Physics of Renewable Energy Systems
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Lecture – 49
Particle Size and Zeta Potential Analysis

In the previous lecture, we had discussed to you about the use of BET to determine the specific surface area of nanomaterials, the pore size, the pore dimensions, the pore volume, which are obtained in these kinds of nanomaterials.

Let us now discuss another experimental technique which is used to actually estimate the particle size of these nanomaterials, the homogeneity in distribution of these particles because you have already understood in the lecture; where we were talking about nanotechnology; the importance of having homogeneous distribution of nanomaterials or nanoparticles.

And we will also discuss today what is zeta potential, why is it so relevant to us when we are discussing devices for energy generation or energy storage devices, which are utilizing nanomaterials. This technique is actually called the particle size analyzer or zeta potential analyzer. And there are various equipments which are available in the market.

And we will be discussing using one of such equipment that is available in IIT, Kharagpur; and will give you an overview of the way you are going to measure the particle size and zeta potential. Why is it important to measure these two parameters, and how do we use the physics of light scattering in making a high end equipment.

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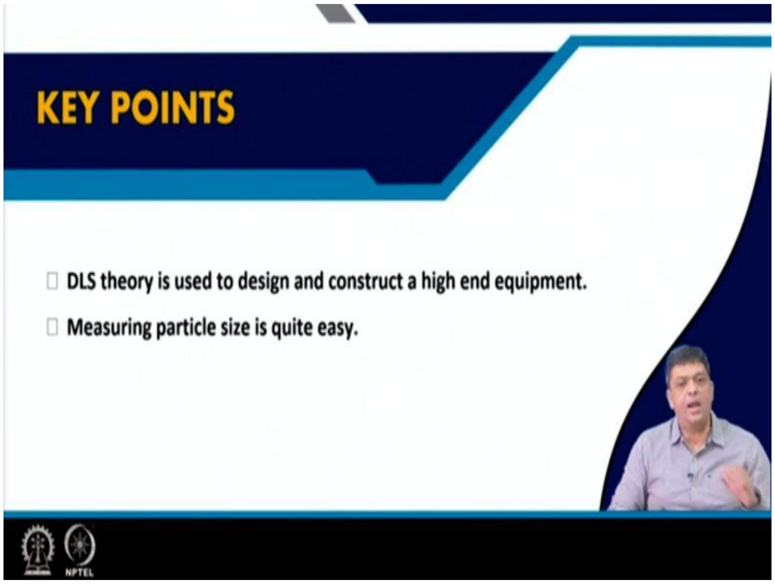

KEY POINTS

- ☐ DLS theory is used to design and construct a high end equipment.
- ☐ Measuring particle size is quite easy.

Hence, it is important to note that you may have various kinds of equipments, but they are all utilizing theories which are taught to you in different subjects. And in this case, the particle size analyzer or zeta potential analyzer uses the theory of DLS. So, it is an interesting example of taking theory to real world application or a high end equipment; and measuring particle size is a very easy strategy, if you are using this theory will also become clear to you.

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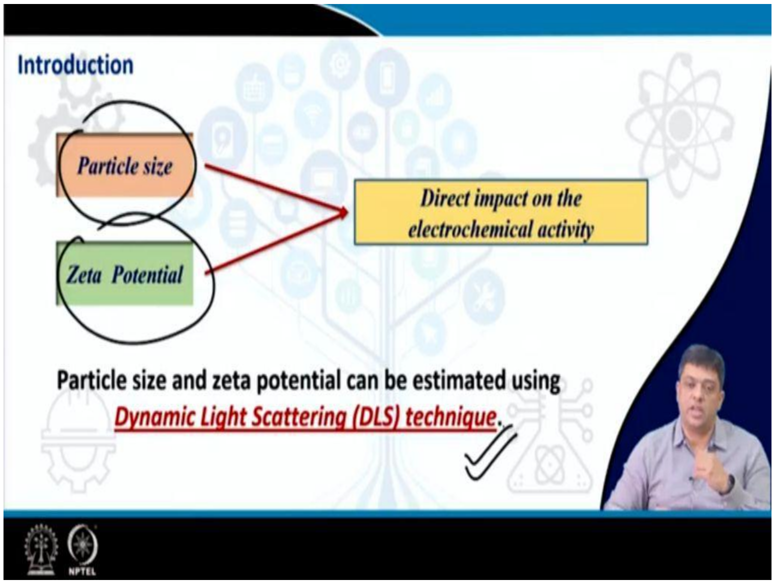

Introduction

Particle size

Zeta Potential

Direct impact on the electrochemical activity

Particle size and zeta potential can be estimated using Dynamic Light Scattering (DLS) technique.

We have discussed the nanomaterials, and how they are utilized in energy storage devices, or many of the energy generation systems also use nanomaterials. There are two additional parameters, which are critical in defining their electrochemical activity; as indicated earlier, they are the particle size and the zeta potential. And both these parameters can be determined using dynamic light scattering technique.

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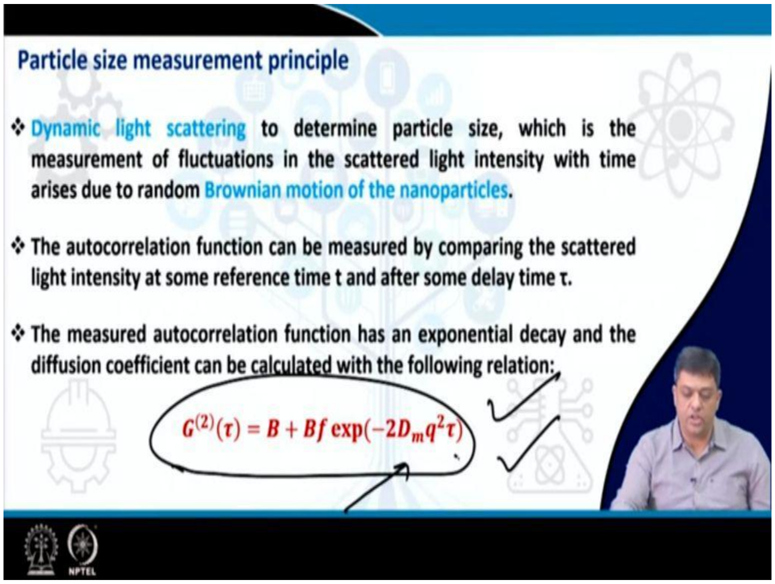

Particle size measurement principle

- Dynamic light scattering to determine particle size, which is the measurement of fluctuations in the scattered light intensity with time arises due to random Brownian motion of the nanoparticles.
- The autocorrelation function can be measured by comparing the scattered light intensity at some reference time t and after some delay time τ.
- The measured autocorrelation function has an exponential decay and the diffusion coefficient can be calculated with the following relation:

$$G^{(2)}(\tau) = B + Bf\exp(-2D_m q^2 \tau)$$

This technique is used to determine the particle size, by measuring the fluctuations in the scattered light in intensity, with time arising due to random Brownian motion of the nanoparticles, difficult to understand. Let me make it easy. So, suppose you take a colloidal solution that is you have dispersed nano size particles in a fluidic matrix or in a fluid; and these particles are randomly moving, so you have obtained a colloidal solution.

And that is at a particular temperature they are having random motion. Now, if you have very high concentration, and then you shine light; will the light be able to cross this turbid solution, or will it not be able to pass? If the size of the particles are very large, will they actually allow the light to pass or will they not allow the light to pass?

And if you have particles which are of small size, they are also randomly moving; and their concentration in this fluid is such that they interact with the light, and they also allow it to pass through, or scatter the light out. Then, depending upon the light which is obtained; that is the scattered light, you can back calculate the size of the scattering or the scatterer.

This is what the whole theory is all about. You actually back calculate the size of the scatter. And this is obtained using the autocorrelation function, which is measured by comparing the scattered light intensity at some reference time t, and after a delay time of tau. So, you measure what happens as a function of time. And if you have the same size scatterer, then you will get the same intensities; and if you have different types of particles coming in the part of the light, then the scattered light will be slightly different.

And then you will get information about the distribution in particle size or the scatterer size. And if they are similar, then the (inten) you will find the intensity variations will be minimal. And if there are various types of scatterers available in this colloidal solution, you will get different intensities and you will get different types of scatterer size.

The measured autocorrelation function has an exponential decay, and the diffusion coefficient can be calculated using the following relation. So, you can use this autocorrelation function, and you will find that the diffusion coefficient can also be calculated as a function of tau.

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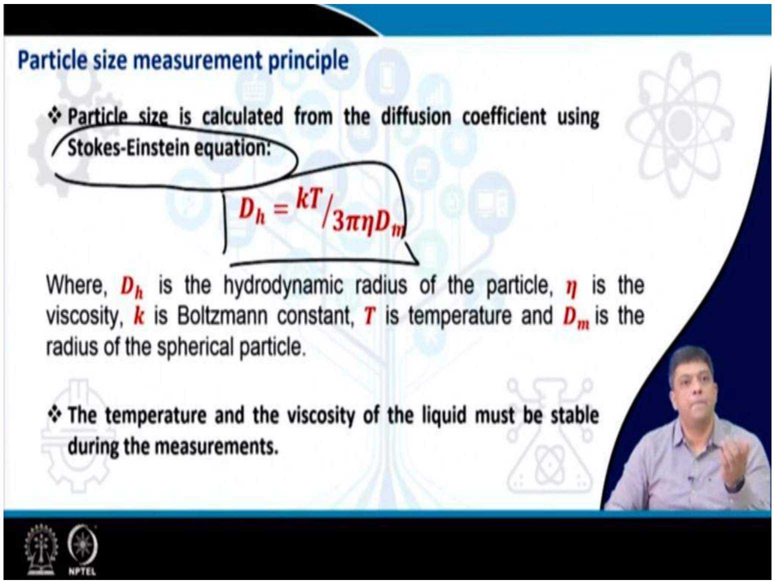

Particle size measurement principle

- Particle size is calculated from the diffusion coefficient using Stokes-Einstein equation:

$$D_h = {}^{kT}/_{3\pi\eta D_m}$$

Where, D_h is the hydrodynamic radius of the particle, η is the viscosity, k is Boltzmann constant, T is temperature and D_m is the radius of the spherical particle.

- The temperature and the viscosity of the liquid must be stable during the measurements.

Once I have the autocorrelation function that is giving me what? It is giving me the diffusion coefficient as a function of time the delay time, which we had mentioned. The particle size can be calculated using the Stokes-Einstein equation; that is the Dh is equal to kT by 3 pi eta Dm, where Dh is the hydrodynamic radius of the particle, eta is the viscosity, k is the Boltzmann constant and T is the temperature, while Dm is the radius of the spherical particle.

So, two things hydrodynamical radius and the radius of the particles come into picture. For example, if I say, you have a system where the viscosity is very large; then if the viscosity is very large, you will you get diffusion coefficient which will be high, or will you get it very low. Obviously, viscosity is coming in the denominator, so the diffusion coefficient value will be much lower, this you can understand.

If the viscosity is high, then the particles cannot move freely from one place to the other; similarly you can explain the effect of temperature. And that is the reason why we say that temperature and viscosities also play an important role in these kinds of measurements.

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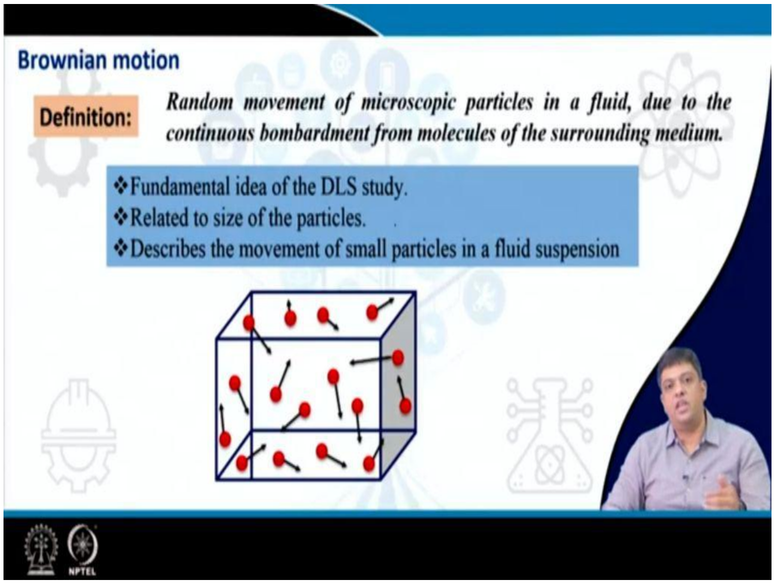

Brownian motion

Definition: ***Random movement of microscopic particles in a fluid, due to the continuous bombardment from molecules of the surrounding medium.***

- ❖Fundamental idea of the DLS study.
- ❖Related to size of the particles.
- ❖Describes the movement of small particles in a fluid suspension

Brownian motion: As all of you understand, it is a random movement of microscopic particles in a fluid due to the continuous bombardment from molecules coming in from the surroundings; or the interaction of a forward moving particle with the walls of the container, where they are confined to move.

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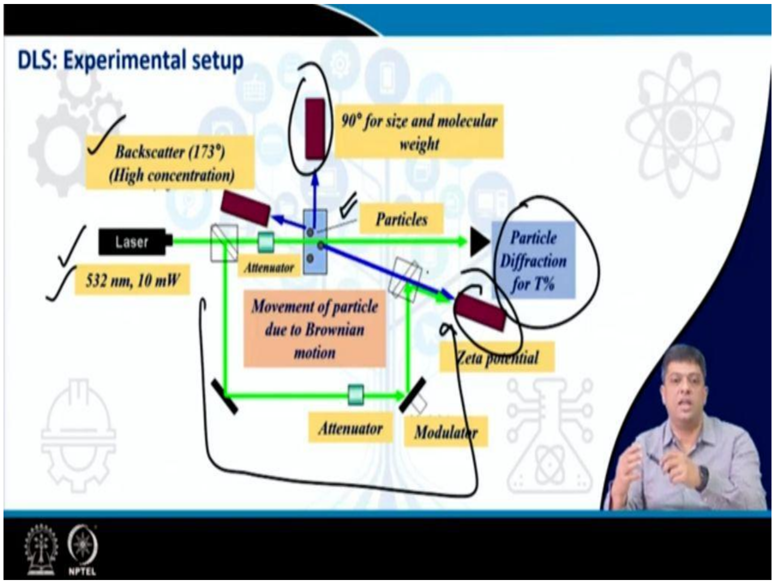

DLS: Experimental setup

90° for size and molecular weight

Backscatter (173°) (High concentration)

Particles

Laser

Attenuator

532 nm, 10 mW

Particle Diffraction for T%

Movement of particle due to Brownian motion

Zeta potential

Attenuator

Modulator

DLS actually utilizes these two concepts; this is the experimental setup of a DLS device. So, you have a laser, a high intensity focused beam, mostly considered to be monochromatic interacting with the particle. And then you can have the various factors, if you have very high concentration. So, if you have very high concentrations the light will come, and then it will get deflected; because you will not have any path to move in, and these will be acting as a reflector services.

So, if you have very high concentrations, then you will have back scattered. If you have reasonable concentration that is low concentration; and for determining the size and molecular weight of the particles you analyze at a 90 degree scattering. And, for when you have transmission. If you measure transmission, then you have the particle diffraction in terms of transmitted beam, which will be investigated.

In addition, if you analyze the two beams, if you split the two beams and then combine; then you can calculate the zeta potential also. So, this is the experimental setup, you can understand it is very simple; you have a glass beaker a light. If it is turbid, you have a lot of impurity in it; the light will not pass through.

And if it is having particles which are small in size, and the concentrations are also low; then the light will get scattered because of this of this interaction of light matter interaction effect. And then you can study the scattered light and investigate, and try to derive information using this scattered wave.

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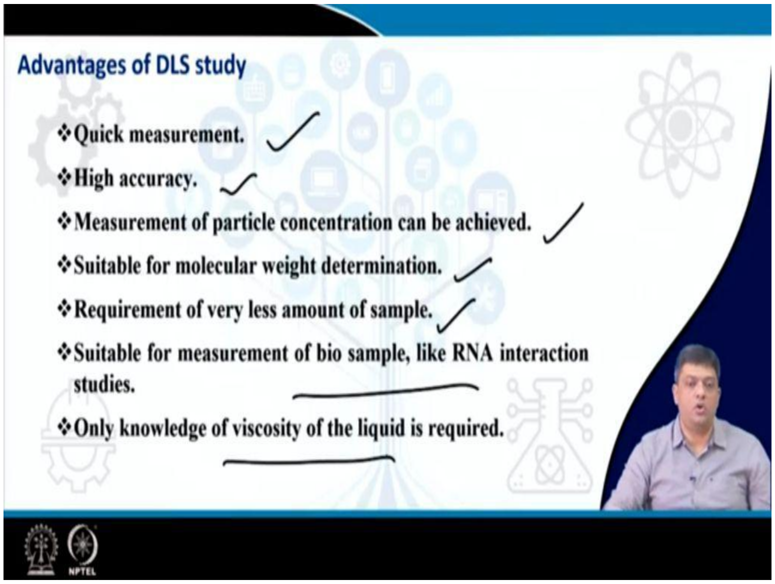
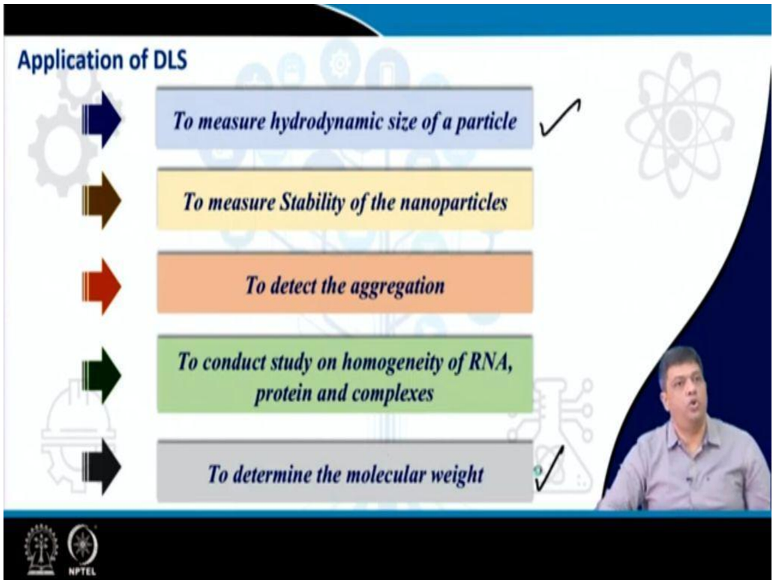


Advantages of DLS study

- Quick measurement.
- High accuracy.
- Measurement of particle concentration can be achieved.
- Suitable for molecular weight determination.
- Requirement of very less amount of sample.
- Suitable for measurement of bio sample, like RNA interaction studies.
- Only knowledge of viscosity of the liquid is required.



Application of DLS

- To measure hydrodynamic size of a particle
- To measure Stability of the nanoparticles
- To detect the aggregation
- To conduct study on homogeneity of RNA, protein and complexes
- To determine the molecular weight

So, light matter interaction, as we know, is near instantaneous and very fast; so the measurement is also very fast, you lead to highly accurate measurements. You can also determine the particle concentrations up to a certain limit; it is used for molecular weight determination. It actually requires very less amount of sample.

Because you are not going to have very high concentration in the fluid or in the when you are making the colloidal solution; you are not going to have very high concentration of these scatterer. They can be used for bio samples, and to obtain the information about the particle size or the zeta (siz) zeta potential.

You only need the knowledge about the viscosity of the liquid, with where you are putting in your particles. And these are the various kinds of applications and they range from measurement of particle size to molecular rate determination.

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Device handling for particle and zeta potential measurement

So, let us show how this equipment actually works; this is a typical particle size analyzer. So, you have a particle size analyzer, just what you had seen earlier in few of the examples we had talked about a light source; so there is a light source that is the laser light. This light has to interact with what? It has to interact with the sample which is dispersed in a fluid; so you have a light source, and you make a solution where you disperse your particles in a liquid.

You know the viscosity of this liquid and then you put this qubit in front of the light. When you switch on the analyzer, you have the cameras at different places 90 degrees, back scattered or for zeta analyzer. And then, by analyzing these scattered rays, you can back calculate the scatterer size using the autocorrelation function.

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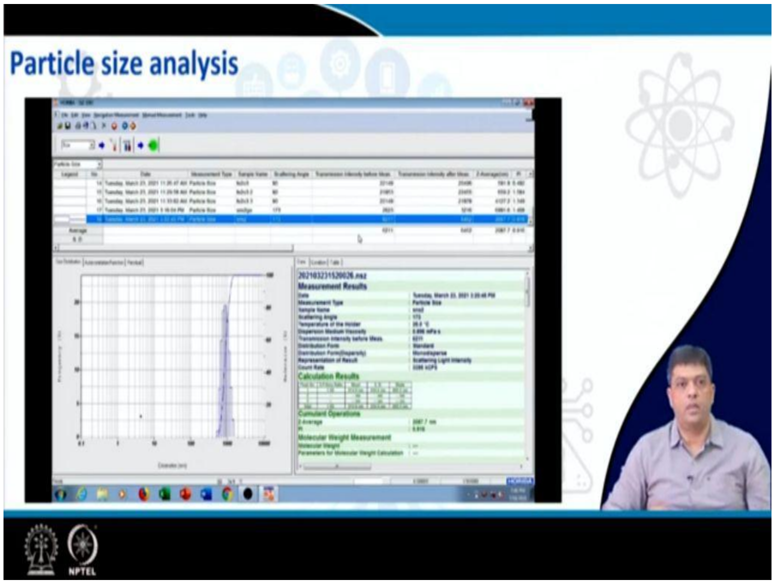
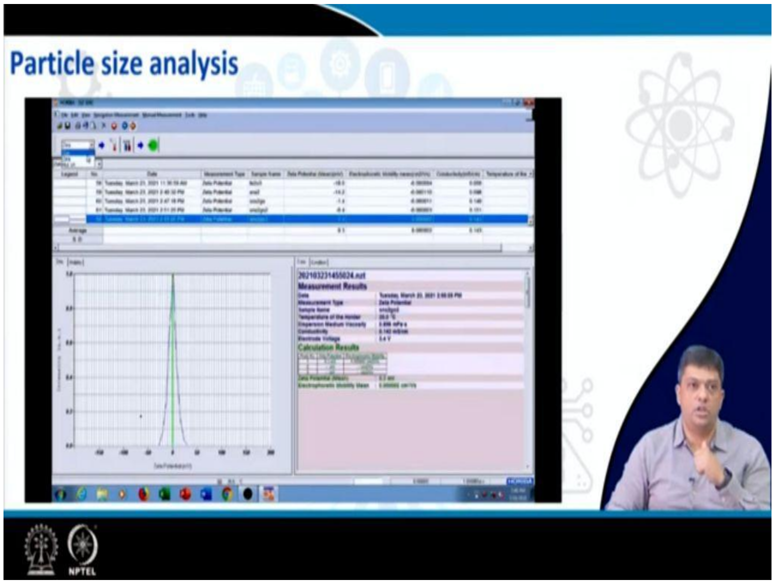

Particle size analysis


Particle size analysis

This is a typical way you start the measurements. So, what we have done? We have taken the sample. We have made a colloidal solution, and for ensuring homogeneous dispersion in the fluid; you generally ultrasonicate this solution, if your materials are stable towards the ultrasonic energy. Then you have to give the various parameters which have to be measured.

So, whether you want to measure the size or the zeta potential. So, let us discuss about the way you would like to measure the particle size. To start the measurement as we have seen that the temperature plays a very important role. So, the device actually turns on, and it sets the chamber temperature to 25 degrees.

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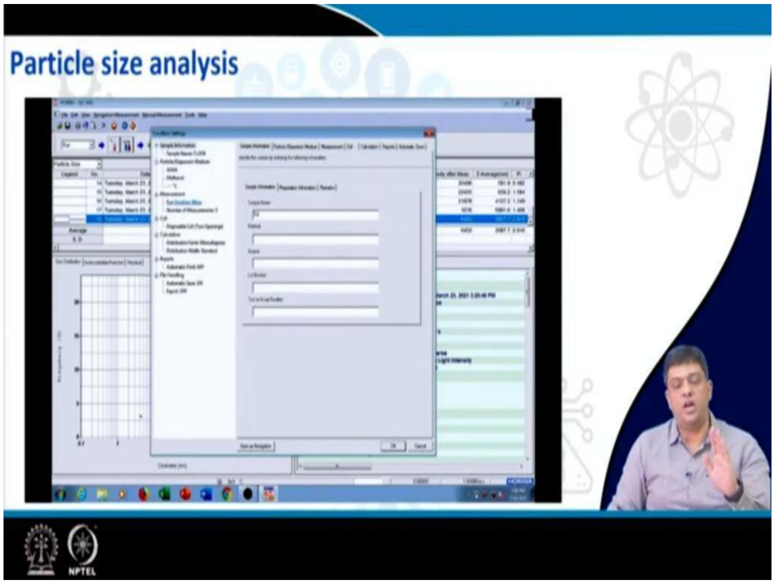

Particle size analysis

So, now your equilibrium condition is obtained, where the temperature around the sample is 25 degrees. Next, we should insert the details about the samples. What is the name of the sample, what is the type of cuvette where we are filling the sample? What is the range in which we are looking for data, what type of particle size are we looking at?

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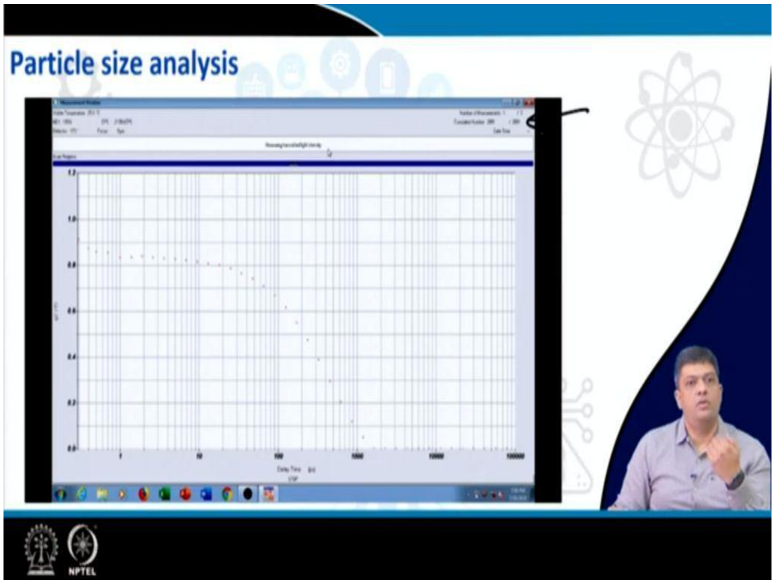
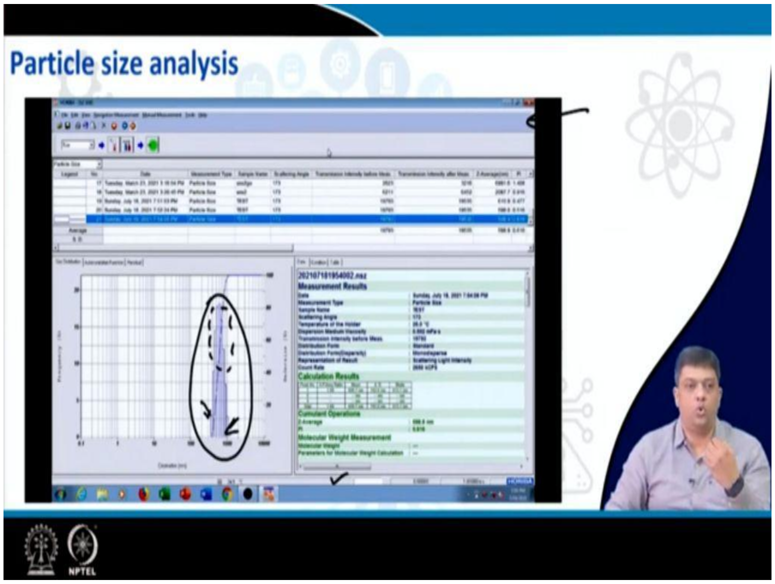


Particle size analysis



Particle size analysis

And then we switch on the measurement. You can see on the top, this is showing one of three. So, the measurement actually starts after the system has reached an equilibrium, and you are going to measure the whole data for three times. Take the average and then get the final values. You can also increase the number of measurements, and then take the average using those measurements.

And for the kind of materials which we are discussing here, what we have obtained is for cobalt oxide nanoparticles. After the optimization process, we knew that measuring for three times gives you reasonably accurate data. There is very little variation after three measurements, average; or you measure it for five times or seven times, or nine times.

And take the average, the results were similar; so, we measure it for three times. Once I have taken and obtained the autocorrelation function that is G 2 tau, as a function of tau what you see, tau and G 2 tau, it back calculates and you can easily obtain the particle size distribution. So, what you interpret?

You have particles, which are mostly in the range of let us say, 800 nanometers or so. But, you also have particles which are in the range of 400 nanometers to 1000 nanometers or so. But you have most number of particles, which are in the range of 800 to 1000 nanometers. So, this kind of bar chart can be calculated using the autocorrelation function, which the software does on its own; and gives you the output.

So, I hope you have seen that, measuring particle size of nanomaterials is actually a very very simple method. And many of you may have actually done the experiments on dynamic light scattering in your M. Sc. physics lab; and now, you will be understanding the importance of that experiment.

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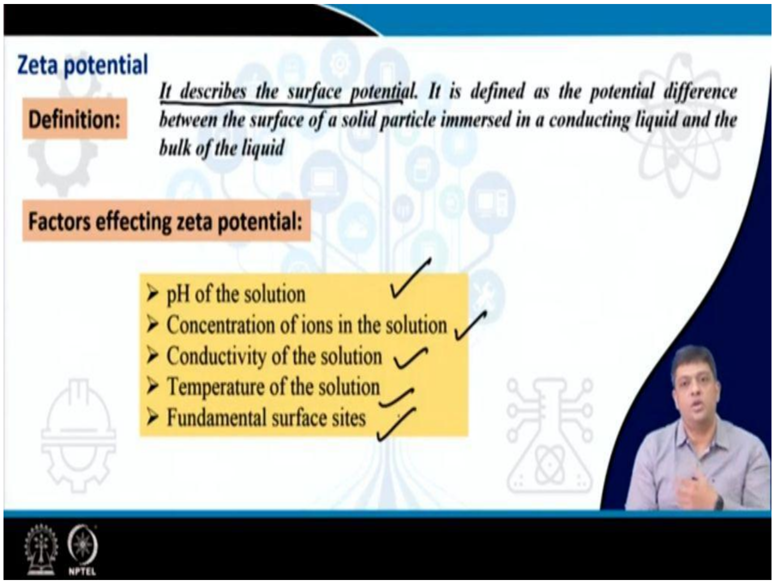

Zeta potential

Definition: *It describes the surface potential. It is defined as the potential difference between the surface of a solid particle immersed in a conducting liquid and the bulk of the liquid*

Factors effecting zeta potential:

- pH of the solution ✓
- Concentration of ions in the solution ✓
- Conductivity of the solution ✓
- Temperature of the solution ✓
- Fundamental surface sites ✓

What was the second term which we said, while stating that there are two parameters, which affect the electrochemical properties of nanoparticles. First one was particle size and second one was zeta potential. Zeta potential: It describes the surface potential. So what is the potential across the surface? It is also defined as the potential difference between the surface of the solid particle, which is immersed in a conducting liquid, and the bulk of the liquid.

So, what is the potential which is near the surface of the particle, and in the bulk of the fluid? Because the potential. There is interface, which is getting formed; and the potential which develops here is because of the charge of the particle. If the particle is negatively charged, what will happen to the interfacial layer?

And if the particle is negatively charged, or opposite in charge to the example which I took in the previous case; then what will happen to the surface near this particle? That is what is meant, and as you move away from the particle, the potential will slowly reduced; because the overall potential is leading to the charge neutrality condition in the liquid. So, this gives you the indication about the surface charge of the particles.

Again, this can change that is zeta potential can change, depending upon the pH of the solution, the concentration of the ions in the solution, the conductivity of the solution, the temperature and other fundamental surface sites associated with nanoparticles, which is being investigated.

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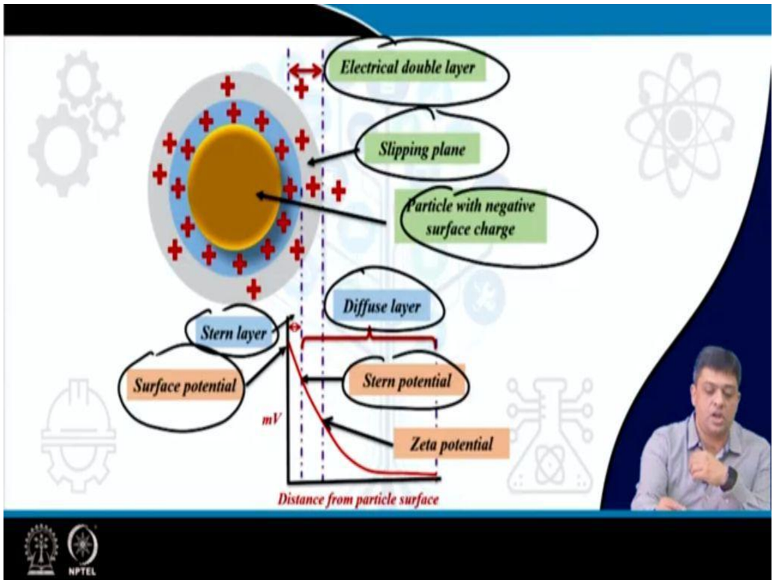

So, this is what it means, if you are very near to the surface. I hope now you understand this stern layer and surface potential concept. These were explained when we were talking about the super capacitors. We had also given you the explanation about the diffuse layer and the stern potential, when we were talking about the stern model. The stern model, which was using the concepts of electric double layer formation (hel); that was given by Helmholtz model.

How that was modified by the Gouy-Chapman model, and then how you obtain the stern model. So, that is what you have seen in the discussion that was presented during the module dedicated to super capacitors. So, you have a particle and then you have the interfaces or the sleeping plane, and then formation of double layer. If you have a negatively charged surface, then a positive charge gets deposited. And if I change the example, can you anticipate or imagine what will be the scenario? I guess it is a very simple question I have given you.

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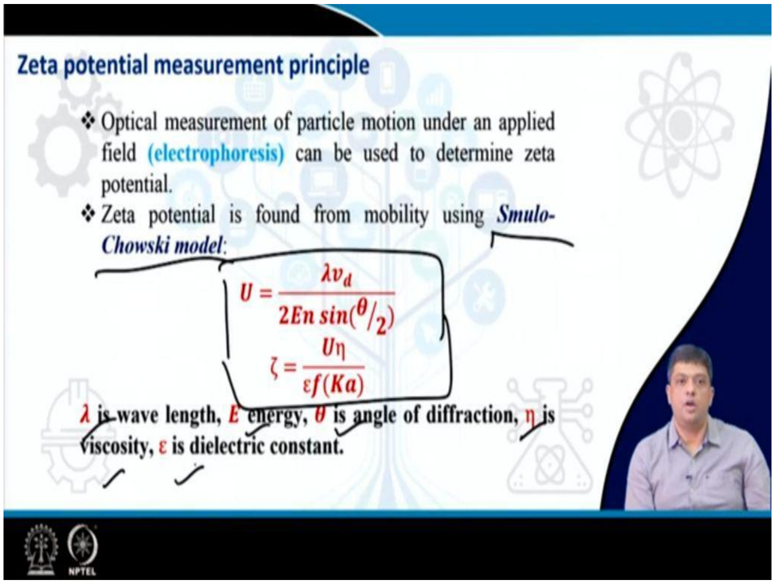

Zeta potential measurement principle

- ❖ Optical measurement of particle motion under an applied field **(electrophoresis)** can be used to determine zeta potential.
- ❖ Zeta potential is found from mobility using ***Smulo-Chowski model***:

$$U = \frac{\lambda v_d}{2En\,sin(\theta/_2)}$$

$$\zeta = \frac{U\eta}{\varepsilon f(Ka)}$$

λ is wave length, E energy, θ is angle of diffraction, η is viscosity, ε is dielectric constant.

This zeta potential is actually determined using the Smulo-Chowski model, which is given by U is equal to lambda vd divided by 2En sin theta by 2; where, lambda is the wavelength is the energy, theta is the angle, eta is the viscosity and epsilon is the dielectric constant. So, we can actually determine the zeta potential.

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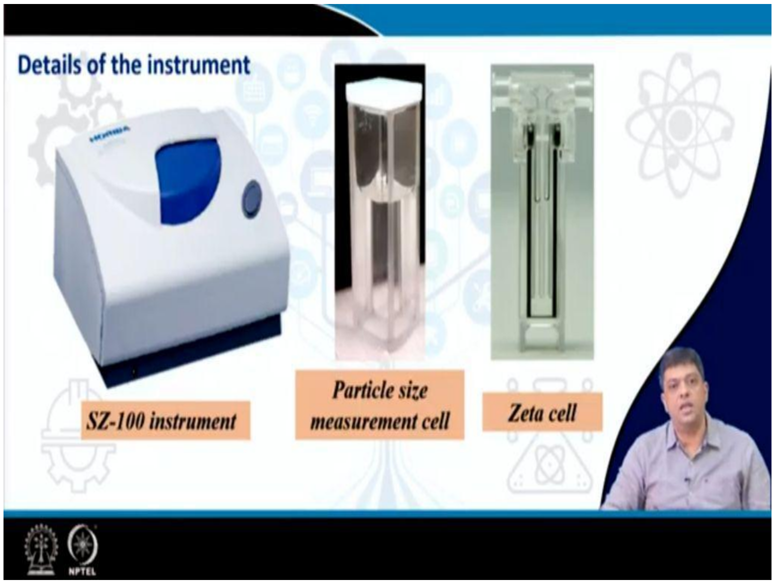

Details of the instrument

The instrument remains the same for particle size measurement or zeta potential measurement. So, we are again using the Horiba particle size analyzer or zeta potential analyzer. The difference comes in the cuvette which we use. So, for particle size measurement, we use the glass qubit with no electrodes; whereas for zeta potential measurements, you use the qubit, which has an way to install electrodes in it. So, you have the zeta cell and the particle size measurement cell.

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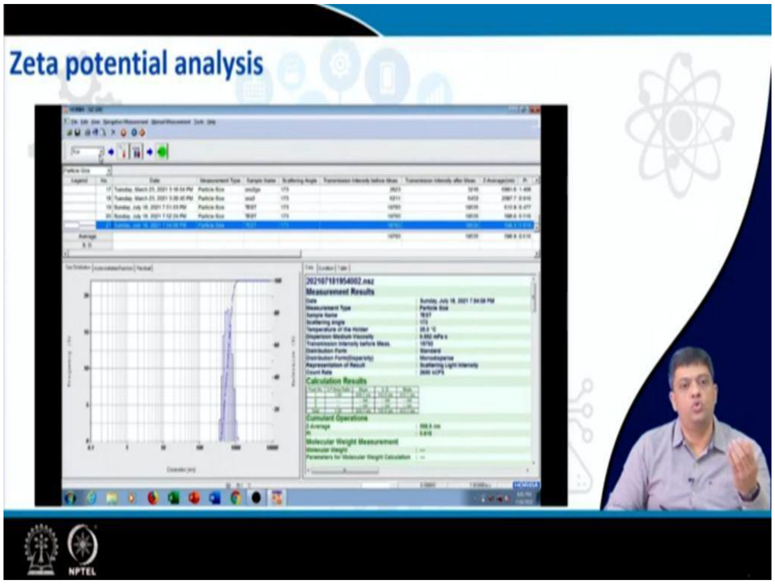

Zeta potential analysis

So, the way you had measured the particle size; you will repeat the measurement in the same order. Here, only the differences that you have now use the zeta cell, in place of the qubit; which was simple qubit used while you were measuring the particle size. So let us see what we do.

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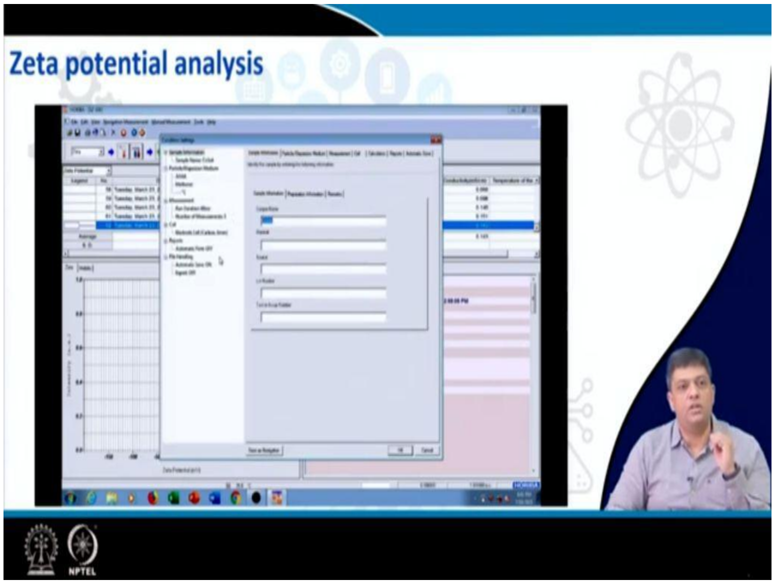
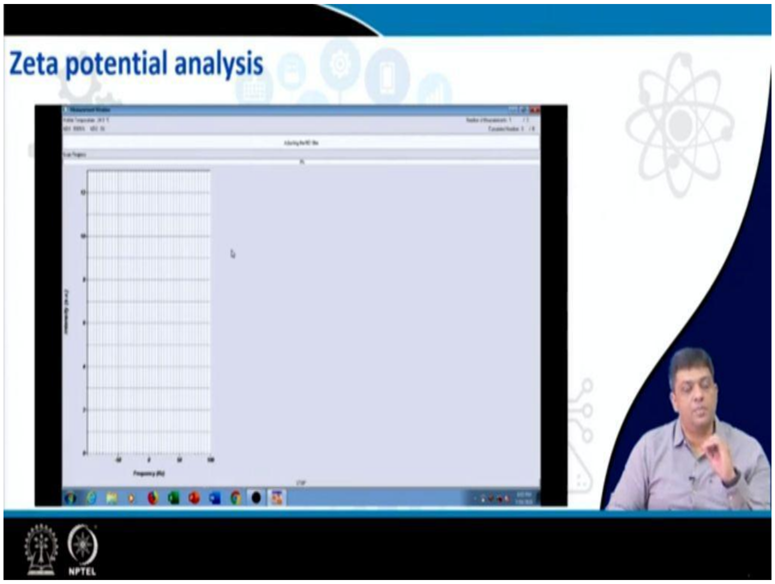


Zeta potential analysis



Zeta potential analysis

So, we have obtained the autocorrelation function; and from there, we can then choose the parameter that we want to measure the zeta potential. We have to insert that for zeta potential determination we are also using the zeta cell. And subsequently, you will initiate the measurements; again, one out of three is shown here. And when it reaches to the end, you will find that it would be three out of three; and the average value will be given to you.

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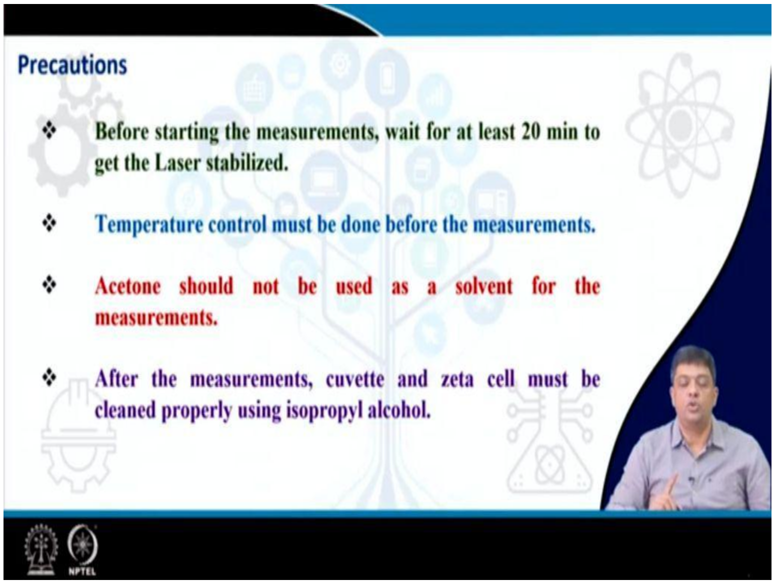

Precautions

- Before starting the measurements, wait for at least 20 min to get the Laser stabilized.
- Temperature control must be done before the measurements.
- Acetone should not be used as a solvent for the measurements.
- After the measurements, cuvette and zeta cell must be cleaned properly using isopropyl alcohol.

So, before you start the measurements, it is also initially important to wait for 20 minutes or so, for the instrument which we are using. This is a specification given by the manufacturer. But for the equipment which we are using, the typical time taken for the laser to stabilize and warm up is 20 minutes; so you should wait for 20 minutes. You must ensure that the temperature control is there. While you are measuring the samples, acetone must not be used as a solvent; because it is continuously evaporating.

Or, it can the acetone vapors can lead to the damage of the cells, or the nearby components which can have plastic or rubber coating on them. After the measurements, the qubit and the zeta cell must be cleaned thoroughly. Otherwise, the next time somebody comes and measures using the same qubit or the zeta cell; then it will give you false results. So, each measurement has certain precautions, which must be followed to obtain the accurate results.

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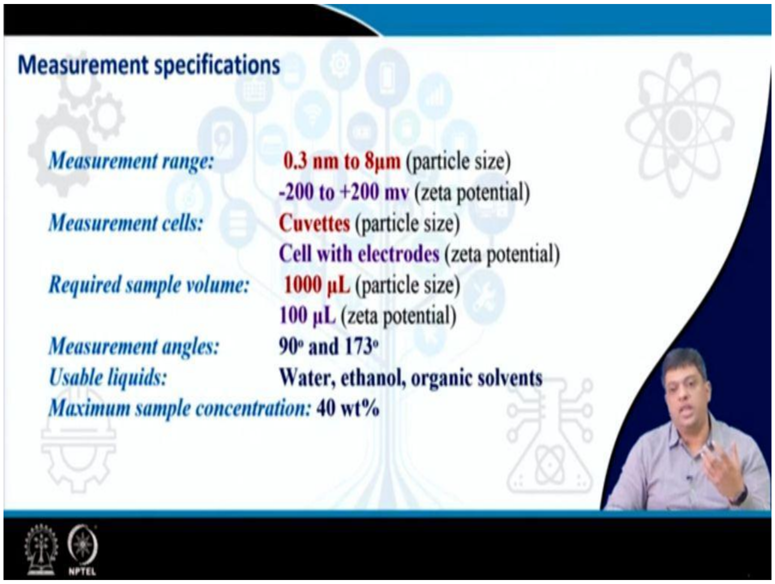

Measurement specifications

Measurement range: 0.3 nm to 8µm (particle size)
-200 to +200 mv (zeta potential)
Measurement cells: Cuvettes (particle size)
Cell with electrodes (zeta potential)
Required sample volume: 1000 µL (particle size)
100 µL (zeta potential)
Measurement angles: 90° and 173°
Usable liquids: Water, ethanol, organic solvents
Maximum sample concentration: 40 wt%

For example, in this case, we can choose the measurement range from point 3 nanometers to 8.micrometers; and zeta potential from plus 200 to minus 200 millivolts. We can have cells of different materials. Generally, after optimization you will find that for the equipment's which I have indicated today, you can have accurate measurement using samples of 1000 microliters for particular size, and 100 microliters for zeta potential.

And the liquids which are used to disperse the particles are water, ethanol, or any other organic solvents; which do not react with the particles, which are going to be dispersed in these fluids. And generally, beyond a certain concentration, the solution becomes so turbid; that it is impossible to get any reliable data out of it.

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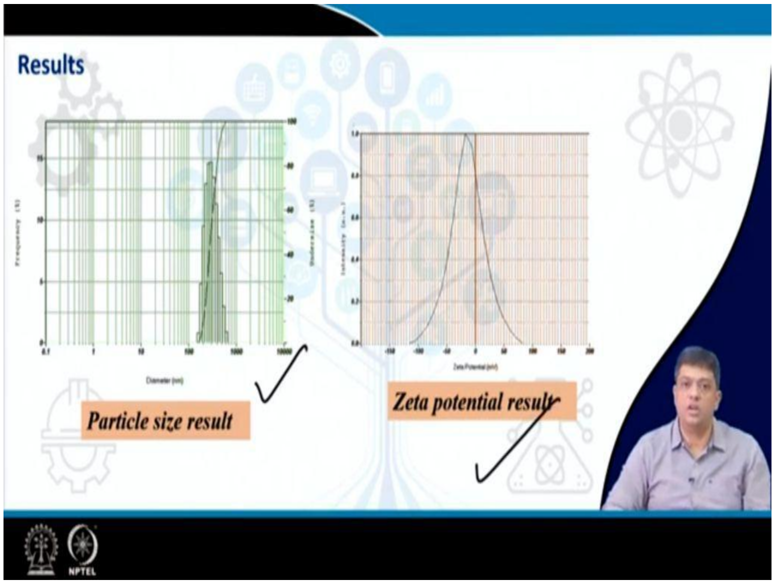

Results

Particle size result

Zeta potential result

So, this is the typical particle size curve and this is the zeta potential results, which you obtain after the measurement. And once you have got the information about the particle size, the surface charges, you can then use them for predicting the electrochemical performance of these particles.

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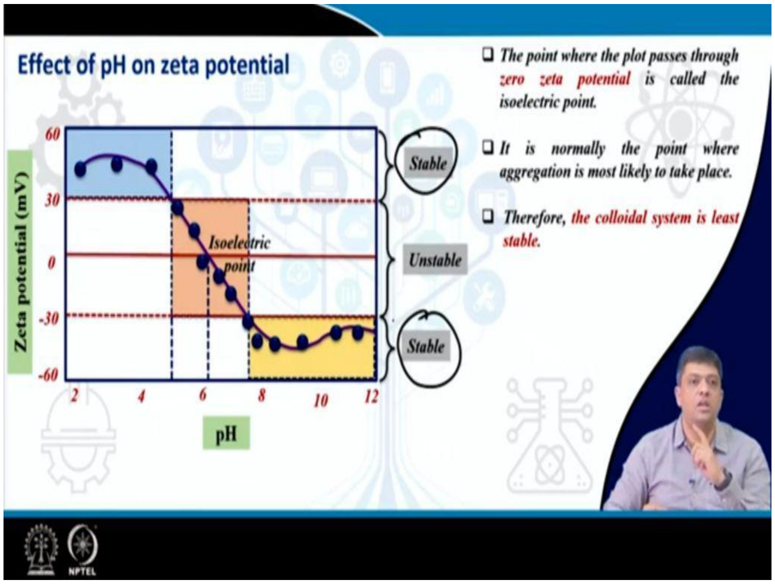

Effect of pH on zeta potential

- ☐ *The point where the plot passes through zero zeta potential is called the isoelectric point.*
- ☐ *It is normally the point where aggregation is most likely to take place.*
- ☐ *Therefore, the colloidal system is least stable.*

Now, why it is important to measure zeta potential at pH values, which are relevant for your sample? Because, suppose you are measuring a different pH, but the range of pH in the real device is very different; then the electrochemical performance may not be the one you have anticipated, after performing the zeta potential measurements at a different pH.

So, it is important that you ensure that the measurements are obtained at pH values, where you are going to use these particles. Along with that you have few points where the colloidal solutions are stable; that means you do not have sedimentation. And for accurate results, you must stabilize these colloids in the pH values, so that you do not see sedimentation.

Otherwise, you will not get the real data; because you would suggest that you have particles on the top, from where the laser light is passing. But because the colloidal solution is not stable, the particles have sedimented to the bottom of the cuvette; and you do not have any particle, which is undergoing a Brownian motion. They have all sedimented at the bottom of the cuvette; and then the results would be inaccurate. And hence, you need to choose the pH values for measuring the zeta potential in the range, when you have the stable colloidal solution formation.

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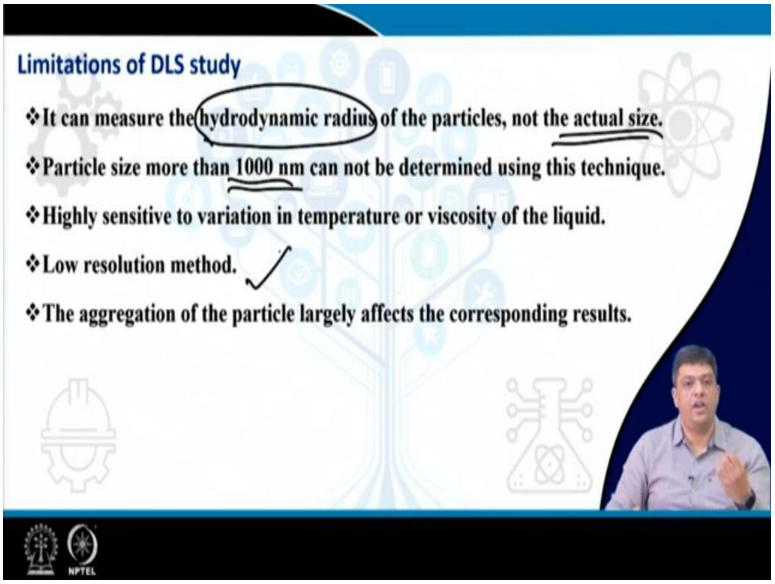

Limitations of DLS study

- It can measure the hydrodynamic radius of the particles, not the actual size.
- Particle size more than 1000 nm can not be determined using this technique.
- Highly sensitive to variation in temperature or viscosity of the liquid.
- Low resolution method.
- The aggregation of the particle largely affects the corresponding results.

Although, this is a very simple technique, very very useful technique, and widely used techniques; it has some limitations. The limitation is that actually measures the hydrodynamic radiation of the particle, and not the actual size. But, then from there you like to get an idea about the actual size. If you have very large size particles, then it is not possible to determine them; or, the size of these large size particles.

As we have seen from the autocorrelation function, you change the value of viscosity or temperature, everything changes. So, if you want to compare the data which were taken at two different places; they should be such that they were obtained at same temperature; and under the condition when the liquid in which they were dispersed have the same viscosity. And it is a slightly low resolution method.

If your particles are very very near to each other; it is difficult to separate their size. And if the nanoparticles all come together, so you may have particles which have 100 nanometer dimensions. But, if they agglomerate, then they become a big chunk; and then they may become like 500 or 600 nanometer sized. And then what you will obtain is not the true picture; but the picture of the aggregated particles. So, you may actually infer wrong information from the measurement.

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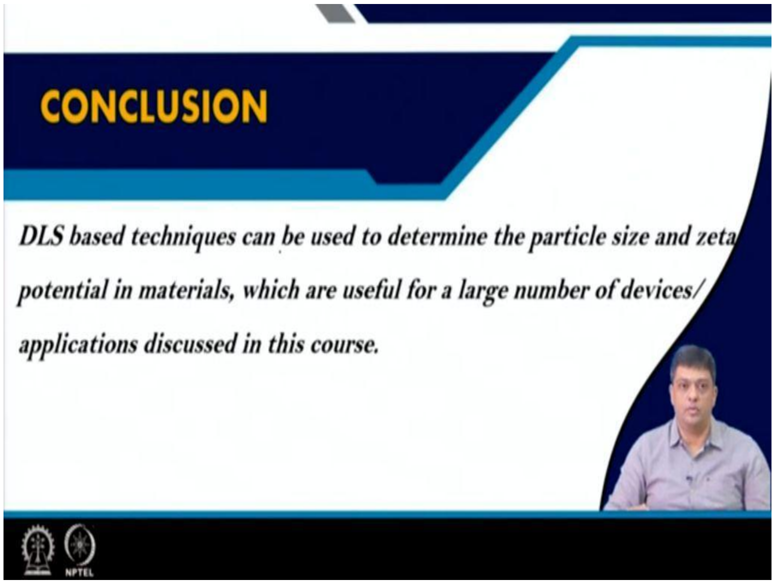
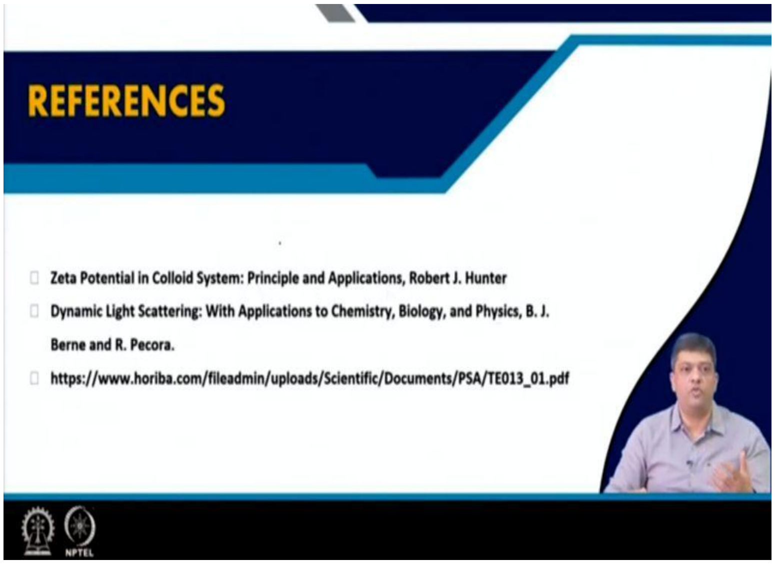


CONCLUSION

DLS based techniques can be used to determine the particle size and zeta potential in materials, which are useful for a large number of devices/ applications discussed in this course.



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Hence, DLS is a very useful technique to determine particle size and zeta potential in materials. Extensively, used in nanomaterials and the kind of materials, which we have used and described in this course, the materials which are useful for large number of devices and applications. Applications such as batteries, super capacitors, catalysis, or any other which we had discussed earlier; but, the technique also has its own limitations.

You should also be very careful when you perform these measurements; because there are certain requirements, which should be followed when you initiate the measurement protocol. These are the places where you will get more information about the technique; and how the theory was developed. With this we have described to you another technique to estimate the particle size of nanomaterials, or particles of reasonably low size. I thank you for attending today's lecture.