Course on Analytical Chemistry
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Module 7
Lecture No 31
Thermal Methods of Analysis - I

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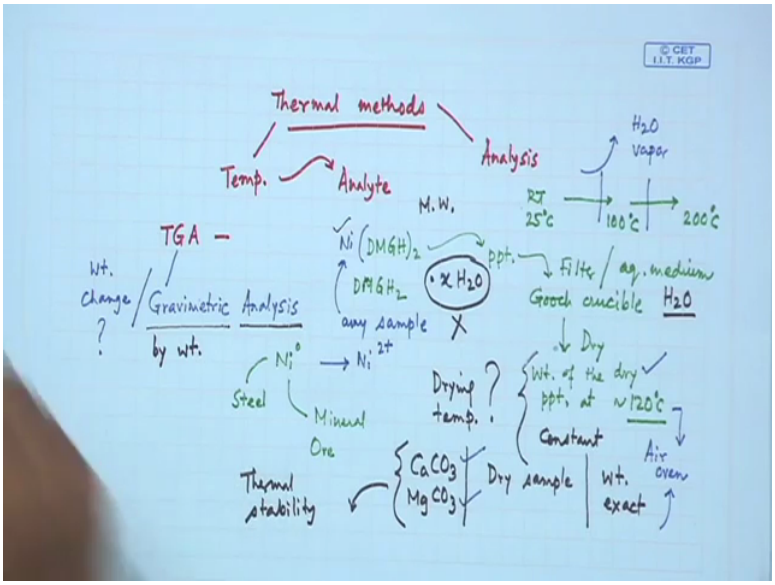

Hello and welcome to this class of thermal analysis in this lecture 31 of week 7 what will just want to say is the thermal methods and obviously those will be different thermal methods that means we will see the temperature effect on the sample or the analyte to change (sun) certain properties such that we can have some ideas about the physical properties as well as chemical properties for our required analysis it is a very useful technique.

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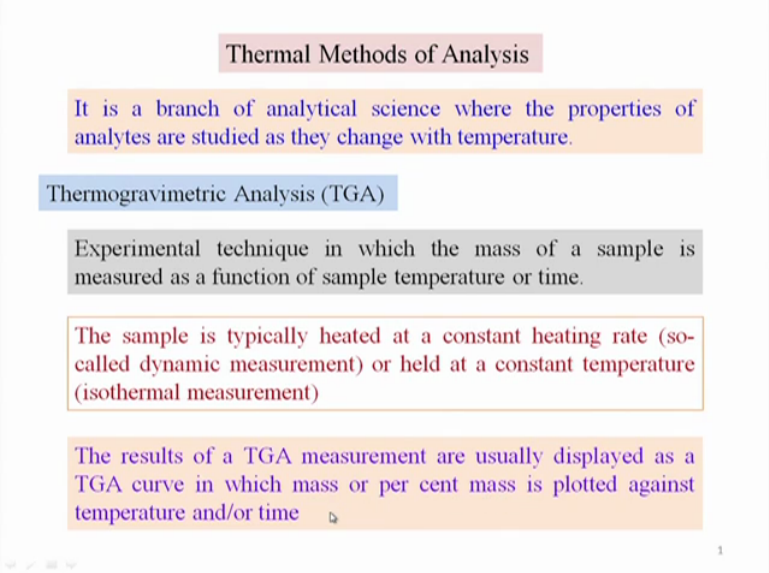

So these thermal methods of analysis can be very useful, why? Is a branch of analytical science basically, people mostly used for the different types of material characterisation, sample characterisation and also the quantitative analysis. So where the properties of analyte so any number of analyte you can handle and study as they change its temperature, if we find that some property can be changed with regard to the temperature that means certain materials is tabled say up to 100 degree centigrade but it can change or it changes above 100 degree centigrade, so the reaction what is happening over there at the particular temperature or the transformed products we can see on this sort of analysis.

So one is such example is Thermogravimetric analysis or thermalgravimetric analysis we call as is abbreviated as TGA. As we all know by now that what is a typical gravimetric analysis and the most well-known and well-studied example of gravimetric analysis we all know which is the corresponding nickel analysis and as I told you earlier nickel from any sample where this nickel is presented as nickel divalent cation that can be taken away from nickel in the metallic state such as from the steel sample or any other source such as a nickel containing mineral or ore.

So what we do there for simple gravimetric analysis is that we use Dimethylglyoxime as the corresponding chiletting agent and we get some rose red color precipitate of Ni DMGH whole 2 and this will get as a precipitate, we filter it out on a gooch crucible and then we dry it to take the weight of the dry ppt or the precipitate at around 120 degree centigrade, so there is the idea about the corresponding introduction of literature so we are doing unknowingly we are doing the gravimetric analysis that means by weight gravimetric means by weight we are

doing some analysis and this particular weight of the precipitate which should be constant at this particular temperature that means it should not be hygroscopic and it should not be decomposed at this particular temperature.

So how do we know the precipitate where we can dry the precipitate to take it exact formula of this that means the formula weight is also important that means we have to use the molecule weight and the molecule weight will also tell you that that much sample will have on atomic weight of your nickel. So this constant weight of that corresponding precipitate you give us some idea that at 120 degree centigrade the precipitate is stable is will not decompose so we can find out the drying temperature.

So how do we find out the drying temperature? So any other material it can be your simple calcium carbonate or magnesium carbonate and we want to get the dry sample of it such that we can take the exact weight of those materials, so what we should concern about all these things is their thermal stability. So this thermal stability is a very important thing for all these cases and if we get this particular nickel DMG and if we try to heat it from room temperature say 25 degree centigrade and we keep on heating at 100 degree centigrade at 200 degree centigrade and this has been filtered out from aqua's medium.

So what was there we have trapped water molecules inside this precipitate, the rose red color precipitate has trapped water molecules, so we have to remove this water molecules initially when the precipitate was there some absorb water is there and is not initially you can have some water uhh crystallization and in this particular case we do not have any water crystallization present in this particular sample but that also we should know whether the precipitate is monohydrate or a dihydrate or a trihydrate where these water molecules are trapped inside the crystal lattice.

So if we can heat it up so this absorb water molecules, so absorb water molecules will go out around this 120 degree centigrade so at this particular temperature we can heat it and then we can keep the precipitate in air oven or we can do something that we heat it the air oven at this particular temperature and keep the precipitate that means we know that when we try the precipitate at this particular temperature the trapped water molecule as the absorbed water molecule will go out and will get the dry precipitate of these because we must have the corresponding exact weight of the precipitate which is dry precipitate.

So if uhh at this point if we get there so the thermal methods of analysis or the thermogravimetric analysis will tell us that if we use the property that means if we can measure the weight change with the rising in temperature along this axis say 25 to 100, 100 to 200 and beyond that whether they will be any weight change or not? And if you find that at this particular range which includes 120 degree centigrade that there is no weight change even for the moisture content of the material because when moisture is going out there will also be weight loss because the water vapor will come out and this water vapor definitely have some weight so there will be some weight loss.

So at this particular temperature range if we find that there is no such weight-loss so we can get that particular temperature as the drying temperature that particular precipitate. So any precipitate end number of precipitate we can have the corresponding drying temperature where we can dry the precipitate in air oven which is applicable to say calcium carbonate which is applicable to magnesium carbonate and many other samples even good materials like plastics and all.

So that is why we have the TGA that TGA analysis we call also the thermogravimetric analysis will be very much useful analysis where we can have a typical experimental technique because we will always think in such a way that when we talk in terms of the gravimetric analysis we must take the weight of the precipitate. So that means a balance is coming into the picture and we must have the corresponding analytical balance which can take the corresponding change in the weight for the mass precisely with the rising temperature.

So what we get that in which the mass of the sample is measured as a function of sample temperature or time. Either you monitor this the rising sample temperature, the mass loss or the sometimes you can also see that if we pull it in a reverse way there can be some mass gain also and if he heating rate of the furnace which is holding the sample over the balance is uhh synchronize with that of our temperature rise means the rate of change of temperature with time is synchronise you can also plot the thing against time instead of temperature.

So the sample or the analyte we can heat it at a constant heating rate that is very important that why we should use constant heating rate so called the dynamic measurement so we have a constant heating rate of say 5 degree centigrade per minutes or 10 degree centigrade per minute or otherwise held at a constant temperature that means isothermal measurement we can hold the sample as the uhh constant temperature so we can monitor also the temperature

rise in terms of the corresponding furnace temperature. So what we get as a result, so result definitely will be getting as a plot, so the results of a TGA measurements are easily displayed as a TGA curve.

So what we are monitoring? We are monitoring a property and the change of that property for any physical change or any chemical reaction, so there will be some curves what we get which mass or per cent mass is plotted against the temperature and or time or is as I told just now that you are temperature is synchronise with that of our time so we can get that thing.

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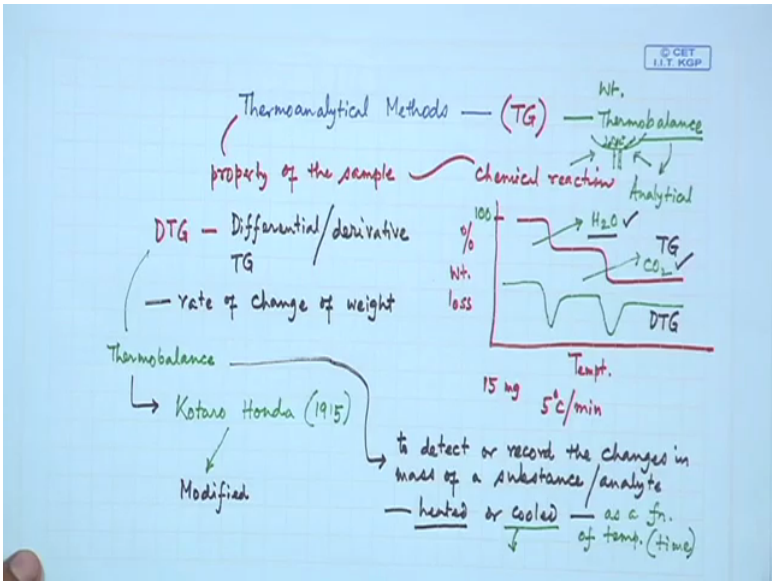

So in another way we can also call particular process as thermoanalytical methods also, so there are different thermal analytical methods we can have and we are just monitoring therefore the property of the sample or sometimes we can find also that we can monitor the temperature change also because a temperature change can also happened with that of our happening the chemical reaction.

So if there is a typical chemical reaction so we can find something that it is associated with sudden temperature change, so this particular analysis so your Tg analysis thermogravimetric analysis we can have and this particular one when we get it also will see that one more methodology which is if we plot this one that means the Tg plot so if the weight loss is like this so there are these are all stair case like plots.

So this is the corresponding weight loss and this is the axis and this is the temperature axis and this is the weight loss in percentage because we standardise it with respect to 100 percent when we start this particular measurement we find that we start from a 100% that means the

weight of the sample uhh weight of the sample say 15 milligram of the sample is taken and is heated as a 5 degree centigrade per minute rate. So this particular one can be synchronised in that way that you have 100% sample, 15 milligram sample will be your hundred uhh percent sample and then we find your uhh percent weight loss because that will immediately tell us what is going out from here and what is going from here as moisture or any other gas.

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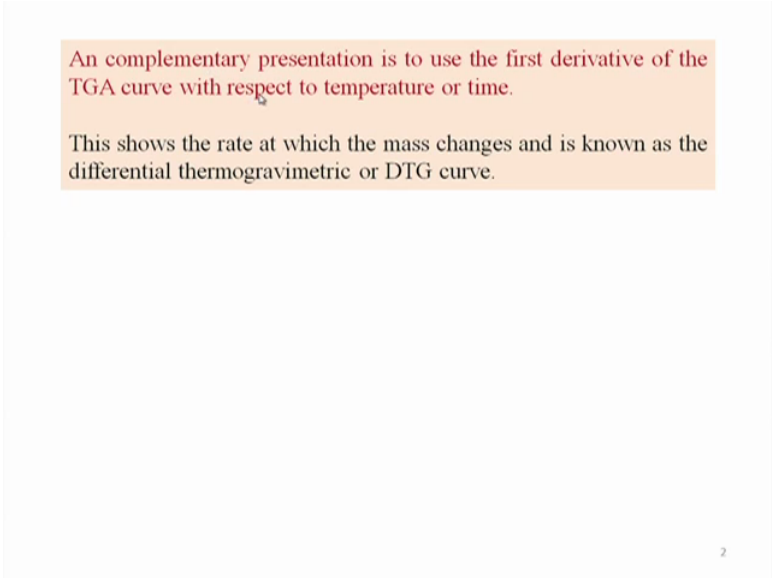

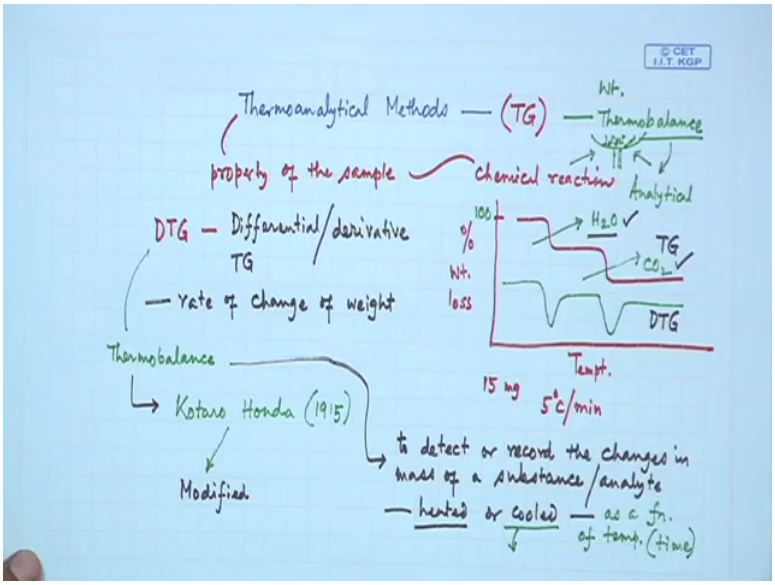

So this particular methodology for this analysis is a we get something which we call as a DTG curve so which is nothing but another form that means a complementary presentation for the corresponding first derivative of the TGA curve with respect to temperature or time. So if we get that so this is the different slots and if we just go for a corresponding first

derivative plot, so the first derivative plot will be like this and this is the corresponding Tg trace and this will be the corresponding DTG trace.

So in this particular DDG which we call as the differential or it is the derivative plot or a derivative plot for the thermogravimetric analysis, so differential thermogravimetric or derivative thermogravimetry where we monitor basically this is the corresponding monitoring of the rate of change of weight, rate of change of weight, so what we require in case of Tg was we are talking about the measurement that means the measuring of weight so we require a thermobalance.

So balance we all know and most of these balances we call is as the typical analytical balances and it can go for a very low weight change monitoring and when it is associated with something where the thermal change at means the sample where we keep the sample in the corresponding uhh sample holder that means the pan we consider because the sample pan we all know and that pan can be heated up that means it is within small furnace. So if we heat the pan where you have the sample on the pan, pan of the balance so and we can have some mechanism for monitoring the corresponding change in the particular weight due to that particular reaction or any other physical change so we require thermobalance for Tg as well as for DTG also we require the same thermobalance.

So how this particular thermobalances have been constructed that all we see because this first thermobalance which is introduced or used for experimental purposes is by Kotaro Honda in the year 1915 and later on most of these has been modified and the modified form of all these thermobalances or who was introduced by Kotaro Honda in 1915 still we use the different modified form of those balances but the basic idea or the basic concept for measuring all these is very simple or very well-known for all these.

What it can do to it can detect the weight change or other same time it can record the changes in mass of a substance which is your analyte which is being heated or cooled as a told you just now that when you heat a there will be a temperature loss means this is the thing if your moisture or water vapor is going out or some gaseous products is going out from the sudden decomposition of the carbonate salts like calcium carbonate or magnesium carbonate, we will take specific examples at what temperature that decomposition and take place it can be any other organic solid also that corresponding pyrolysis reaction we call if it is the organic solid and organic compounds all we know that they can burn so the burning of any other organic material so also related to the products of these 2 that means when they burn uhh any organic

material or any food material or any pharmaceutical sample we all know that the corresponding decomposition of carbohydrates also they form water as well as carbon dioxide.

So these mass changes related to any other sample whether you have the trapped water molecule or the product of a particular reaction even the corresponding carbonate salt if we heat also then we can have the carboxylates organic carboxylates or inorganic carboxylate salts the metal salts like copper acetate, iron acetate or nickel acetate if we heat and if they decompose if you carbon dioxide with the remaining or the leftover nickel oxide, all these things we can monitor very nicely.

So this is during heating something is going out but when same material is cooled in some environment that means some environment of those things that means those gashes products which were going about and during this heating process can also be trapped back by those materials so when it is cold there will be weight gain and weight gain is due to the entrapment of carbon dioxide or your water molecule. So we can have a very good idea about using the thermobalances with regard to the corresponding change in mass as a function of temperature or time if it is synchronised for this temperature change.

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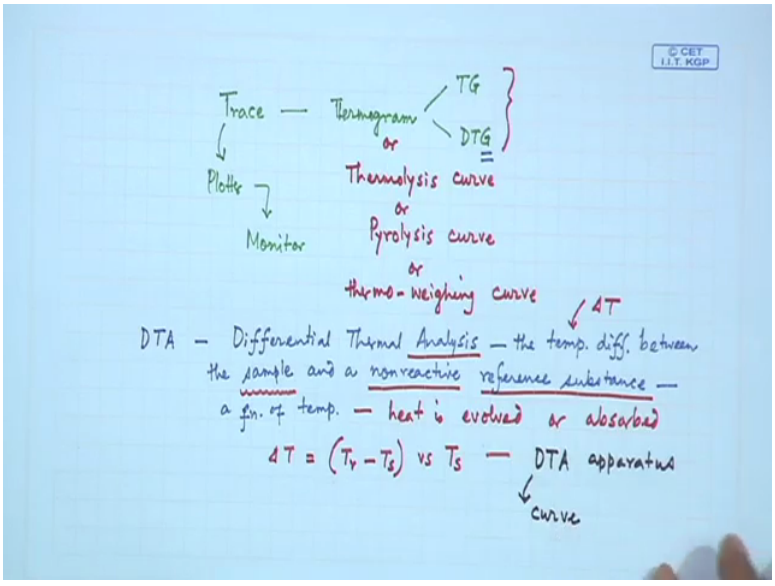

So by doing so they will get this curve so this particular curve we get and that trace we plot, so we must have a plotter or nowadays the computer monitor is fine to measure all these things and we term those as the corresponding thermogram, so those will be the thermogram so your Tg can give you the thermogram your DTG can also give you the corresponding

thermogram, so this can also be known as because we are talking something in terms of corresponding uhh decomposition in terms of temperature rise so it will be can also thermolysis curve or if we consider that we are seeing something where the pyrolysis is taking place so it will be pyrolysis curve also or thermo-weighing because ultimately what we are doing you are seeing the temperature effect on the sample by weighing in a thermobalance, so thermo-weighing curve.

So all these things related to the very basic and the first 2 techniques will go in detail while we do the sample wise the Tg technique and the DTG technique but we can have also the other processes one such is the DTA process which is known as its differential thermal analysis technique, do not confuse it with you DTG technique is a thermogravimetric G is there but is typically the analysis and in this particular the temperature difference will be monitoring so the temperature difference we have 2 monitor between the sample and a non-reactive reference material or substance is again monitored as a function of temperature.

So they are (())(24:23) something else that means we bring some non-reactive reference substance so it can be a simple very thermal stable material by Alumina or any other oxide so with respect to that so if you have 2 sample as well as that say reference material and within the same chamber that means within the same furnace chamber we try to heat it but temperature rise for one is different to that of the other and we basically go for the corresponding uhh delta value that means the temperature difference we uhh try to monitor this as the delta T and as a function of temperature or the control temperature of the 2 substances so how this rise in temperature of the 2 substances are taking place such that what we are trying to monitor that heat is evolved that means the temperature for the sample will be more or will be absorbed where the temperature of the sample would be less compared to your reference substance because the reference substance will not undergo any such heat evaluation or heat absorption.

So it will be basically an inert nonreactive reference material for over DTA analyses or differential thermal analysis because analysis is already included in the DTA term. So what we get, we get basically from there is a measurement for delta T where the delta T is nothing but the temperature of the reference minus temperature of the sample, so we have sample as well as your reference material is plotted versus the temperature of the sample we plotted against the temperature of the sample and now we uhh need something just little bit elaborate one where we just do not use the uhh simple thermobalance for monitoring this thing, so DTA

is an inbuilt says or the instrument is also dedicated for your differential thermal analysis and we thus we can have typical DTA apparatus and that DTA apparatus will be useful to monitor all this things and we get a corresponding DTA curve or the DTA plot by the (())(27:07).

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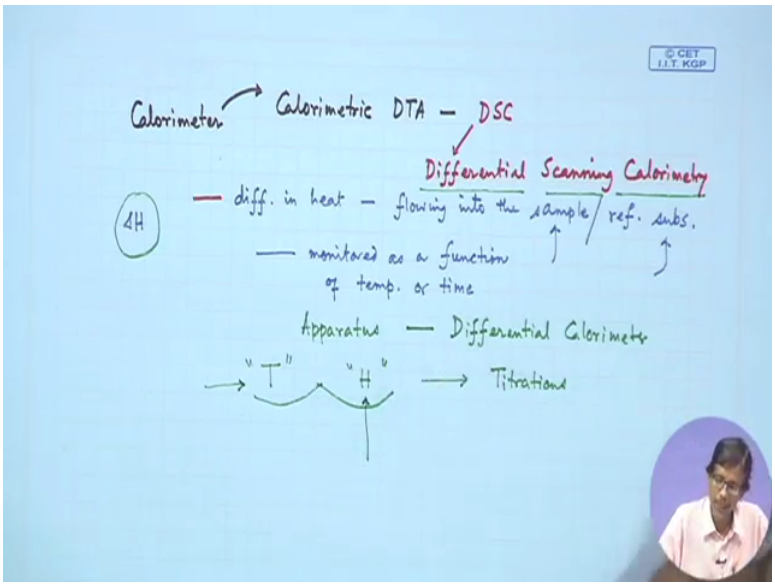

So after this DTA we can do we can do something whose name is also related DTA but we bring something we know that the thermal effect we can monitor by a calorimeter. So calorimeter when we bring into the picture of the DTA and we consider it as calorimetric DTA so it has a special name for that also which is the technique will be known as DSc and name will also tell you what is that so is differential scanning cause we are scanning all the time the temperature or the (())(28:11) and this calorimetry so it is differential scanning calorimetry or DSc.

So DSc is also sometimes very much useful if you require sometimes more information related to heat not only the temperature, so it is the difference in heat basically, what is flowing into the sample or the reference substance flowing into the sample or the reference substance, so heat is flowing both to the sample as well as to the reference substance and this particular change in the particular how much heat is gain by sample as well as the (subs) uhh reference material we can have the corresponding temperature rise and monitored as a function of temperature also the amount of heat so it is the amount of heat or delta H will be plotted against the temperature or time.

So is monitored as a function as a function of temperature or time. So now what we have a have now the corresponding differential calorimeter because the process is differential

scanning calorimetry the name immediately will tell you what is your apparatus to do that it is the corresponding differential which is slightly different from simple calorimeter because we are seeing something where we try to monitor not only the H but the delta H between the sample as well as the corresponding reference substance or the reference material.

So differential calorimeter so we monitor these things, so in all these cases what we are discussing so far is the corresponding temperature effect or the heat effect will see then we can introduce this two things to something where we all know that the analysis is (())(30:58) if we do not talk about in terms of the corresponding titrations, simple acid-base titrations and all these things but we do not know when we go for acid-base titration what is the corresponding temperature change or the reaction (())(31:13) and what is the heat effect for the corresponding neutralisation reaction, so that we will see in our next class that how we can define say these 2 that of our standard titrations. Thank you very much.