Characterization of Construction Materials
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Lecture – 53
Spectroscopy Techniques – AAS, AES – Part 2

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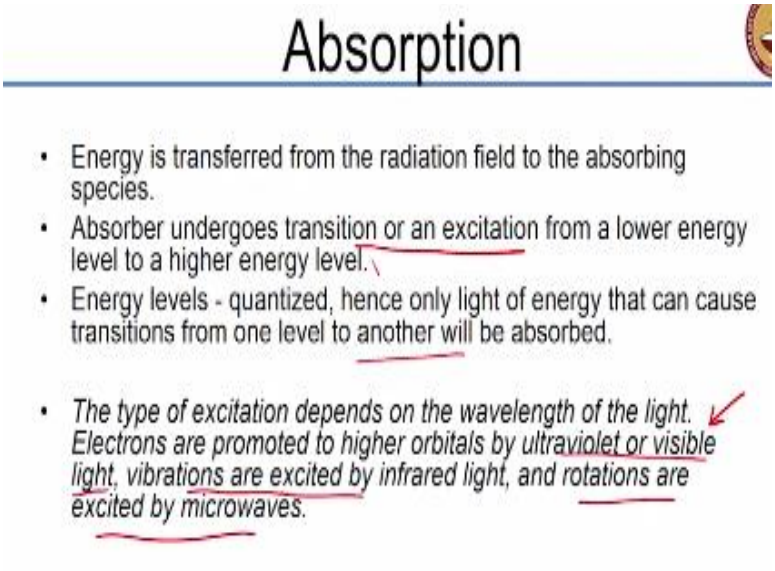

So, nuclei in atoms have spins because they sometimes may have an unbalanced number of neutrons and protons. In that case, they will have a spin. When they have that nuclear spin, when you are supplying the microwave energy to this nuclear spin, it absorbs that energy and changes direction and that is what we are trying to detect by microwave or Nuclear Magnetic Resonance Spectroscopy, NMR spectroscopy. So, these are basically the guiding principles for absorption of different radiation and the use of different types of spectroscopy.

- So, when you are talking about electronic promotion to higher orbitals that happen by ultraviolet or visible light, we are talking about UV-Visible light spectroscopy.
- Vibrations are excited by infrared light that is basically your Fourier Transform Infrared Spectroscopy
- Rotations excited by microwaves – this is your Nuclear Magnetic Resonance Spectroscopy.

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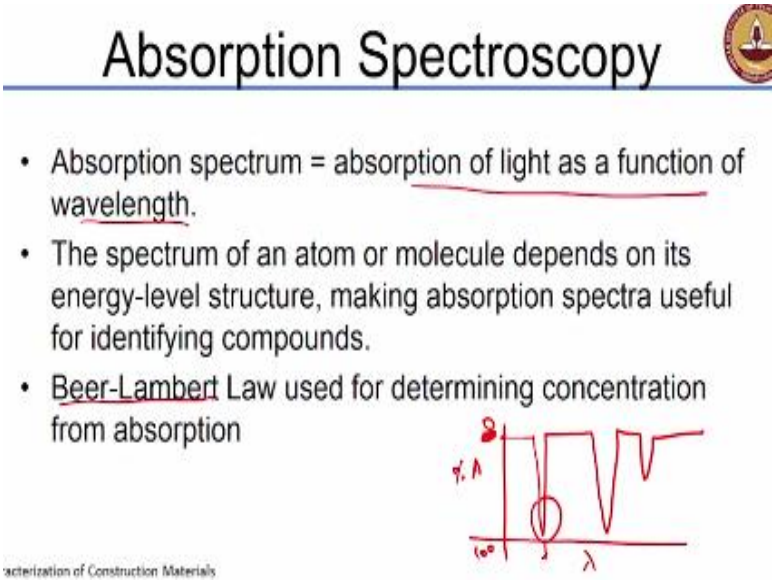

So, absorption spectroscopy or absorption spectrum is nothing but absorption of light as a function of wavelength. So, all you do is you have a plot between percentage absorbed versus wavelength (as shown in graph drawn). Percentage absorbed, 100% may be absorbed in some cases and there may be some peaks like that, at certain wavelengths it is absorbing, this is 0 and that is 100% (as shown in ordinate axis). So, at certain levels you get absorption of the radiation and those peaks can be related to the wavelength of the radiation and then you can actually identify standard elements which will produce that kind of absorption at the specific wavelengths. So, the spectrum of an atom or molecule depends on the energy-level structure, as you already know, which makes absorption spectra useful for identifying compounds. And you can actually apply a law to determine the concentration from absorption that is called Beer-Lambert law. We will see this law briefly.

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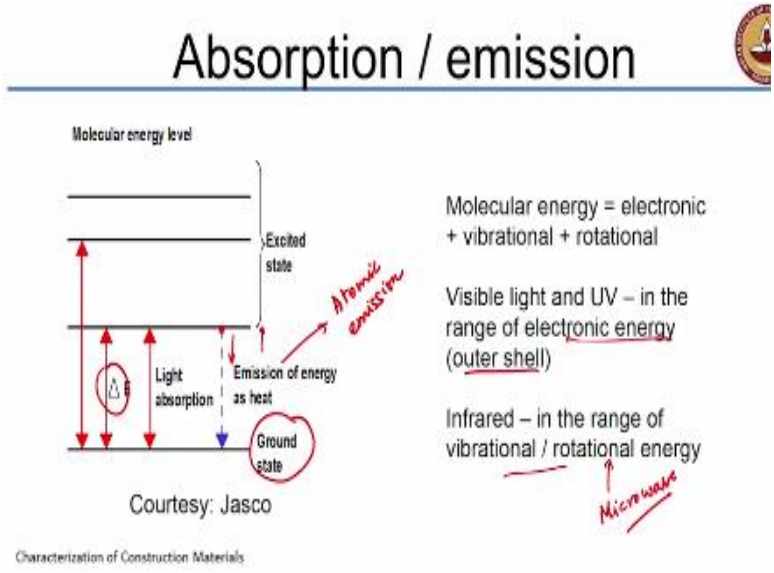

Before that, just to give you a schematic representation of absorption and emission, so that is the ground state of your atom (as shown in diagram). So, because of absorption, your atom is going up to a higher state, an excited state, which could be at different levels. Atom or molecule is going to an excited state. So, this ΔE that happens when you go from ground state to excited state is directly related to a specific wavelength that has been absorbed. So that will help you characterize the material.

Alternatively, if it goes to a higher state and then wants to emit energy as heat and then come back, that is basically your atomic emission spectroscopy. The molecular energy is a sum total of the electronic energy, vibrational energy and rotational energy. So, as I said earlier, visible and UV light are in the range of outer shell electronic energy. You cannot create inner shell transitions by UV and visible light spectroscopy because the wavelengths are too large or alternatively the energy is too low to cause those kinds of transition take place. Now, outer shell electrons are too far away from the nucleus. There they are not really held by a very strong bond with the nucleus. So, outer shell electrons can be knocked off quite easily or promoted to higher orbitals quite easily by ultraviolet and visible light spectroscopy, but you cannot do that with inner shell electrons. For inner shell electrons, the kind of radiation you need is X-rays or high-speed electrons.

Infrared is in the range of vibrational or rotational energy, and microwave is more characteristic of rotational energy.

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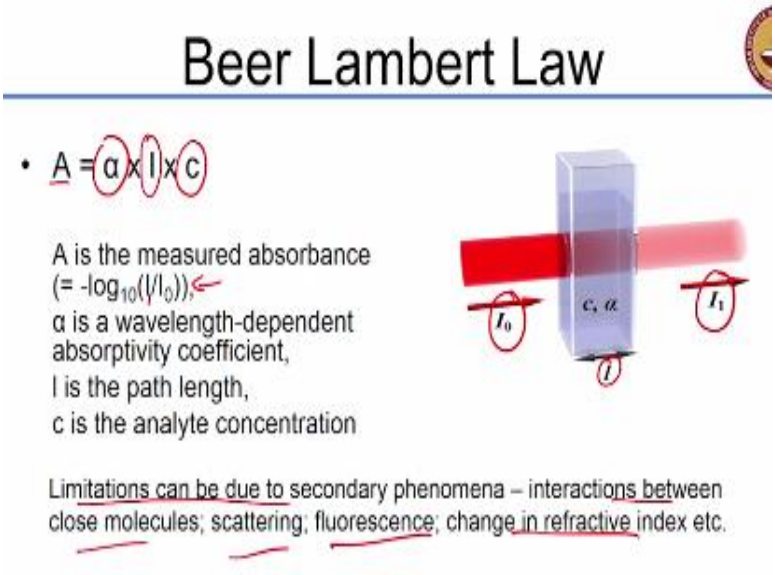

So, now how do we use this to calculate the intensity of the element that you are trying to observe in your sample? So, Beer Lambert law is nothing but it states that the measured absorbance (A) is equal to a coefficient α which is a wavelength-dependent absorptivity coefficient, the length of travel within the material (l) and the concentration of the species that you are trying to analyze (c).

$$A = \alpha * l * c$$

So, suppose you have a sugar solution, sugar and water. So, if you put it in a tube, the length of the tube will be 'l'. 'α' will be the absorptivity coefficient of the sugar solution and 'c' will be the concentration the sugar in solution. The incoming intensity of the radiation is I_0, outgoing is I_1. So absorbance $A = -\log_{10}(I_1/I_0)$. So, it is the negative log of intensities of outgoing to incoming wavelength.

Now, this is a simple phenomenon just like what we have for typical absorption of radiation inside samples. In general, even if you look at design of nuclear shielding devices, again the same sort of principle is applied where you are relating the energy of the material absorbed to some sort of an absorptivity coefficient of your material that depends on density, here it depends on the wavelength of the light that is being transmitted through the material.

But there are some limitations. You can have secondary phenomenon inside. For instance, you can get interaction between closed molecules. So this assumes that each and every molecule of your analyte or the material that you are trying to quantify will be independent of each other and it will interact separately with the radiation, but it is possible

that you may actually get some secondary bonding between the atoms inside the sample and that may actually create some deviations from this law. Then you have scattering because not all the radiation that goes in will be able to come out just after absorption, some of it will get scattered. Fluorescence - what is fluorescence? Radiation that is getting generated by the atoms in the sample, because of the high energy radiation that is coming in, it is able to excite some sort of a change transition happening inside that will be fluorescence, which is nothing but emission. Fluorescence is nothing but emission. And you can have a change in refractive index of the light that is actually coming in because of the difference in the type of medium that is inside your sample. For example, if your original intensity is in air or vacuum and then you have a liquid medium through which your light is going to be traveling, then obviously there is a change in refractive index, that may change your overall law, which relates the concentration of the species to the extent that is getting absorbed. So, if you have, for instance, some dissolved species in a solution, then this law is quite easy to apply. It is quite easy to apply, but we will see later that in typical atomic absorption spectroscopy studies, applying this law directly is very difficult, we will see why.

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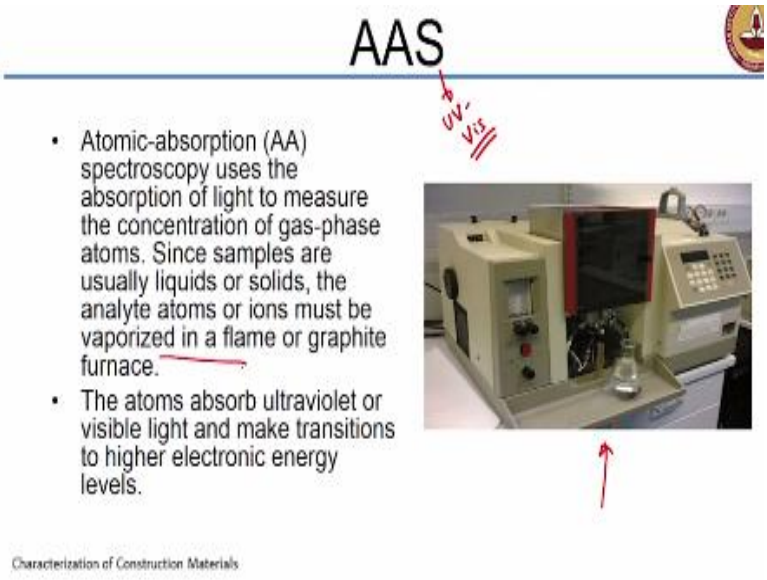

So, one of the common instruments that are used in materials research is atomic absorption spectroscopy. Now, this is a typical instrument, this is the one which we have in our Environmental Engineering Laboratory. You will actually get to see the instrument that we have in Geotechnical Engineering Laboratory.

So, atomic absorption uses the absorption of light to measure the concentration of gas phase atoms. Now, please remember that the energy levels in solids, the ground state in solids is of such a nature that to excite the atoms of a solid to a higher energy level, it may take a lot of energy input and that may not be possible by typical radiation in the ultraviolet or visible light range. So, atomic absorption also uses ultraviolet and visible light range of wavelengths. So, in that range you will not be able to excite solid atoms to absorb radiation. What you need to do is convert these solid atoms or atoms in the solid sample into the gaseous phase. So, what happens when you convert into a gaseous phase? Molecular distance increases. There is a lot higher Brownian motion and so on, you have learned about this before. So essentially there, the atoms are excited, and at that level getting the radiation absorbed or new radiation emitted becomes much easier. So that is basically one of the major initial steps that you need to do in absorption spectroscopy, you need to actually transform these solid atoms into gaseous state.

Now, how do we do that, we will just see that in a minute. So samples are usually liquids or solids, we do not usually analyze gases, we usually analyze liquids or solids. What we do is the analyte atoms or ions must be vaporized in a flame of graphite furnace. So, we are just burning the material off and then pushing these atoms or ions which are in the solid or liquid species into a stream of gas, which can then be analyzed. So, the atoms absorb ultraviolet or visible light and make transitions to higher electronic energy levels. So again, we are talking about outer shell electrons moving to further higher shells by absorption of the incoming ultraviolet or visible light radiation.

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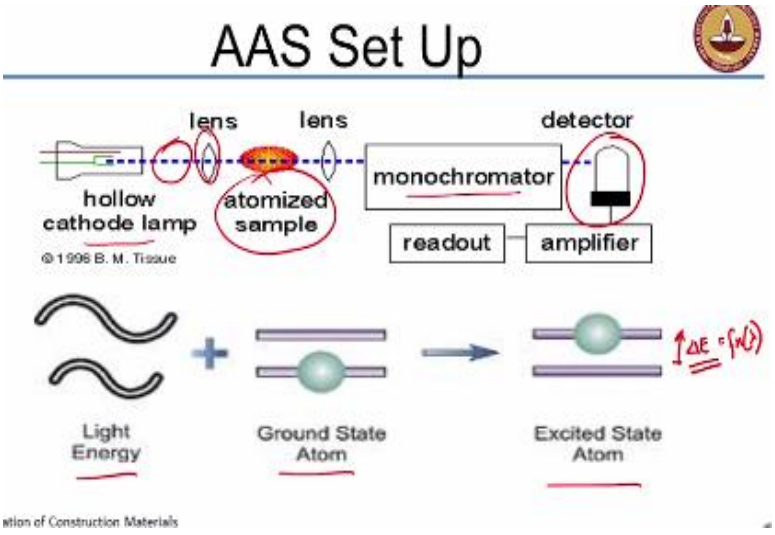

So, this is the typical setup. You have a hollow cathode lamp, which is a source that produces light with the intensity of ultraviolet or visible light. Then it is obviously sent through a lens because we want to ensure that we have a convergent beam that goes right through your atomized sample. Again, we want to ensure that all the intensity coming out of the atomized sample is directed towards a detector. The detector itself consists of a monochromator. What do you think is the function of the monochromator? So, monochromator means it is isolating separate wavelengths from the emitted light, and then of course, you have a detector, which can be amplified to get you a proper readout. So, the idea of a monochromator is that you are trying to separate, because light coming out will be composed of several wavelengths. So, you are actually trying to extract information about different wavelengths that are actually coming out.

What wavelength do you want? You want this wavelength that was coming in. You want to actually select that wavelength, only then you will be able to understand the intensity of this light and the intensity of the light that is coming out. Other wavelengths may be from emissions and fluorescence that you do not really want to collect. So, we want to isolate this wavelength and collect it, so that you can analyze the energy of the incoming and outgoing radiation only of that particular wavelength.

So essentially, again, just to repeat the principle, you have light energy and a ground state atom leads to the excited state atom and this ΔE is perfectly related to the wavelength of the incoming radiation because there is a quantized energy difference, you can actually relate it perfectly to wavelength of the incoming radiation.

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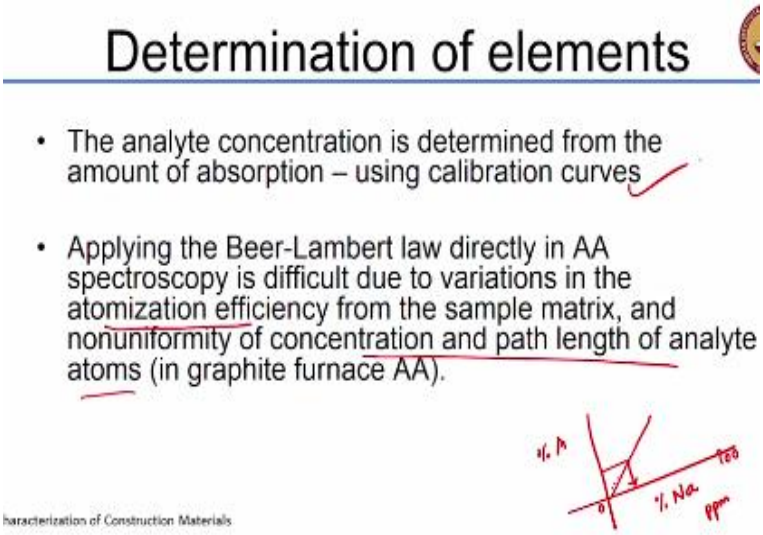

So, again analyte concentration is determined from amount of absorption using calibration curves. We earlier said that you can use Beer-Lambert law, but the problem with atomic absorption spectroscopy is we have an atomized sample. We do not have all the elements of the solid which probably get atomized or converted to gaseous phase to the same level. So, we do not know about the atomization efficiency of the system, and we also do not know the concentration and path length of the analyte atoms. What do you mean by that? So here, if you have a liquid filled inside a tube, we know exactly the length through which the light has to pass through, but in a furnace when the atoms are getting excited to the gaseous state, we do not know if the gaseous atoms or ions are perfectly lined up all along the length of this furnace directly in the path of the intensity of the beam. So we do not know that length for sure. So because of that, application of Beer-Lambert law in typical AAS studies is not easy.

So, what we need to do is prepare calibration curves. So, we prepare mixtures of the species that you are trying to observe. For example, let us say you want to observe or you want to detect the amount of sodium present inside your cementitious paste sample. So, what you do is you prepare known solutions of sodium or known samples of sodium at different concentrations and prepare a curve. So, percentage absorption versus percentage of let us say sodium (Na) from 0 to 100% and you have to actually do a calibration curve. Obviously, you cannot produce 100% sodium, you will be using very small parts of sodium, so usually we talk about parts per million (ppm). So, our points will be only somewhere here okay and then you prepare a calibration curve, which is nothing but a regression line through the points to ensure that you get, then you can read out for whatever absorption level you get, what is the specific percentage of sodium that you have in your sample, that is a calibration curve. You are actually producing known samples, just like what you do with the chloride electrode in the lab. We prepare chloride solutions with different concentrations of chloride ions and then use the electrode to determine what the voltages for specific concentrations of chlorides in your solution. Similarly, we prepare a calibration curve in this case. So that is how you will determine the concentration of the analyte inside the gaseous system.

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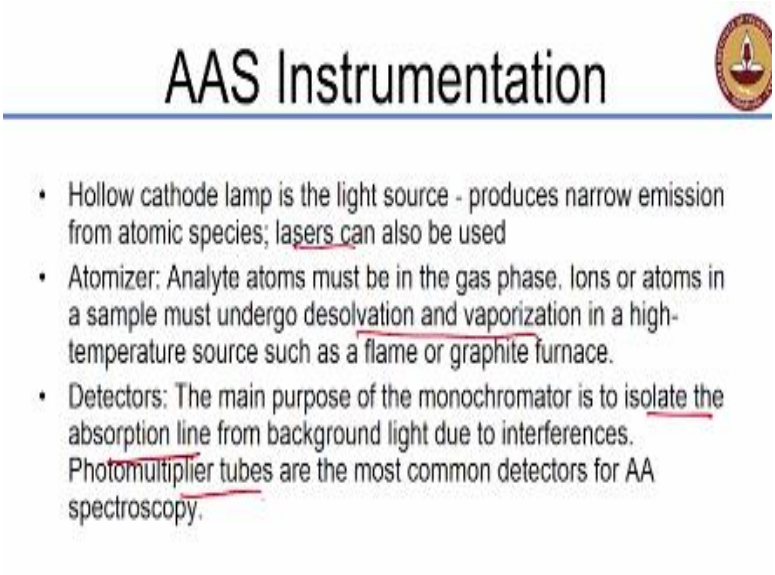

So, again hollow cathode lamp is the light source. It produces narrow emission in the range of ultraviolet and visible light. You can also use laser. Laser can also be used, it produces intensities in the same range or wavelengths of the same range.

Atomizer: the analyte atoms obviously are going to be sent into gas phase. So, ions or atoms in a sample must undergo desolvation and vaporization in a high-temperature source such as flame or graphite furnace. So, we do not send solids directly into gas form. Typically, we dissolve the solids into a solution or prepare a solution of the solids and then send it into a vaporized phase. So, it is a 2-step process. So, to determine sodium in your sample of cement paste, you first need to extract the sodium from the cement paste. How do you do that? Typically, sodium is presented in the pore solution. So, to extract that, you might have to just compress the paste and extract the pore solution out of it. Because you will get only a small quantity, you can then dilute it with more and more water and prepare a larger solution and then sending this into the gaseous phase becomes much easy. You do not have to heat it up to very high degrees to send the sodium ions into a gaseous phase.

So, detector basically, the main purpose of monochromator is to isolate the absorption line from the background light due to interferences because we want to only isolate the incoming radiation. We know exactly the wavelength of that and we want to only isolate that, so that we can attribute it to absorption by the specific species. And again photomultipliers are used to ensure that we are able to amplify the intensity of the outgoing radiation sufficiently, so that we can show that as a result.

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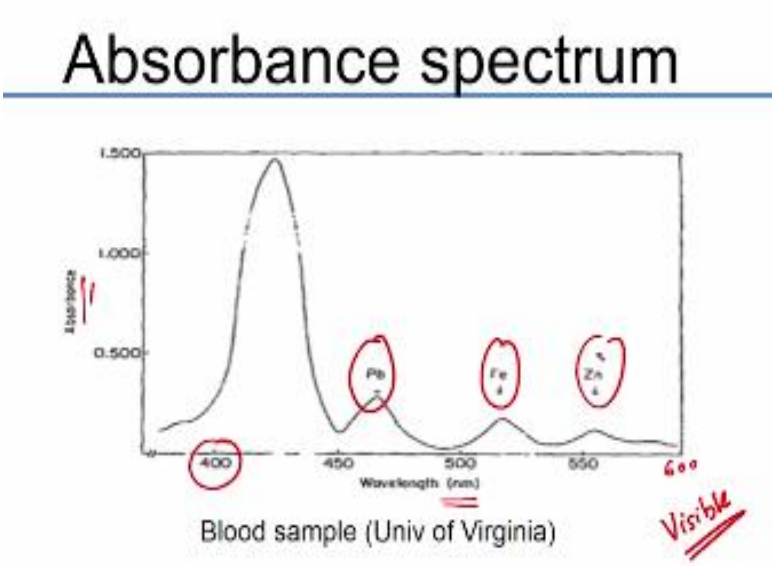

So, this is a typical absorbance spectrum. So, here absorbance is given in some arbitrary units from 0 to 1.5 and this is a sample of blood, which has been taken from University of Virginia, and you see here that the wavelength is plotted on the X-axis. Again see the wavelengths 400 to about 600 nm, which is in the range of visible light, which is typically 400 to 700 nm. In that wavelength, you are able to identify the presence of lead, iron, and zinc in the blood. So, obviously this may have been an investigation into the lead poisoning and lead is being found. Iron will definitely be found in your blood (in haemoglobin essentially).

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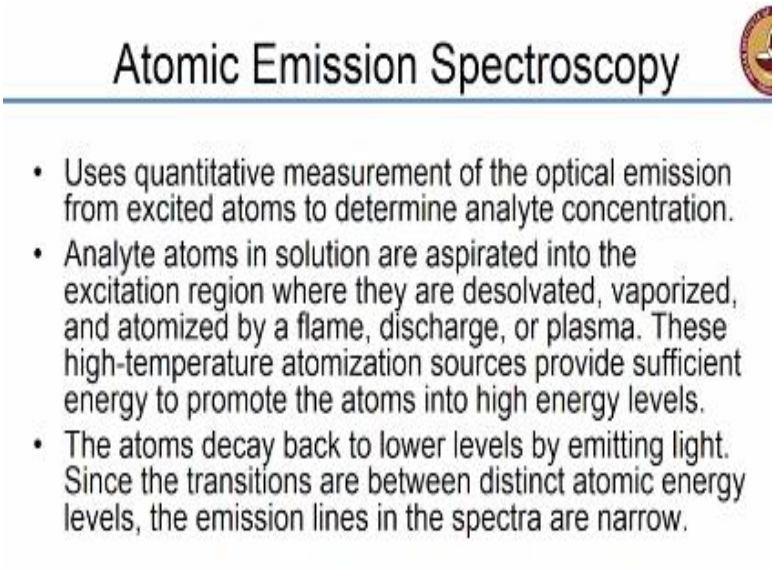

So atomic emission is utilizing the same sort of an apparatus as the atomic absorption spectroscopy, but in this case, you do not need the incoming radiation. You do not need incoming radiation in this case; there is no need for hollow cathode lamp. You only need to

desolvate, vaporize the atoms inside the liquid, and then because of the vaporization providing that energy to send it to a higher energy level, the difference in the higher and ground state energies will now be released, will be emitted and that is what is being captured.

So essentially, we are talking about a system that has nothing but an excitation source and a wavelength selector to isolate the wavelengths that are coming out from the sample. So, for example, if you are trying to analyze for sodium, your wavelength selector will only select the radiation that corresponds to sodium.

So, this is emission spectroscopy and one of the common ways to actually look at emission spectroscopy is your firecrackers. In firecrackers, we produce a lot of different colors, and each color obviously is representative of a certain wavelength. And because of the elemental species that are present inside the firecrackers, you are able to emit different colors. When you are burning what are you doing? You are basically converting to gaseous phase, and that is actually able to emit wavelengths of a certain level and that creates the color in your firecrackers. What are the common ingredients in firecrackers? Potassium is there, also magnesium, the same kind of species that we actually want to observe inside cement also. So very often when you actually do the analysis of emission, you see very nice colors coming out when you have sodium, potassium or magnesium.

So again, the idea is just to look at the optical emission from excited atoms to determine the analyte concentration. So, this is without an incoming radiation, we just look at the outgoing radiation from the system. Now, because we are going to be desolvating and vaporizing with the furnace, we may want to actually produce a much higher level of energy from the furnace that is able to excite these atoms to the gaseous state without an influence of an incoming radiation. We do not have an incoming radiation here. We are directly sending it to an excited state. So, that means the efficiency of the burning system will be very high. So, again analyte atoms are aspirated into excitation region, while they are desolvated, vaporized and atomized by a flame, discharge, or mostly we use plasma, in this case, and that is the basis of your ICP - Inductively Coupled Plasma; that is able to generate very high temperatures of burning in the region. I will show you the different types of temperatures that you can actually generate. The high temperature atomization sources provide sufficient energy to promote the atoms into higher energy levels, without the absorption of other radiation, you are simply heating up your sample to a level that is high enough to promote the

electrons to higher energy levels, and when they come back to their ground state, they emit specific wavelengths of energy that can be detected using your wavelength selector.

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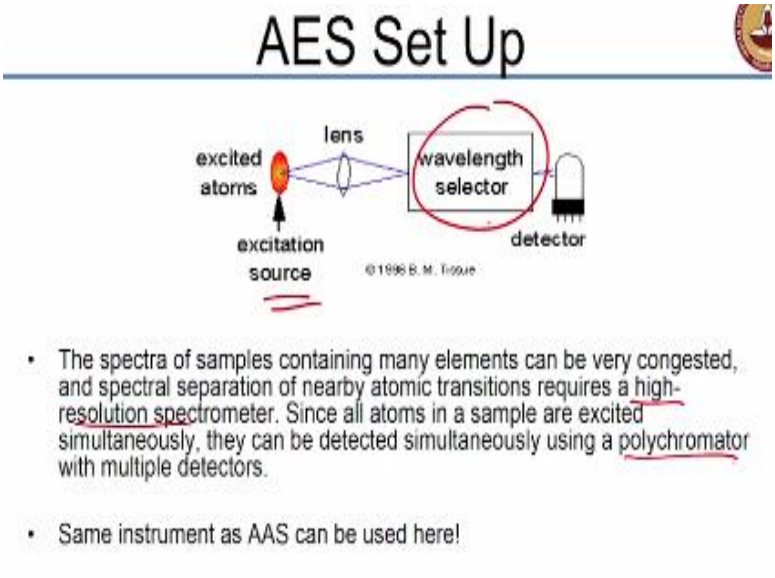

So, again, spectra contains many elements that can be very congested. What you need to do is the wavelength selector can be a high-resolution spectrometer which may be able to capture all the radiations that are getting generated and isolate the wavelengths from different elemental species. So, you can use a polychromator to detect all the elements simultaneously also, because in a sample of a cement paste or pore solution, you will have sodium, potassium as the primary species. You may have some calcium present in them also and all of these will generate some specific intensities or specific wavelengths of radiation, and if you want to detect all at once, then you need to have a specific polychromator, which is able to separate out different wavelengths at the same time.

So, as I said earlier, the same instrument as atomic absorption can be used here except that you need to increase the efficiency of the burning system. So, in the atomic absorption, we saw that the burning system was essentially a graphite furnace, but when you go to emission spectroscopy, you may need to provide better excitation sources.

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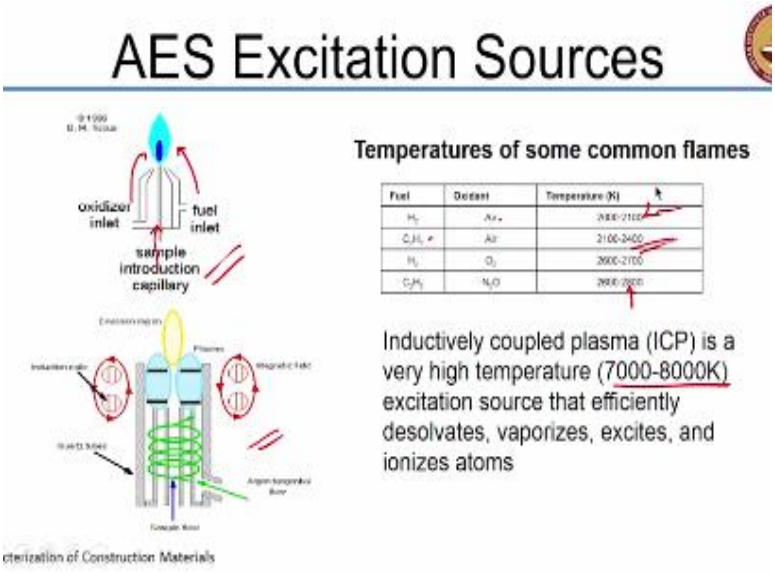

So, a typical flame for instance when you use hydrogen as a fuel and air as an oxidant produces a temperature of 2000 to 2100 K. You might have used in your chemistry and physics laboratories in high school in Bunsen burners where they use a combination of oxygen and acetylene for instance, or acetylene and air to produce temperatures of nearly 2400 K. But if you use inductively coupled plasma which works with the generation of this high energy emission from an applied magnetic field in that case, the temperature can be as high as 7000 to 8000 Kelvin. Inductively Coupled Plasma can have 7000 to 8000 Kelvin and that can be efficient for a wide range of solute atoms. All kinds of solute atoms can be actually vaporized at 7000 to 8000 Kelvin.

This is a typical layout of an excitation source (top-left figure). So you have a sample introduction capillary. The sample is aspirated in a liquid state up this capillary. You have an oxidizer and a fuel that combine to produce the flame at that temperature, and the sample can be burnt at that temperature to create a vaporization from ground state to gaseous state.

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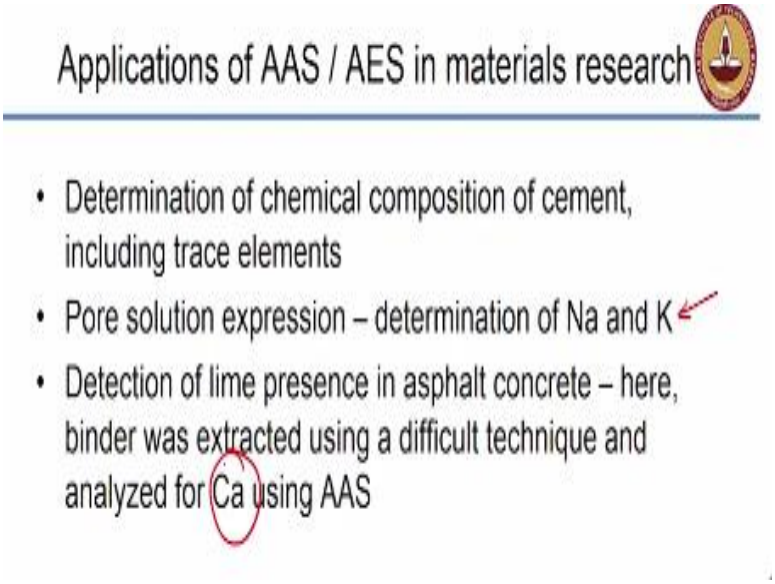

So, some examples are provided here, I will show you a more detailed example in the next lecture. Essentially, determination of chemical composition of cement including trace elements can be done using atomic absorption/emission spectroscopy. So, what I will show you in the next lecture is the determination of sodium (Na) and potassium (K) from pore solution expression. Essentially, we are creating a special device to squeeze out the cementitious pore solution from inside a hardened cement paste or concrete sample. By squeezing this out, we will then be able to analyze the extent of sodium and potassium that are actually present inside the pore solution.

And again, it can also be applied in certain cases to transportation materials like asphalt concrete. So here, extraction of the binder becomes very difficult from the asphalt concrete, but then you can analyze the calcium (Ca) in the binder that is your asphalt and isolate that using atomic absorption spectroscopy; it will tell you whether lime was used as a binder inside the asphalt concrete. Why is lime used inside asphalt concrete? To improve the bond between the asphalt and the aggregate, so lime helps in improving the bond between asphalt and aggregate. So that is where lime can be used as an additive inside asphalt concrete and you can actually detect the presence of lime and the concentration of lime by looking at the atomic absorption spectra from samples that are collected. But in that case producing the sample is quite difficult, it is not that easy.