Quantitative Methods in Chemistry

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Lecture-11

A Look At Uncertainties in a Measurement Taking An Example

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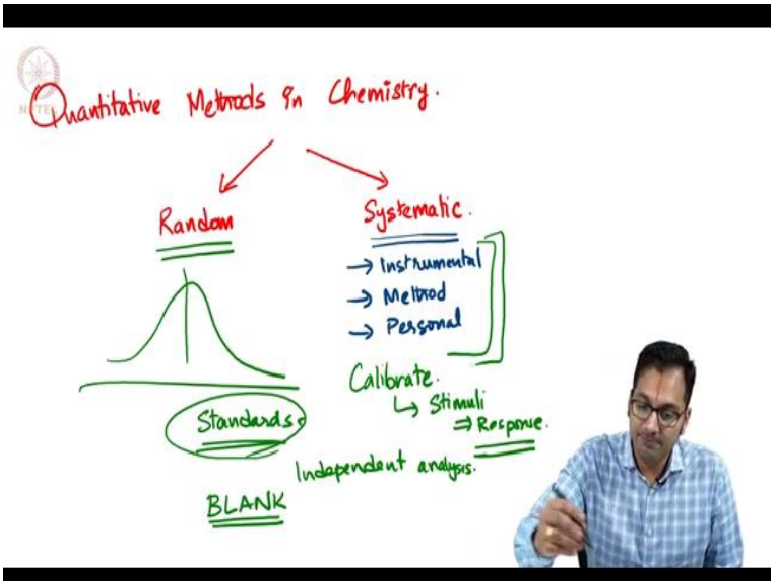

In the last class, we started to understand how the uncertainties from different measurements come out. And in that regard, we saw 2 major ways that one can categorize errors. One is random errors. The other is systematic errors. And in systematic errors, we learned that this is something that comes up because of what we do in the experiment and because the reason why it comes up and it results in a biased analysis.

So, one must avoid trying to do systematic errors. And out of this, these were characterized into instrumental errors, method errors and personal errors. So, what did we mean by each one of this instrumental error could be one where the instrument misbehaves. For instance, different equipment tend to work in a given temperature range, or in a certain level of humidity. But let us say that those things changed this will result in an unreliable measurement and they would result in systematic error.

Even something as small as the voltage fluctuations might result in variability in measurement. On the other hand, method errors are one where one has to carefully follow protocol and steps have to be done in such a way that they do not change the order of the steps or change something without a rhyme or reason. Method errors could be cause also due to the fact that let us say you add a unknown agent in your solution. For instance, it is quite common practice to add an indicator in your titration experiments in order to find the endpoint.

But we make a huge assumption that the indicator does not change the endpoint. But when you think about it, it does interact with the chemical that you end up adding, meaning that let us say you are adding phenolphthalein as the indicator and let us say you are adding sodium hydroxide. It does interact phenolphthalein does interact with sodium hydroxide, so small but a seemingly negligible amount of sodium hydroxide reacts such that it does change range, it could change the end point to a small extent.

On the other hand, personal error comes from our own bias, meaning that we might have assumed a certain value that we might end up getting, and we tend to do the experiment, assuming that that is what we are going to get. On the other hand, random errors are one which results in ending getting the bell curve or the normal of the Gaussian distribution, which we discussed in detail.

And this could be something that is not very easy to minimize or in certain ways one cannot minimize it. This could be the inherent error that comes up from the measurement by itself. Since we have discussed this in detail I am not going to do this further in this week, however, we will be trying to look at how analysis could be done to delineate these types of errors. But before going forward, let us try to also understand how the systematic errors can be detected or even minimize.

Let us say you start to have a feeling that the instrument is misbehaving. The first step that one ends up doing is to calibrate the instrument. I have used this word calibrate a lot. What does this calibration mean. Generally, the way we work is that we give a stimuli and we expect a response

from a system and as long as we have a clear standing between what stimuli is given and the response that we expect is obtained, we understand that the instrument is working properly.

As an example, I did give you an example of how the pH meter works, pH meter generally has an electrode which is immersed into a solution, and you are expecting to read out a certain pH value. In order to calibrate that what we end up doing is to use standards. This is the same way one could also check for systematic error. If you start realized that, for instance, let us say you take potassium dichromate, which has an beautiful yellow color.

Let us say that there is analyte that you are trying to analyze using let us say UV visible spectrophotometer, then you see that the color comes on, you are able to estimate a certain number but you are not very sure whether it is indeed working right. So what you could end up doing is buying a standard and making up the necessary concentration of this potassium dichromate.

And actually you vary your own values in terms of control experiment, meaning that where you know what you are going to change, and you would expect to see the response that you are already thought out, let us say that is not coming up, then what you end up doing is to calibrate the instrument such that the stimuli and response go hand in hand together. Once that is done, you end up repeating the analysis that you have done before, just to see whether the variation comes up after having recalibrated the instrument.

On the other hand, one could also do an independent analysis. Let us say instead of using spectrophotometric way of determining concentration of this potassium dichromate, you could use other techniques such as analysis of chromate concentration using other techniques, where it is an oxidizing agent. So you can add a reducing agent and you could stoichiometrically determine how much of dichromate was present.

So therefore, you will be able to estimate it in an independent fashion. If you are able to estimate this in an independent fashion, you can compare it with what measurement you are made in order to analyze whether it falls in the right place. On the other hand, if you think that whatever is in

the solution, except for the analyte is causing trouble, people trend generally tend to resort for blank measurements. What do we mean by black measurements.

This is a solution which has everything apart from the analyte and is subjected to the same experimental technique. And you see what measurements come out. Now, let us say the measurements without the analyte already gives the response that you do not expect, then this clearly indicates there is a problem either the blank already has something in the background that is giving such signal, or it could be something wrong that has been added into the solution.

If you realize all the things that I have been mentioning, could fall into any of these different systematic errors that could come and a vigil experimental list would ensure that these are minimized.

Now to move on to the next portion of today's lecture, I would like to actually take an experiment and first show how the results come up and how can we understand what various things that we have discussed so far. We can look at repeatability; we can look at whether okay where all errors could come. In order to do this, I am going to take a simple example. I am sure all of us have heard of entities called surfactants.

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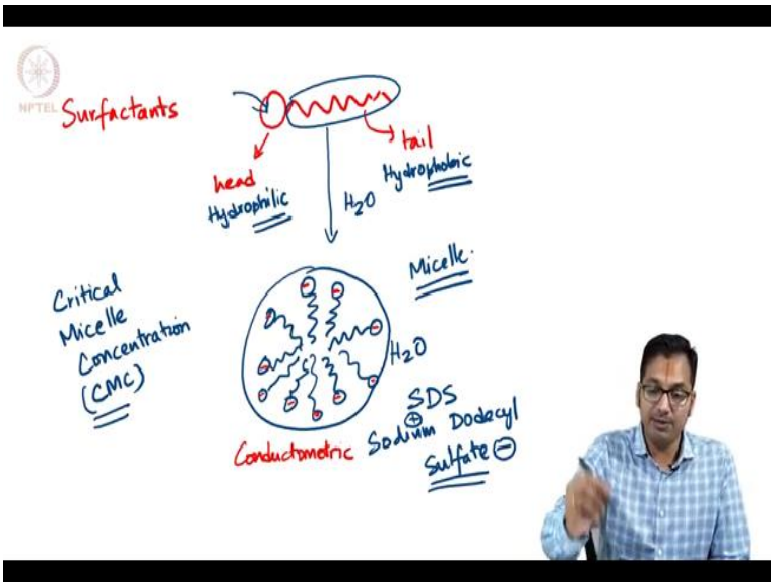

These are generally chemicals that tend to change the surface properties of the liquid that they are added to. For instance, the soap that you end up taking and dissolving in water when you are taking math is indeed a surfactant. I am pretty sure all of us are played by making bubbles which is nothing but a surface phenomenon, which is generated by these agents. So these are generally characterized by hydrophilic head and hydrophobic tail.

I am using some terms which I assume that you would already know where hydrophobic means fear of water by hydrophilic means water liking. So these kind of molecules, when you add a lot of them, what it tends to do in solution, let us say you are adding them to water. What happens to them is that all the hydrophobic groups bunch of together by the hydrophilic head groups point towards water.

So this kind of an assembly is called a micelle and the reason why I am taking this as an example is because there are complimentary techniques that one could use to understand at what concentration this micelle forms and such a concentration is called critical micelle concentration. Of course, this has nothing to do the course, but all that we are trying to do is to take up an example such that we can understand whatever we are spoken in English what is actually does it mean in the laboratories case okay.

Now that you see such a system as the concentration keeps on increasing these aggregates tend to form not aggregates this micelle tend to form then we would like to know at what critical concentration do they actually found the species. So, for this instance we will be taking example of the surfactant called SDS. This is sodium dodecyl sulfate, acid able to realize that dodecyl will be the hydrophobic tail while the sodium sulfate will form the head.

And as you are able to realize, again, that the sulfate will give it a negative charge, which is neutralized by the sodium ion. So in this case, what you are able to realize the head groups are negatively charged. And this gives us a handle to measure it through conductometric experiments. You do not have to worry whether you know conductometric experiments.

I will briefly introduce them to you, conductometric experiments are nothing but trying to determine the rate at which they move when they are certain an electric field and this is nothing but how much conductance does the ions help passing through alright. So you can think of them as electrolytes which held them pass the current and in this case, what you are able to realize is that SDS is charged you could set it to conductometric experiment.

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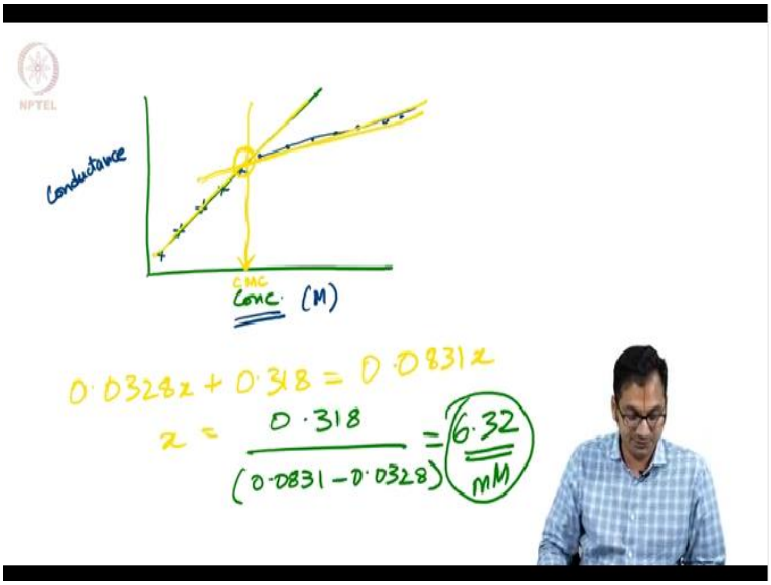

So, what are we trying to understand here, the migration of these surfactants will depend upon whether they are formed micelle or not, as you keep increasing the concentration. So what are we expecting as we increase the concentration of these surfactants. Let us say in molar, you expect the response of conductivity or conductance to increase because as you keep increasing concentration, the number of negatively charged ions in the solution keep increasing.

So, as it keeps increasing, you are going to see a nice increase in its conductance. However, the moment they start forming the micelle, you are able to realize the size increases, so therefore, the migration might start reducing. And that would be indicated by the change in conduct and so what is going to end up happening yeah, it will still conduct as you keep increasing concentration will still conduct.

But what is going to end up happening is that there is going to be a break in this curve, which results in the fact that, at this concentration, the micelles are indeed form. So that this is the

concentration that we are looking for in this experiment. So why do not we take a little look at a data set and understand how does this behave okay. **(Video Starts: 12:26)**

So this is the measurement that I was talking to you about. Of course, I told you that you have a conductometer that helps you do it. Let us first look at the results and try to understand each step where mistakes could come up in such an experiment. And what you are seeing here is that this row or this column has the variable that you are able to change meaning that the concentration of the surfactants and this is the measurement that you are making, meaning that the conductance.

How does the conductance change. So let us see whether this is indeed true that when we plot concentration of the surfactants, the conductances of function of concentration of the surfactants, what happens, you are able to nicely see the fact that okay, until this point, the slope was quite steep. And after a certain concentration, you are able to realize the conductance is indeed increasing as a function of concentration, but not as much as it did before.

So this indicates that probably after that concentrations this surfactants tend to form a micelle and therefore the migration is reducing, therefore the conductance is also reducing. Now let us try to use this data set to analyze, we are able to realize that the initial point you can assume that very less micelles are formed, predominantly the conductance is coming from the monomeric form.

On the other hand, as the concentration is at the maximum, you can tend to believe that almost all of them have started to form micelle beyond the critical micelle concentration and let us try to see where is this concentration. So I am going to use the first 4 points to determine what is the slope and the intercept. One is able to understand in the absence of SDS, pure water does not conduct as much.

So when we fit this curves a curve fitting will be seeing in some time, but when we fit this curve we can set the intercept 0. And the first thing that you are able to realize is that you are getting the slope us 0.831 times the concentration. On the other hand, let us use the last set of data to

understand what is the slope and the intercept that comes there. So let us use the last set of data points and fit them to see where the CMC comes up.

So what you are able to realize is that there are 2 separate curves. There are 2 separate lines here, one that goes this way. The other that goes this way, I would like to remind you the same thing that we ended up seeing a moment back. So if you are able to realize we have a curve that goes this way, and another curve that goes this way, the point of intersection tells us what is the concentration at which micelle are formed.

So in this case, you are also seeing a parameter called r squared, you will be taught in the subsequent lectures, what is this r squared, what is fitting, you will be taught in the forthcoming lectures what is data fitting, and how to analyze whether the data that you fit is reliable. But for now, I would request you to assume that the dotted line that is added as a trend line nicely fits the experimental data that has been measured.

So, now all we have to do is that we have 2 equations and we need to find where they meet. if you have 2 curves where do you how do you find whether where they intersect is to equate them one to the other. So, that is exactly what I am going to be doing right now $0.0328 x + 0.318 = 0.831 x$. So, this would mean $x = 0.318$ divided by $0.0831 – 10$, 6.32 of course, since the concentration is used in millimolar, you tend to save the critical micelle concentration from this data set works out to be 6.32 millimolar from conductometric measurements. Let us see with the same critical micelle concentration is obtained by another researcher.

In order to do this, we will take a data set from another researcher. Let me remove all the curves that are present here okay, let us first see whether the similar dependence is what we observed. Yes, you are able to see the fact that there is a line that goes here and another line that has a quite a different slope alright, let us analyze the data the exact same way. So, let us assume that the initial few points, the conductance comes purely from the monomer that has not found. **(Video Ends: 17:39)**

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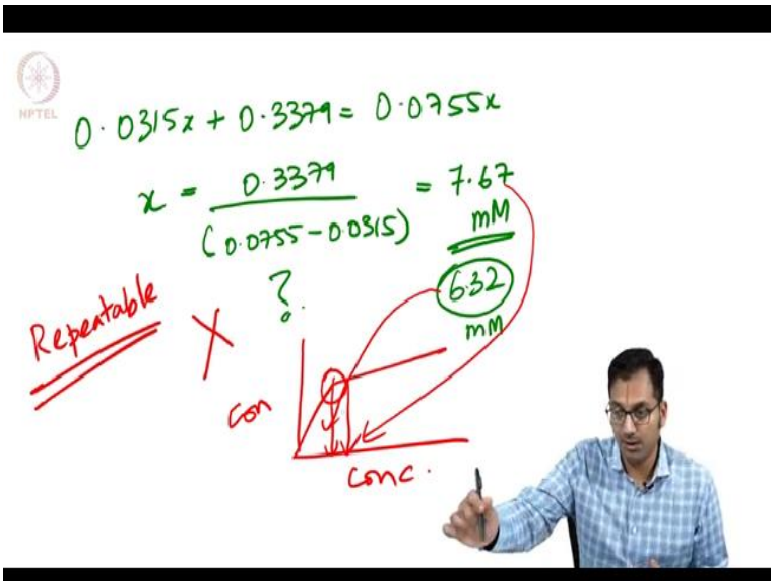

So what do we get here, we get a slope of 0.0755 0315 x + 3379 = 0.0755 x. So x therefore would be equal 0.3379 divided by and you get a number, like 7.67 millimolar. It is quite interesting if you see the previous page they get 6.32. On the other hand, this measurement says it is 7.67. So which one is correct. So, first point that we are able to realize the experiment is not repeatable.

The repeatability does not exist for this experiment and that is a problem, right meaning that if the same measurement with the same equipment is done by the same person, multiple times and what values do we get as what we are trying to look and what you are able to realize is that was the curves for both the cases look looks as anticipated. Meaning that conductance is a function of concentration showed a steep change.

But the problem is where do the lines meet seem to be quite different for these 2 measurements, while one claims it to be 7.67, the others claiming this to be 6.32, so which one is correct. So now, this calls for the fact either a third person ends up repeating it, or one has to repeat it using an independent analysis. For today's class let me take an example of an independent analysis that comes to our rescue.

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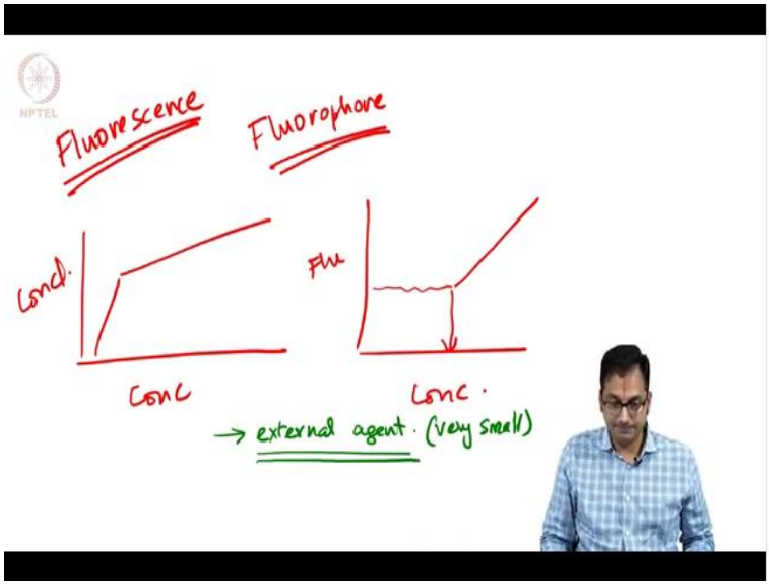

So, in order to do that independent measurement, then we can try to take fluorescence spectroscopy where you can assume this is a technique that is quite different from that of conductance where conductance looks at conductivity of charged surfactant on the other hand here we will end up adding a fluorophore are people who do not understand what is fluorescence and a fluorophore.

You can think of this as an indicator that will help us analyze our sample that we have gotten. And the fluorophore in general, tends to absorb light only when it is encapsulated inside the micelle, meaning that if the micelle are not formed, the fluorophore is going to be free. And the signal that we read out from the spectrometer is actually going to be constant. But the moment micelle start to form, this fluorophore gets arrested within these micelle.

And the signal tends to increase. While in the previous case, we saw conductance as a function of concentration, which had a discontinuous goal like this. In this case, what you are expecting fluorescence as a function of conductance will be more or less flat, and then it is going to increase. So this point of break will help us understand what does the critical micelle concentration. Of course, I would like to make you guys understand.

These 2 measurements are certainly different, largely because what is ending up happening is you are adding an external agent in this example. If you really want to compare the

measurements from conductometry and this fluorometry, then you should have repeated the conductometric experiments with this external agent added. But let us assume you add a very small amount that this does not affect the overall measurement.

And let us go ahead and see when this experiment was repeated for the fluorometry what kind of results do we get.**(Video Starts: 21:41)** So, the data that is given is here. Remember in none of the calculations I did, I wrote them in significant figures. We can only write about significance figures when you have an estimate of precision. So far the repeatability has not worked out, which is why we are committing to the 2 decimals in concentration. But here of course the researcher has given multiple decimals. Let us go with it concentration in millimolar and then fluorescence signal.

Okay, so now let us plot these 2. Yes, you are able to realize yes, it did indeed does happen. You have a until a concentration where there is no change and after a concentration it increases. And for such curves, it is prudent enough for us to fit the last few data points and understand where they meet the initial point. So let us fit this, we will once again discuss more about fitting as we go forward. But for now it suffices to understand that the fit that we are performing helps us analyze the data. **(Video Ends: 23:12)**

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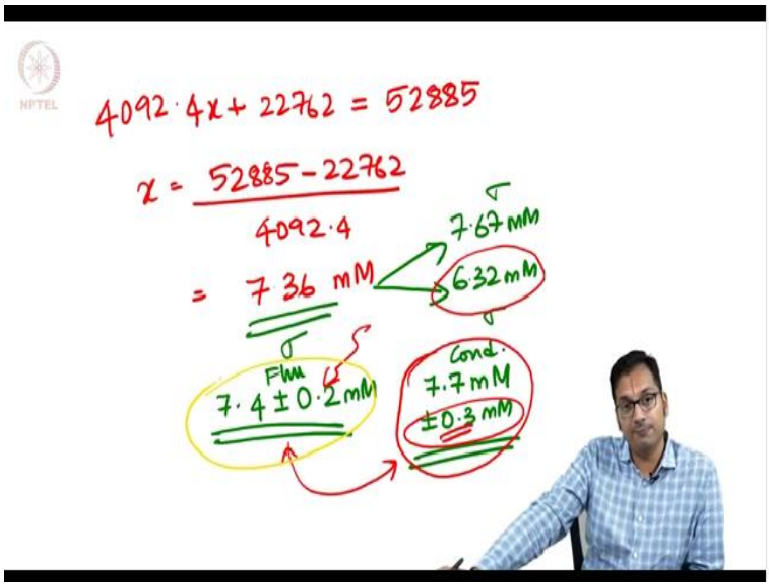

So, what do we get, we get something like 4092.4 x + 22762 is equal to the y factor. And now one has to understand this, we are trying to find where it meets the basal value and in order to find the basal value, we can actually try to take the average of the first few points, the average of the first few points works are to be 52885 and therefore, your x is going to be this is equal to I would like to recollect what values did we get.

We got 7.67 and 6.32. And you realized this value is in between these 2 values now, which is correct. So, once again, I hope this makes you understand, one has to understand what is the precision of each of this measurement, so, that we can try to compare the numbers across without doing further add, it was observed that from conductometric or fluorometric experiments, this was the value that was obtained and with reliable measurements.

This is fluorometric, this is conductometric where the student ended up getting + - 0.3 millimolar. So, what you are able to realize here after a thorough analysis, you are able to understand do repeating the same measurement in 2 different ways helps you ascertain what is indeed the true value. On the other hand, this scientist probably did a few mistakes. What we will end up doing is to enlist the steps that were done in the next class to set up this experiment.

So, that one by one we will take a look at what all mistakes could have happened and which could have been reduced in order to ensure that such systematic errors could be reduced. On the other hand, you want to realize that the random error that arises from all of this cannot be minimized less than this of course, this can be only done after multiple attempts with a protocol that is well written and multiple labs trying the same thing across different techniques.

I just showed you an example where measurement becomes repeatable, then you actually check for replicability, meaning that same set of conditions are given to other scientists, which helps you ascertain whether a given measurement is replicable and followed that you are able to see the similar measurement can be made reproducible with an alternative technique. Thank you