Characterization of Construction Materials
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Lecture – 52
Spectroscopy Techniques – AAS, AES – Part 1

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Spectroscopy Techniques

AAS, UV-Vis, FTIR, NMR

Hello everyone, today we will begin discussion of a new topic. We have so far talked about microscopy and image analysis and how they can be used for studying construction materials phases, the internal structure of materials, trying to get an estimate of the quantitative phase composition of given materials and so on. Now, of course, you talked earlier about X-ray diffraction in one of the previous lectures and X-ray diffraction is also a kind of a spectroscopy technique. Now, spectroscopy is a broad name which is given to any technique that uses some characteristics of the electromagnetic spectrum, X-ray spectroscopy or X-ray diffraction uses X-rays. X-rays are one part of the electromagnetic spectrum. They are very high energy rays, but apart from X-rays, there are several other types of rays that make up the electromagnetic spectrum. We talked about optical microscopy that uses visible light. So, even that, light microscopy is also some sort of a spectroscopy technique. You will see later when I define the kind of interactions that are possible in spectroscopy, that all these techniques feature one way or the other in the spectroscopy techniques. But for the purpose of discussion in this chapter, we will talk about Atomic Absorption Spectroscopy, UV-Visible light spectroscopy, Fourier Transform Infrared Spectroscopy, and Nuclear Magnetic Resonance. These techniques are applied to a wide range of materials and they are quite popularly applied in cementitious materials analysis also. So, we will look at the principles of these techniques and how we can actually make use of the information that we get from the absorption or scattering or transmission of the radiation from different types of species.

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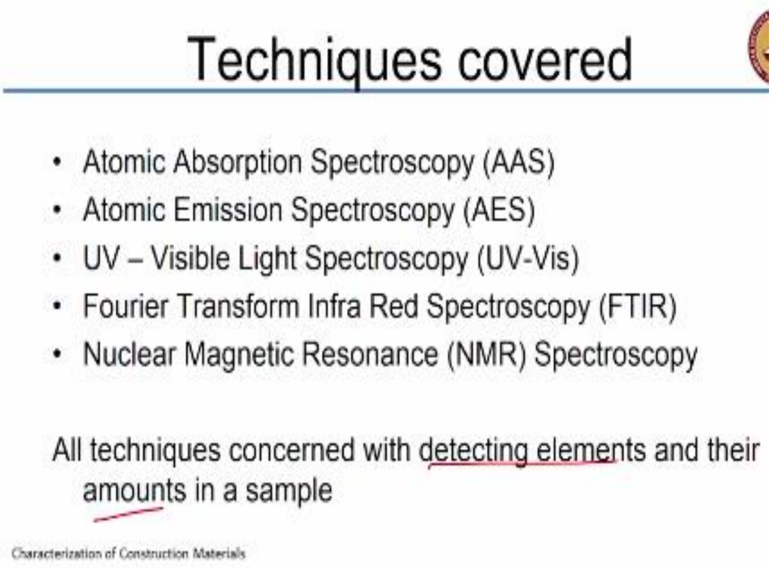

Techniques covered

- Atomic Absorption Spectroscopy (AAS)
- Atomic Emission Spectroscopy (AES)
- UV – Visible Light Spectroscopy (UV-Vis)
- Fourier Transform Infra Red Spectroscopy (FTIR)
- Nuclear Magnetic Resonance (NMR) Spectroscopy

All techniques concerned with detecting elements and their amounts in a sample

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So, essentially the techniques we are trying to cover here is Atomic Absorption and of course, together with absorption, you will also have Emission Spectroscopy, UV Visible Light Spectroscopy, Fourier transform infrared and Nuclear Magnetic Resonance spectroscopy. So, all the techniques are concerned with detecting elements and their amounts in a sample, just like any other technique, we want to apply these for qualitative and quantitative analysis of the phases in the sample.

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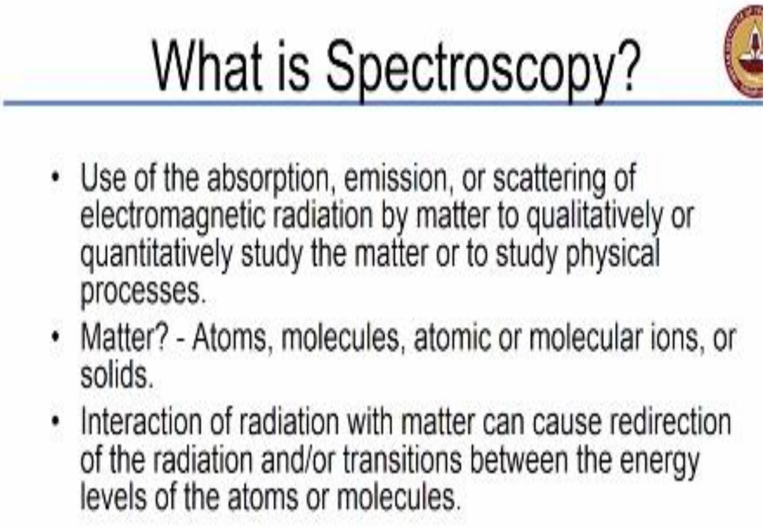

What is Spectroscopy?

- Use of the absorption, emission, or scattering of electromagnetic radiation by matter to qualitatively or quantitatively study the matter or to study physical processes.
- Matter? - Atoms, molecules, atomic or molecular ions, or solids.
- Interaction of radiation with matter can cause redirection of the radiation and/or transitions between the energy levels of the atoms or molecules.

So, generally spectroscopy is nothing but the use of absorption, emission or scattering of electromagnetic radiation by matter which could be atoms, molecules, atomic or molecular ions or even solids for that matter to quantitatively study the matter or to study physical processes that are ongoing inside the material that you are trying to observe. So, the interaction of electromagnetic radiation with the matter can cause redirection of the radiation, like you saw an X-ray diffraction, the presence of certain crystalline planes in your sample is able to diffract and produce constructive interference of the outgoing X-rays which is captured in your detector.

So, essentially interaction can cause redirection of the radiation, but at the same time, the interaction can also cause transition between the energy levels of the atoms or molecules. You saw earlier in X-ray diffraction that X-rays are actually produced because of high speed electrons bombarding a target metal, which leads to the ejection of an inertial electron from the target metal and that space is occupied by an outer shell electron. The resultant difference in energy is released as heat and X-ray. Now, heat is also one form of radiation. Heat is also one form of radiation; you will see later that typical heat that is given out from human bodies for instance is of the order of the infrared wavelengths. The wavelength of heat coming out of human body is of the order of infrared.

So, again, you are generally utilizing the property of electromagnetic radiation to either get absorbed or scattered by the atoms or molecules which are present inside the system. In doing so, what would happen is you are changing the state of the atom. You are changing the state of the atom or molecule that you are trying to observe. So very often, we see how much the state has changed to try and understand the type of element that is actually present, or after changing its state, if the atom wants to jump back to its natural state, it would then emit radiation and that emission can also be captured and analyzed to understand what kind of element and how much of the element we are actually looking at.

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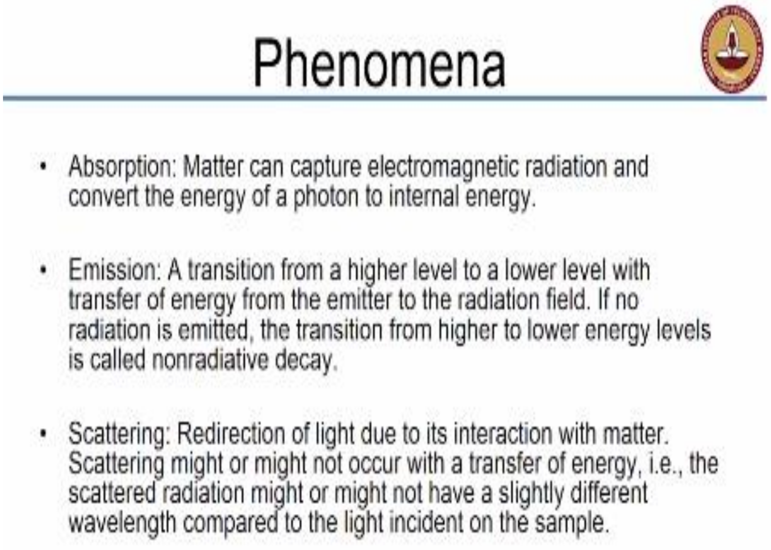

Phenomena

- Absorption: Matter can capture electromagnetic radiation and convert the energy of a photon to internal energy.
- Emission: A transition from a higher level to a lower level with transfer of energy from the emitter to the radiation field. If no radiation is emitted, the transition from higher to lower energy levels is called nonradiative decay.
- Scattering: Redirection of light due to its interaction with matter. Scattering might or might not occur with a transfer of energy, i.e., the scattered radiation might or might not have a slightly different wavelength compared to the light incident on the sample.

So, different phenomena are involved as far as interaction of electromagnetic radiation with matter is concerned. You know these phenomena quite well. Absorption is nothing but absorption of the electromagnetic radiation and conversion of the energy of the radiation into internal energy. That internal energy can do anything; it could lead to transitions in the electron shells within the atom. It can lead to probably ejection of outer shell electrons, for instance. So that is basically absorption of the radiation.

Emission happens when internal changes in the system lead to an emission of an electromagnetic radiation. The atom or molecule is in an excited state and to come back to its natural state, it emits radiation which is in a specific wavelength. That wavelength is characteristic of one of the different types of electromagnetic radiations. So, *emission* is a transition from a higher level to a lower level with transfer of energy from the emitter (that is the atom or molecule) to the radiation field.

In some cases, there is decay possible of the atoms without any radiation being emitted. So that is basically called nonradiative decay. If the transition which is happening inside the elements is leading to some generation, then it is called emission. If it does not generate anything, it is called nonradiative decay.

Scattering, you have all seen before, when you have backscattered electrons, basically these are the ones which are scattered almost 180° from their path by the nuclei of the atoms that you are having in your sample. So, backscattered electrons are basically one of the scattered electrons that you find in scanning electron microscopy. So, *scattering* is redirection of light or electromagnetic radiation due to its interaction with matter. Scattering might or might not occur with a transfer of energy. You may or may not transfer any energy, that is, scattered radiation might not have a slightly different wavelength as compared to the light incident on the sample. Now, what does this mean? When you get an elastic scattering of the backscattered electron, there is almost no loss in energy. It is almost completely reflected back with the same speed. But if it is actually having some inelastic collisions, for example, if it is not exactly in the same direction, if it is getting scattered elsewhere, there may be some loss of energy from this outgoing electron. So loss of energy, obviously energy of an electromagnetic radiation is related to its wavelength. So if the electron that is going out has a different level of energy as compared to the incoming electron, then obviously that would be characterized by a different wavelength of the electron. So, scattering can happen when electromagnetic radiation interacts with the atoms or nuclei or electron shells of the species that you are trying to observe.

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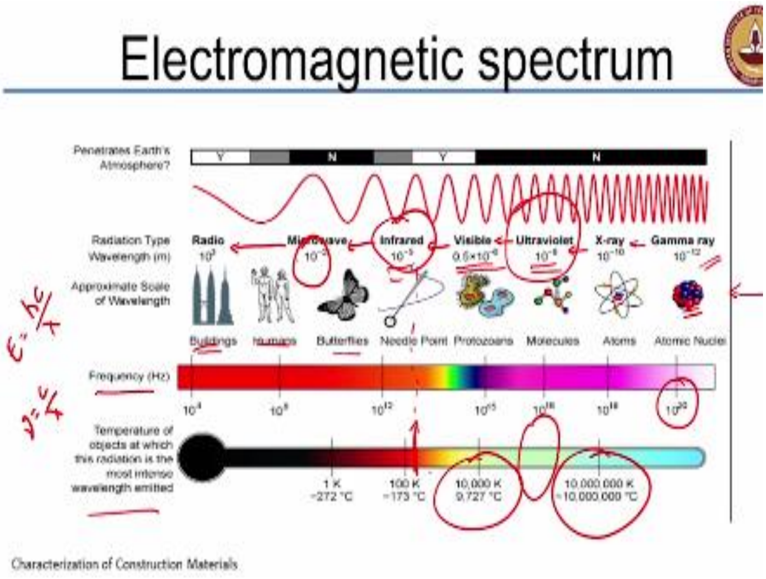

Electromagnetic spectrum

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Just to give you again a glimpse of what the electromagnetic spectrum has, of course you know very well that, at the smallest end, that means of wavelength, smallest end of wavelength, what does it mean in terms of energy? Smallest wavelength means highest energy. Smallest wavelength means the highest energy because energy (E) is:

$$E = \left(\frac{hc}{\lambda}\right)$$

where c is the speed of light in vacuum, that is 3 $*10^8$ m/s.

All electromagnetic radiation will move at the speed of light in vacuum (that is $3*10^8$ m/s), λ depends on the type of rays that you are having in your electromagnetic spectrum. So Gamma rays have 10^{-12} metres as the wavelength. So you can imagine they are very high energy electromagnetic radiation. Then if you come from gamma rays down to X-rays, you are reducing the energy by two orders of magnitude that is about 10^{-10} m is the wavelength, Ultraviolet as compared to X-ray is again reduced by two orders of magnitude (10^{-8} m). Visible light is again two orders of magnitude lesser than ultraviolet radiation ($0.5*10^{-6}$ m), and then you can come to infrared, and then microwave and then radio waves. If you look at radio waves, the wavelengths are of the order of kilometers, (10^3 meters).

So, what scale of wavelength is given by the kind of materials that are in the same range as the wavelength of the electromagnetic radiations. For example, if you are looking at radio waves, these are building size, like Burj Khalifa for instance is 828 meters. So we are in the range of radio waves. Humans, we are typically about 1.5 to 2 meters. So we are in the range of microwave to radio wave transition. Butterflies, how big are butterflies typically? About few centimeters, may be about 6 to 7 centimeters. So, we are in that start of the microwave range. So, as you are trying to utilize different categories of electromagnetic radiation, your capabilities of measuring with that radiation are different. So if you have to measure in kilometer scales, obviously you have to use radio waves. For example, when you have to locate the position of an aircraft, it is done using radio waves (RADAR - Radio Detection and Ranging). If you have to detect under the sea objects, you do SONAR - Sound Navigation and Ranging. So, idea is simply that you apply the right type of radiation to study the kind of phenomena that you want to.

Now what is also given is the frequency in Hertz (Hz). What is the frequency (ν) ?

$$\nu = \frac{c}{\lambda}$$

So that is basically your frequency here. We are talking about 10^{20} Hz in the case of gamma rays. At that frequency, you can actually resolve very small features of the atomic nuclei. So, we are talking about extremely small sizes of resolution with gamma rays. X-rays, again you can resolve atomic sizes; ultraviolet, you are looking at molecular structures; visible light, just like what we use in light microscopy, you can actually see the structure of amoeba for instance.

So again, the capabilities are different. And again, temperature of the objects at which the radiation is the most intense wavelength emitted. Talking about the human body, what temperature are we at, 37 °C, which is about 310 degrees Kelvin. So if you are talking about 310 degrees Kelvin, we are somewhere in this range here, if you come to this range, we are talking about infrared radiation. One of the examples of human body emitting infrared radiation can be seen in the movie predator. I do not know if you have seen the movie Predator, where the alien comes down to earth and is able to make out humans in a dense forest because of the heat signatures emitted from the humans and alien has an infrared sensor in the eye. So that is basically one of the forms of characterization that aliens probably use to detect us humans in otherwise dense foliage which is very difficult to find. So anyway, infrared is the range of wavelengths that are emitted when our bodies are at 310 degrees Kelvin.

So if you heat your material to extremely high levels, for example if you are able to heat to 10,000 Kelvin or 9727 °C, we are talking about generating a wavelength that is significantly high to produce visible light. What is the temperature of the surface of the Sun? It must be on the same level or probably more because sun generates ultraviolet radiation and that ultraviolet radiation can be generated when you are at a temperature range somewhere between 10,000 and 10 million Kelvin. So that is again two orders of magnitude different temperatures.

But X-rays, we are talking about 10 million Kelvin temperature to really generate the X-rays. Now this kind of heat can only be generated by very high speed electrons, for instance, when we have electronic transitions happening between the shells of the atom, that is able to generate the X-rays. So you can imagine the energy that is emitting that X-ray, it is significant. That is why in an X-ray source, one of the common things provided is a cooling tube. You have water circulating to cool the metal because otherwise these high speed electrons and the interactions that they are generating are also liberating a lot of heat, not just X-rays, they will actually, I do not know the exact percentage, but apparently more than 90% is actually getting released as heat and only some small fraction is emitted as X-rays. That is obvious because when you are going to be generating X-rays, you are talking about temperatures that are extremely high, so you need to ensure that you are cooling down your target metal. Of course, we do not heat to 10 million Kelvin, but the temperatures are significantly high when you bombard a very high speed electron beam onto the target metal to generate the X-rays.

This was just to put things in perspective as to where we are with respect to different types of light. Now, from this, you can basically get a small understanding about what we should use to detect different signatures in materials. Now, for example if we have to see through a material, we need to have a very high energy radiation. What do we use typically to see through materials? X-rays, the energy produced by X-rays are high enough to actually travel right through solid species. And if there are any defects present in the solids, they will be transmitting more X-rays and the dense and solid parts of the solid will actually absorb more X-rays. So the difference in absorption and transmission of the X-rays will generate the kind of radiographs that you are commonly familiar with when you actually go to take a medical X-ray. But please remember, the medical X-ray is a very weak X-ray, because you cannot expose human bodies to very high energy X-rays. But there are obviously solid structures like concrete or steel, which are a lot denser as compared to the human body, and because of that you will have to use higher energy X-rays to penetrate to any depth in concrete or steel. The higher the density, the lesser is the penetration of x-rays or even gamma rays.

That is the reason why in nuclear shielding materials, in nuclear reactors we provide a shielding material to ensure that the harmful electromagnetic radiation does not make it out in the atmosphere. We try to ensure that we have a very high density material in the lining or in the shell of your nuclear reactor, so that all these rays are absorbed significantly and do not get transmitted out of the reactor. So, typical materials used for shielding, if you talk about metallic materials, it is usually lead (Pb) - lead has a very high density, but lead is very expensive. So, one alternative that people have is high density concrete. In high density concrete, they replace the conventional aggregates (siliceous aggregates) with iron bearing aggregates like haematite or magnetite or ilmenite or barite (barium sulfate) also is a very high density aggregate. These aggregates provide extremely high densities that increase the overall absorption capacity of the concrete with respect to X-rays, and that acts as a good radiation shielding material.

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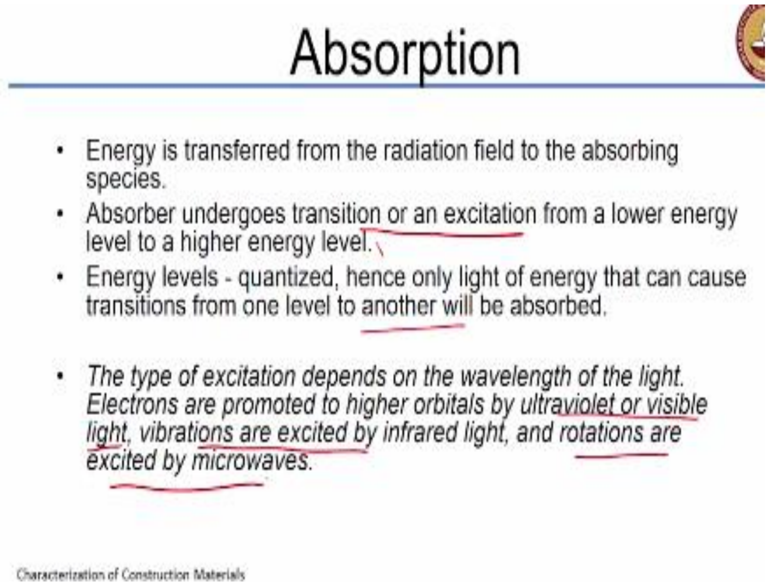

Absorption

- Energy is transferred from the radiation field to the absorbing species.
- Absorber undergoes transition or an excitation from a lower energy level to a higher energy level.
- Energy levels - quantized, hence only light of energy that can cause transitions from one level to another will be absorbed.

- *The type of excitation depends on the wavelength of the light. Electrons are promoted to higher orbitals by ultraviolet or visible light, vibrations are excited by infrared light, and rotations are excited by microwaves.*

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So, let us look at these phenomena in isolation. Absorption is the energy transferred from the radiation field to the absorbing species or the object that you are trying to measure.

What the atoms or molecules in your object are going to undergo, is a transition or an excitation from a lower energy level to a higher energy level. You are supplying it energy. So it adds up to the energy level and brings it up to a higher level. Now, you know very well from the atomic structure that was deciphered by Niels Bohr that each of these levels that the atom is capable of having, are quantized. That means there is only a certain value that these energy levels can actually have. So when the atom absorbs certain energy and goes to a higher energy level, the difference in energies can be perfectly quantized. You can actually get a single answer for that, it is not really some uncertain type of an answer. So, when you know the exact wavelength of the energy that is getting absorbed, which is creating that transition, then you can actually clearly understand what the element that is causing the transition is. For example, in calcium, if an electron is supposed to be promoted to a higher shell by the absorption of energy, you know exactly the energy difference between the higher and lower shells and you can relate that energy difference to the absorption of a certain wavelength of light. So, you can relate the transitions in the material to the absorption of specific wavelengths of light, which is basically absorption spectroscopy.

So, energy levels are quantized. Hence, only light of energy that can cause transitions from one level to another would be absorbed. So for instance, I want to have a transition from the L shell of the electrons to the M shell. The difference between L and M shells is very clearly quantized, you have learned earlier in your electronic structure, the formula for calculating energy of electrons in different shells. So, difference in energies can be related directly to $\left(\frac{hc}{\lambda}\right)$ and from that you know exactly what λ is, which is getting absorbed to create that kind of a transition.

So, the types of excitation obviously depend on the wavelength of the light. Electrons are going to be promoted to higher orbitals when you use ultraviolet or visible light. When you use radiation that has energy that is sufficiently high to be ultraviolet or visible light, you have electrons promoting to higher orbitals.

Vibrations are excited by infrared light. So again, coming back to this absorption spectrum, so your ultraviolet light has 10^{-8} m as the wavelength, whereas infrared is 10^{-5}m. So, it is three orders of magnitude lesser in energy as compared to ultraviolet. So it cannot excite electrons to go into higher orbitals. It is not possible for infrared to do that. However, it can generate vibrations because you have bonds. You have bonds between elements in a material and these bonds are basically at a certain equilibrium length. If you remember your structure of materials before, essentially these bonds are at an equilibrium length, which is the lowest energy configuration. Now, when you supply infrared to these bonds, these bonds can start vibrating, stretching, bending, or rotating. You can have different types of movements of the bonds. We will see some of these later. That will create absorption of that energy. So, because of the absorption of energy, the bonds are not exactly the same position, they are moving, so that is the power of infrared light.

Rotations are excited by microwaves, because microwave radiation is again having high wavelength (10^{-2} m), we are talking about centimeter wavelength. So, at that level, the energy is not sufficient to create the kind of transitions that can be possible with ultraviolet or X-rays or infrared. So we are in the range where we can only produce rotations.