Atomic and Molecular Absorption Spectrometry for Pollution Monitoring

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Lecture – 19
Quantitative analysis – III

We continue our discussion on the composition of the complex ions last. Yesterday I had explained to a little bit essentially I was telling you that there is method of continuous variation mole ratio method and slope ratio method.

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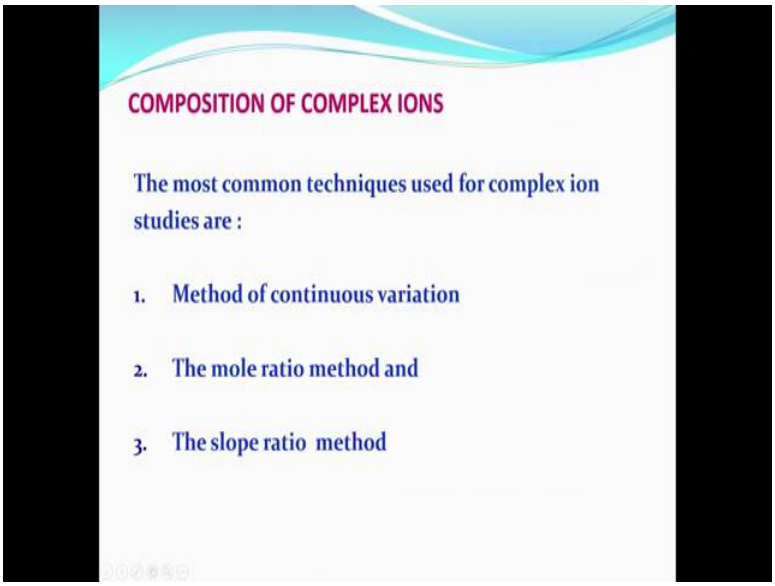

So, in the method of continuous variation, I had explain to you that we get a curve something similar to what we had seen earlier this figure.

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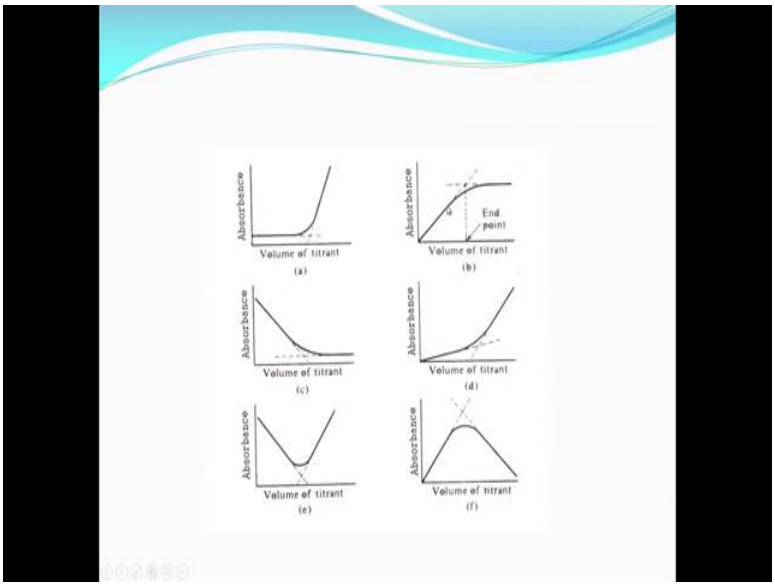

We end up with a figure something like this, you take known more molar concentration of the metal ion and then keep on adding the reagent in the same molar concentration and wherever you get infraction point that would be the composition of the complex.

So, if you get one more if you start with one molar substance, and you have the inflection point at one molar volume of the titrant then it is one is to one complex. So, if it is one is to two complex, the inflection point would shift to 0.66 or something like that. So, depending upon the mole ratio you will get the composition of the complex.

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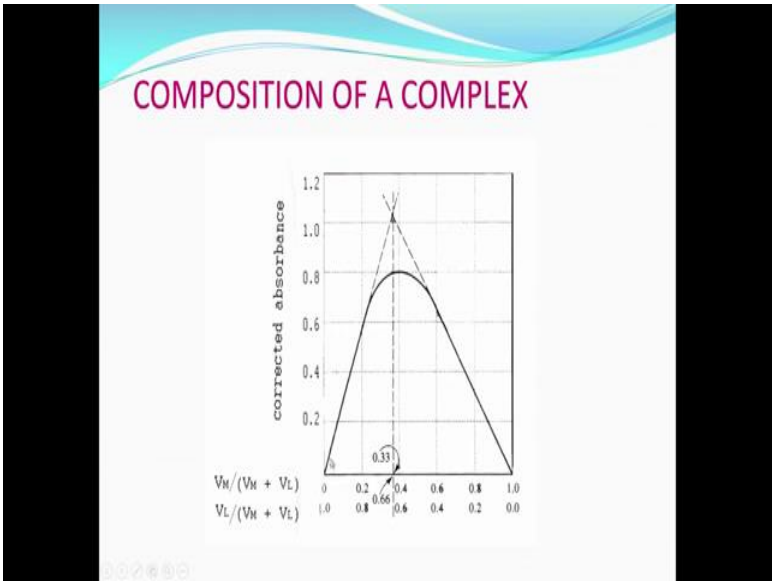

Now, the other methods are the mole ratio method, here what I do is I take the reagent 100 percent and metal 0 percent. So, here V m is 0 percent and V n by V l I compute and I keep on increasing from 0.2, 0.4, 0.6, 0.8, and 0.1 since it is a ratio maximum is one only. So, if I take 100 percent of the reagent vl, Vl refers to ligand if I take 100 percent of the ligand there is no metal and no complex formation; as it I increase this to 2 percent and V l is 8 percent 80 percent where mole ratio what I get is 0.2. So, I get some amount of complex will be formed.

But unless it is optimum I will not get a inflection point. So, I keep on increasing 0.2, 0.4, 0.6, 0.8, 1 0 similarly I can do for the ligand there when V n is 0, Vl would be one and when V m is 0.2 this would be V 8 something like that. So, if I plot the absorbance versus the mole ratio at the inflection point I calculate where is this. So, suppose my Vm is 0.33 it automatically fixes the Vl concentration to 0.66; that means, it is 1 is to 2 ratio suppose it is 0.5 the infection would be somewhere here one is to one complex at 0.5, and then similarly if it is 1, 2, 3 you can calculate where the inflection point would be coming and we can always determine using this method this is a very well known method and this my you again complex jobs ratio method is a very well known and full proof method.

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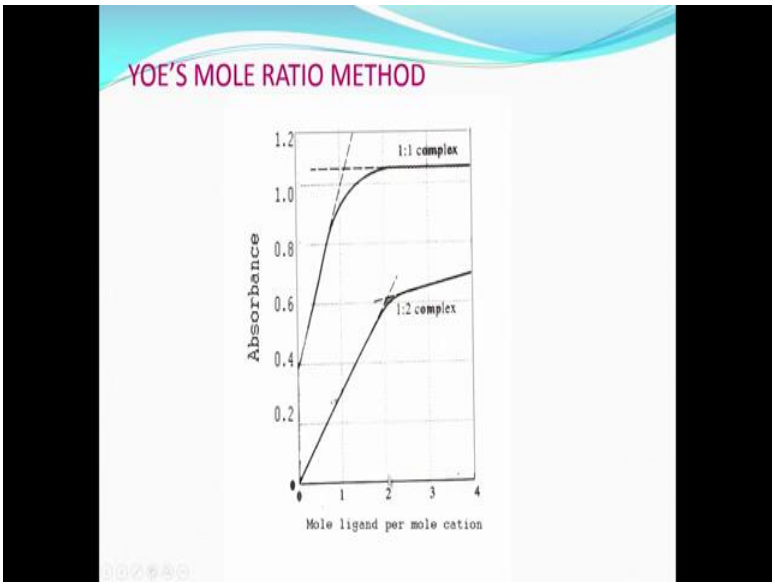

Then there is another this is essentially the same thing what I have told you more continuous mole ratio method, here moles per ligand per cation. So, 1 is to 1 if I have

any inflection point, the and here it would be 1 is to 2 if the inflection point occur somewhere here then it would be 1, 2, 3 something like that you can have le ligands combining up to 1 is to 6 ratio also octahedral complexes.

So, this is a very simple straight forward method and the slope ratio method I will not explain to you it is given in regular text books, what I would like to do it I will give you an assignment based on the slope how to determine these slope composition of a complex using the slope ratio method, which I had indicated here. This I will not be explaining to you, but it will be some sort of an assignment for you.

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So, another application we move on to another application of the spectrophotometry; nowadays since 1980s I want take the to explain to you this now a days since 1980s there are continuous requirements of measurements of the pollutants and things like that and whenever an industry is letting out an effluent, then it is necessary required that effluent be monitored continuously not regularly, not at regular intervals. So, if it is a continue there are there is a there has been a tremendous demand for continuous monitoring methods, even in India since last one year a central pollution control board has mandated at almost all the industries must monitor the effluent screen on a continuous basis, and this could be electrochemical method or it could be spectrophotometric method or it could be any other method suitable for a particular pollutant.

But whenever metal ions are involved and b o d and c o d and several other pollutants are involved, it is important that a spectrophotometric method provides you a very cost effective method even for continuous analysis. So, this is something a slight modification of a spectrophotometer what you will be doing is you will be creating a manifold.

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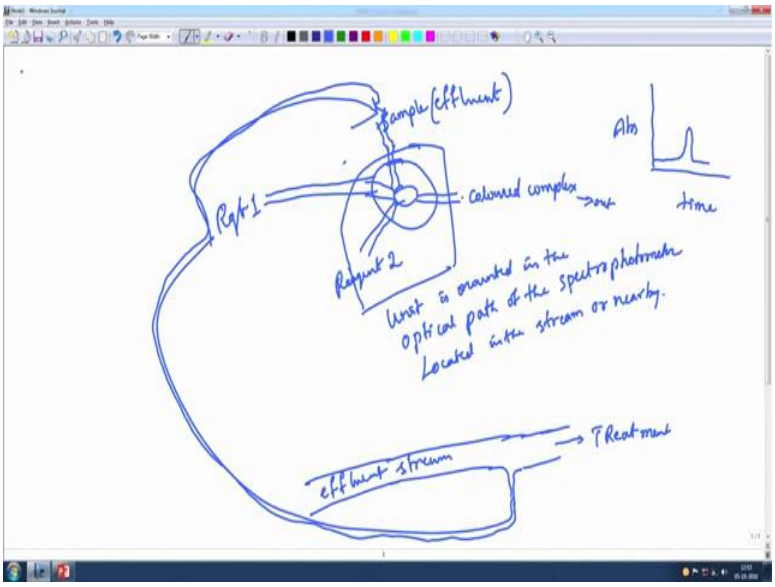

The I run a continuous stream of a reagent, and then I create a manifold and here the sample will be coming, here I can add a reagent this is reagent this is the sample or the reagent I have already here, sample that is the effluent, and here I can add reagent I can say reagent 1 and reagent 2, this could be an organic reagent this could be a buffer and all these things will mix and then I have a continuous stream flowing out this is the coloured complex; this whole unit, this unit is mounted in the optical path, path of the spectrophotometer located in the stream or nearby.

Normally, what people do is if I have an effluent stream, this will be going for treatment and I take a small sample out of this and then connect it to the sample here connecting to here. So, this is a type of arrangement we normally look for in a spectrophotometer whenever you want to do the sample analysis. Generally what happens is you can even take a small sample from a syringe and then inject it here injected in the manifold.

So, the or you can take injected through this sample or this port reagent, reagent 1 and reagent 2will be flowing continuously and the sample can be injected and measured whenever there is no reagent they are they still be acting as a reference solution and

whenever there is a reagent there will be given a certain amount of time the you will be getting a coloured complex. So, in a continuous flow injection analysis in a continuous analysis, the curve of absorbance versus time would show a reference and then complex will form and then as it is fed out of the system, this is out as it is sucked out of the system the colour will come down and then it will again reach the reference level.

So, this is known as flow injection analysis, this flow injection analysis abbreviated as FIA there are several spectophotometric manufacturers who will give you a manifold made of Teflon and other things, which will give you accessability for flow injection analysis. So, basically what it involves is the that the measured amount of small amount of liquid is moved into a non segmented stream of the reagent, and has the injected sample and reagent career proceeds down the narrow tube into the manifold.

The reagents are pumped and the normal coloured complex formation takes place, but display takes place under dynamic flow conditions; that means, it passes through a flow cell attached to the spectrophotometer continuously. So, the sharp signal develops followed by a trailing edge, that just like what I showed you earlier.

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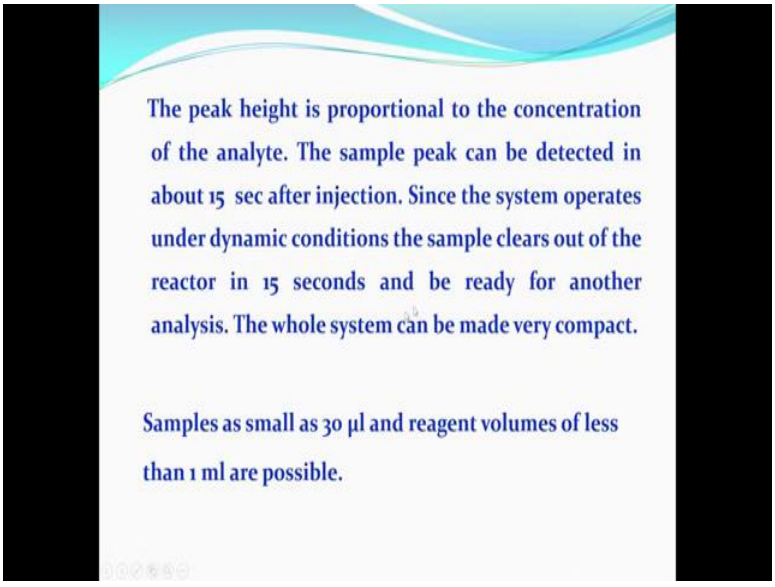

The peak height in this case the peak height is proportional to the concentration of the analyte, the sample peak can be detected in about 15 seconds after the injection, and this much of time delay you can always give whenever you are operating a machine in flow injection mode.

Since the system operation under dynamic condition, the sample clears out of the reactor in about 15 seconds and be ready for another injection. So, the whole system can be made very compact and samples as small as 30 micro liter of the sample and reagent volumes of less than 1 ml; normally in a are possible to use, normally in a spectrophotometer we expect the sample to be of minimum size of a about 5 ml for normal 1 centimeter cells and of course, smaller volumes if the path length is less and higher volumes if the path length is more. But in a FIA we handles samples as small as 30 micro liters and total reagent volume itself would be approximately 1 ml.

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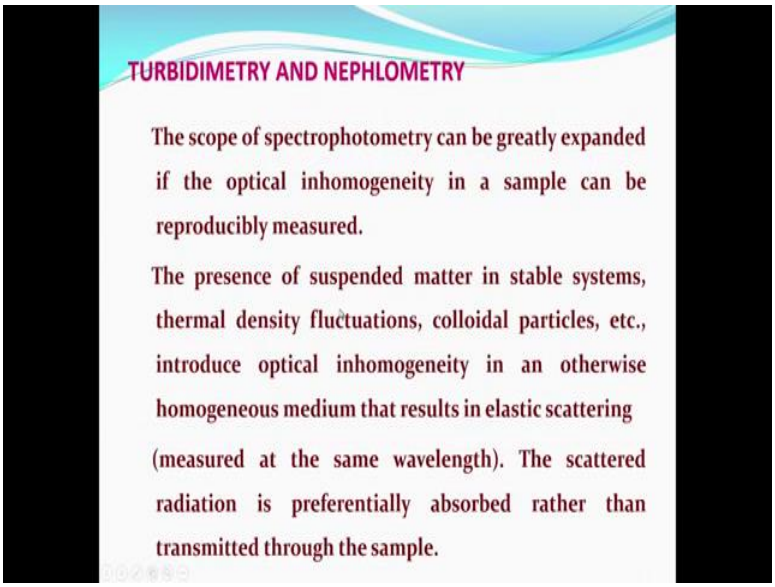

So, we move on to another application of spectrophotometer, this is known as Turbidimetry and Nephelometry. Basically spectrophotometer measures the colour. So, one of the pre conditions for a spectrophotometer measures for measurement for a spectrophotometric measurement is that the solution must be absolutely free from turbidence; in the initial stages when I was teaching you about the spectrophotometry I had written that the effect that the fate of the electromagnetic radiation is the sum of radiation absorbed, some of it is transmitted, some of it is scattered, some of it is reflected, some of it is refracted like that and it is not be I had not written Turbidimeter turbidmetric solutions.

But, basically a turbid solution means it is interference or the sample is in the form of a precipitate. Now beer lamberts law does not apply to turbid solutions; now you will

come across real life situations where turbidity is part and parcel of our life for example, the precipitation of barium sulfate and silver chloride, all these substance substances precipitate whenever there is chloride insulation. So, they can precipitation titration reactions be made part of spectrophotometric arsenal, the idea is if I can make the precipitate in a reproducible manner and make it stable, all other variables being constant if the precipitate is having a specific colour, then I should be able to determine the precipitate, the sample in the form of a precipitate itself or as a turbid solution itself provided I do not have any other variables; even though this is a violation of beer lamberts law empirically I can make it work like this.

So, the conditions for such a precipitation reaction would be that the precipitate should be in the form of a very fine powder, it should not be colloidal of course, because collides do not settle, but precipitates do settle that is the main difference between the colloids and precipitation. And some time for colloids also we have the same title is given Nephelometry and we will come to that in a minute. So, the basic idea is to have a very small concentration of the precipitate in the form of a suspension the so that the suspension does not settle down, it should not if it settles down your absorbance value will be wrong.

So, it may be scattered or it may not be scattered it may be just transmitted etcetera, but still if the precipitate is held in solution without much movement then I can get an empirical correlation of the absorbance versus concentration. So, if such a thing is possible then I can go ahead with the determination of the analyte in the form of a precipitate itself. So, this opens up a large number of chemical reactions which can be made amenable to spectrophotometric determination.

So, the scope of spectrophotometry can be greatly enhanced, expanded if the optical in homogeneity in a sample can be reproducibly measured. So, the basic idea is the presence of suspended matter in stable systems and thermal density fluctuations; temperature is a big parameter in this and colloidal particles all these things introduce optical homogeneity, in homogeneity in an otherwise homogeneous medium that results in elastic inelastic scattering.

So, inelastic scattering means measured at the same wavelength, elastic scattering means measured by different wavelengths. So, the scattered radiation is preferably absorbed

rather than transmitted through the sample. So, in turbidimetry you can make the measurements as absorbance, but not as transmittance this is a major difference with respect to spectrophotometery. In spectophotometry we can either make me measurement either as absorbance or transmittance, where as in turbidimetry we will make the measurement preferably preferentially as absorbance.

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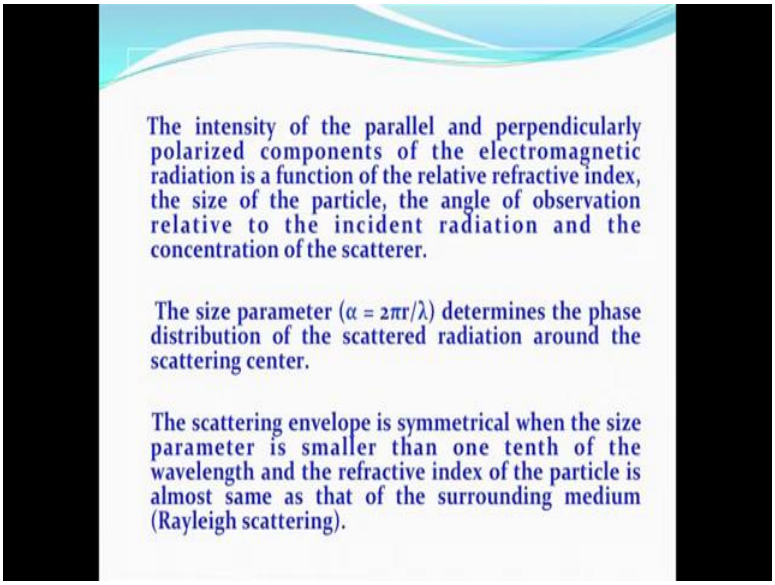

So, the intensity of the parallel and perpendicularly polarized components of the electromagnetic radiation is a function of the big is a basic function of the relative refractive index. This we have seen earlier, but it is also a function of the size of the particle, if we are measuring making any turbidimetry measurements. So, the angle of observation that is also important with respect to precipitates, because many of the precipitates are not in the form of spherical shape, they may be conical, they may be square they may be hexagonal and so many other types.

So, the angle of observation relative to the incident radiation is also an important factor, and the concentration of the scatterer that is the precipitate is also some sort of a factor for the linearity of the concentration. So, the basically the size parameter if we assume that the it is of a spherical shape, then I can say this alpha is equal to 2 pi r upon lambda this is size parameter determines the phase distribution of the scattered radiation. So, the scattering envelope is symmetrical when the size parameter is smaller than the smaller than one tenth of the wavelength. This is very important concept; that means, if the size

parameter is one tenth of the wavelength of my of the size, basically wavelength is also a type of a measurement of length.

So, if it is one tenth of that size and the refractive index of the particle is almost same as that of the surrounding medium that is Rayleigh scattering. So, we have a very nice measurement possible. As the size parameter reaches one fourth of the wavelength suppose the particles aggregate and then coagulate, then the particle size becomes bigger and bigger.

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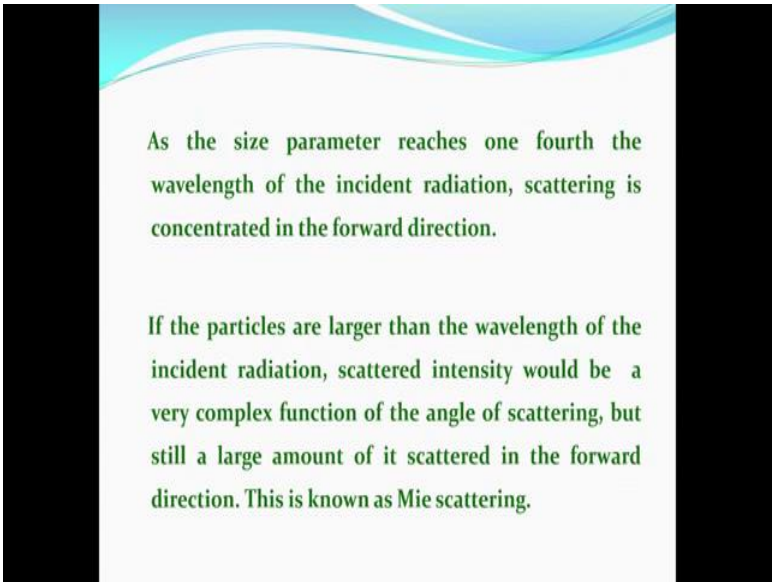

So, as the size parameter reaches approximately one fourth of the wavelength of the incident radiation, that is I choose the incident radiation using a monochromator know. So, the monochromator if I choose a particular wavelength I know what is the size of the radiation. So, the scattering is if it is reaches in about one forth then the scattering is concentrated only in the forward direction, this is very important because I am going to measure the turbidance only in the forward reaction that is a forward direction. So, it is not measured in all the directions, only along the direction of the electromagnetic radiation. So, if the particles are larger than the wavelength of the incident radiation scattering will be obviously, through in a in all directions and the scattering intensity would also be a very complex function of the angle of scattering.

But still a large amount of it is scattered in the forward direction only, still we can make the turbidimetric measurements even if the particles are larger; this is a very gratifying

factor because this opens up the determination of almost all types of particles precipitates, for spectrophotometric determination, this is known as Mie scattering. So, which scattering permits one to use the turbidimetry as a monitoring method provided the precipitates are coloured and scatter in the UV visible region.

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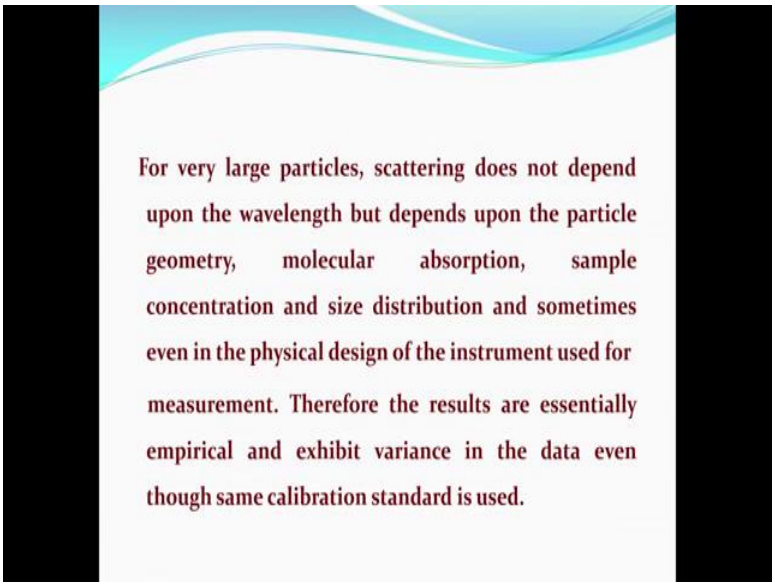

So, for very large particles suppose they really concentrate and do not move around; the scattering does not depend on the wavelength basically of course, it has no meaning for very large particles because they may block the radiation also.

So, scattering does not depend upon the wavelength, but depends upon the particle geometry. So, if it is round shaped square shaped etcetera cubicle then it also depends upon the molecular absorption and then sample concentration, the particle size distribution, because we know that from experience that most of the chemical reactions produce a precipitate very indeed size, they are not always of the same size. So, the size distribution also becomes very important in the most of the turbidimetric measurements.

And sometimes even in the physical design of the instrument used for measurement that is sample compartment physical design of the instrument means sample compartment, it is used for measurement, therefore the results are in any case 100 percent in and chemical turbidimetric methods they are always empirical. This we have to understand very clearly that it is not very easy to correlate the absorbance values to be a lamberts

law or any other non-laws, and they exhibit variance in the data even though the same calibration standard is used.

Suppose we use a precipitation standard may today and tomorrow you make the same so precipitation another one more reaction, make the same measurement again it will show you a different absorbance but within certain limits. So, this is the catch in all spectrophotometric reagents are using turbid matter Turbidimetry; because the results are essentially empirical, there is no guarantee that you may get the same absorbance every time.

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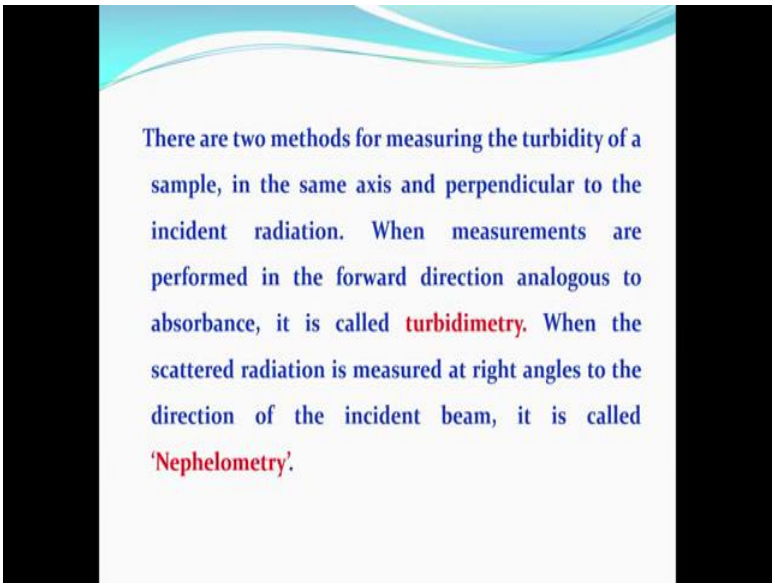

So, there are two methods for measuring the turbidity of a sample in the same axis, and also perpendicular to the incident radiation.

So, when measurements are may performed in the forward direction just like spectrophotometry, that is in the direction of electromagnetic radiation analogous to similar to absorbance it is called turbidimetry, but suppose I measure the absorbance at right angles to the direction of the incident beam it is called Nephelometry.