Quantitative Methods in Chemistry
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Lecture – 09
Introduction to Use Spread Sheets to Analyse Errors

Welcome to the last class in the second week of quantitative methods in chemistry, in this class we will be once again reiterating some points of what is significant figures, how to determine them and use some computational tools to understand what is reproducibility, why should somebody repeat the experiment and topics of that sort.

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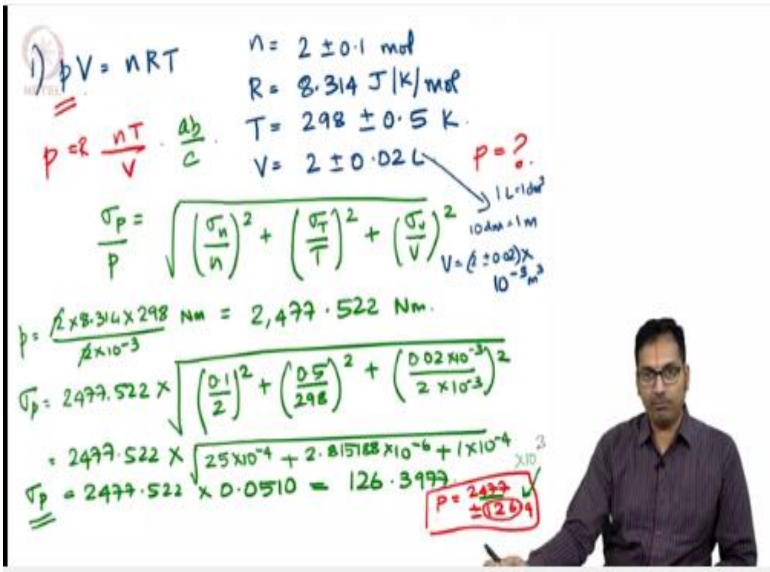

To start with last week, we solved a problem, where we try to use the ideal gas equation with the variables given for the ideal gas equation with varying level of standard deviations and we did spend some time calculating and there is a small error here, the whole answer should be multiplied by with 10 power 3 anyways, let us take a relook at the same problem but instead of using our tools of writing it stepwise, why do not we take a quick look at how software could be useful in this regard.

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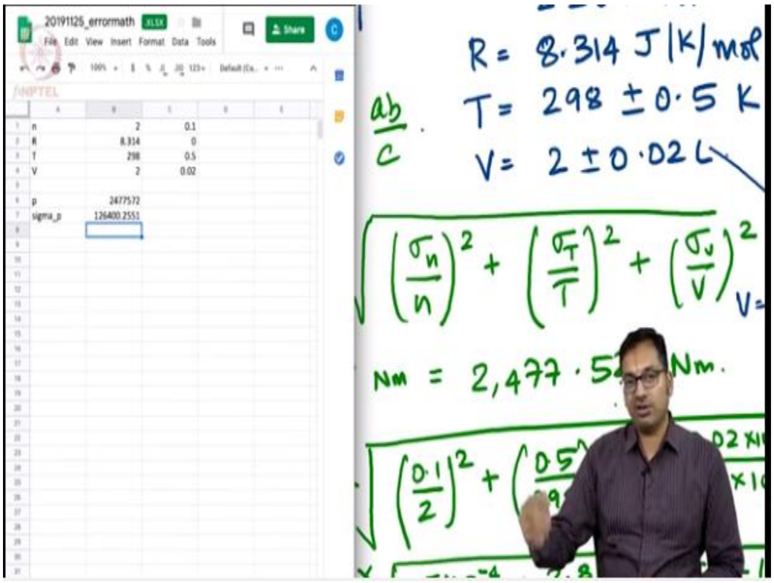

So, what I am going to be end up doing today is to show you how to do the same maths, so let us have the problem properly defined, the number of moles n here is given as 2 plus minus 0.1, you might ask how can the number of moles be a non-integer number, here we are trying to say maybe the precision at which you measure the mass or any other parameter like pressure induces the error in it.

Let us assume that there is no error involved with the measurement or the constant that we use for universal gas constant, the temperature is at 298 Kelvin plus minus 0.5 Kelvin and the volume is 2 litres and that has an error of 0.02. So, then we want to find what is pressure and let us say pressure here now, can be calculated by the product of n times R times T divided by the volume.

But of course, we have to convert the volume into SI units as we just realised last time, 1 litre is 10 to power - 3 meter cube so, this is going to be to the power of - 3 meter cube, so the volume here comes up in SI units as we did figure out last time, the pressure was founded to be 2477.522 but in reality is actually, we have missed the 10 power 3, so therefore the answer turns out to be 2477.572 basically order; 3 orders of magnitude higher, okay.

Now that we determine this, why do not we redo the formula to find what is sigma p, where sigma p is the error involved in such a measurement as we are able to see N, R and T and V are all either multiplied or divided, we remember the formula as written in the as shown here that it is nothing but the square root of sum of squares of the ratios between the deviation to the actual value.

So, in this case what is going to end up happening; this is going to be the deviation on N divided by the actual value square plus deviation on R is going to be 0, so therefore we are not going to be putting that N square plus deviation on V, one might always ask why is that we are not including the 10 power 3, you are going to have the 10 power 3 in the numerator and the denominator, so that is going to get cancelled out.

Now, the square root has been taken this times product where the value of the pressure itself, so what you end up getting is exactly the same thing that we got last time of course, with the 10 power 3 because we missed the 10 power 3. So, one thing that you are able to realize is how to use software to make your work easier.

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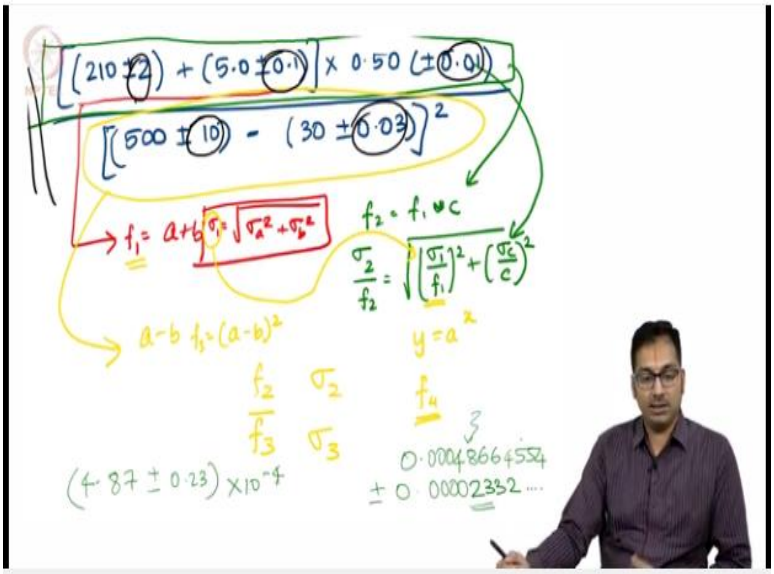

So, similarly we also asked a more difficult question and the question here was what is the error involved in a measurement that has multiple variables that go together in this fashion? So, I am going to write all of this; 210 plus minus 2 so, 210 plus minus 2, 5 plus minus 0.1 0.5 plus minus 0.01, then you have 500 plus minus 10 and 30 plus minus 0.03. So, in this case you are able to realize we can calculate this step wise where we said F1 is nothing thing but the sum of these 2.

So, let us calculate that really quickly, so F1 is going to be given by sum of 210 to 5 with their error, so let us calculate what it is so, F1 is going to be 210 + 5, however the error on it is going to be given by square root of squares of the standard deviations, there you go so, this becomes 215 plus minus 2, okay. Now, you are multiplying that with 0.5, so what is that going to be?

This is going to be equal to star 0.5, this is the actual value but the standard deviation since it is a product is going to be given by the square root of variation of F1 to the original value square plus the variation of the measuring value 0.5 which is 0.01 square root times the value by itself. So, what do you end up getting; you get 107.5 plus minus 2.4, alright. So, now those 2 are done, the next thing that we need to calculate is the denominator.

And the denominator is what we called as F3 right in the last class so, F3 is going to be given by 500 – 30, so that is going to be equal to 500 - 30 okay, of course the error here is going to be square root of the deviation and 500 plus their of square of the deviation in 30, okay so that becomes 470 plus minus 10 and I would like to remind you, you need to have an F3 square.

So that is going to be nothing but square of this value and if you might remember, if Y is equal to a power a power n, then sigma y will be given by n times a power n - 1 times sigma a, this we derived in one of the earlier classes, so I am going to end up using this here n is equal to 2. So, this is nothing but 2 times a that a is this, times the deviation in a, so what you are able to realize is that now this variable comes with the quite an amount of uncertainty.

Now, the final thing that you would like to calculate is nothing but f2 divided by the square of f3, so the reason why we are doing this in this class is that although, I gave this problem in the previous class, you should understand that doing this arithmetic in by paper and pencil could get difficult, so we are making use of computers, so that to make our process easier. So, what is this going to be; this is going to be equal to f2 divided by square of this, so that is the actual value.

But now let us take a look at the error, one must understand it is a division, so therefore it goes back to square root of the error involved in f2 divided by the actual value itself the whole square plus the error involved and f3 divided by the; f3 square divided by the actual value of f3 square the whole square times the actual value. So, what you end up getting here, let me make a note of this.

So, now what you see here is that after all this arithmetic, you end up getting something like this and we are able to realize the uncertainty comes in this given value because these 2 digits are what is uncertain. So, the final answer for this problem would be 4.86 actually, you can actually write it as 4.87 plus minus 0.23 times 10 power – 4. So, once again what I have shown you is to use arithmetic.

But instead of us doing it in the calculator, we make use of a spread sheet to do this and we are going to see how we are going to exploit such a feature of computers as we go forward in this course, okay. Now, that those 2 are done, let me quickly also review the concepts that we learnt in significant figures. So, there are some rules that go with it although, I did not enunciate it in this class, I will try to say those rules out clear.

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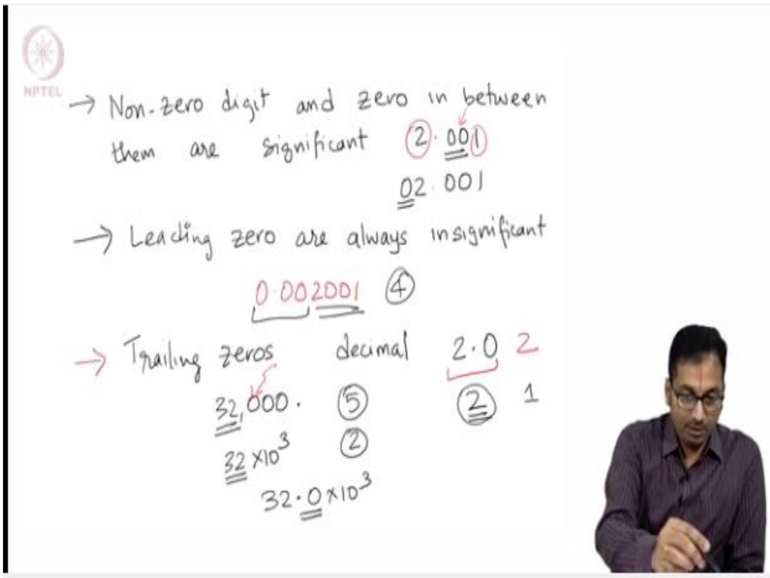

Any non-zero digit and 0’s in between them are significant this just means that if you are having something like 2.001, these 0’s are indeed significant but on the other hand, this 0; the leading 0, it is not going to be significant, so that is our next point of course, let me reiterate the first point. These 2 are non-zero digits and 0’s in between them are indeed significant and any number, so let us talk about leading 0’s.

Leading zeros are always insignificant, so what do I mean by that is that let us take an example, let us say we have 0.002001, in this case these 0’s are not significant and these 4 digits are significant, so this still reminds us something like this. Now, let us ask about trailing zeros, so one has to be a little careful here, let us say there is a decimal point involved.

So, let us say we are talking 2.0 and if this is given as 2.0, then this has 2 significant figures, on the other hand if somebody just writes us 2, this indicates that this number itself is significant or rather the insignificance or the variability in uncertainty comes from that value itself of course, there are times where this could be ambiguous, let us say we write a number 32,000.

Now, how many of these are significant so, this is a little tricky to determine, this could be ambiguous as well, if somebody puts a decimal point here definitely, 5 digits are significant but on the other hand, let us say there is no dot here, it could be that only 2 values are significant in which case people generally, write this as 32 into 10 to the power of 3, in scientific notation indicating that the error comes up here itself.

On the other hand, let us say the in significance comes from this value, then people would end up writing the same number as 32.0 into 10 to the power of 3, this indicates the uncertainty comes from this so, this is the scientific notation we end up using and if you realize in the previous example that we saw that is the kind of notation we ended up using where we realize, there are a lot of digits that come here but how many digits make sense depends upon the level of uncertainty that you get.

And here we are able to realize that uncertainty comes here, so we tend to give one more value that comes after that and we say this is the level of uncertainty, alright.

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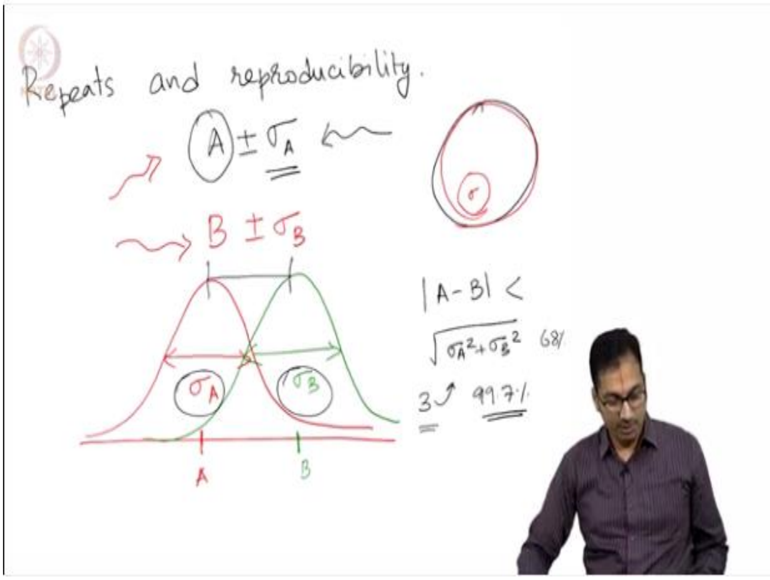

So, now that these 2 are done, let us get to the next topic of repeats and reproducibility, this is important because we keep saying that in a measurement, a person gets a certain value and if this is repeated enough let us say, we take a parameter A and then if a person repeats it enough, we are going to get something like the standard deviation and this is important because one is able to realize what is the level of uncertainty associated with that given variable.

Now, we are able to realize that we are talking about standard deviation here but remember, standard deviation could be population or sample standard deviation meaning that population standard deviation means taking the variance across every possible entity in the population versus the sample standard deviation where you have a given set of values that could be obtained but you take a small sample set to get your standard deviation.

So, these 2 could be slightly different and of course, when the sampling size goes to the entire population you tend to see the truth that comes out of the uncertainty in a measurement. So, now that you have taken something like this, let us assume that the same thing was repeated couple of times and you had the luxury of only taking the sample standard deviation in terms of sigma A and sigma B.

So, now what ends up happening the first question that comes is okay are A and B similar, so I want you to remember every time we talk about a variable and its standard deviation, the first thing that should come to your mind is the Gaussian distribution that comes up. So, in this case, this is A with the width given by sigma A and let us say, B that is given with a width sigma B and this is its average.

So, now the question is; how far are these 2 peaks in comparison to the standard deviations that come up and depending upon that, we will be ascertaining the fact whether A and B that were measured for the same parameter are agreeing or not. So, in this case when you have a mod A - mod B that is less than sum of squares of sigma A squared + sigma B square, this is within one standard deviation remember that.

Then you would say, A and B measurements agree with each other but you could always have a case where you have 3 times this product, even then that could be the case what happens when you are trying to look for 99.7% of the data points inclusive of course, if you are using only single standard deviation, you are only taking into account 68% of the points that might come up when queried upon, okay.

So, now that we understand why do not we do a quick simulation to understand how repeats matter, so to do this I am going to take you to a very quick small simulation?

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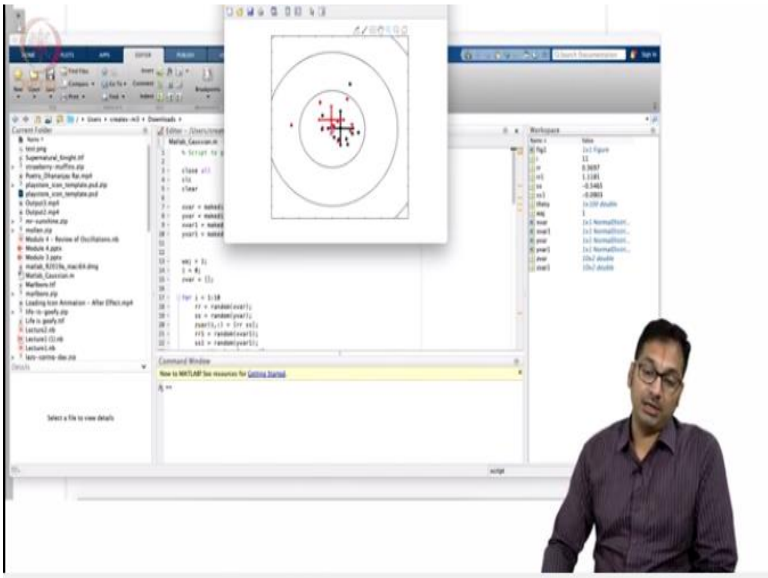

You have seen a similar kind of simulation before, this is the same simulation done when we were thinking about the dartboard where you are trying to have the air ways that get in so, let us quickly redo that simulation, so that we understand what we are talking about and recollect our the past that we have spoken about. So, basically this was the example that we were trying to take.

Here, I am trying to emphasize the same example with 2 different measurements; one in black and the other in red but you are able to realize here there is a distribution of values that come up and if this distribution falls on top of each other, then both these measurements agree with each other. In the dartboard, we took the example of hitting the centre of the dartboard and you realize that almost all the points in black and red are going on top of each other.

Of course, this in this simulation we used about 1,000 points, let us see what happens if you keep reducing the number of points, here we are using just 100 points now, you start to see a spirit that comes up and you are able to realize that all those simulation is just repeated with the same normal distribution you see that the red and the black do not fall on top of each other and this is for 100 points.

Let us try to reduce it another order of magnitude here, for this measurement you are just doing it 10 times to repeat in 2 possible ways, so what you are able to see here the average of the black dots; the average and standard deviation is given by the cross hair in black and the average and standard deviation for the red is given as in the cross hair in red and once again, as we are able to see not all black and red dots fall on top of each other.

In fact, if you pay close attention, none of the dots fall on top of each other, however the measurement of red and the black, the average; the both the black and the red points are close enough such that the standard deviation of each of this measurement already agrees with these 2 measurement. What do I say, what do I mean by this? Is that A minus B let us say red minus black, the average of red minus black is less than the standard deviation of square root of the black and red put together.

And you are able to realize that they are within the error, so therefore you can say both are measuring the same thing, meaning that the red and the black values agree with each other and one important aspect that you must observe here is that there are still data points that fall outside this single standard deviation, this should not be a point of concern because we are just plotting one standard deviation.

If you go to 3 standard deviation, I am pretty sure you are able to realize that this will fall within the measurement and of course, do not be flustered if you are having still one data point that falls outside 3 standard deviations because it could be belonging to the 0.7% of the population although, less likely to happen, it could happen depending upon the experimental setup.

However, the only way to determine that is doing more repeats but one is able to understand is that as the number of data points start to go lower and lower, you realize that the spread could be anywhere. Let me repeat the same simulation again without changing any parameters for 10 data points, you start to see the spread is changing. So, this spread depends upon the experiment that you are doing at that given point of time.

So, this is why repeats are important meaning that if you repeat the same experiment multiple number of times, the average and standard deviation could slightly differ but overall, the measurements that you have done should go on top of each other, so this is an important aspect called repeatability. So, what is repeatability? When the same experiment is performed by the same researcher using the same setup and within a very short interval of time, you should have the variables that agree with each other.

This is one example that we are able to see that does come up in such a fashion okay, so but let me go ahead and try to reduce this even further, let us say you do not have the luxury to measure 10 times and you can just measure it 2 times, so let us zoom in and what you are able to realize, the pink dot is actually the centre of the dartboard and you are able to realise the 2 measurements that you did in red and black are quite different from each other.

And you start to realize, it is possible that the red and black are not on top of each other and this is a very important observation to make although, it was exactly the same measurement and done by the same person, you are able to realize 2 different things come up, this could be because of the fact that this student did it in 2 different days but does this mean the answer is different.

So, this could be very tricky and which is why people keep on saying try to have as many data points as possible, so let me repeat it with the same distribution but with 4 data points. Now, what ends up happening; let us zoom in again, what you are able to realize along the vertical axis, the 2 measurements agree and along the horizontal axis as well the experiment start to agree.

This is an important point once again to emphasize the point how when you add more and more data points, you will be able to measure something more meaningful, so let us repeat the simulation again to so that you are able to appreciate the fact that not always, so this is an exaggerated simulation where you are able to realize only along one of the axis, the data points agree with each other, that is along the horizontal axis they agree with each other.

But along the vertical axis, you are clearly able to realize they do not agree with each other and interestingly enough, the red value at least goes close to the centre of the dartboard while the black does not, okay, this is a very, very important conclusion. So, let us try to increase it to 10 and see what happens.

Here, you start to realize that both are indeed getting to the average and the spread across the average does encompass the centre of the dartboard, making you understand if that is the true value the both measurements kind of agree with each other.

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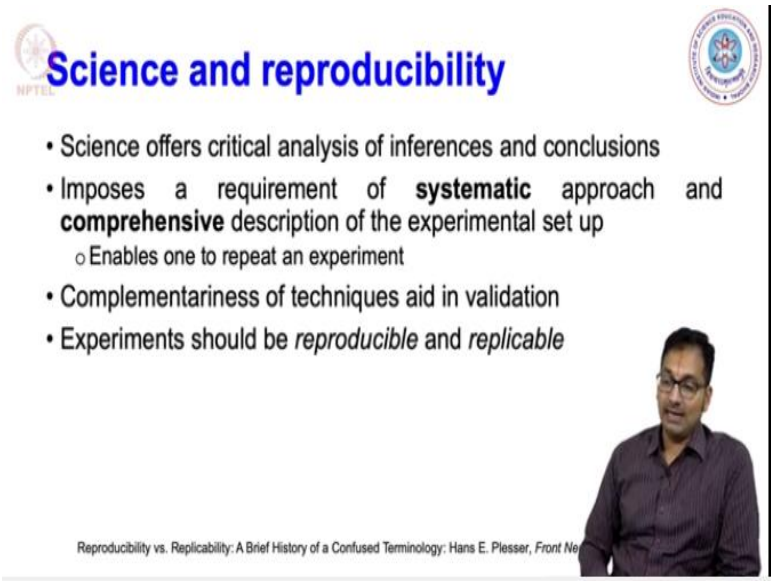

So, now let us actually go towards understanding what these different variables are so, let us reiterate some of the definitions which we did, remember we said science is nothing but building hypotheses based on observations and these observations are made out of coherent experiments that are set up to understand one thing or the other so basically, this the same thing we are trying to repeat here.

Science offers critical analysis of influences and conclusions this means, that when a person writes an inference based on a measurement that has been made, we can do a critical analysis by repeating to make sure things are okay and the conclusions that are drawn on such analysis could also be tested and such an analysis imposes that one should have a systematic approach and must comprehensively describe the experimental setup.

What do we mean by a systematic approach; meaning that you should build up your experiments such that the ones that are going to vary the most are the first ones that are varied and probably, the only ones varied you should not be varying multiple parameters at the same time. On the other hand, a comprehensive description of the experimental procedures is important.

Meaning that if you are setting up an experiment, every small detail or what is a temperature, what is the pH that you are setting it in, what is the ionic strength and all these parameters should be carefully documented, so that when somebody wants to repeat this experiment, this can be done and most importantly, in order to validate we would require complementariness of the techniques used.

For instance, let us say you made a measurement through a liquid chromatography and if you are able to make a similar study based on some other technic let us say, fluorescence spectroscopy or NMR spectroscopy and you are able to make the same conclusion, this helps in validation; meaning that the data is obtained with the different technique but does represent the truth or the truth that is very close enough in these 2 methodologies.

And this all takes us to the fact that experiments should be reproducible and can be replicated so, we will go into closer details of what this is.

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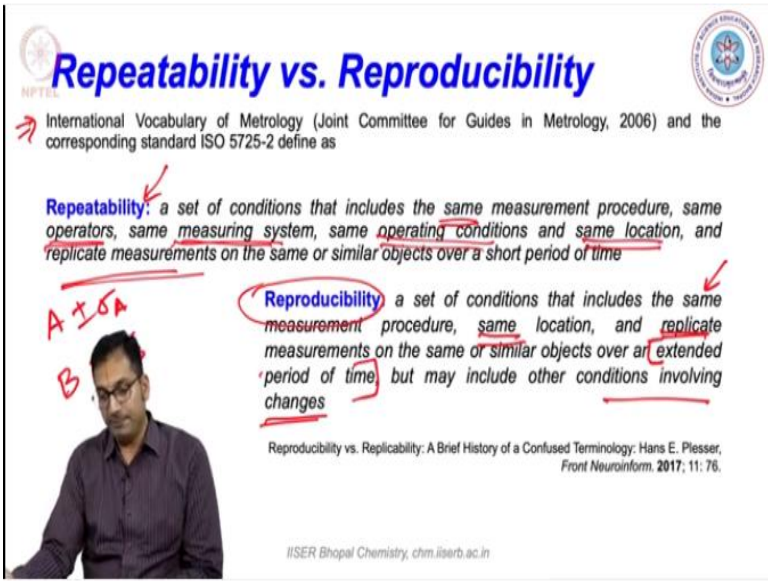

And this has been defined by various committees in this case, it is the International vocabulary of metrology and by this what do they mean by repeatability; is that repeatability a set of conditions that includes the same measurement, same operators meaning that the same kind of person doing it and same measurement system.

Meaning that if you are taking a certain weighing balance, you take the same weighing balance, the same operating conditions in terms of temperature, pressure, pH, ionic strength, the same location meaning that you do it in the exact same laboratory that you do it and replicate measurements so, this is essentially what they are trying to mean; meaning that if you keep repeating with everything remaining same how much variability comes into place.

On the other hand, reproducibility is defined by the fact that the same measurement procedure is done in the same location in the replicate measurements or similar objects over an extended period of time, so this has to be noted, meaning that one repeats it over a period of time with the exact same setup but may include other conditions involving changes. Meaning that you performed it at a time where temperatures could be slightly different.

But you still maintaining the temperature and things of that sort so, let us say some small deviations come up and still if we are able to measure A and B, which agree with in their given values, then you tend to say this is reproducible.

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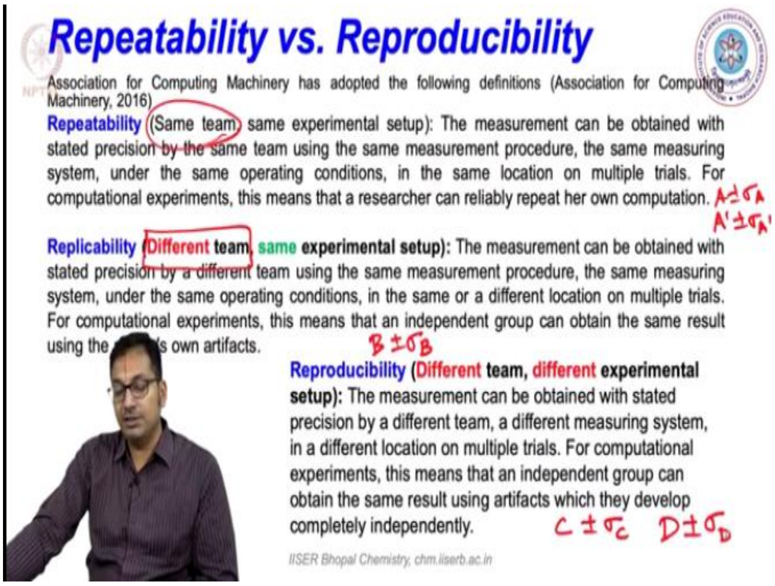

A similar rigorous definition is also given in by the computing machinery, where the repeatability is the same definition as we gave before that is the measurement can be obtained with stated precision; precision here is uncertainty during the measurement by the same team using the same measurement technique, using the same measuring system under the same operating condition in the same location on multiple trials.

Meaning that the same person repeats at the same time, multiple times and you get something like an average and standard deviation on the other hand, repeatability is one where different team does the experiment but under the same experimental conditions as above, okay. So, in the previous case as the same team that repeats at under same setup but here a different team repeats it with exactly the same setup.

And let us say they measure B plus minus sigma B, on the other hand reproducibility is one where the team is different and the experimental procedure also can be different, meaning that as I gave an example previously, let us say you do something with liquid chromatography and try to replicate it let us say with NMR or fluorescence spectroscopy.

So, then what ends up happening is that now, you measure this C with a certain precision, then you tend to say you compare A with B and A and B agree with each other, then it means that you are able to replicate the measurements of course, A when repeated with another measurement say, A prime within the same lab which has a certain deviation and A and A prime agree with each other you say, that the measurements are repeatable.

If A and B agree with each other and A prime and B prime agree with each other, this means that the data is replicable, on the other hand if you are using a different team using different experimental parameters and measures C and C agrees with A and B, then it means that the measurement is reproducible, okay. Now that we have understood what is repeatability, replicability and reproducibility.

Let us take some examples to understand the same, I was just giving you an idea; if A plus minus sigma A is obtained and the same team repeats and they get A prime plus minus sigma A prime, then when do you say these replicates; this repeats are okay, is when these 2 values agree with each other. Let us take a scenario when they do not agree with each other, what problems could that be?

It could be the problem that the team; the second team or the first team that is doing it; is doing it and slightly different procedure although, they think that they are doing with the same way but it could also be the case that the experimental setup is changing and they have to pay closer attention to it and have better details that would help them repeat the experiment by themselves.

This is a very important step because without this, one cannot be sure of the experiments or the results that they have obtained. On the other hand, let us say that the replicability that we get as B plus minus sigma B, let us say that A and B agree with each other of course, then you say the experiments and the results are replicable but on the other hand, let us say they do not agree with each other.

Now, what is clearly happening is probably, the protocol that has been shared across these different teams are; is not enough, so that they are able to replicate these measurements and this could happen in science often because when somebody writes a paper, the amount of details that goes into materials and methods matter a lot, this is why people want to give as much information with high level of precision.

So, that mistakes happen less and on the other hand, let us say a team tried to reproduce it with another complementary experiment and let us say A and C do not agree with each other, this could be the case where when you measure A from a certain experiment, I mean you measure C from the other experiment, these 2 experiments are seeing something different altogether, this is not new in science.

This happens quite often not because of errors but just that sometimes, experiments and the technology views could be phenomenologically different. So, what do I mean by that? Let us say, let us take an example of a certain molecule that you wanted to study and you wanted to understand the structure, you solve the crystal structure and you study it in solution with NMR, it could happen many times that the solution state structure and the crystal structure are different from each other.

This is not surprising because it could be that the crystal structure had some crystal packing forces that took it to that given structure while an NMR, it is flexible enough where you are able to see that structure but in addition you see other structures that go with each other, this is per se not a problem but helps you understand what information is obtained in different let us say time scales are in different conditions.

And this just enhances the understanding, what third complementary technique which will help us measure the same thing with D sigma plus minus sigma D would help you put both together, so basically the complementariness of the experiment is exploited to see and validate theories that exist on the other hand also, get information in under different conditions which once again help us refine our system and better our understanding further, with this we stop and we will be trying to solve some examples in the assignment to understand this further, thank you.