Atomic and Molecular Absorption Spectrometry for Pollution Monitoring

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Lecture – 20
Quantitative analysis – IV

So, there are 2 methods for the determination of absorbance in a turbidimetric methods, and as you can see, we can make the measurement in the same wavelength in the same direction of the electromagnetic radiation, after this is radiation passes through the sample then it is known as turbidimetry and when I make the measurement perpendicular to the electromagnetic radiation then it is known as nephelometry.

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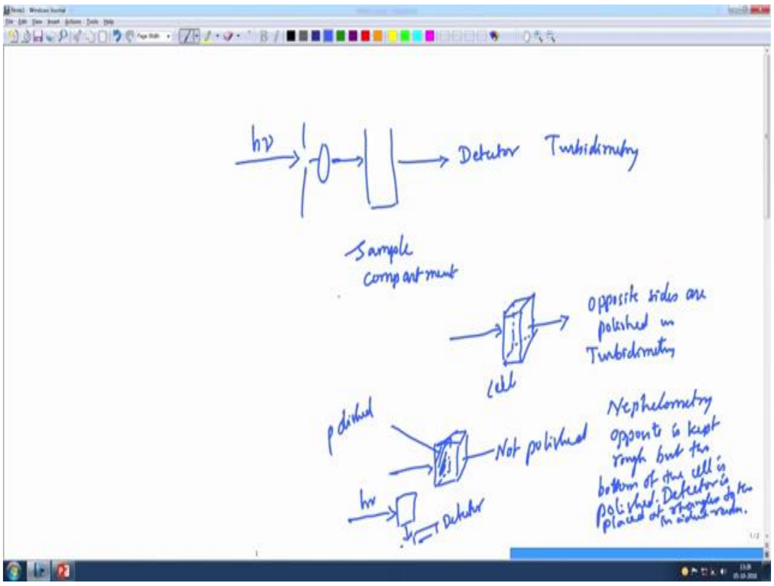

opposite sides are polished in Turbidimetry

Nephelometry opposite is kept rough but the bottom of the cell is polished. Detector is placed at right angles to the incident radiation.

I can show you a simple example. So, this is my incoming radiation corresponding to a particular frequency that is h nu, and then after all this (Refer Time: 01:23) etcetera and then other things I have the sample compartment here.

Then I have the detector. So, this is the basic schematic diagram of a spectophotometer. So, if I am measuring the radiation in the same direction that is along this direction then it is known is Turbidimetry. In Turbimetry generally what happens is the opposite sides of the side are polished the cell are polished this is cell, opposite sides are polished in turbidimetry, but in nephelometry one side of the opposite side is not polished only one side is polished.

So, if I have a cell like this incoming radiation this is polished and this side is not polished and this side is polished. So, in Nephelometry opposite side is kept rough, but the bottom side of the cell is polished. So, the radiation will enter like this go through the cell and then the detector displaced at right angles to the incident radiation, this is the major difference between the a two cells between turbidimetry and nephelometry.

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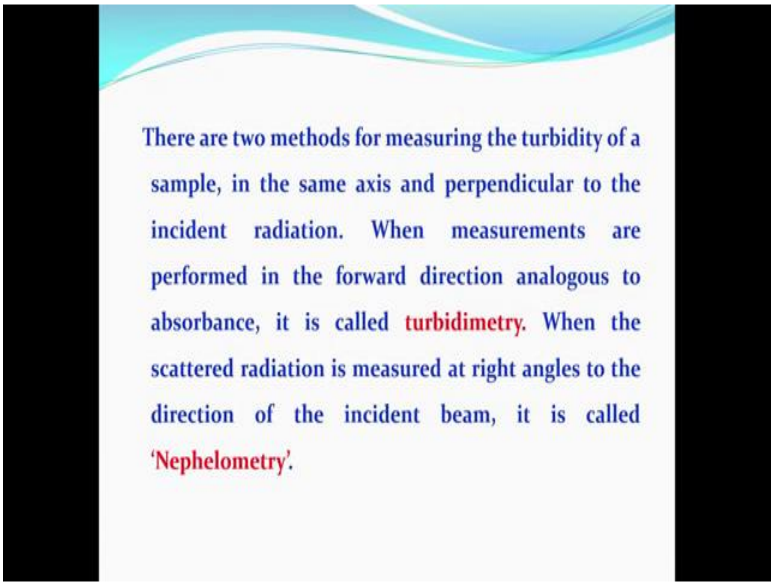

There are two methods for measuring the turbidity of a sample, in the same axis and perpendicular to the incident radiation. When measurements are performed in the forward direction analogous to absorbance, it is called turbidimetry. When the scattered radiation is measured at right angles to the direction of the incident beam, it is called 'Nephelometry'.

So, but otherwise there is not much difference except that the measurements are the optics and designed for nephelometry is slightly different from the turbidimetry only in this aspect it differs.

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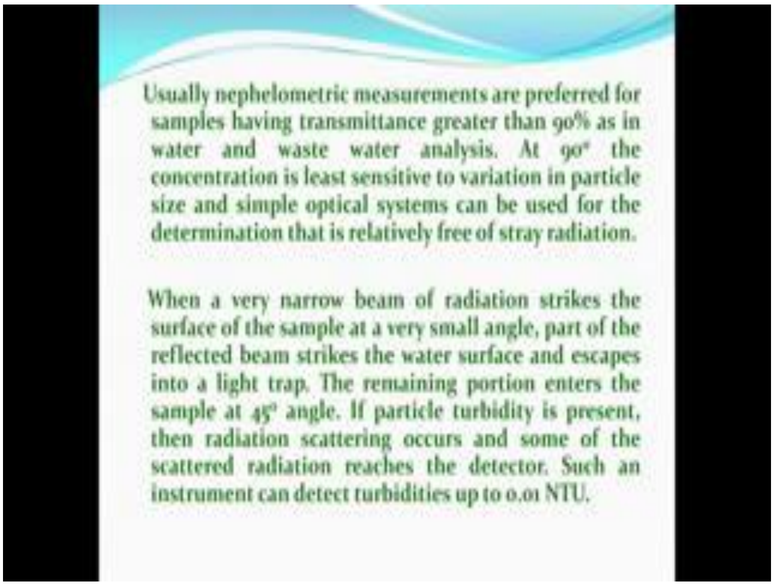

Usually nephelometric measurements are preferred for samples having transmittance greater than 90% as in water and waste water analysis. At 90° the concentration is least sensitive to variation in particle size and simple optical systems can be used for the determination that is relatively free of stray radiation.

When a very narrow beam of radiation strikes the surface of the sample at a very small angle, part of the reflected beam strikes the water surface and escapes into a light trap. The remaining portion enters the sample at 45° angle. If particle turbidity is present, then radiation scattering occurs and some of the scattered radiation reaches the detector. Such an instrument can detect turbidities up to 0.01 NTU.

So, usually nephelometric instruments are preferred for samples having transmittance greater than 90 percent; that means, for very low concentrations in water and waste water samples. So, at 90 degree 90 percent the concentration is least sensitive to variation in particle size. Because the concentration is so slow. So, low that be getting a linearity curve is not a big problem at all and then sometimes simple optical systems can be used for the determination that is relatively free of sterilization. For this reason a nephelometers are basically filter photometers, but with a slight design change, and turbidimeters can be ordinary spectrophotometers. So, in many times in spectrophotometery there is no model or a there is no accessory for turbidimetry, but there will be an accessory for nephelometry, on the other hand the for nephelometry there may be a dedicated instrument available whenever you need one.

So, normally spectrophotometric cells are also monitor, are also need to be useful for nephelometry. So, when a narrow beam of radiation strikes the surface of the sample at a every small angle paet of the reflected beams strikes the water surface and escapes into a light trap, the remaining portion enters the sample at 45 degrees and if any particle turbidity is there then radiation scattering occurs and some of the scattered radiation which is the detector.

So, the positioning of the detector is also very important in a turbidimetry, such an instrument as can detect turbidities up to 0.01 NTU. NTU is a unit turbidance emits nephelometric in turbidimetry turbidimetric unit known as 0.01, there are standards for water analysis where the turbidity is described defined in terms of turbidance emits entails, and platinum chloride is one of the standards used for calibrating the turbidence units.

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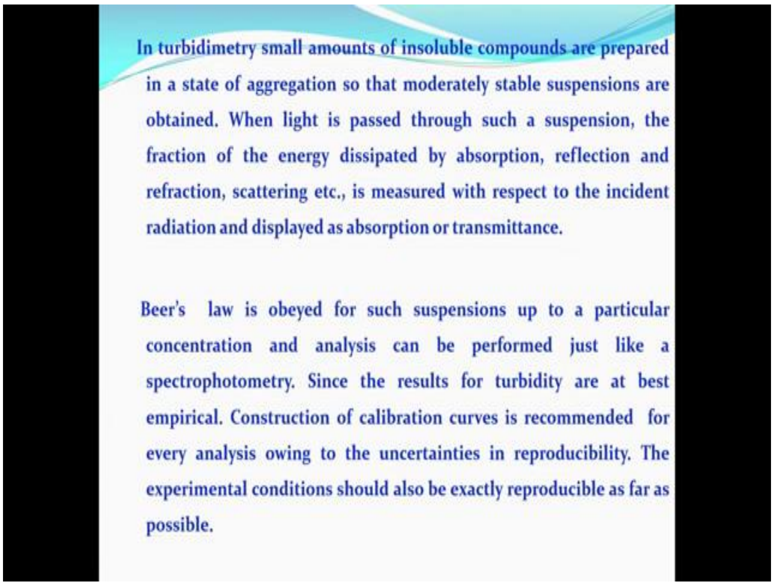

In turbidimetry small amounts of insoluble compounds are prepared in a state of aggregation so that moderately stable suspensions are obtained. When light is passed through such a suspension, the fraction of the energy dissipated by absorption, reflection and refraction, scattering etc., is measured with respect to the incident radiation and displayed as absorption or transmittance.

Beer's law is obeyed for such suspensions up to a particular concentration and analysis can be performed just like a spectrophotometry. Since the results for turbidity are at best empirical. Construction of calibration curves is recommended for every analysis owing to the uncertainties in reproducibility. The experimental conditions should also be exactly reproducible as far as possible.

So, in turbidimetry small amounts of insoluble compounds are prepared in a state of aggregation.

Now, we come to the chemistry of the method. So, what do we do whenever you want to make the measurements in turbidimetry all you have to do is continue doing a chemical reaction as if you using your standard flask chemical reaction reagents etcetera, for which we will come that again in a at a later stage and the we are prepared what you have to do is to prepare the reagent and standards and mix them in suitable prepositions and their optimum ph conditions etcetera, temperature conditions, ph conditions, shaking conditions etcetera and once you make the standards ready then you have to pass the light through such a suspension, and the fraction of energy dissipated by absorption reflection refraction scattering etcetera its measured with respect to the incident radiation, and displayed as the ratio of the p by naught or absorbance or transmittance.

Now, in percept suspension Beer Lambert’s law is obeyed up to a particular concentration, and analysis can be performed just like spectrophotometery. Since the results for turbidity are at best empirical as I have explain to a number of times whatever way you prepare the standards. Next day if you come and prepare unless the conditions are extremely critical and exactly same, we will not get the same absorbance therefore, the results for turbidity are at best empirical only so; that means, the error margin with respect to the concentration is fairly large with respect to compare as compared to spectrophotometery, and there is no sound theoretical basis to determine the absorbance theoretically; there is nothing like molar absorptivity or epsilon value and like that in spectrophotometry with respect to turbidimetric precipitation methods.

So, the construction of calibration curves is always recommended every time you want to do as turbidimetric determination, we recommend that you prepare your calibration curve on the same day same time. Whenever you want to make your measurement unknown measurement at the same time the standard should be prepared and standard should be mixed along with the sample under similar conditions, and that data will hold good only for that set of samples and an calibration standards as for as turbidimetry is concerned.

Next day again you come and do the calibration do the measurement and continue working with the say with the same solutions even if you prove the reagents are all same the absorbance will be different. So, we say we recommend strongly that every time you everyday every time you make a measurement check the calibration first, and adjust it accordingly for small experimental variations because you 99 percent of the time it is only a empirical correlation. So, the experimental conditions should also be exactly reproducible as for as possible.

So, what are these kinds or what are these absorbance conditions; for in turbidimetry we need to follow the conditions, something like concentration of substances participating in the reaction.

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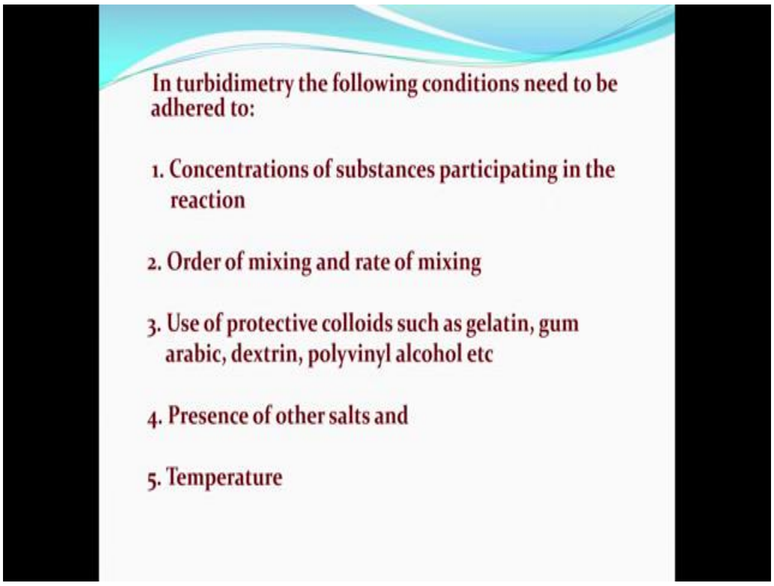

In turbidimetry the following conditions need to be adhered to:

1. Concentrations of substances participating in the reaction
2. Order of mixing and rate of mixing
3. Use of protective colloids such as gelatin, gum arabic, dextrin, polyvinyl alcohol etc
4. Presence of other salts and
5. Temperature

The standards must be prepared scriplesly and then substances other re agents also must be prepared very accurately. So, prefer there is no need to over emphasize that all the standards and reagents must be particle free, you know it should be of very high clarity standards there should not be any suspended particles and dissolved substances etcetera in the reagents that is number 1; number 2 is order of mixing and the rate of mixing.

Sometimes we take metals, then add buffer, then add reagent and if you do then a stabilizing agent to keep the small took particles in suspension. Now the order, order of mixing can change I can change it take the reagent first add a stabilizing reagent, and then add your metal add the buffer etcetera we can prepare the precipitate in a four factorial ways, but it is important in all turbidimetric methods that order of mixing should be exactly same, for the standard and for the sample sorry otherwise there will be variations in the recordings in the absorbance measurements. Then we need to use protective colloids such as gelatin, gum Arabic, dextrin polyvinyl alcohol etcetera these are all basically viscous solutions which will make the particles move slow as slower.

So, what happens if I take the substance if I take the substance in a bottle, and then I add a protective colloid to that sustain becomes viscous. So, the viscous solutions if I mix the then by gentle shaking something like this slowly something like this shake 1 2, 1 2 this way you can check or I can shake it like this or I can shake it like this you (Refer Time: 15:09) I mean put it in a machine to shake it like this then a different ways of shaking, and once you put the viscous solution and the shaking should be very uniform and very gentle that is very important.

So, the all these things are approximately in about 1 percent I had to use; gelatin, gum Arabic dextrin these all basically gums and high molecular weight substances. So, that is important for us and then there we also should be worried about the presence of other salts that is a basic concept of spectrophotometer that is matrix matching; what are the substances in your standards it should be there in the sample also, or whatever or other way around whatever is there sample matrix we should try to match it in the standards.

So, presence of others salts is important and also we need to determine the temperature at which we carry out the reaction; because we know that solubility of a precipitate is a temperature dependent function, as the temperature increases solubility will increase and if the solubility increases absorbance is going to be affected and so you will get lower absorbance. But if the solid temperature decreases solubility will decrease, and that there will be more particles, more scattering, more transmittance and you may get higher reading.

So, in all this case is these 5 parameters 1 has to look carefully with respect to making a standard measurement.

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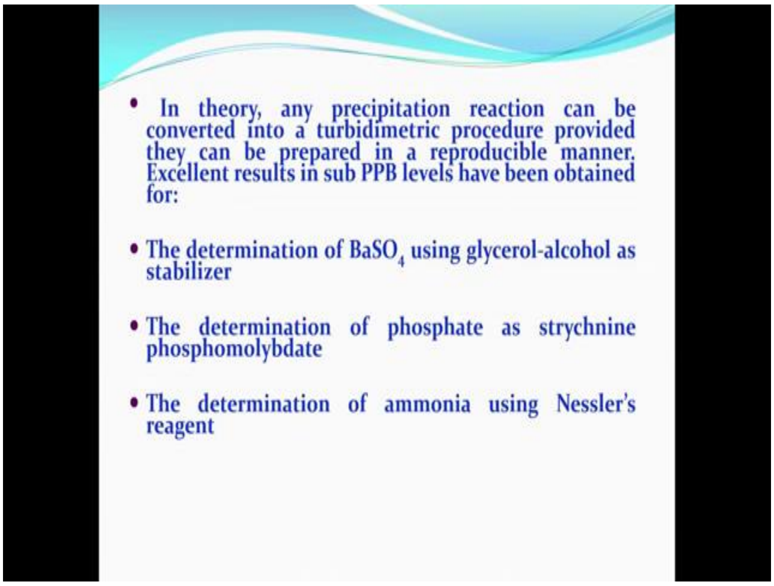

- In theory, any precipitation reaction can be converted into a turbidimetric procedure provided they can be prepared in a reproducible manner. Excellent results in sub PPB levels have been obtained for:
- The determination of $BaSO_4$ using glycerol-alcohol as stabilizer
- The determination of phosphate as strychnine phosphomolybdate
- The determination of ammonia using Nessler's reagent

In theory I can make any precipitation reaction amenable for spectrophotometric provided, they can be prepared in a reproducible manner and we know that there are several millions of chemical reactions including pharmaceuticals etcetera which are precipitation reactions. So, excellent results in sub parts per billion level, have been obtained for some of them I am listing below here that is determination of barium sulfate using glycerol, alcohol as a stabilizer.

Now you will be surprised that how many times we do the determination of sulfate in water, actually the presence of sulfate in drinking water is a subject of regulation and standards effluent standards. So, there is if the water is very hard drinking water is very hard, we suspect that calcium and magnesium sulphates are the cause and in drinking water it should not exceed more than 200 ppm. So, the sulfate 200 ppm means you cannot do the determination by titration and other things even though ADPA can help in such matters.

But this is an excellent example of how a simple and analyte that is sulfate ion can be determined using spectrophotometery. Now all you have to do is take sample containing barium sulfate, add a little buffer to adjust the ph, add barium chloride solution. So, you have barium sulfate and precipitate; to keep the precipitate in solution what you should be doing, you should add using glycerol alcohol you can add polyvinyl alcohol also and then several others other gums big streams etcetera can be added and this is one example where the gravimetric or a spectophotometric finished a gravimetric method can be easily adopted.

The advantages in such case is you can finish the spectrophotometric analysis in about one- tenth of the time that is required for gravimetric determination as barium sulfate, and also it is possible to reduce the time and accuracy will be much better. In our laboratory you have developed these methods and standardized and we have prepared a cookbook which will tell you what should be the absorbance approximate absorbance within working error what you should do looking for. So, going back to this the another example is determination of phosphate has strychnine phosphomolybdate this is also a very important concept for the determination of phosphate strychnine phosphomolybdate precipitates as a yellow powder and then if it is in water it can be held in suspension using a for using polyvinyl alcohol approximately 1 ml of 1 percent in 25 ml that is that is the range in which you will be working.

So, most of the stabilizers are 1 percent solutions. So, we need about 0.5 ml or 1 ml in a sample of about 10 ml, 25 ml, 50 ml like that to keep the precipitates in suspension. So, ammonia is another example which is a very well known pollutant and a chemical used in day today life also, and an excellent method exists as Nessler's reagent and Nessler's reagent produces a precipitate of potassium mercurate, potassium ammonium mercurate and that can be determined using Nessler's reagent, this is also a very good method for the adoption of turbidimetry in the in spectophotometery. So, these are some of the examples which will give you a sub ppb levels.

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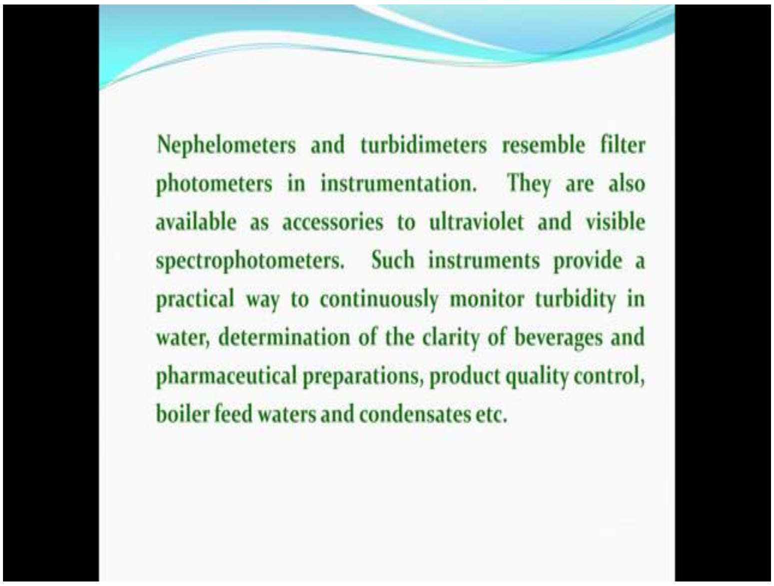

Nephelometers and turbidimeters resemble filter photometers in instrumentation. They are also available as accessories to ultraviolet and visible spectrophotometers. Such instruments provide a practical way to continuously monitor turbidity in water, determination of the clarity of beverages and pharmaceutical preparations, product quality control, boiler feed waters and condensates etc.

So, that is less than microgram per ml and srs instrumentation is concerned I have already explained to you that turbimeters and nephelometers resemble filter photometers in instrumentation; they are also available as accessories to ultraviolet and visible spectrophotometer, such instruments provide a practical way to continuously monitor the turbidity also just like a fia in water flow injection analysis, and determination of the clarity of beverages: coca cola, fanta and all these drinks beverages can be their quality can be controlled using turbidimetry. And there are several pharmaceutical preparations quality product, quality control, boiler feed waters, condensate kind of for all these things phosphorus phosphate is required sulfate is required analysis and turbidimetry could be 1 of the best methods for easy and fast determination of such samples it is ok.

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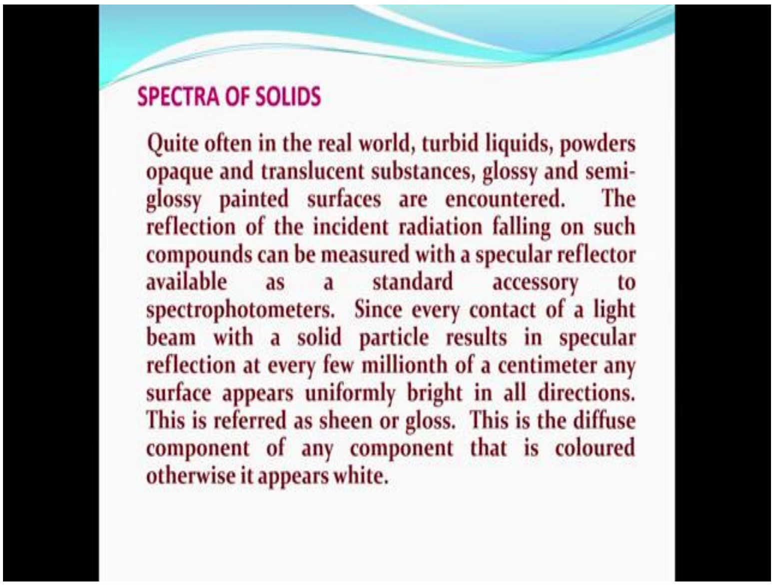

SPECTRA OF SOLIDS

Quite often in the real world, turbid liquids, powders opaque and translucent substances, glossy and semi-glossy painted surfaces are encountered. The reflection of the incident radiation falling on such compounds can be measured with a specular reflector available as a standard accessory to spectrophotometers. Since every contact of a light beam with a solid particle results in specular reflection at every few millionth of a centimeter any surface appears uniformly bright in all directions. This is referred as sheen or gloss. This is the diffuse component of any component that is coloured otherwise it appears white.

Now, I will not say more about the turbidimetry and a nephelometry, but we will move on to another aspect spectrum solids. Now, I want you to concentrate on what I am going to show you tell you rather what I am going to tell you. Sometimes it is possible for us to monitor the colour of the solid particles quite often you would see a nicely painted car on the road we will be tempted to look at it, oh how nice the car is in rates etcetera etcetera.

But you will be a wiser to know that several parts of the car are painted with a specific paint: black, blue, red etcetera etcetera and it is important for us to know the quality of the painting especially in a big machine. Because a big machine containing several components may be painted or a different time scale, 1 part may be painted today another part may be painted 3 months after, and 1 might have been painted 2 years before. So, all those parts come together whenever there is an order for a big machine all those parts are put together to make the car or whatever is the machine, and then at that time the painting quality of 2 years before and to a 1 month before and right now today everything should match.

Otherwise it is a big car or a big machine will look like an assemblage of different colours, which is not aesthetically good and that the quality also suffer therefore, it is important for us to determine the quality of the paint or the surface reflectance. So, if the reflectance whenever light falls on the metal plate reflect it reflects part of it. So, the reflectance spectrum can be taken as a qualitative quality component for many of these things. So, we need to do this spectra of the you know solids, and in the real world we have turbid liquids, powders, opaque materials and translucent substances like polythene and other things and then a glassy paints, and a paints applied on metals glasses and walls so all these things, we need to have a uniform quality of the paint all over the surfaces.

So, it is important for us to check the reflection properties of the paints and solid other solids also, quite often we do have to do that. So, let us have a look at what are the things involved in the spectra of solids; quite often in the real world as I told you that turbid liquids powders opaque and translucent materials are encountered, there may be a glassy or there may be semi glassy, and there may be non glassy also.

So, the reflection of the incident radiation falling on sets of compounds can be measured for quality control. So, what do we do? We take a make a circular reflector available as a standard accessory to spectrophotometer one more accessory for a spectrophotometer. So, this accessory should be able to tell us how the surface of a painted material or plated material electroplating also is done on number of materials and the quality of the plating can also be determined by the reflectance spectra.

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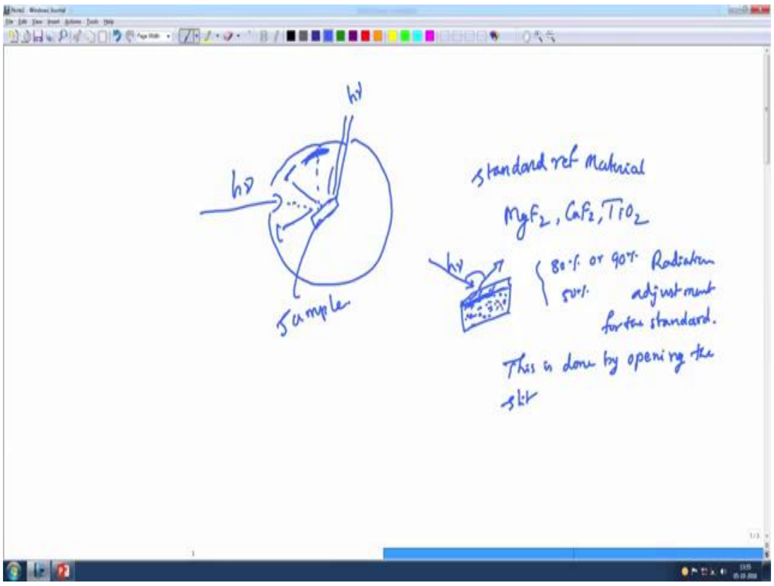

standard ref Material

MgF_2, CaF_2, TiO_2

80% or 90% Radiation
50% adjustment
for the standard.

This is done by opening the slit

So, what I want to show you is how we go about doing this, what you want to do is prepare incoming radiation is like this hp, and then I have small compartment and I have the sample maintained here then there will be the radiation you will be following on the sample surface and then it will be reflected; and if I fix a mirror here then again it will reflect and then again it will go back and then again reflect back with like that, the constant if I keep a hole its somewhere here the radiation h nu can be determine which is a reflection which is a quality and a reflection of the material which is posted on the sample here. Normally what I do is I would if I have to standardize a given material what I do is I take a standard reference material, this could be magnesium fluoride calcium fluoride T i o 2 titanium dioxide or any of the standard materials this is a white material.

So, this white material I take it in a cup and then put it here and press it. So, this gives me a uniform phrase on which the radiation will be coming in and then will be reflected. So, the angle of reflection I put we I connect the radiation at the angle of reflection. So, it is as simple as that, what I can do is for a given sample that is for a given painting I can adjust the out coming radiation reflected radiation to about 80 percent or 90 percent or maybe 50 percent. By adjusting the incoming radiation this is radiation adjustment for the standard how do I do this? This is done by opening the skit, if I open more it will be adjusting to about 90 percent; if I open less it will be adjusting to around 80 percent something like that and once this standard is set all other materials can be tested according to the preset standards.

So, this is the normal mechanism and accessory to this effect will be available in spectrophotometer, but you will have to ask for it. Normally whenever you meet somebody who is trying to sell your spectrophotometer he will not tell you that an accessories like this will be available, 99 percent of the time people do not want to tell you what are the accessories because it will affect their sales business. So, if you buy a special equipment for every application there the seller will be happy, but a buyer will be happy if he does more applications with a single instrument. So, it is your duty and to have to know about such things.

So, coming back to the spectra of solids quite often we come across situations like there and then the sample compartment needs to be modified with respect to solids, because if we have to make the colour measurements. Since every contact of light beam with a solid particle results in specular reflection, as at every few millionth of a centimeter; any surface appears uniformly bright in all directions. So, the quality of the painting or electroplating or a thin film are prepared in a laboratory, all these things can be refer can be standardized using reflectance term that is known as shwen or glass; shwen is a s h w e n and glass is of course, I think many of your familiar with the word this is the glass is the diffuse component of a any material that is coloured otherwise it appears white ok.

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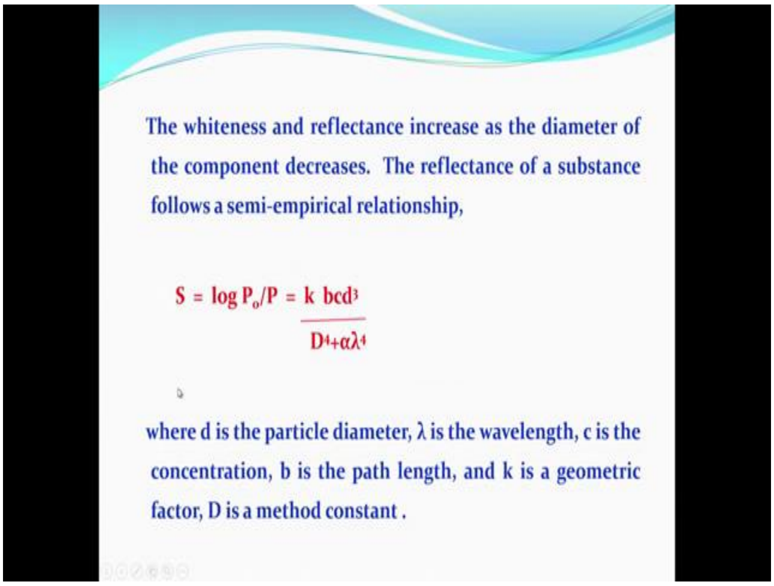

The whiteness and reflectance increase as the diameter of the component decreases. The reflectance of a substance follows a semi-empirical relationship,

$$S = \log P_o/P = \frac{k\ bcd^3}{D^4+\alpha\lambda^4}$$

where d is the particle diameter, λ is the wavelength, c is the concentration, b is the path length, and k is a geometric factor, D is a method constant.

So, that is the definition of glass. So, the whiteness and reflectance of a increase has the diameter of the component increases this is a very simple conclusion you do not have to be a mathematician to say such things, but the reflectance of a substance is also a semi empirical relationship. So, in this case what happens? The write a term known as s that is the ratio of log of p naught by p that is a just likes Beer lamberts law, but that is a function of a constant k into bcd cube divided by D raise to 4 plus alpha into lambda raise to 4, the relationship is somewhat a complicated and your small d refers to the particle parameter here I have the small d that is d cube and lambda is the wavelength c is the concentration here I have it in the numerator and b is the path length, k is a geometric constant and d is a method constant.

So, for every whether we use a calcium fluoride or a titanium fluoride capital D will be different in the for slide what I had shown you earlier. So, alpha is again a method standard parameter that is related to lambda. So, known values of lambda alpha are available for each wavelength we choose. So, if my alpha is different for uv, different for visible different for br ir like that, and basically you can see that log of P naught by P that is absorbance is a function of all these things here path length is constant path the particle size is constant you should try to keep it that way most homogeneous way, and capital D that is method constant is automatically fixed and lambda is fixed then if lambda is fixed alpha is fixed, and k is a proportionality constant right it is a geometric factor.

But basically it is a proportionality constant. So, we can say that log of P naught by P is proportional to concentration. So, that is how the painted materials can be determined.

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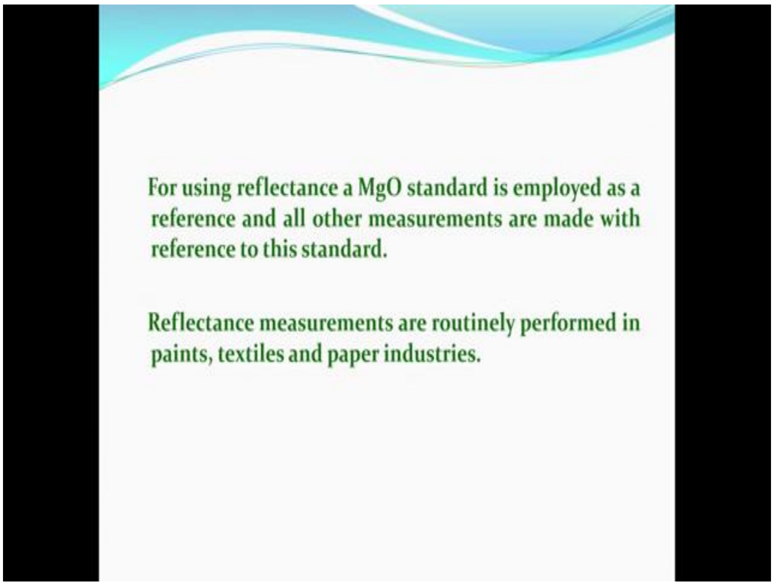

For using reflectance a MgO standard is employed as a reference and all other measurements are made with reference to this standard.

Reflectance measurements are routinely performed in paints, textiles and paper industries.

So, for using reflectance as I had told you a magnesium oxide standard is employed as a reference, and all other measurements are made with reference to a standard. And the applications definitely include paints, textiles, paper industries, thin film industry and any other large surface area preparation with different colours, that is how we should be going about it. I want to take you to another level of spectrophotometer practice of spectrophotometry. Now that is fluorescence and phosphorescence spectrophotometry.

Normally we are now normally we are concerned in 99 percent of the time about the changes in colour as far as the spectrophotometer is concerned, but whenever there is a radiation impinging on a substance the substance when it absorbs the radiation the naturally the radiation that is coming out will be less than the incident radiation because part of it is observed. Now there is another phenomenon known as known as fluorescence; fluorescence what this fluorescence does is it will give out different colour radiation than the incident light this phenomenon is known as a fluorescence.

Now, you have seen fluorescence in your day to day life number of times number of places; quite often you will see the a fluorescence phenomenon in on the highways whenever your car is going by it falls on a reflecting plate, it will show you the road signs etcetera in different colours. So, if you go to airport or in your own city at in the at night when the traffic police or somebody who is functionary where they will be wearing a different coat with a green colour, red colour etcetera; and whenever there is red light falling on the any light falling on the persons coat or something it will show different colour and it makes him appear specifically focused for a particular job to be done, this sample what I had shown you earlier is also a phenomenon and if you look at it from the bottom you can see there is certain amount of blue colour associated with this otherwise from the top it looks reddish.

So, different colours are possible to generate from the same incident radiation. So, this fluorescence phenomenon can be instantaneous taking place very fast within a matter of about few seconds, and then you do not see from your practice from the practical stand point of view the moment you see the person wearing a fluorescent shirt or shirt and pant fluorescent shoes, fluorescent road sign etcetera even though there is a time gap up gap of about 10 raise to minus 8 or something like that 10 raise to minus 12 also seconds, then your eye will not see a time gap. So, you will see instantaneously there are different colours of fluorescence and many of you may remember at homes the in the older times clocks used to give you visible numbers at night without any light.

So, there they were also known as fluorescence flourishing clocks and you, but they contain radioactive materials which used to give out radiation. So, that is also a kind of fluorescence only, and sometimes what happens is this fluorescence may take more time it may take about 10 seconds 5 seconds like that from several minutes, once the radiation impinges the radiation that comes out may come out after a few after a small delay. So, that can be that is visible and; that means, you can experience the time delay also such a phenomenon is known as phosphorescence. Now fluorescence and phosphorescence both are sort of extension of the spectrophotometry, and quite often the accessory for fluorescence is available with many manufacturers.

So, if you are in this business of measuring colour it would be good to have a fluorescence accessory, but over the years fluorescence has developed as a separate special new science and dedicated fluorometers are also available, but essentially principle remains the same. So, what I would like to do is in the next class next 2 classes I would like to teach you a little bit about the phenomenon of fluorescence: how it occurs, why it occurs, what are the instrumentation etcetera and what are the components and then we will move on to the applications of spectrophotometer to different parameters in water monitoring.

Thank you.