Analytical Chemistry
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Module 10
Lecture No 49
Electrochemical Methods 2 (Contd)

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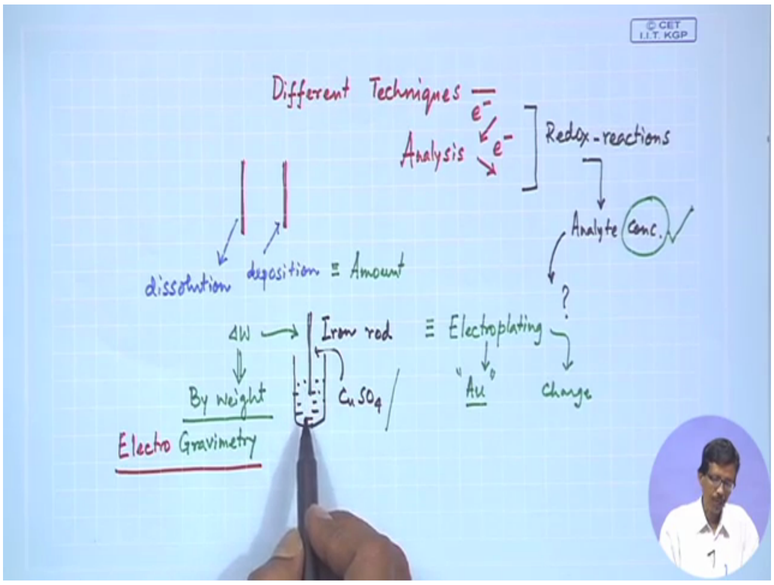

Good evening everybody, so we were talking about the different techniques which are useful for particular type of analysis where we can go for oxidation or reduction ok. Means we basically looking for some very interesting and very important reaction is that the different redox reactions because these understandings are also very much important in developing any kind of that sensors based on the electron transfer reaction, so these redox reactions we want to monitor in terms of the corresponding analyte concentration that means it can be any solution which has something which we want to determine.

And if it goes for say electron loss or electron gain in terms of its corresponding oxidation and reduction we will find that the number of electron transfer it also be directly proportional to the analyte concentration present in the solution. So since we are talking about this electrode reactions and what we have seen in other cases like the potentiometric analysis and all these that we have two electrodes and these electrodes we have seen earlier also that these are your cathodes and anodes and these electrons can nice be utilized in terms of the corresponding electron acceptance or electron donation and if we try to monitor this analyte concentration from the very early stage of this electrochemical analysis classes, what we have seen there that you can have some electrodes and either we can go for some deposition or that electrodes can go for dissolution due the corresponding electron transfer reaction.

So how we can correlate this that means if we have an analyte and in one such case we have seen that a iron rod or iron nail if we deep it within a copper sulphate solution and we have seen that there will be some deposition of this copper on this iron rod, so now if we can try to correlate these things that means your analyte concentration which is your unknown thing and the amount of deposition.

So if there is some deposition so what should be the corresponding amount so amount of deposition that means if we can wave out the amount which is getting deposited on this iron rod or we know that a very practical application of this particular technique is the electroplating technique. Something we get some trophy or some model are all these things it can be finely electroplated on the base metal by say gold plating so the amount of gold required for gold plating can be controlled by knowing the corresponding charge which we have to provide for this particular type of electro deposition.

So anything of that kind that means electroplating or this deposition of metal iron on the iron rod because there we can find the weight difference of this particular electrode initially how much wet you have and finally how much weight you get that the difference will give you corresponding amount of copper which can be deposited on this iron rod. So by weight what we are looking for is that something we want to measure by weight or taking the weight difference of the electrode and we will try to correlate that with that of your concentration.

So by weight analysis we know that is known as gravimetry, the gravimetric analysis which we have seen earlier that how we can differentiate this from that of your volumetric analysis, so we can have these things one after another that means you have the corresponding electrolysis or the electronic charge transfer then we have some things should be reduced or oxidized then if something is reduced and oxidized on the electrode surface we can take the weight change of that particular electrode and we can go for the gravimetric estimation but by using something which we call as the electronic charge so electro gravimetric analysis or electro gravimetry that means by doing something that means by sending the charge or for a particular electrode which can be cathode or anode.

We have to go for the corresponding calculations in terms of the corresponding change in weight, so we find that this particular technique that is basically your electro gravimetric analysis or electro gravimetric method. So if we go for electro gravimetry then we will get the electro gravimetric methods for this particular type of analysis.

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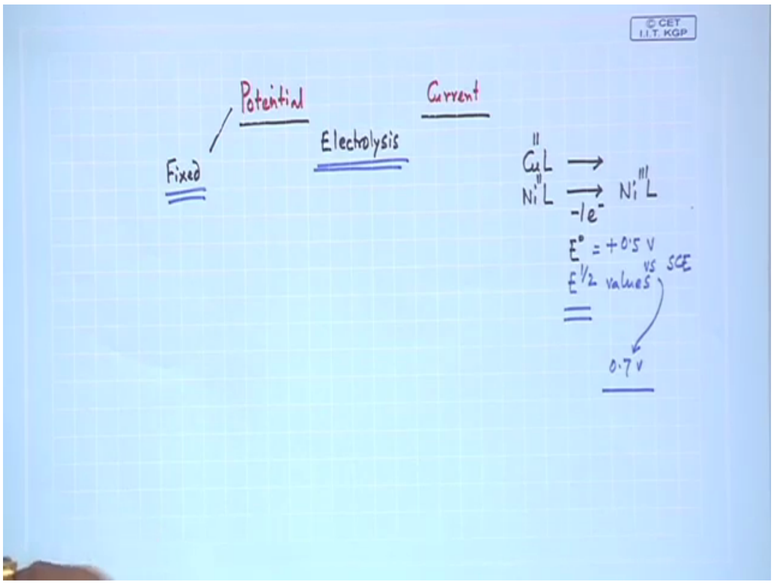

So the next thing what we can define in terms of the control potential electro gravimetry that means two things what we have seen so far that what you have you have the corresponding potential change or the measurement of the potential as we have seen in the potentiometric method that means potential and we also can measure the corresponding current what is passing through this cell whether you have a corresponding galvanic cell or an electrochemical cell.

So what we do that we want to go for some electrolysis, and if we go for that particular electrolysis at fixed potential value that means if we want to go for certain oxidation or reduction suppose you have some copper or the nickel complex we know that very good example for all these because it is bound to some of the ligand, so you can have CuL or NiL. Then what we can do that we should know the corresponding oxidation state where it is stabilized by this particular ligand. So what we get that if it is stabilized in copper 2 or nickel 2 and if we go for oxidation that is – 1 electron loss that means you get a corresponding nickel 3 compound of that particular ligand but in the trivalent state.

So if we can go that means if we have to measure the corresponding E0 value or the corresponding half wave potential for reversible oxidation and reduction reaction because most of these reactions are reversible in nature. E0 or E half values and if we can put these E half value or the E0 value as the fixed potential for your electrolysis and by doing so if we get the corresponding deposition or dissolution of a species, we get the corresponding electro gravimetric method but it will be controlled by a fixed potential value.

So at a fixed potential value suppose this particular one is oxidizing at a E half value of say + 0.5 volt versus SCE saturated calamine electrode. So we have seen also that we can have that ohmic potential values and the corresponding polarization factors and all these so your potential for electrolysis should be higher than that of this particular magnitude of half web potential so it can be 0.6 or 0.7. So at 0.7 volt we can go for the corresponding electrolysis for getting the entire copper sample what you can have to be converted to the trivalent state.

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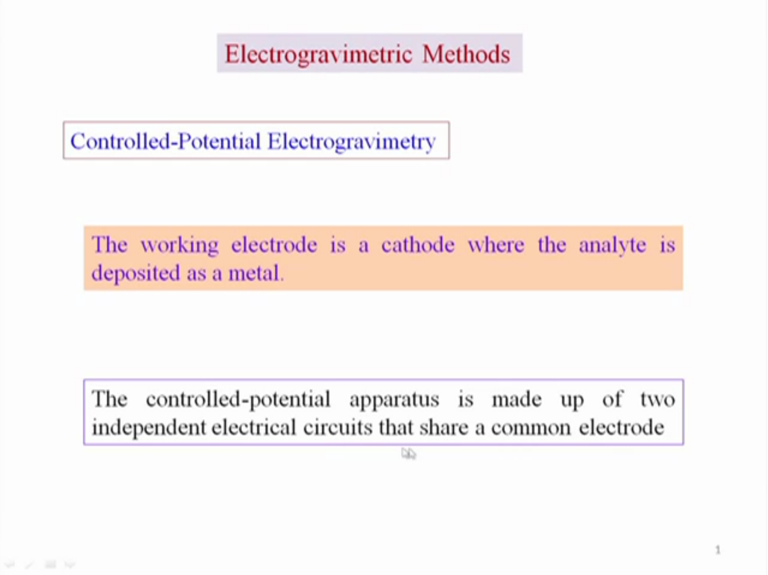

Electrogravimetric Methods

Controlled-Potential Electrogravimetry

The working electrode is a cathode where the analyte is deposited as a metal.

The controlled-potential apparatus is made up of two independent electrical circuits that share a common electrode

1

So what does it mean basically then we see that what is that control potential electrogravimetry that means you have the gravimetric estimation and this gravimetric estimation is done at a constant potential or a control potential because control potential is a very useful term because you can control the potential change also but at some potential you go for sometime then you change the potential for other values to a different type. So if you have a working electrode now we define this as the working electrode which is basically going for your oxidation or reduction reaction but if it is a cathode one as I just now told you that if it is a cathode one where you can expect the corresponding analyte to be deposited at the corresponding metal that means when the iron rod or iron nail is immersed or is inserted within the copper sulphate solution that can be function as a corresponding cathode because it can give rise to the corresponding required number of electrons for the reduction of copper 2 + to copper 0.

So obviously that can function as a corresponding cathode so it is a natural tendency for that iron to be oxidized to ferric iron and the number electrons released in that way can be used for your reduction reaction of the solution where the electrodes is inserted. So in this particular case now if you go for electrolysis that means you have the electrochemical cell and we are looking for something which is controlled potential electro gravimetric measurements or the methodology.

So control potential apparatus should have two independent electrical circuits that share a common electrode, now by definition we are making little bit complex at this point that we can go for control potential apparatus or the electrochemical cell but it will have two independent electrical circuits, we are not talking in terms of two electrodes. We all know that we can have a cathode electrode or an anode electrode but now what we see that we can have two independent electrical circuits but some combined form we are trying to get as we have seen in case of your glass electrode that the (())(12:43) of that glass electrode we have seen that you can have one half cell that E half cell for the right electrode or E half cell for the left electrode which can be combined together.

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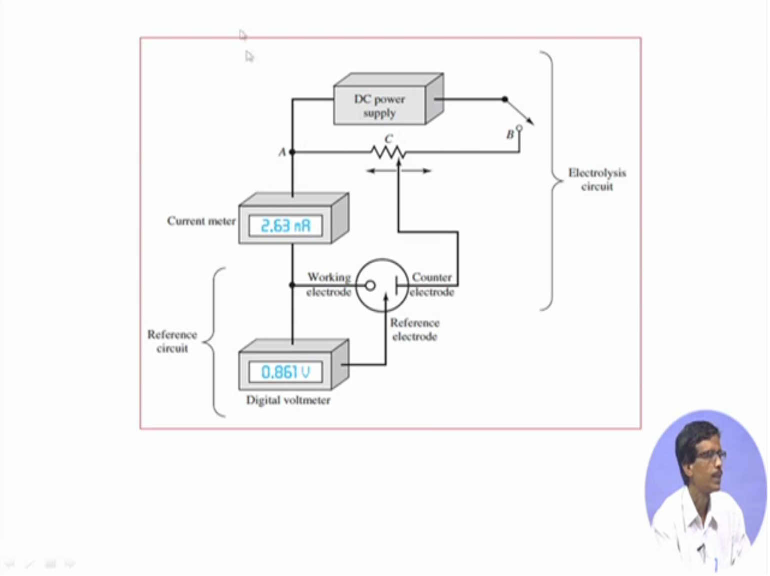

So this is something like that you can have a common electrode and two other electrodes such that you can have two electrical circuits for this particular purpose. So what we see that schematically there schematic presentation of these things where we can go for some reactions that means some solutions should be there is this particular thing that means your electrochemical cells is the circular one, that the circle is designated your electrochemical cell and instead of talking in terms of two electrodes, now we are talking in terms of three electrodes system.

And throughout our discussion in this class or the next class or beyond that also we will be talking the arrangements of these three electrodes and their sign also all three are different one is the corresponding circular one, one having arrow and another having vertical line and these three electrodes combination is a very useful one for all these measurements and just now what we defined for this is that we have defined two electrical circuits. So as we know that one cathode and one anode if we have you can have a corresponding circuit here and if we connect this working electrode with the counter electrode you can have a different circuit for that.

So if we do these basically and we find that the working electrode is responsible for your electrolysis. Suppose you have the cathode as your working electrode so how this particular reference unit that means for reference electrodes can do and what counter electrode can do that give rise to two different measuring things that means this current metre which is in the unit of milliampere some amount of current that we previously we have discussed also in case of potentiometric analysis that this current can be 0 and we can measure the corresponding volt in terms of the corresponding cell potential when we have a cathode and an anode inserted within the solution.

Now what we see that we do something where we get a potential value so a voltmeter and is a current metre is nothing but your ammeter we all know that ammeters are required for measuring your current and the volt metre is required for the voltage. So between working electrode and the reference electrode if we consider that working electrode is going for functioning one half salary action and reference electrode is for another function so with reference to reference that means in reference to reference electrode your working electrode can have some potential value which is 0.861 volt.

So we put some potential value which is equal to 0.861 volt on working electrode but with respect to the reference electrode that means that potential is versus your reference electrode. Your reference electrode can be your normal hydrogen electrode it can be your saturated calamine electrode or it can be your silver-silver chloride electrode. So we get this so reference electrode once you have reference electrode and working electrode is fine that you can measure the potential for that cell or that electrochemical cell.

Now what does it means over here on the other side that means in working electrode is connected with the counter electrode, so counter electrode we define something as an auxiliary electrode which is required for passing the corresponding current. So you have the DC power supply and that power supply is there and we have something some that potential potentiostat or the potential bridge is there such that we can change from one arrow head to the other position. We can change that means we can monitor the corresponding amount of current which is passing through the other circuit.

So you have the upper part you have the electrolysis circuit basically that means which is required for your electrolysis that means what amount of current we are getting and the reference circuit. So basically from this block diagram what we see that we can have two parameters we get one is your current what we measure we can measure from this particular arrangement and another is the corresponding potential. So if any situation we get that where we can have this thing that means how the current is changing with respect to the change in the potential values.

So both these two parameters can be dynamic one so you just can the potential and how the current within the circuit can change also that will give rise some important or some interesting information related to that of our electrolysis. So this basically gives us some ideas that is that block diagram is very simple block diagram only the connections you have to remember that give rise to the corresponding thing for your control potential electrolysis theme, that means if you have a fixed potential you go for the electrolysis and the electrolysis once you go the corresponding electrolysis will find that this current will not remain constant because if it is a fixed one or a controlled potential value.

So potential will remain fixed at a constant value but your current will change depending upon your analyte concentration so if you go for exhaustive electrolysis that means the presence of analyte within the solution medium is nil or zero when you go for complete electrolysis in terms of oxidation or in terms of reduction.

So if we go for complete oxidation or if you go for complete reduction at a particular potential we find that particular magnitude of current definitely will be deducing and will be proportional to that of our electro active analyte, the species which is getting say oxidized or reduced that means as its concentration is decreasing with time your current value will also be decreasing with time.

So that will see that within that electrolysis circuit now what we have seen that whole circuit now will see how we can explain the typical circuit so this circuit will have a dc source a direct current source definitely is not a alternative current because if you have the alternative current then it basically moves from one direction to the other particularly that corresponding nature of your electrodes will also change.

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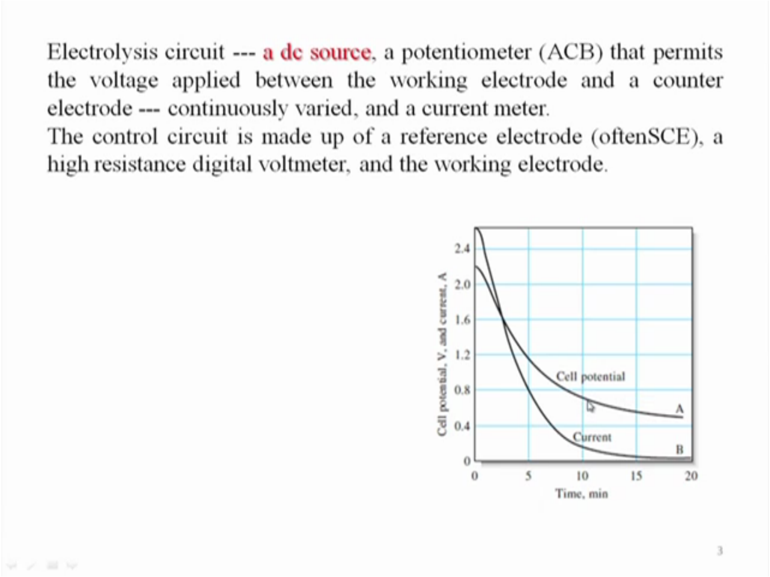

Electrolysis circuit --- a dc source, a potentiometer (ACB) that permits the voltage applied between the working electrode and a counter electrode --- continuously varied, and a current meter.
The control circuit is made up of a reference electrode (oftenSCE), a high resistance digital voltmeter, and the working electrode.

Then what I was talking to that the zigzag line for your potential with the aids that ACB so this permits the voltage applied between the working electrode and the counter electrode, so if you have the corresponding the potentiometer will control the corresponding voltage between the working electrode and the counter electrode remember it, that means the magnitude of current which is passing between the working electrodes and the counter electrodes is being monitored by these potentiometers and is continuously varied and a current metre is showing the magnitude of current, then a control circuit is made up of a reference electrode often SCE that means a saturated calamine electrode you have.

So the other circuit will have RE the reference electrode which is nothing but a high resistance digital voltmeter also and the working electrodes. So your working electrodes have two connections one having the connections with the counter or auxiliary electrode and the other one is for with that of your reference electrode, so when we are talking in terms of the corresponding circuit with reference electrodes we will be taking about the measurement of the potential and when it is talking in terms of the corresponding counter electrode or the auxiliary electrode we will be taking in terms of the corresponding passage of current that means the maximum amount of current can be flown through the counter electrode or the auxiliary electrode only and your reference electrode will not sense much current otherwise the corresponding magnitude of the electrolytes present in the reference electrode will change due to the electrolysis given by the corresponding current flowing through the reference electrode that we should avoid.

Now we see how these two parameters what we have seen that the current as well as the potential can change with time as we go for electrolysis. Suppose we are doing some electrolysis for say 20 minutes, so 0 to 20 is the time for your electrolysis and in one point for the potential you see that A is the cell potential. So cell potential in volts basically will be measuring that and definitely with respect to some reference electrodes it can be your SCE just now what we have seen.

So this cell potential initially you see the potential was around 2.2 when you start the electrolysis, so at the beginning when time is 0 only so your potential is 0 so with time it is decreasing initially in a very sharp manner but after that is not that way that means the rate of decrease of cell potential is not a very linear one or is not going monotonously but it can ultimately reach over here say around 18 minute or 19 minutes. It is reaching at say 0.5 or some value so 0.5 is going to reach there.

So starting from 2.2 we are reaching at a point of point 5 so this is a corresponding decrease in the corresponding cell potential and so one circuit what was measuring your cell potential can also be seen by the other circuit is the circuit for your current measuring device so you see the current reaches there. So is in the ampere scale so this we are using both the two scales on this left hand sides otherwise you should have a in this axis and current in this axis so y in two axis but if we consider that it is also in ampere and which is also say 2.6 or something like that, but you see in case of current this is a very sharp decrease and it is approaching close to zero at an time interval of 20 minutes.

So at the relapse of 20 minutes time basically the current is going to almost 0 the negligible current that means you can go for exhaustive electrolysis by this way when the analyte concentration in the cell or in the medium or in the beaker what we use a electrochemical cell is almost negligible that means all the things that means whatever we are doing for that has been oxidized or reduced that means electrolysis is complete. So we get these changes for A and B during a control potential deposition of copper basically if we consider that throughout the experiment thus we have seen we started our discussion in this class also that like the putting your iron nail or iron rod in copper sulphate solution

But in other way also you can have the deposition of copper on any other type of electrode sometimes, we can the electrodes which is made up of some inert material such as your platinum or the carbon electrodes so when you fix the potential at – 0.36 volts versus SCE this potential is fine for your control potential deposition of copper, but remember that your cell potential is decreasing as well as your current through that particular circuit is also decreasing, so we will be able to deposit the whole amount of copper to a particular electrode.

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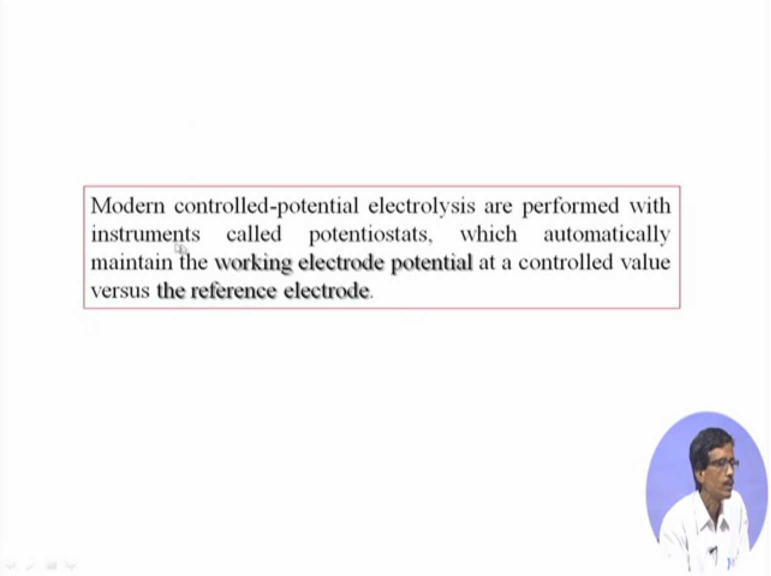

Modern controlled-potential electrolysis are performed with instruments called potentiostats, which automatically maintain the **working electrode potential** at a controlled value versus **the reference electrode**.

So by doing so what you get that during this particular process that modern control potential electrolysis what you perform are performed with typical instruments called the different potentiostat that means you have the static potential the potential you have the static potential values that means a fixed potential values or control potential values which automatically maintained the corresponding working electrode potential at a controlled value versus a reference electrode. So these potentiostat are responsible to give you a working electro potential, so we maintained a particular working electrode potential at a constant value versus the reference electrode.

If we require that you can have a 0.7 potential value and sometime we also require that your potentiostat can scan this particular range also say + 0.2 volt to say + 0.7 volt, so when we scan and what will happen to the electrodes which are dipped into the solution that means with regard to the corresponding current which is available over there within the circuit can be measured so if we have in one axis that means you have the potential and in another axis we will be able to measure the corresponding current. But what you see that the potential is falling and the current is falling for during the during your electro deposition so that amount of electro position we can measure for your electro gravimetric measurements. So what we get therefore that if we have not a single one that means your copper, you can have many more metal ions together so if we have a mixture also that can also be determined

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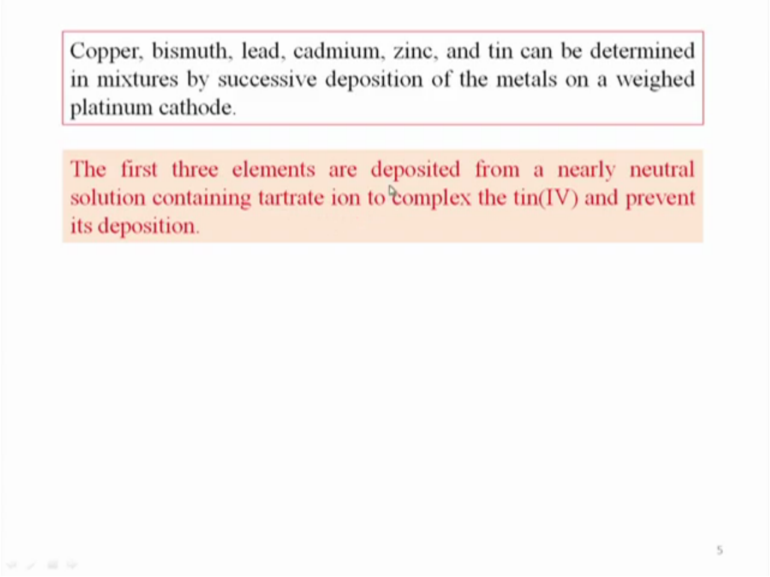

Copper, bismuth, lead, cadmium, zinc, and tin can be determined in mixtures by successive deposition of the metals on a weighed platinum cathode.

The first three elements are deposited from a nearly neutral solution containing tartrate ion to complex the tin(IV) and prevent its deposition.

So all these metal ions in some oxidation state that means copper in bivalent state, bismuth in trivalent, lead in bivalent state cadmium, zinc tin all are in bivalent state. So if they are in mixtures so these mixtures can be handled nicely for your electro deposition in a weighted cathode, so this is your inert cathode now what I just told now you that you can deposit copper on platinum but you can deposit all other metal ions on the same platinum cathode but how do I do that. So therefore we should know the corresponding potential values for these electro deposition because copper is know just now what we have seen for the copper deposition at a particular potential.

But for the other one also we do not know there is a first three elements are deposited nearly neutral solution only thing that you vary the corresponding potential and when you have the one particular anionic species like your coordinating one or the binding species that means the tartrate ion to the complex, so if it complex to the tin 2 or tin 4 it prevents its corresponding deposition. So tin will remain in the solution all other elements can be deposited in this particular fashion.

So in our next class therefore we will find that how we get these particular selectivity for deposition of these metal ions one after another so if you have a fixed potential for deposition of one particular metal ion say copper you can go for that potential and complete the deposition of the entire copper which is present in the solution so metal ion number 1 can be deposited selectively then you can go for the metal ion 2 or the metal ion 3 or the metal ion 4 in this fashion ok, Thank you very much.