Course on Analytical Chemistry
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Module 7
Lecture No 33
Thermal Methods of Analysis – I (Contd.)

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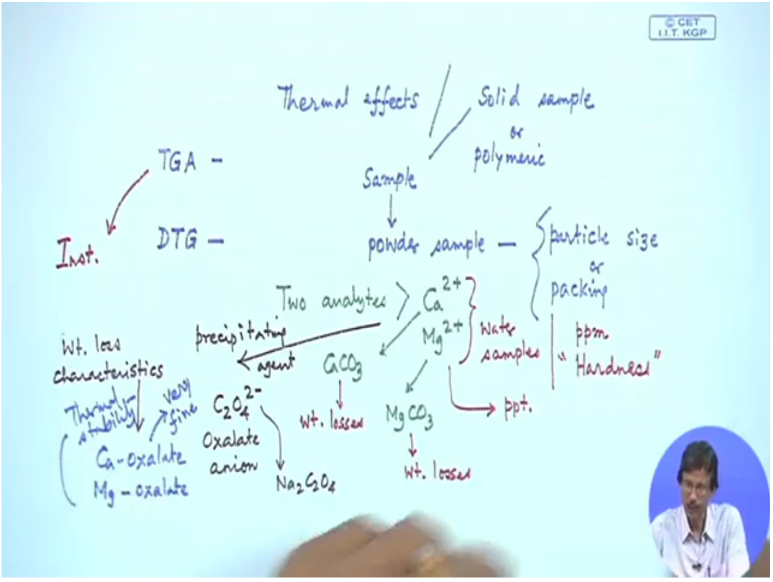

Hello and welcome to this class of thermal analysis where we have just seen the thermal effects on some samples which can be your solid samples or something else, can be a polymeric sample also and what we can discuss nicely for your thermogravimetric analysis what we have abbreviated as TGA thermogravimetric analysis and one also we have started discussing is the corresponding derivative one which is the DTG process and the nature of this particular sample that means the sample characteristics is very important. Suppose we have some powder sample and which is finely powdered so the particles what is present and the type of packing both are important.

So what we can see now at if we have 2 analyte is which we want to determining and these 2 allies are slated if we consider that we want to find the 2 metal ions one is calcium 2 plus and another is magnesium 2 plus and we all know they are very much present in the groundwater in other water salt water samples what we use everyday so if they are present in water sample and at what concentration level sometime we define some unit which is parts per million unit and that parts per million unit if we can apply to some calcium and magnesium samples present in water that gives us the hardness of that particular water sample.

So if you want to measure the corresponding hardness of these samples what we can do we can measure the corresponding amount of calcium and magnesium 2 plus present in the sample as calcium carbonate as well as magnesium carbonate. Now we want to see if we can have something where it can convert these 2 from the solution to some insoluble names the insoluble in water medium which will be your good precipitate and whether this calcium and magnesium samples are very useful but we can use also for standardising any thermogravimetric instrument.

So if we have the instrument and that instrumental have to be standardised in terms of its corresponding change in mass or the weight loss with respect to the temperature change and how it is standardise for that particular sample because if we have some well-known sample we know that that corresponding weight losses if we heat these 2 samples also. So weight loss is if we know when we can find out the corresponding percentage or the amount of calcium and magnesium present in those samples.

So these as well as something which we can add as the corresponding precipitating agent, so which is the precipitating agent, the precipitating agent can be C2 O4 2 minus which is your oxalate anion which has a 2 negative charge which is the anionic form dianionic form of oxalic acid or sodium oxalate what we can use, so directly we can use Na2 C2 O4. So with the bivalent cation calcium 2 plus or magnesium 2 plus, the immediate (())(5:18) and give rise to the corresponding precipitates of calcium oxalate and magnesium oxalate.

So this one is a different one where we get that, that corresponding precipitation of calcium and magnesium can be used for standardisation of the instrument for analysing the amount of calcium and magnesium is not in the sample and also the weight loss characteristics, this is very important that means the weight-loss characteristics will also be useful to know the corresponding nature of our calcium as well as magnesium oxalate because we have added the oxalate anion as the precipitating agent and that anion is binding the corresponding cation calcium and magnesium, so the study will also tell us that we can see the nature of their thermal stability.

So first thing what we can see is their thermal stability and as I discussed in some of our previous classes that when we add some precipitating agent and this separation of this calcium and magnesium oxalate take place from the solution medium and from the solution medium if it is insoluble in that water medium or the aqua medium where we do the reaction so in that particular (())(6:57) the solid what is separating out as calcium oxalate so these are very fine precipitate.

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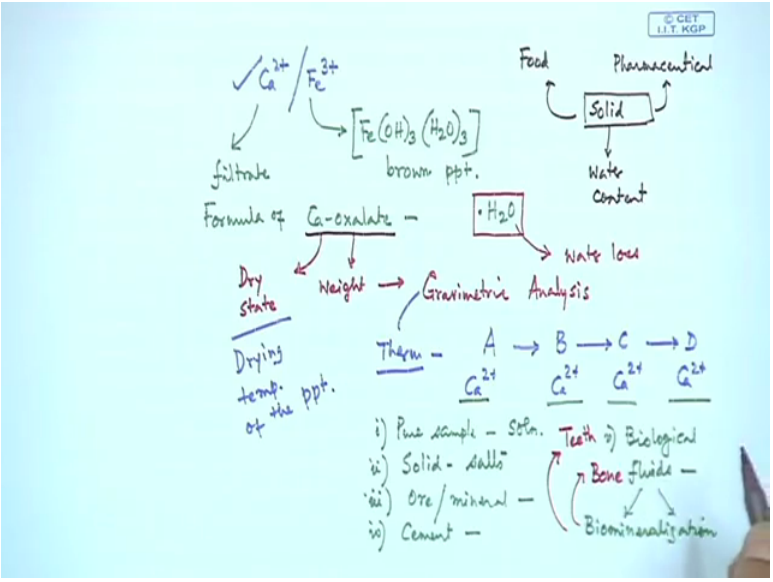

We use this particular technique for gravimetric estimation of calcium also and that calcium can be present with a solution of say iron 3 plus. So what we do there we basically separate out this first say as the precipitating of ferric hydroxide which we also write nicely as this, so this is brown precipitate so from the filtrate we get the calcium 2 plus and then we add the corresponding oxalate anion and we precipitate that.

So if you try to get the corresponding formulation that means the formula of calcium oxalate that means the corresponding molecular formula which can be very useful to know because the number of water molecules present as water of crystallisation is also very important to study because we have seen that 2 types of sodium carbonate we can have the washing soda, when freshly precipitated or freshly prepared sodium carbonate we have has 10 water of crystallisations but if you keep it for longer period even in air, it can lose 9 other water of crystallisations and it remains with that of your monohydrate species that means sodium carbonate monohydrate.

So the water content that means water of crystallisation also is very important knowledge or information or characteristics of this particular sample, so any other solid sample it can be useful for any other samples like liquid, gas et cetera or if we have a solid sample and it can be polymeric sample it can be a cement sample it can be any other solid sample, so the information regarding the water content is always very important. Even that solid sample can be your food sample, food materials or it can be your pharmaceutical samples pharmaceutical samples.

So this water content is always very important and we want to know to know when we go for TGA analysis of any of these samples because at a particular temperature this will go for the water loss which is the first step and that we can apply that information as we have discussed earlier in case of drying the precipitate of nickel DNG nickel dimethylglyoxime in air oven so we should say a particular temperature and we should know also at what particular temperature we can dry the corresponding sample of nickel DNG.

Similarly this particular calcium oxalate if we want to go for the corresponding measurement or the analysis based on the drying of the sample and taking the weight that means the gravimetric estimation, the conventional or the traditional gravimetric analysis can be useful know about the corresponding amount of calcium oxalate on the crucible or on the filter paper in dry state.

So this thermogravimetric estimation is directly related with the typical gravimetric analysis and if we put that therm that means the temperature the thermometric part, temperature when we add and if we go for the corresponding weight loss of the whole sample. What we find that with regards to the temperature not only the drying temperature because this will also give you the drying temperature of the precipitate.

So that particular profile can also give you the species that means the thermal stability of the calcium oxalate, so any other thing any polymeric sample and is cement sample any ore or any solid or the pharmaceutical sample the should know its corresponding thermal stability because we have 2 even that particular sample at a particular temperature. If it is unstable room temperature or little bit higher temperature than that of our room temperature, we have to be very much careful about its thermal stability.

So if A is there and with temperature is converting to B and since in all these cases we are talking about that calcium, so if we have a compound which (())(12:35) calcium 2 plus so calcium bearing one species then that can be converted to another species, then it can go to another third species or it can go to the last one which is another one based on (())(12:56). So these are therefore the conversion of A to D, if we have on to measure or if we want to find the corresponding calcium content of the pure solution. So you can have that calcium present in some of your sample which is in solution, it can be in some solid calcium bearing salts, it can be in ore of calcium or mineral of calcium or it can be in some cement sample.

So all our these opportunities we can have and also end number of things can be there in our body also in our biological fluids. We require calcium presents of calcium and its proper assimilation for the corresponding one for a particular process we call is biomineralisation that means the calcium bearing useful species or the material what we can have now body which can also be termed as biomaterials but the presence of calcium from the food material and its typical absorption can give rise to the corresponding formation of our bone in our body or our teeth or several other useful forms.

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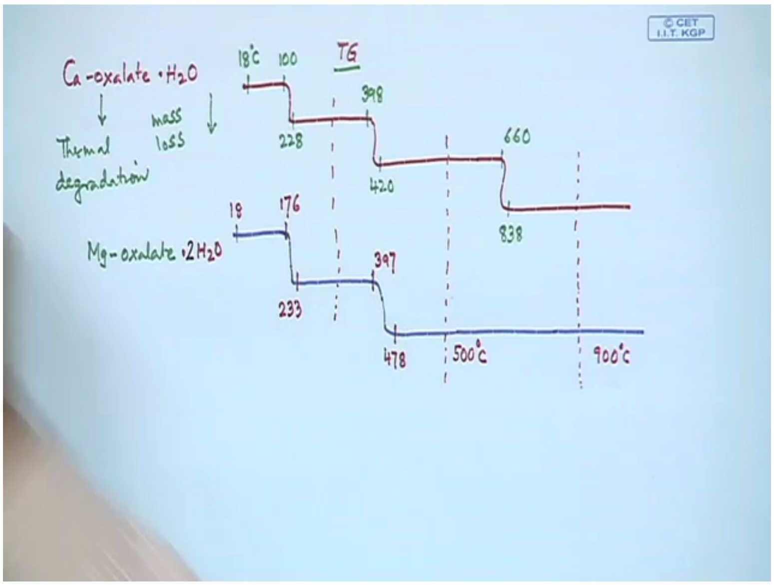

So this particular thing that means calcium is forming A, B, C, D all these things so depending upon their thermal stability we can start with say calcium oxalate and the formulation also do not know that means what is the number of water molecules present in it, whether it is a monohydrate or dihydrate or trihydrate, so we can go or its corresponding TG plot.

So it is TG plot will give rise to corresponding plot which is like this. So instead of leveling all these in terms of the corresponding axis because this is your corresponding mass loss, we just simply level the temperature in the start from the room temperature which is 18 degree centigrade all will be in degrees centigrade, then next is 100 then it is 228 it is 398 this is 420 then it is 660 then is 838 and so on.

So immediately seeing this particular thermogravimetric plot of calcium oxalate we see that of 100 degree centigrade dehydrate form of the calcium oxalate stable means if we want to measure the corresponding weight of calcium oxalate in the hydrated form or if we want to keep that in hydrated form also we should preserve that particular sample below 100 degree centigrade and above 100 degree centigrade monotonously you will have a weight loss characteristics and that weight-loss will continue till 228 degree centigrade, you see this is a pretty high temperature.

Initially it goes this particular one so that means the water molecules and the mass loss at this particular mind whether that will correspond a single water molecule or a double water molecule or triple what the molecule also signifies the number of water molecules present with this calcium oxalate sample. So what we see that this particular thermogravimetric plot or thermogravimetric characteristics can give rise to the information or it gives us the information about their weight losses and at which particular pleasure which one is stable and if there is some formation that means the calcium bearing compound A is going to calcium bearing compound B going to calcium bearing compound is C and calcium bearing compound D.

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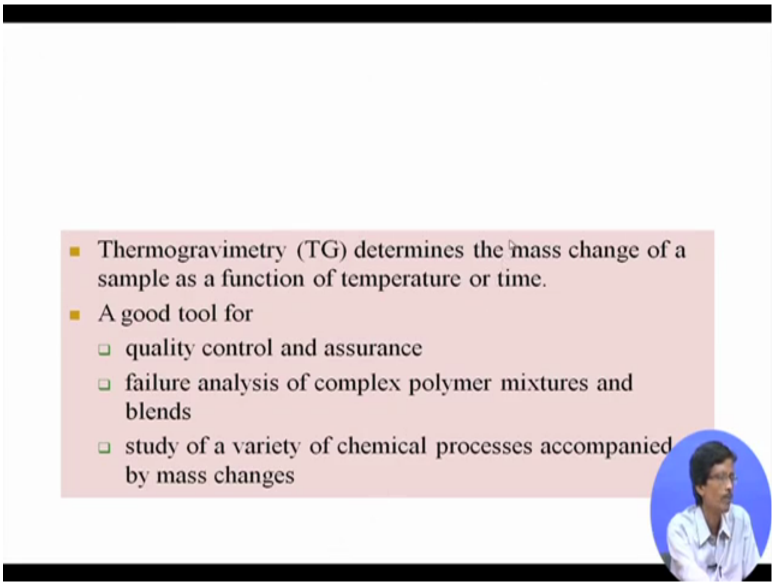

So before going to that exact analysis, what thermogravimetric tells us that we just seeing from our previous class that it determine the mass change of a sample as a function of temperature or time so if we have this that means if we want to measure the corresponding mass change all that particular sample which is your calcium oxalate and we will also take immediately that one other one that means the magnesium oxalate, so this particular instrument or the technique or the machine will be a good tool for quality control and assurance also.

Just now I told you that if we want to use the TG for our industry important sample of cement or the another pharmaceutical industry important sample is your medicine that means the solid tablet and the capsules are solid materials or the solid ingredients what we used for making the pharmaceutical samples because you must have the corresponding quality control and the assurance in terms of the simple presence of calcium iron in water molecule in water samples for the quality of the cement in terms of the presence of the calcium that means the percentage of calcium should be known to us in terms of a cement sample or any other calcium bearing medicine or drug or anything.

So calcium solid tablets can also we analysed for their presence. And failure analysis of complex polymer mixture so if you have a polymer mixture and that polymer mixture and blends also so polymeric samples just now I told you also that we can handle polymeric samples also nicely with this particular technique so if we have polymer mixture and blends and their thermal stability is also very important because at that particular temperature whether it is we are using below 50 degree centigrade or we are using the particular sample or the car component because the car engines and body and all these things they are doing some variable power consumption as well as the temperature rise for their all these components.

So this polymer mixture and blends and how good they are so for this complex species we can go for the thermal stability analysis and the failure analysis of these polymer mixture and the blends will discard them for their useful use and also we can use this for a variety of chemical processes accompanied by mass change, so we will just take that example we have taken this particular example that calcium oxalate what we have seen that a chemical process that means the thermal degradation, that thermal we can consider it as typical chemical process so this thermal degradation will accompany some mass change also.

So along with this calcium oxalate if you take another sample because both the 2 metal irons are present in the water samples so we can precipitate it together which is your magnesium oxalate, so this magnesium oxalate when we heat that particular one also in a similar fashion, so but to a high temperature extent, it will go like this. So compared to the sample of calcium oxalate here we see we have 1, 2, 3 breaks in case of calcium sample, in case of magnesium sample we have 2 breaks only and if we level the temperatures, this temperature can be leveled over here.

So this is also the starting point 18 degree your room temperature then we have we can reach little big beyond this temperature so it is 176 degree, so it has got thermal stability compared to your calcium sample then this one is in the (())(22:27) of the previous temperature what we obtain in case of calcium oxalate which is 233 degree then we have 397 degree then 478 degree then there is no change beyond that that means whatever is formed at this point…so we have A then B then C and previously in case of calcium oxalate what we have seen that we can get this 1, 2, 3, 4 samples that means compound A compound B, compound C and compound D and all these the transformation from A to B, B to C, C to D all accompanying some mass loss.

So now if we have this axis basically and now if we just…this temperature we can have so it will be between these so it will be close to 350 to 400 degree centigrade but these 2 temperature are very important, it can be considered as the drying temperature so this is our 500 degree centigrade and this is our 900 degree centigrade. So this calcium oxalate and magnesium oxalate have something in difference such that thing what we can get for the optimum temperature range what we can try to find out where we try to dry our condition this precipitate for gravimetric analysis so if we try to get this and if we find that is first weight loss in both the 2 cases are you to the loss of this water of crystallisations and we find that this particular deep is much more.

So the mass loss in case of your magnesium sample is more as compared to your calcium sample that immediately signifies that you are the have more number of water of crystallisations which is a dihydrate come back to your calcium oxalate which is a monohydrate. So the calcium oxalate monohydrate a stable up to 100 degree centigrade whereas magnesium oxalate dihydrate is stable up to 176 degree centigrade and as a result is 2 temperatures if we select those are the temperature ranges useful temperature ranges for our gravimetric analysis.

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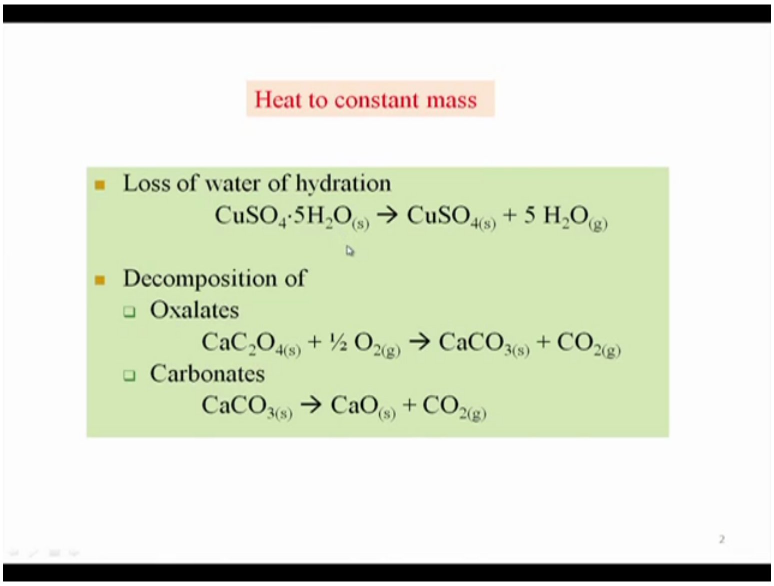

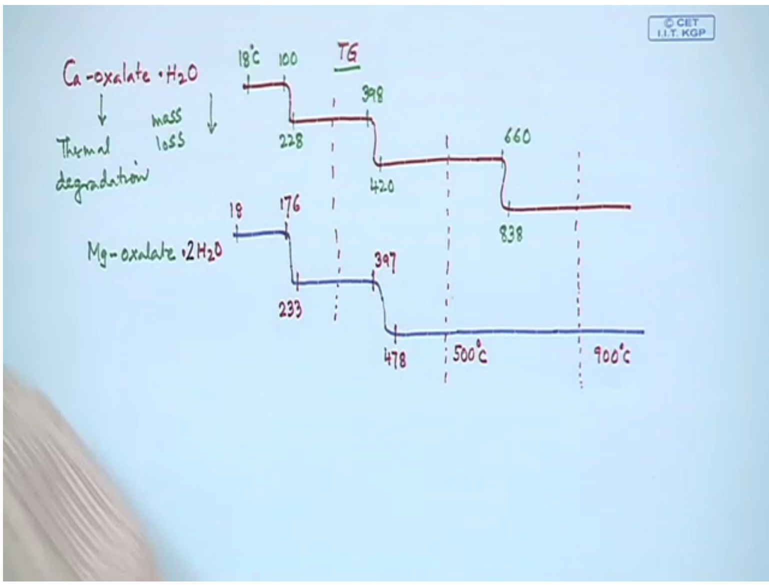

So how do we go for the corresponding thermogravimetric analysis that what we are looking for, we are looking for a heat we are giving to the sample to get some constant mass and this particular constant mass is also an important terminology over here that which particular range you can have a constant mass as it is have a constant mass in this particular range of 18 to 176 when a constant mass within the range of 233 to 397.

That means whatever sample is formed as compound B of coming from magnesium oxalate is stable in this particular temperature range and third one that means A, B, C the compound C from magnesium oxalate is also stable in this particular temperature range above 478 degree centigrade that means it is stable at 500 degree centigrade there is also stable at 900 centigrade of giving you any mass change so the mass will be constant in this range, this mass will be constant in this particular range. So what we find over here that if we just simply talk in terms of corresponding loss of water hydration, so loss of water hydration will give rise to something where we find that we take the simple sample like copper sulphate pentahydrate.

In one of our previous classes we have just discuss that water are that water present is many more there are 5 pentahydrate we know that this copper sulphate pentahydrate if we he did so not that all 5 water molecules will go out in a single step, one is different compared to other 4 so initially we get the sample which is copper sulphate monohydrate and we see also the color change so that is another indication good indication of those samples which are coloured unlike your calcium oxalate or magnesium oxalate sample which are white in color.

So this one it will immediately show some color change for the monohydrate formation and then monohydrate will go ultimately to the anhydrous copper sulphate and the temperature ranges which is known to us for the omission of monohydrate copper sulphate and the corresponding anhydrous copper sulphate is important because some of these samples are very useful, even they are in small amount they can show some catalytic thing in any organic transformation in the biochemical transformation or any pharmaceutical preparation we can use 3 different types of copper sulphate therefore and if I ask you to make these 3 samples, how will make it?

When a copper rod or copper that copper strings all so ordinary copper foil is given to you, so for metallic copper which has been obtained from your overall mineral of copper so that can be solubilised in presence of sulphuric acid and the sulphuric acid we all know that unlike nitric acid but sulphuric acid some oxidising power also which will oxidise this foil to give you the copper sulphate but if we want to prepare the corresponding copper sulphate in the monohydrate form and the anhydrous form so this anhydrous from when it gives rise to all 5 water molecules out.

So it is colourless species and these 2 things now what we want to see that the plots we have seen, these are basically the 2 important studies what we can make or thermogravimetric analysis is the corresponding decomposition and degradation of calcium oxalate to cash carbonate and this calcium carbonate to calcium oxide. So here we see that starting from your hydrated salt and this is hydrated so calcium oxalate is also hydrated one which we just now have seen that it is monohydrate one, that monohydrate will give rise to the corresponding anhydrous form of calcium oxalate.

Then that particular calcium oxalate can break down over go for the corresponding one where it can in presence of plenty of oxygen because oxygen supply if it is there be another gaseous product which is coming out from this thermal degradation is your carbon dioxide. Otherwise what we find in absence of this oxygen or in presence of some inert gas like nitrogen or argon, carbon monoxide can come out.

So that carbon monoxide coming out from the sample of calcium oxalate is a well-known fact and that will give rise to a different kind of weight loss compared to the heating of the sample of calcium oxalate in presence of air or oxygen. So once this calcium carbonate is form because the clinkering process what we know for making cement samples, several carbonate or oxalate and all these things are heated together in the furnace and we get a very complex has structure of this oxide or hydroxide which can be hydrated or dehydrated in cycling manner for all the cement samples and we all know that this calcium carbonate and all these things also very much useful for…it is their setting properties.

So this particular elimination of carbon dioxide and all these hot only from your calcium oxalate but also from calcium carbonate is very important step to think of where we can see that the gases which is coming out from those samples we can also analysed those gases very nicely that in one case you get the carbon monoxide so if the particular thing can be connected to your gas chromatographic analysis or gas chromatography attached to the mass spectrometric analysis also the GCMS instrument so that this gas analysis can immediately tell you whether you have the cash wages coming out from heating of the sample is carbon monoxide or carbon dioxide.

Similarly while heating this particular one so in this particular case in the second step we do not need any kind of oxygen for their decomposition, it is directly going out so calcium carbonate will be degraded to calcium oxide. We know that the use of calcium oxide we know that when it is trapping water we get (())(32:03) and all these things, so this also can give rise to the carbon dioxide from the particular sample.

So this gave rise to a very important information to us because in detail we will just talk in our next class about the degradation not only for your calcium oxalate but for the magnesium oxalate also that particular degradation losses will also tell us about the corresponding stability of these 2 important compounds because many number of bivalent metal ions can give you the carbonates.

Sometimes we can give rise to the basic carbonate then the hydroxycarbonate the copper carbonate, copper hydroxycarbonate and like magnesium oxalate several other salts also known so all these metal ions can be analysed by getting its corresponding either oxalate salt or their corresponding carbonate salt. Thank you very much.