1	1.2
Cement C2 +LS-C1	250X	250X	2.2	2.0
Cement C2+PCE-D1	250X	250X	0.4	0.4
Cement C4+PCE-D1	250X	250X	1.3	1.0

Good correlation between loss in fluidity and adsorption of SP

Jayasree, 2009

So, while this result is not entirely 100% accurate, but what it is tending to show you is that there is a good correlation between loss in fluidity and adsorption of superplasticizer. The greater the tendency of the superplasticizer to get adsorbed on the cement particles in the beginning itself, the faster is the loss in fluidity. So, what we generally come to notice in this case is that, the systems which have polycarboxylate ether in them tend to have a larger amount of the superplasticizer remaining in solution, even after 90 minutes of the mixing of cement and water.

So, that simply tells you that the greater effectiveness as far as dispersion is concerned would be obtained from these kinds of molecules. So, I would not completely expect this result to be 100% correct because again, look at the extent of dilution that was necessary in several cases, because the amount of solution that you collect even after centrifuging is going to be only minimal. So, in this case, the solution is diluted 1000 times. So, you need to ensure that you are reading your data correctly with respect to the kind of solution that you have extracted. So, if you get only 1 milliliter, if you want to have a substantial amount ready for your analysis, you need to dilute that to 1000 milliliters in this case.

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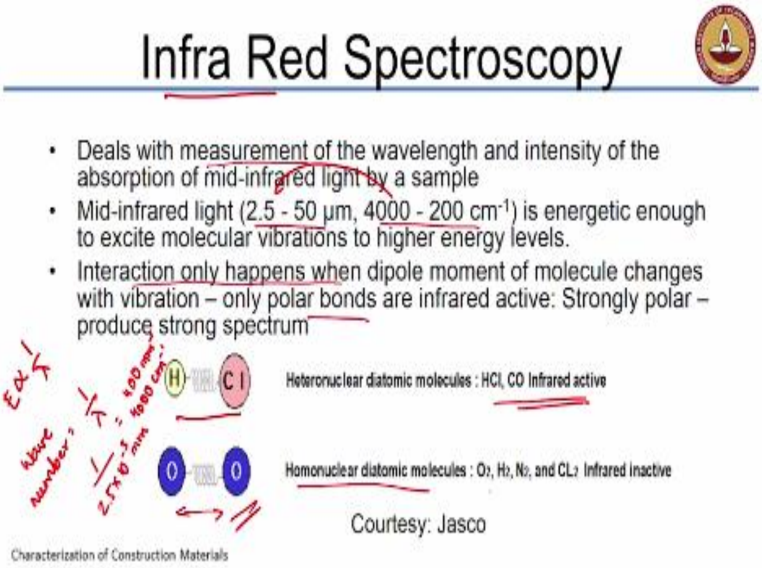

Infra Red Spectroscopy

- Deals with measurement of the wavelength and intensity of the absorption of mid-infrared light by a sample
- Mid-infrared light (2.5 - 50 μm, 4000 - 200 cm^{-1}) is energetic enough to excite molecular vibrations to higher energy levels.
- Interaction only happens when dipole moment of molecule changes with vibration – only polar bonds are infrared active: Strongly polar – produce strong spectrum

Heteronuclear diatomic molecules : HCl, CO Infrared active

Homonuclear diatomic molecules : O_2, H_2, N_2, and CL_2 Infrared inactive

Courtesy: Jasco

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I did not spend that long on ultraviolet-visible light spectroscopy because we are operating nearly in the same range as you do for atomic absorption or emission spectroscopy. However, when we want to look at organics present in the system or when we want to look at the types of bonding for the compounds that are present in the system, we move on to a different range of spectroscopies based on infrared. So, infrared obviously has a wavelength that is higher than visible light, because of which its tendency to induce electronic transitions becomes lower and lower. At the extent of energy that infrared radiation has, you can only excite vibrations in molecules.

So, essentially, infrared spectroscopy deals with measurement of wavelength and intensity of absorption of mid-infrared light by a sample. So, we have 3 regions in infrared. We have near infrared, mid-infrared and far infrared. So, in this case, we are talking about mid-infrared region which is essentially 2.5 to 50 µm of wavelength and very often as far as infrared spectroscopy is concerned, the wavelength is referred to by wave number. Now, what is wave number?

$$Wave\ number = \frac{1}{\lambda}$$

So, 4000 cm^{-1}corresponds to 2.5 µm. So, wavelength has to be expressed in millimeter in this case. So, wave number is nothing but just another representation of reciprocal of wavelength. Why is this sort of representation chosen? Because energy is proportional to $(1/\lambda)$. So, energy in this case is proportional to the wave number.

Now, there are several types of molecules that your system may have, some of these are molecules that are not going to be active as far as infrared is concerned. What do you mean by that? If you have homonuclear diatomic molecules like oxygen, hydrogen, nitrogen or chlorine, these will have no response to the radiation because they are going to be inactive as far as infrared is concerned. Now, when do you consider system to be inactive? Interaction only happens when dipole moment of the molecule changes with vibration - only polar bonds are infrared active and the stronger the polarity in the system, the stronger will be the infrared spectrum that is produced by these materials. What do you mean by polar? When there is a separation of charges happening between the elements that make up the molecule. Can you give me examples of other polar compounds? What about water, is it polar or nonpolar? Water is polar, right. There is a separation of charges that happens at the bond and the stronger the difference in polarity, the higher will be the absorption spectrum produced in infrared.

So, in this case of homonuclear diatomic molecules like oxygen, nitrogen, you have almost neutrality as far as charge is concerned, but here (heteronuclear diatomic molecules) there is a charge imbalance because of the relative sizes of your hydrogen and chlorine atoms inside the HCl compound. So, there is a charge imbalance that leads to polarity and this polar system will definitely be infrared active.

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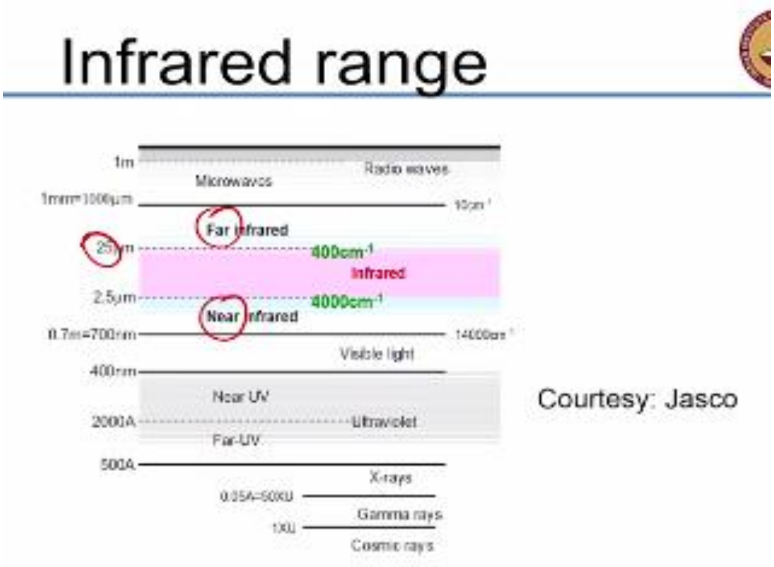

Infrared range

Courtesy: Jasco

So, the range of infrared we are talking about from 2.5 to about 50 µm. So, this is the mid infrared system, of course here (in figure) only 25 µm is marked, but 2.5 to 50 µm would be the mid-infrared region. Beyond that becomes your far infrared, less than 2.5 µm is near infrared that means which is closer to visible light.

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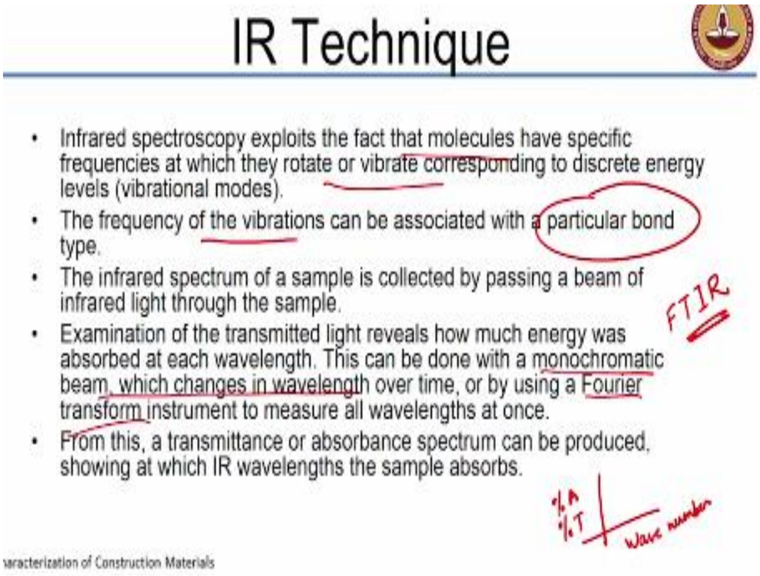

IR Technique

- Infrared spectroscopy exploits the fact that molecules have specific frequencies at which they rotate or vibrate corresponding to discrete energy levels (vibrational modes).
- The frequency of the vibrations can be associated with a particular bond type.
- The infrared spectrum of a sample is collected by passing a beam of infrared light through the sample.
- Examination of the transmitted light reveals how much energy was absorbed at each wavelength. This can be done with a monochromatic beam, which changes in wavelength over time, or by using a Fourier transform instrument to measure all wavelengths at once.
- From this, a transmittance or absorbance spectrum can be produced, showing at which IR wavelengths the sample absorbs.

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So, what happens as a result of absorption of this infrared radiation is that polar molecules tend to start vibrating because of the different types of vibrations that may actually happen in the molecule. So, since there is a charge imbalance, when you supply radiation to it, there are different kinds of things that may happen. The bond may start extending or it may start bending or rotating. So, a lot of different things can happen to the bond because of this absorption of the radiation.

So, IR spectroscopy simply exploits the fact that molecules have very specific frequencies at which they can rotate or vibrate corresponding to discrete energy levels. Once again, any transition that happens, either in electronic system or a molecular system happens at very discrete energy levels. So, for example, if you have a hydrogen and chloride bond and you are talking about the specific energy that will excite the stretching of this bond, there will be only one single value for that energy that creates this stretching. If you are talking about the water molecule with 2 hydrogen and 1 oxygen atom (H_2O), so you have the oxygen at the center and the hydrogen attached to it. So, there can be stretching of the hydrogen atoms, there can be bending of the bond and so on, but each one will happen only at a specific energy, because energy levels are always discrete as far as atomic structure is concerned. So, what you are simply doing is looking at what specific frequencies do this particular transition occurs? In this case, by transition I mean vibration. Then you can relate that to the specific elemental species that are present in your system.

So, the frequency of the vibrations can be associated with a particular bond type. Infrared is collected by passing infrared light through the sample and how much of the energy that gets absorbed or transmitted can give you an indication of specific wavelengths at which you can induce vibrations happening in the system.

Now, we have seen several systems, we saw that you need to actually isolate the wavelengths to send them through the sample or you can have in the case of UV-visible spectrometers, we talked about the array-detectors in which case you can collect all the wavelengths together at the same time. Similarly, in the case of Fourier transform, to make the technique a lot more robust, either we can use a monochromatic beam, which changes in wavelength over time, that means you disperse the wavelength to specific ranges or you can collect all the wavelengths together and do a Fourier transform, to measure all the wavelengths at once. So, that is why today, what we typically call IR spectroscopy is FTIR spectroscopy, Fourier Transform Infrared Spectroscopy. The idea is that you can isolate all the frequencies or all the wavelengths at once, rather than having to individually choose wavelengths of infrared light to be passed through the sample.

So, the spectrum here is quite similar to what you had in the case of absorption spectrum seen previously. So, you plot the absorbance or the transmittance on the Y-axis and the wavelength on the X-axis, but in this case we do not plot the wavelength, we plot the wave number. So, we plot the wave number on the X-axis and the % absorbance or % transmittance. Once again, at specific wave numbers, we will be generating certain peaks that will be indicative of the species that are present inside the system.

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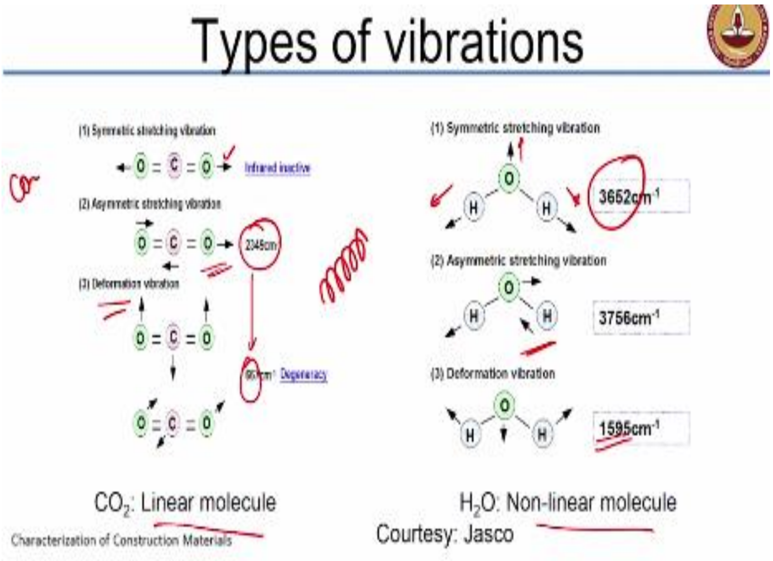

Types of vibrations

CO_2: Linear molecule

H_2O: Non-linear molecule

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Courtesy: Jasco

So, this is just an example of the different types of vibrations that can actually happen. So, considering the CO_2 molecule, which is nothing but a linear molecule, because there is no angle in the bonds between carbon and oxygen, so in this case, we have a symmetric stretching. That means both sides are stretching equally. That means you do not really get a charge imbalance in this case. So, because of that this sort of system will be infrared inactive. On the other hand, if there is asymmetric stretching, that will be corresponding to specific energy absorption of infrared light and that happens specifically at 2349 cm^{-1} wave number.

Deformation vibrations which lead to a change in the linearity of the structure can happen at 667 cm^{-1}. So, is the energy higher or lower here? Where is the energy higher, in the asymmetric vibration or in the deformation vibration? So, the higher the wave number, the higher the energy. So, in the case of asymmetric stretching vibration it happens at higher energy levels as opposed to deformation vibrations which are possible at lower energy levels.

Now, if you consider a nonlinear molecule like water, H_2O, so here you can have symmetric stretching vibrations, where the oxygen goes this way and the hydrogen go in its specific direction, but even in this case, this would also be infrared active because there is no balance in this case also. So, because of that, this specific stretching vibration actually happens at around 3652 cm^{-1} wave number. Asymmetric stretching vibration happens when you get differences in the way that these bonds are stretching.

Now, for ease of understanding, just imagine that these bonds are springs. So, what happens when you stretch the spring or when you compress the spring? When you stretch two springs together at the same time equally or when you stretch one spring with one force and other spring with a different force and so on so, that creates your stretching which is either symmetric or asymmetric. Deformation vibration happens when you have change in the structure of the material, and again in this case, these are possible at lower wave numbers like 1595 cm^{-1}.

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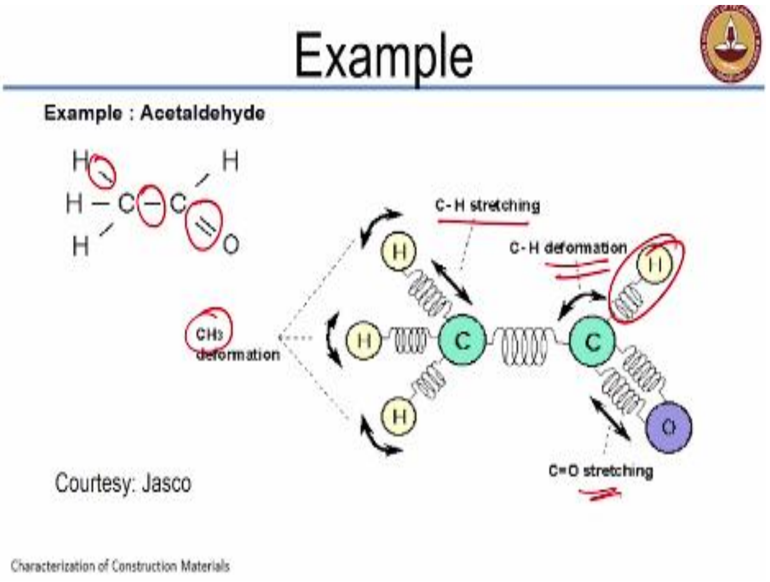

Example

Example : Acetaldehyde

Courtesy: Jasco

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So, just to give another example from the structure of acetaldehyde, so here of course we have different types of bonds, we have carbon-hydrogen bond, you have carbon-carbon bond and carbon-oxygen double bond. Each of these will have specific vibrations associated with the stretching or deformation of these bonds. So, here for instance the carbon-hydrogen stretching can happen. Here, again the bonds are represented by springs. So, stretching simply means extension of the spring. The CH_3 itself can deform as a single unit. The carbon-hydrogen can deform; the relative angle between carbon and hydrogen with respect to the horizontal axis may get changed. The carbon-oxygen double bond may also stretch, okay. So, for each of these transitions, you will actually get a specific absorption of the IR in your absorbance spectrum. So, with this what we are trying to do is deciphering the structure of the molecules that we are interested in.

Now, in the case of cementitious materials, what would you expect to see? What kind of bonds are there in cementitious materials? We have Si-O, then aluminium-oxygen, you may get carbon and oxygen from carbonate species that are present in the system. Then you have O-H (oxygen and hydrogen) and so on. So, for each of these specific bonding systems, you will get a signature as far as your FTIR spectroscopy is concerned.

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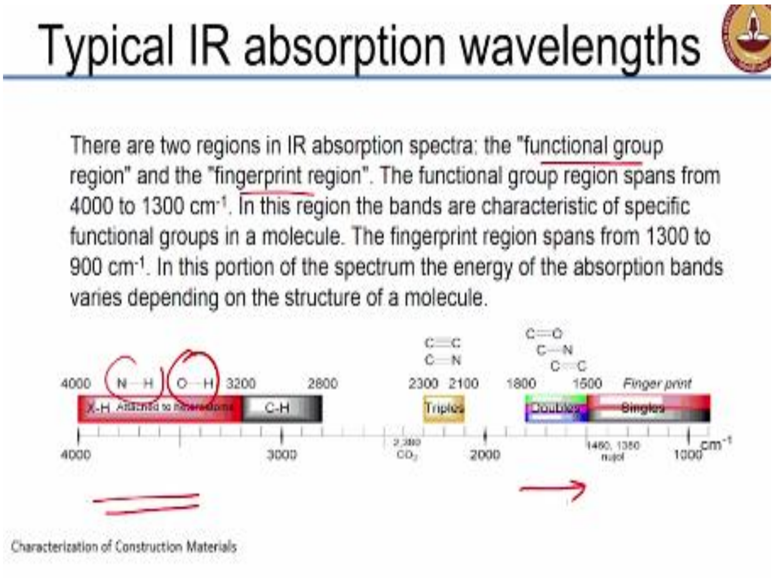

Typical IR absorption wavelengths

There are two regions in IR absorption spectra: the "functional group region" and the "fingerprint region". The functional group region spans from 4000 to 1300 cm^{-1}. In this region the bands are characteristic of specific functional groups in a molecule. The fingerprint region spans from 1300 to 900 cm^{-1}. In this portion of the spectrum the energy of the absorption bands varies depending on the structure of a molecule.

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So, the typical IR absorption wavelengths are divided into 2 groups, one is called the fingerprint region, the other is called the functional group region. At the higher end of the absorption spectra, that means at higher wave numbers what you get are called functional group regions. So, here nitrogen-hydrogen (N-H) group, alcohol group (O-H) and so on. These are essentially the functional groups that may be present in your systems.

On the other hand, when you go towards the lower end of the wave number, what you get is the fingerprint, which essentially corresponds to the presence of single bond, double bond or triple bonded systems. Based on the specific sets of wave numbers at which you get these transitions, you can then approximately estimate the composition of your structure of the material.

Now again, you will obviously need to compare with the database to try and understand what each peak signifies. For most of the standard bonding systems like carbon-

carbon triple bond or carbon-carbon double bond, there are very specific locations at which transitions happen like stretching or bending and so on and you can associate that with the peaks that you observe for your sample and then figure out what actually is present in your sample. We will see some examples in just a minute.

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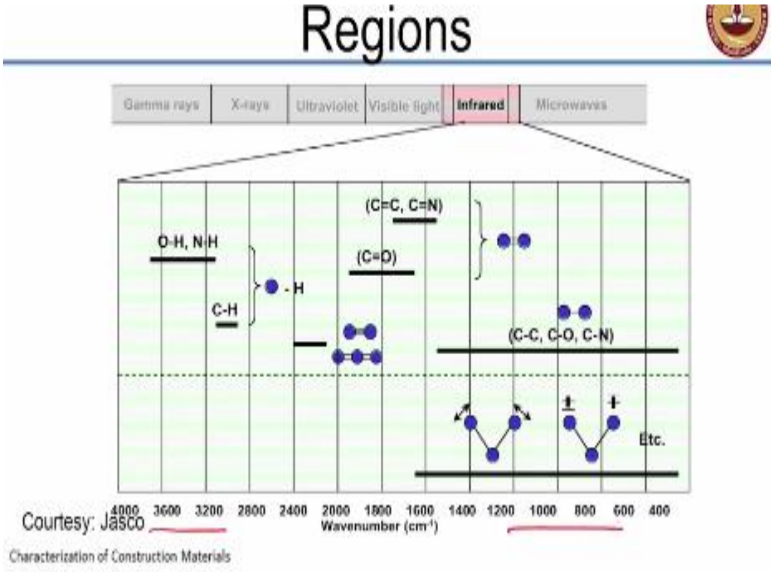

Regions

Courtesy: Jasco

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So, these are the different regions as I said, in the infrared spectroscopy, you have the functional group region on the left and the fingerprint region on the right.

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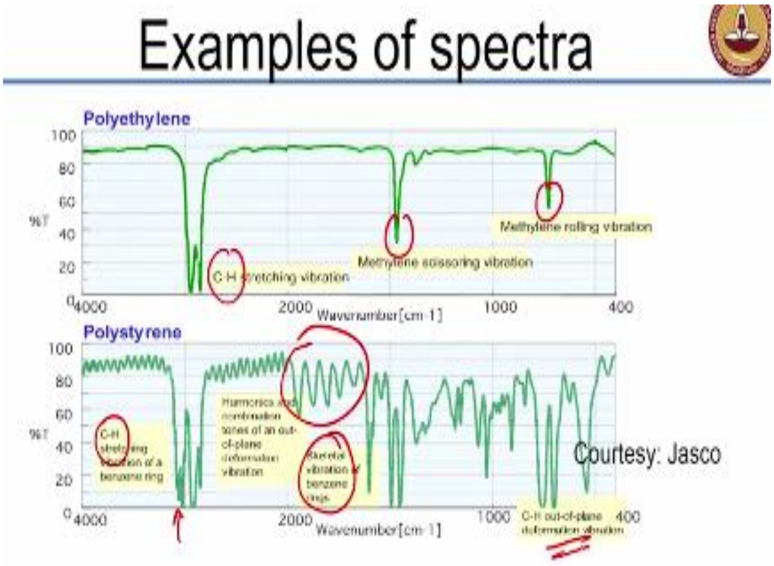

Examples of spectra

Courtesy: Jasco

So, this is an example of spectra. This is the polyethylene spectra on the top and polystyrene at the bottom. What is the essential difference between polyethylene and polystyrene? Polyethylene and polystyrene, the primary difference is polyethylene is aliphatic and polystyrene is aromatic. So, you will have benzene rings in polystyrene. In polyethylene, you have carbon-hydrogen stretching vibration, which is being measured at close to 3000 cm^{-1} wave number. You have the methylene scissoring vibration and rolling vibration.

Whereas in styrene, you will have to somehow differentiate the effect here, the stretching of vibration between carbon and hydrogen happens inside the benzene ring in this case. So, because of that, your specific frequencies or wave numbers at which these kinds of transitions happen are going to be quite different from the carbon-hydrogen stretching which happens in the case of polyethylene. You can also get skeletal vibration of benzene rings, the complete vibration of the rings itself that can produce such kind of IR spectra, and you can also get out of plane deformation vibration of carbon-hydrogen bonds which are recorded later, but you can see the spectra becomes a lot more complex for structures like benzene, whereas for simple aliphatic structures like polyethylene, you get very specific peaks that mark the presence of certain type of compounds.

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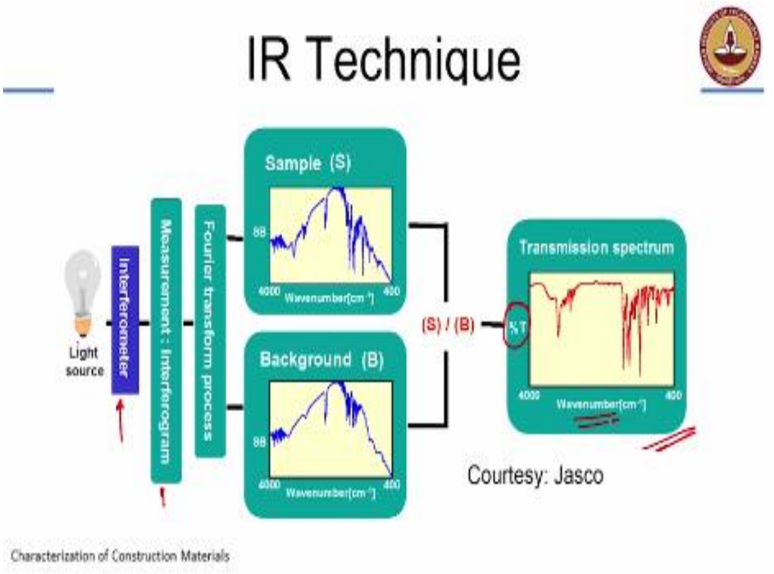

IR Technique

Courtesy: Jasco

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So, just a little bit more information on the technique itself, just to try and understand how these spectra are produced and what does Fourier transform actually do in the system. So, again, you have the light source. This light then passes through an instrument called the interferometer. The interferometer essentially brings out light rays that are either completely in phase or out of phase based on the movement of some mirrors, which are inside the interferometer. This light that comes out of the interferometer, then passes through your sample and creates what is known as an interferogram, and this interferogram is then subjected to what is called the Fourier transform process. Now, Fourier transform is something you have learned in mathematics, but we will again just go through what is going on here.

So, once again, we have a background presence in the sample. We are operating at infrared wavelengths, so, there is sufficient amount of infrared radiation in the background also which needs to be removed from the system to actually get a clear understanding of the absorbance spectra for the sample itself and ultimately we get what is known as the transmission spectrum. So, here the percentage transmittance is plotted against the wave number on the X-axis. So, how do we actually generate this light that passes through the interferometer?

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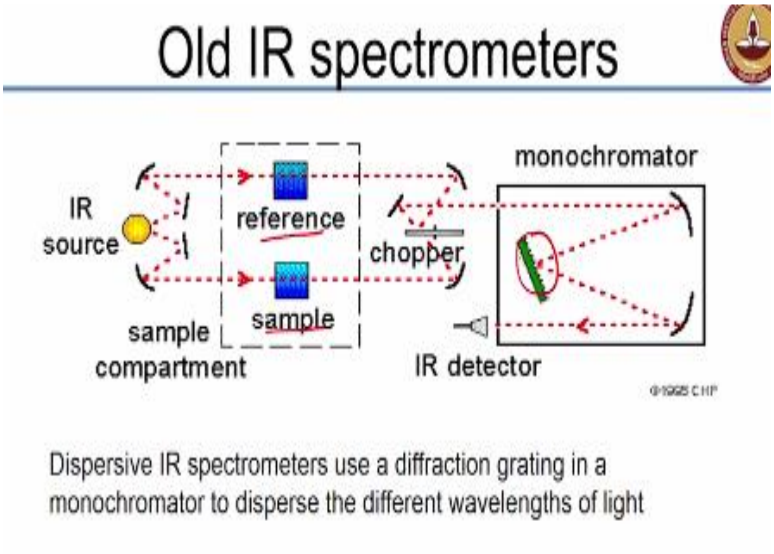

Old IR spectrometers

Dispersive IR spectrometers use a diffraction grating in a monochromator to disperse the different wavelengths of light

So, these are old IR spectrometers which were quite similar to the layout that we saw earlier for the ultraviolet-visible light spectrometers. So, here, the infrared source radiation is actually sent separately through the reference and through the sample and then you basically send it through a monochromator to isolate specific wavelengths and detect the specific wavelengths at which absorption has happened.

Now the problem here is it is a very cumbersome technique because for every wavelength you need to actually adjust your diffraction grating to ensure that you are actually able to capture the wavelength. A more robust and sophisticated technique is actually to capture everything at once and determine by Fourier transforming the signal as to what are the frequency components present inside your light.

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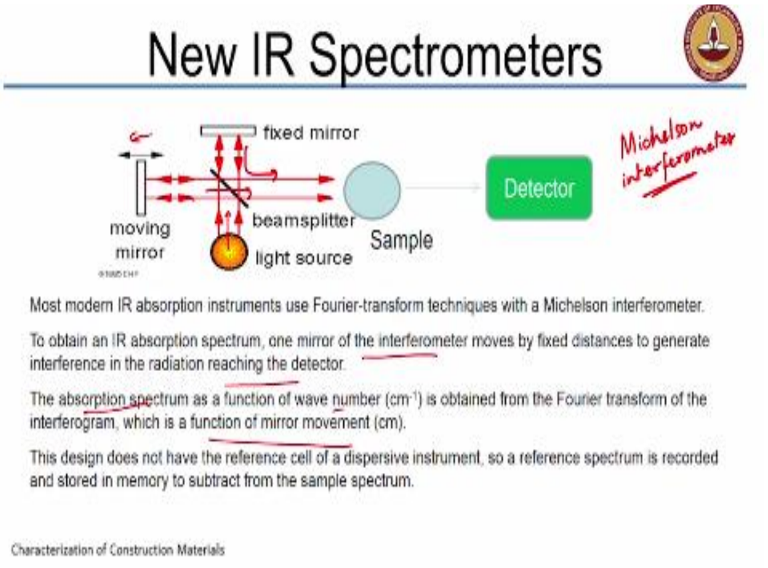

New IR Spectrometers

Most modern IR absorption instruments use Fourier-transform techniques with a Michelson interferometer.

To obtain an IR absorption spectrum, one mirror of the interferometer moves by fixed distances to generate interference in the radiation reaching the detector.

The absorption spectrum as a function of wave number (cm^{-1}) is obtained from the Fourier transform of the interferogram, which is a function of mirror movement (cm).

This design does not have the reference cell of a dispersive instrument, so a reference spectrum is recorded and stored in memory to subtract from the sample spectrum.

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That is what we are talking about with the new IR spectrometers. So what is happening in this case? So, this sort of an interferometer is also called a Michelson interferometer and this is something that you have learned before in physics in school, but I am sure that you would have forgotten this. It would be a good idea to actually look at Michelson interferometer designs on the internet, you get very good information from Wikipedia itself about this.

So, what happens in this interferometer is that you have a fixed mirror and you have a moving mirror. So, light is going from this light source onto a beam splitter that sends the direct beam to the fixed mirror and the reflected beam to the moving mirror. So, what will happen at a specific location is that the light beam that is coming through the fixed mirror towards the sample and from the moving mirror towards sample will be completely in phase, but at certain lengths of the moving mirror, there will be some out of phase as far as the two beams are concerned. Now, as a result of this, you will produce light which comes out from this beam splitter going towards the sample, which has some constructive and some destructive sort of wave nature.

So here to obtain the absorption spectrum, one mirror moves by fixed distances to generate interference in the radiation reaching the detector. So, what you are simply doing is instead of sending the beam directly through the sample, you are causing it to have components that have constructive or destructive interference while you send it through the specific sample.

The absorption spectrum is a function of wave number obtained from Fourier transform of the interferogram, which is a function of the mirror movement. So, if you can compute the distance over which the mirror is moving, you will actually generate specific wavelengths at which there is constructive interference which go right through the sample. Only at certain lengths of the moving mirror, you will produce a constructive interference and because this function of the mirror movement can be captured as the specific wavelengths over which absorption occurs, then you can actually generate what is known as the interferogram. So again, I think we are out of time, there is a lot more information that I wanted to give you here. So, let us continue this in the next lecture.