Quantitative Methods in Chemistry
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Lecture-29
Standards And Volumetric/Gravimetric Titrations Part 01

Yeah, welcome back to week 8 of this course quantitative methods in chemistry. This week we will be covering the topics related to the concept of standards, primary and secondary standards internal and external standards. And then we will focus on understanding the practical and theoretical concepts related to various titrations basically volumetric and gravimetric titrations where pH or any property undergoes change as an analyte or a reagent is added.

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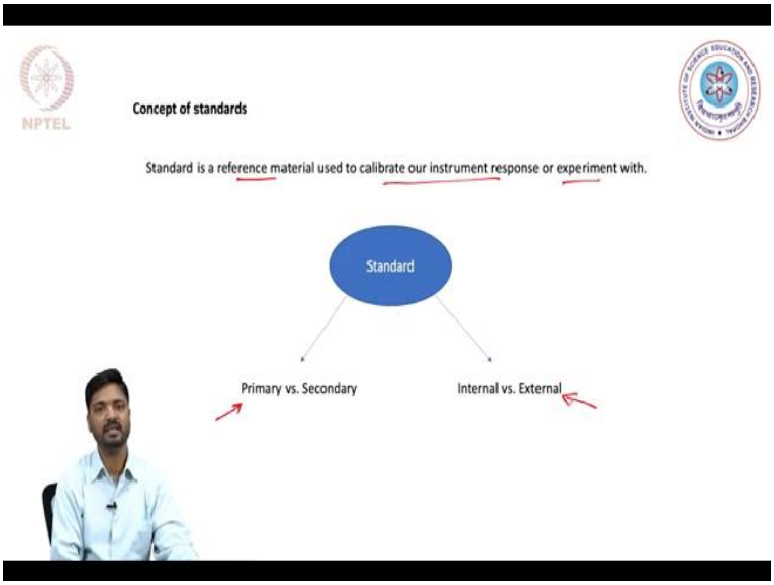

So, let us get ahead with the concept of standards. So, standard is any reference material that is used to calibrate our instrument response or the experiment with. So it is some sort of a reference standard reference material that we use. So, this standard can be of 2 types, we can consider standard as a primary standard or a secondary standard. Similarly, a standard can be internal or external based on whether it is present within the sample or is externally employed.

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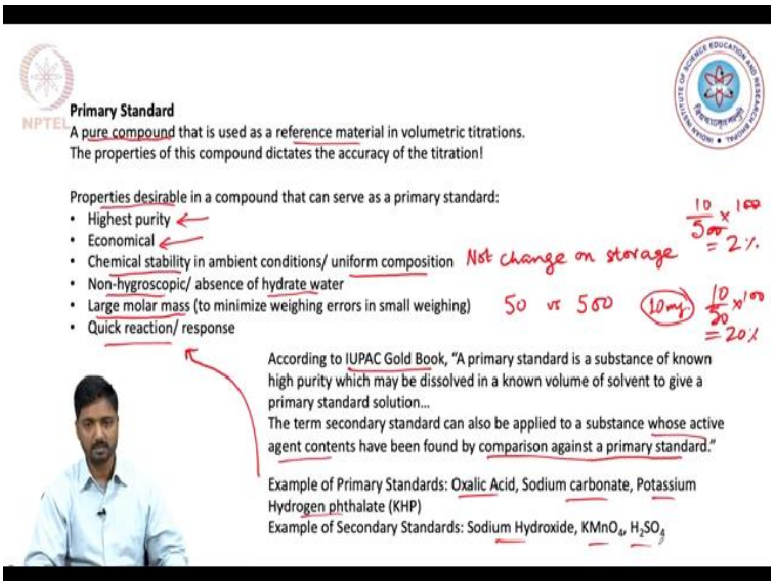

So, let us quickly understand what is a primary standard. A primary standard is a pure compound. So, obviously a standard has to be pure compound or a compound of high purity and it is used as a reference material in volumetric titrations or any analysis and the properties of this compound, the primary standard dictates the accuracy of our titration. So, we would want our primary standard to have certain desirable properties and what are these desirable properties.

So, this compound should be available in highest purity, this goes without saying and of course, for practical considerations, it should be available economically, it should be not very costly, so that we can continue using it regularly. And another important aspect with regards to practical utilization of primary standards is their chemical stability under ambient conditions. So, what we want specifically in our primary standards is that they should have a uniform composition.

And this composition should not change upon storage. So, let me mention that. Now, one way through which this can be done is to have the primary standard which is non hygroscopic and in which the hydrate water is not present, because as you can think that any hygroscopic material for example, sodium hydroxide or sulfuric acid will absorb moisture from the atmosphere and will undergo changes in it is composition.

Similarly, the hydrate present in many of the salts will either get decomposed or undergo changes, which are not considered good for a primary standard. Now, one more practical

requirement for good primary standard is that they should have a large molar mass. So, this is required in order to minimize any weighing errors when we are weighing small samples of this primary standard.

So, for example, if we have primary standard which has a molar mass of 50 versus another primary standard which has a molar mass of 500 and we are weighing it on a balance which has say least count of 10 mg, then if we are weighing 50 mg on balance of least count of 10 mg, then we are under going about 110 by 50 into 100 is equal to 20% error. Now, that is a large error, but if the same or if a different primary standard has the same mass as 500 then we see that the error reduces to only 2%.

Now, of course, when we are undertaking titrations we would want that our primary standard undergoes a quick reaction, or the response that it generates is very rapid. Now based on these criteria, the IUPAC gold book has come up with a definition of a primary standard. And it says that a primary standard is a substance of known high purity, which may be dissolved in a known volume of solvent to give a primary standard solution.

And this solution is what we will use in our titrations. The term secondary standard according to the same IUPAC gold book can be applied to a substance whose active agent contents have been found by comparison against a primary standard. So, for a secondary standard, we need to utilize a primary standard for making a standard solution. What are the examples of primary standard oxalic acid, sodium carbonate, potassium hydrogen phthalate.

These are 3 examples of chemical compounds, which are considered primary standards based on the properties that we have and listed here. And similarly, secondary standards are compounds such as sodium hydroxide, potassium permanganate, or sulfuric acid for the reasons that were enlisted in our previous discussion, mainly these compounds are either hygroscopic or undergo compositional changes upon storage, which implies that they cannot be used as primary standards.

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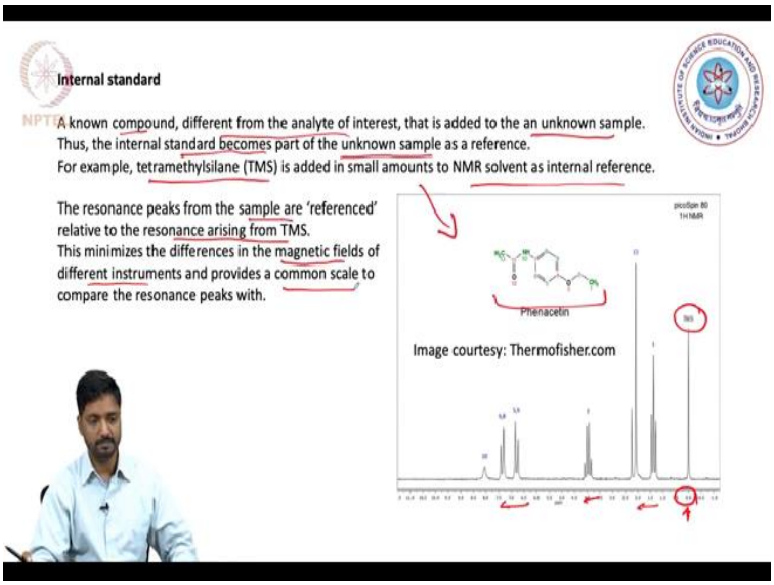

Now, let us look at what do we mean by an internal standard. An internal standard is a known compound. It is different from the analyte of our interest and it is added to an unknown sample as a reference material. So, in other words, the internal standard becomes part of the unknown sample as reference. A very common example for an internal standard is the tetramethylsilane which is abbreviated as TMS, which is added in small amounts to NMR solvent as internal reference.

For example, this is the NMR spectrum of this particular compound. And you can see the TMS peak is shown here at position of 0.0. So, the resonance peak from the sample are referenced relative to the resonance arising from the TMS internal standard. So, the TMS internal standard is set as reference value of 0 and all the peaks of the sample are referenced relative to it. So, why this is to be done, this is to be done because this process minimizes the differences in the magnetic fields of different instruments. And it provides a common scale to compare the resonance peaks with.

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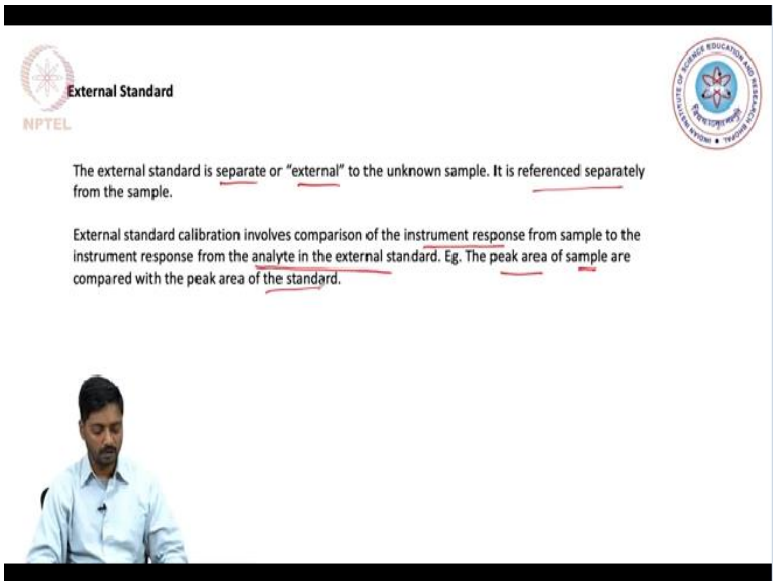

Now, opposite to that would be an external standard, which is separate or external to the unknown sample. So, the external standard is referenced separately from the unknown sample and the external standard calibration involves comparison of the instrument response from sample to the instrument response from the analyte in the external sample and for example, a very simple way through which this is done is to compare the peak areas of the sample with that of the standard. Now, whenever we are comparing 2 peaks or 2 responses.

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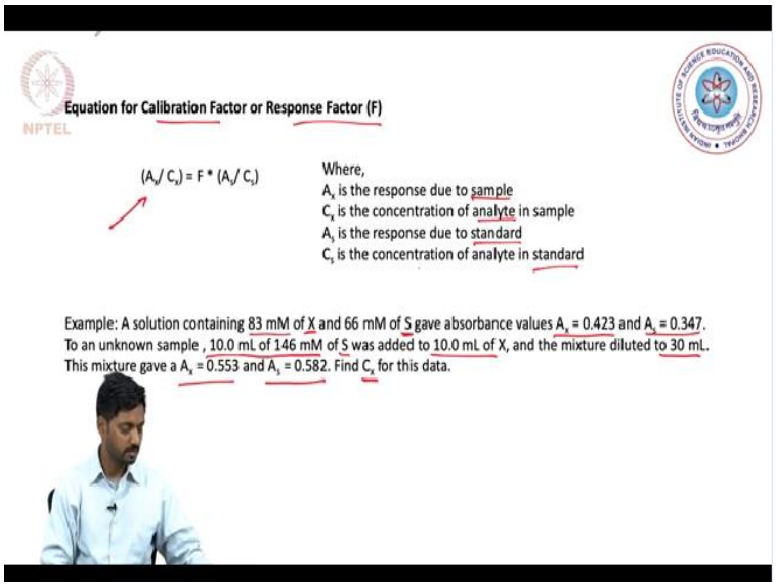

We need to consider what is known as a calibration factor or a response factor F and this is given by the equation shown here. So, what we have is the A x as the instrument response due to the sample and C x is the concentration of the analyte in the sample. Similarly, A s the subscript s

corresponds to the standard. So, A s is the response due to the standard and C s is the concentration of analyte in the standard.

So, based on this, we will now solve an example, where we are told that a sample containing 83 millimoles of an unknown compound X and 66 millimoles of the standard gives absorbance values of A x as 0.423 and A s coming from the standard as 0.34 sample. Now, to an unknown sample we add 10 ml of 146 millimolar of the standard and this was added to 10 ml of unknown sample X.

And this mixture was finally diluted 3 times to a final volume of 30 ml and when this sample was analyzed, now we have added a standard to it, it gives the absorbance value due to the analyte in the sample as 0.553 and due to the standard as 0.582. Based on this data, we need to find out what is the concentration of the analyte in the unknown sample. So, let us quickly go to the board and try to solve this okay.

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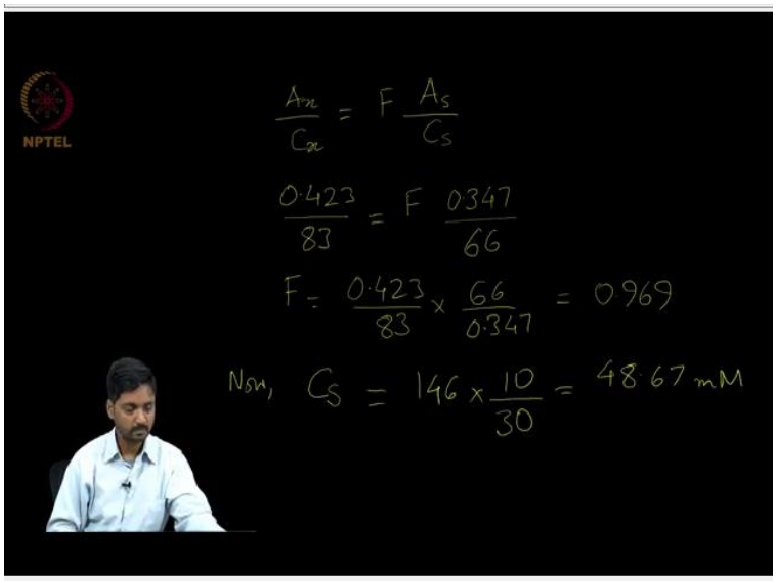

So, what we are given is that A x by C x is equal to the response factor into absorbance due to the standard divided by the concentration of the standard. And in the initial phase we are given that A x = 0.423, and when the concentration is 83 millimoles. And we do not know at this point the F value, so that is what we will calculate the absorbance due to the standard was coming as 0.347. And the concentration of the standard was 66 millimoles.

So when we solve this out, we get an F value of 0.423 divided by 83 into 66 divided by 0.347. And this ultimately solves out to be 0.969. Now in the next step, we had the concentration of the standard as 146 millimoles of 10 ml finally diluted to 30 ml and this turns out to be 48.67 millimoles.

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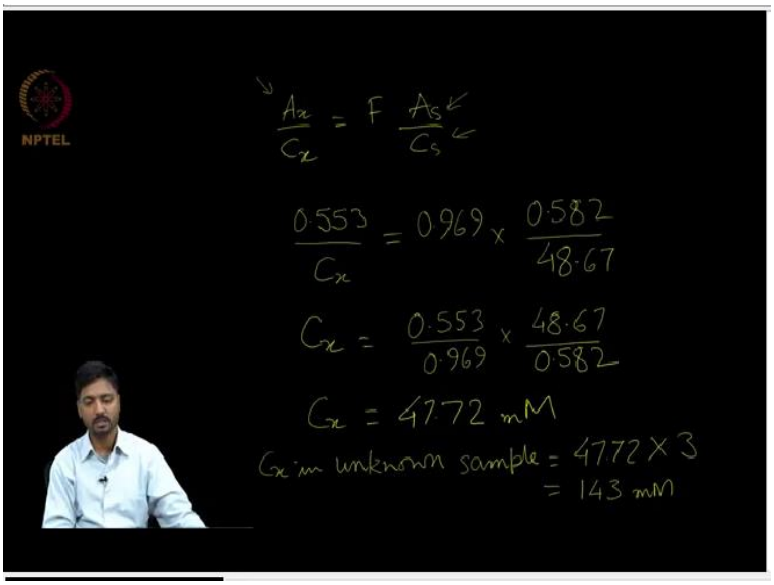

And we have A x by C x = F A s by C s, now we know the F value, we know the A x value, and we know the A s and the C s value. So we can plug in those values to find out what is the C x value, let us do that quickly. So the absorbance due to the sample was 0.553. At this moment, we do not know the concentration of the sample in this 30 ml volume. And the response factor was 0.969. And the absorbance coming from the standard was 0.582.

And the concentration of the standard that we just calculated was 48.67 millimoles. Now when we resolve this out, we get this. And finally, when we solve this out, this turns out to be C x = 47.72 millimoles. Now, this is the concentration of the sample which was diluted 3 times that is from 10 ml to 30 ml. So the actual concentration in the unknown sample is equal to 47.72 into 3 is equal to 143 million moles.

So, here we see how we have utilized the response of the signal coming from our standard and compare that with the response coming from an unknown sample to calculate the concentration of the analyte in the unknown sample. Now, let us go back to the presentation.

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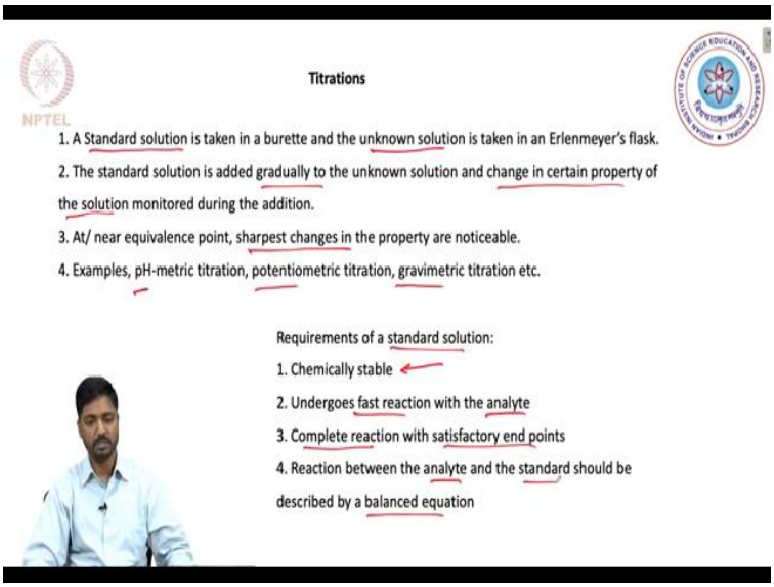

Start talking about titrations. So, as all of you must be aware that in a titration, what we need to do is to take a standard solution and that is added to an unknown solution which is taken in an Erlenmeyer's flask or conical flask and the standard solution is added gradually and the change in the property of the reaction mixture of the solution is monitored during this addition. And what is observed is that at or near the equivalence point, say the acid and base concentrations are similar.

We observe the sharpest changes in the property. And some of the properties that can be easily monitored are the pH of the sample or the potential of the sample or using the gravimetric titration. So, what are our requirements with regards to the standard solution, we want our standard solution obviously to be chemically stable in the conditions in which the iteration is being performed.

And we want a quick reaction or a fast reaction to happen between this kind of solution and the analyte of interest. For example, when we add acid and bases the reaction is generally very fast. So, this obviously becomes a very commonplace example of undertaking titrations. However, in

case the reaction is sluggish, for example, when we are taking weak acids or weak bases, sometimes heating may be utilized to accelerate the reaction between the analyte and the standard solution.

Now, we also need that the reaction between the analyte and the standard goes to a completion with satisfactory and points. That means, the reaction should be in some senses stoichiometric and we should have a clear end point and the end point should be noticeable through a change in property. And finally, we should have a balanced equation through which we can describe the reaction between the analyte and the standard.

Again, acid base reactions are the most straightforward examples of reactions where the analyte and the standard undergoes stoichiometric reaction, which can be explained by a balanced equation.