Trace and ultra trace analysis of metals Using atomic absorption spectrometry Dr. J R Mudakavi Department of Chemical Engineering Indian Institute of Science, Bangalore

Lecture – 06 Interaction of EM radiation with matter I

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So the energy of the photons should not be confused with brightness or intensity of the source; for example, the people have a may have a feeling that the energy higher the energy lower is the brightness that is wrong notion, the energy has nothing to do with the brightness or intensity of the source, but you does it does relate to the color of the light yes to some extent it thus relate to the color of the light. The power of a light source is given by P is equal to number of photons and photon energy. So, if the number of photons are more if the photon energy is more than the power of a intensity of the light will light source will be high.

So, it is the energy of a beam of radiation that reaches a given area per second not the given point. So, intensity of a radiation what it is; is the power emanating per unit solid angle how much of the energy is coming out in a particular solid angle just like when you point a torch, if you point it very near the earth it will be a small spot, but if you rising and then open it into space it will describe a bigger arc. So, that is what we mean

here intensity of a source of ray is the power emanating from the unit solid angle that is how we can define it.

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Now, we come to having understood the properties of electromagnetic radiation we will consider how the transmission of radiation occurs. So, the radiation rate of propagation of electromagnetic radiation through a transparent medium such as atoms, ions, molecule particles etcetera should be less than that of vacuum, this is understood sort of in a rough way because if there is vacuum there nothing to stop the a corpus cell. A photon passing through a vacuum and then reaches reaching the other end, but if there are atoms and molecules and other things gases in between that space, then it will be interacting with them and proceeding at the at a lower pace.

So, the normal expectation is the rate of propagation of electromagnetic radiation through a transparent medium is less than that of the vacuum, but if it is not a transparent medium question does not arise because it will become it will look opaque; however, frequency change will not be observed which means that the permanent energy transfer to the medium does not occur. See if the earlier we have said frequency corresponds to any frequency corresponds to fixed amount of energy. So, if a radiation passes from one end to the other end (Refer Time: 03:44) and still having the same frequency it means the medium has not interacted with the photon. The permanent energy transferred to the medium does not occur at all therefore, the interaction involved must be only temporary.

So, how do we define that? It can be due to temporary deformation of the electronic cloud associated with atoms and molecules. So, this interaction occurs between 10 raised to minus 14 to 10 raised to minus 15 seconds, within that space of time span of time if you know what is a second right 10 raised to minus 14 seconds the whole interaction occurs and it is completely over.

So, the velocity of the radiation in the media is the wavelength dependent on the refractive index of the media. If the refractive index of the media is one there is apparently no change in the velocity. The variation of the refractive index with respect to wavelength that is known as dispersion; what are you saying now the variation of the refractive index of the medium with wavelength of the incoming radiation if it if there is a variation, then we say that the electromagnetic radiation is dispersed. So, this is how transmission of radiation occurs.

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Now, you can imagine that dispersion is not a simple phenomenon at all, dispersion curves usually show two reasons one is normal dispersion that results in the gradual increase in the refractive index with increasing frequency, and anomalous dispersion occurs at frequencies at which sharp changes occur. Coinciding with natural harmonic frequency of some part of a molecule or atom or an ion leading to an absorption of the photon or absorption of the radiation or absorption of the beam; in spectroscopy dispersion curves are important for optical components such as lenses; why? Lenses should show minimum dispersion and, but uniform dispersion.

Most suitable components for the manufacture of lenses are those in which refractive index should be high and constant if the refractive index is high; that means, a thinner material would suffice for the job. If the refractive index is low the I need a thicker this thing you can imagine in a when an old an older person will require a thick glass, a younger person if at all if he reads a glass specs is he requires a very thin number because thin glass because the number would be small. So, similarly if the dispersion is uniform and dispersion is very high then their components of a spectroscopic instrument would become thinner that is the beauty.

So, we look for materials which are having a high refractive index. So, most suitable components for the manufacture of the lenses whose refractive index is high and it should be constant also, this results in reduced chromatic aberrations. What is the chromatic aberration? Near the edge of the lens or something like that there will be the image transmission will not be proper. So, it may be either elongated or short end or something like that you would have seen in a number of a day to day examples where the you go and look at any curved mirror near the edge the image is always distorted. So, for the regular spectroscopic components, we need materials which are having high refractive index because the image of the substance should not be disturbed.

Now, the fabrication of prisms therefore, refractive index should be large that also highly frequency dependent. So, prisms lenses mirrors these are all parts of our spectroscopic instruments. So, that is why I am teaching you all about the optical components now with the interaction between the electromagnetic radiation. So, initially we have described what is known as electromagnetic radiation, how we characterize it, now we are coming to properties of the electrical magnetic components interaction with different material.

Now, we are talking about air and that is transmission through the refractive index. Air has got refractive index similarly if I allow a radiation to pass through water, then water is also having refractive index like that we are talking about this thing. So, if I want to transfer electromagnetic radiation through a prism, then without I can chose the particular frequency because their refractive index of a prism is a function of the material.

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So, now we talk about reflection. So, reflection of a radiation or it means we are familiar with the whole phenomena; mirrors reflect the radiation, falling on them without any loss of the incident radiation power. So, that means, if you stand in front of a mirror you will see the reflection, then the reflection should be as true as possible otherwise you yourself will feel am I really like this.

So, without any loss of the incident power if the mirror works, then you will get a very high quality image hence they are used as optical components of a spectrum of a spectrometer. Concave mirrors reflect the radiation as well as concentrate the reflection reflected radiation at its focal point. If you pass the radiation through a concave mirror all the image all the radiations will focus on a particular point and at that point the image will be perfect and short and sharp etcetera.

So, when radiation crosses an interface between the media resulting in a refractive index of some amount of reflection always occurs. So, for a beam entering an interface at right angles if I have a (Refer Time: 11:34) like this a radiation entering at right angle straight away perpendicularly, the reflection the right angles the fraction reflected is given by I r by I 0 is equal to n 2 minus n 1 whole square divided by n 2 plus n 1 whole square this is all high school physics I am not teaching you anything brand new, but all these you would have studied in your high school, but I am just refreshing your knowledge with respect to reflection refraction radiation etcetera, because it is later on when we study

above study the instrumentation I do not want to go into detail regarding the component optical component I will simply say that it is reflected it has got so many reflectors like that I can proceed.

So, in this expression I r by I 0 is equal to n 2 minus n 1 whole square divided by n 2 about plus n 1 whole square, the I 0 is the intensity of the incident beam, I r is the reflected incident intensity and n 1 and n 2 are the reflective refractive indices ok.



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So, this is how a refraction phenomena occurs; you can see the this is a glass and then this is perpendicular to the glass. If I allow the light ray to pass through this it will not proceed in the same direction, but it changes direction depending upon the refractive index of the glass. And then when it change the when it gets out of the glass again the reflective index will change, and it will be joining the same direction, but not the same point in the space.

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So, when radiation passes at an angle through the interface between the two media having different densities an abrupt change in the direction occurs this is called refraction. But owing to the changes in the velocity of the radiation in the two media, the extent of refraction is given by Snell's law what does it say? Sin theta one bar sin theta two is equal to n 2 by n 1 in that should be equal to velocity of the radiation in a medium 2 and that to the ratio of velocity in the medium 1. So, in vacuum we generally consider it as having 0 the velocity. So and n 1 is unity, so n 2 vacuum is given by sin theta 1 vacuum divided by sin theta 2.

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SCATTERING OF RADIATION Momentary absorption of radiant energy by atoms, ions, or molecules followed by reemission of the radiation in all directions is known as scattering. Particles having comparable dimensions to that of the incident radiation

all directions is known as scattering. Particles having comparable dimensions to that of the incident radiation removes most of the reemitted radiation by destructive interference except those traveling in the original direction. A very small fraction of the radiation is transmitted at all angles from the original path & its intensity increases with particle size.

Scattering by molecules or aggregates having smaller dimensions than the incident radiation is called Rayleigh scattering.

So, refractive index of various materials are measured with air as reference, not vacuum which are available in data bases if you look at google if you hit google and find our refractive index you hit Google refractive index of material, you will see so many refractive index of water and then air, liquid vacuum, acetone, benzene like that and all such data are useful at some particular point of time during the construction of the electromagnetic radiation. So, similarly we can talk of scattering of radiation. So, what is scattering? Scattering is momentary absorption of radiant energy by atoms ions or molecules, followed by reemission of the radiation in all direction; that means, if I have a particle here radiation comes and hits, and then the radiation will be dispersing in all directions that is scattering.

Now, you would have seen a number of examples like this, that if you put a glass of glass ball in front of a on a table and allow radiation to come and hit all the area around it is eliminated. Such things you would have seen number of times in all your day to day in your day to day life, and even water can act as a point of scattering. Now the point is particles having comparable dimensions to that of incident radiation; removes most of their radiation by destructive interference, what happens is if the radiations are the are moving everywhere some of them will interact constructively increasing the light, some of them will destroy each other because the frequencies are not matching. So, this is again a high school of physics experiments you would have done.

But what is important is a very small amount of fraction of the radiation is transmitted at all angles from the original path and which intensity decreases with particle size, if the particle size is smaller intensity decreases in increases. So, scattering by molecules are aggregates having smaller dimensions than the incident radiation is called Rayleigh scattering. That means, scattering by molecules or aggregates having smaller dimension than the incident radiation; that means, incident radiation must be reacting with atoms and molecules and electrons and things like that, then it is called Rayleigh scattering larger molecules scatter radiations in different quantities in different directions this is called as Mie scattering.

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So, the two types of scattering, one is Rayleigh scattering another is Mie scattering. And when the scattered radiation is quantized like those occurring in vibrational energy level transitions in molecules, as a consequence of polarization process then it is called Raman scattering. We are not going to study any of these scattering phenomena in our atomic absorption spectrometer course, but it is a part of the optics of the instrument that is why I am describing you some of these experiments.

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So, now we should also know about polarization of radiation. An ordinary beam of light consists of electromagnetic (Refer Time: 18:25) this I have already told you a number of times and then it consists of a bundle of electromagnetic radiations in which vibrations are equally distributed among a huge number of planes centered along the path of the beam, this is the general picture of how an electromagnetic radiation moves.

Now, we would end on that is if you stand at the end at on one end and see an electromagnetic radiation proceeding towards you, it looks like an infinite set of electric vectors fluctuating from 0 to maximum amplitude A.



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I have shown here, here you are I assume that you are standing here on this point you are seeing a radiation coming here this side you can see that number of vectors are pushing towards you, if you are stand this side. If you stand this side you with of course, with a different phenomena, but what I am saying is the vector in any one plane say x y can be resolved into two mutually perpendicular components though we have already said that also, because we have said the particles will move from it has got two components perpendicular and horizontal. So, removal of one of the two resolved planes that is one either horizontal part or the vertical part, it produces a plane polarized beam this occupies a single plane.

So, radio waves emanating from an antenna and micro wave produced by klystron tube are plane polarized this is for your information. What is a plane the cause with another part is removed. So, radio waves how do we remove that. We put an absorber so it will absorb only the vertical component or the horizontal component. So, example is radio waves coming from an antenna and micro waves produced by klystron tube are plane polarized. So, polarized ultra violet and visible radiation is normally produced by passing the electromagnetic beam through a media that selectively absorbs reflects or trans refracts that vibrates only in one plane, that is plane polarization.

So, you can imagine now here this is this part is incident beam, it has contain it has all components, but in space all the components are in space and they are scattered everywhere. Now I put a polarizer and this polarizer is nothing, but a small piece of mica or something like that transparent mica what it does, it removes all other parts components of the electromagnetic radiation, but allows only one direction. Single direction vertically this is known as vertically polarized light wave. So, here I can put one more and remove what is there at the bottom also, and then I can have one more this thing.

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So, now this part which I have explained to you just now is useful in the atomic absorption instrumentation which we will describe and as the Zeeman effect atomic absorption spectrometer. Shall I stop here or continue another 5-10 minutes Avinash.

Student: (Refer Time: 22:13) one hour over sir.

Over shall I stop?

Student: (Refer Time: 22:17) 5 minutes sir.

Huh?

Student: You can continue for 5-10 minutes sir.

5-10 minutes ok.

Student: Sir.

Right, I will continue.

Student: Sir you can continue.

Yeah. So, in continuing our discussion what you will you are going to do now is describe an electromagnetic radiation with respect to dispersion and dispersion as I have told you earlier it is a complex phenomena, dispersions occur usually in the they show two reasons one is normal dispersion in which there is a gradual increase of refractive index with increasing frequency, and there is another part that is known as anomalous dispersion that occurs coinciding with natural harmonic frequency of some part of a molecule or atom or a ion leading to the absorption of the beam. So, the dispersion can be of two types one where there is no a change, and one the when another part is part of the this radiation is absorbed; that means, the intensity of the light coming out of after dispersion would be lower than what is there in the intensity of the light differ.

So, in spectroscopy especially dispersion curves are impact on for optical components again such as lenses. Most suitable components for the manufacture of lenses are those in which refractive index should be high and constant. So, there is always a search for good refractive index materials in spectroscopy, they could be called glass or cards or something like that and the refractive index can be changed by preparing glasses with different kinds of compositions of the silica component, and then a layered that gives still clear glasses. Most suitable components are those in which refractive index should be high and constant, these results in again in reduced chromatic aberrations. For the fabrication of prisms what we need is a refractive index should be large, but also should

be highly frequency dependent. If the frequency dependency is high on the refractive index then it is a better material for spectroscopic components.



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Now, I am trying to show you here what is known as normal dispersion, another is anomalous dispersion. Normal dispersion this is this part is known as normal dispersion because we know that these this these are the frequencies on the x axis, 10 raised to 13, 10 raised to 14 and 10 raised to 15, this is in infrared, this is in again in infrared, this is in visible this is in ultraviolet, and here you can see the refractive index is high here and it is very uniform here and then here in this range it is not at all uniform.

So, the anomalous part is between this range area and normal dispersion is in this area very uniform.

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So, the diffraction of radiation; so, this is also another important aspect of radiation usually diffraction refers to the bending of a parallel beam of electromagnetic radiation as it passes through a sharp barrier or a narrow opening. It is just like prism you send the radiation through a prism it starts bending, and it is the consequence of interference because diffraction which can be easily demonstrated in the laboratory. So, all these things we know in a high school physics and college physics, but lot of experiments have been done and you also would have done if you have passed a intermediate science with physics as one of the subjects; even in high school level they try to teach you all these things but here we are only trying to refresh ourselves.

So, when a parallel beam of light is allowed to pass through a pin hole, two closely spaced pin holes are seen on a screen placed across it. This is a very standard phenomena you can do the experiment even at home. So, if the radiation is monochromatic; that means, if the we use a radiation containing only one wavelength that is monochromatic, its one wave single wavelength light is known as monochromatic light.

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So, if the radiation is monochromatic radiation a series of dark and light energies appear perpendicular to the plane of radiation; very common example is like this, what you do is you take a this is not there you take a plain paper and make a pin hole and in allow the radiation to pass through and put a paper on the other side ok.

So, this is how this whole experiment has been done you can see the picture now. Now in this picture the light radiation is coming out like from this end and then there is a small hole here, and you can see a range of dark and white patches all along the radiation, but you can also see that the light is proceeding from like this, again light is proceeding coming from this side it enters the pin hole and then proceeds like this describes a bigger and bigger angle. So, the angle here is very small and the angle here is bigger that is the range area is bigger. So, this is the phenomenon of refraction diffraction and this occurs because of the constructive and destructive interferences of the light that is emanating from the same pin hole.

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So, in the above figure this figure you can see that if you draw a picture of the geometric picture you will see that I do not know whether I have put it or not I will try to show you in the next class; what it is the two beams are in phase at the end it is necessary that they should correspond to the wavelength of the region, and two beams which are not in consonants they destruct themselves and shows zero or dark patch. Now the white patch is also seen at different wavelengths two lambda 3 lambda etcetera. So, we can arrive at an expression known as n lambda is equal to BC sin theta, where n is a number called as the order of interference.

So, we will continue our class in the next class we will continue our discussion about this in the next class, and then we will proceed to determine the other components of the optics of the spectrophotometer or a spectrometer for that matter.

Thank you very much.