Analytical Chemistry
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Module 11
Lecture No 51
Electrochemical Methods 3

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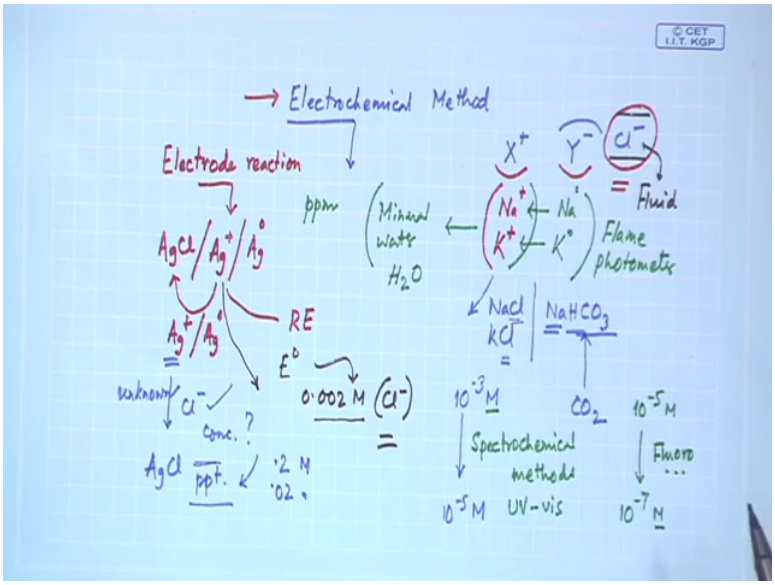

Hello, good morning everybody, so we were talking about the electrochemical methods of analysis and as I told you that we will be basically talking about the electrochemical effect or electric chemical signals what we can find to determine some unknown analyte, it can be X + or it can be Y – because always for us when we study analytical chemistry courses, always we must have some good idea about the identification first then quantification of the species like X + or Y –. So when you take the help of electro chemical methods definitely we should go for some electron transfer reaction on cathode and anode as we are discussing.

So the species like this the cationic species we all know that in common water what we drink, our drinking water and we always very much concern about the presence of sodium ion and potassium ion because these 2 ions are very much important for our health for our well-being, so the concentration of sodium ion as well as potassium ion we determine basically in our drinking water or the bottled mineral water that we take, so the problem to us should be how we determine the corresponding concentration of sodium ion and the potassium ion in mineral water, so if we think that we can solve this problem by doing some electron transfer reaction on it that means if you reduce it to sodium 0 and reduce it to potassium 0 then the

problem will come that how will you go for the corresponding determination of the atomic state of sodium and the potassium.

So all this things are related for that particular type of analysis where you know that the mineral water bottle is written with some amount of ppm values of potassium or ppm values of sodium as in the ionic form because they are all mineralised that means the required quantity of sodium ion or the potassium ion is mixed with that pure water which is only H2O so this should be difficult in that way for measuring the signal in terms of their electrons transfer behaviour, but we can go for some other technique, we know that we can use it by simple flame photo meter to analyse this particular species.

But today in this class what we will be talking about is not that your sodium + or potassium + because this analysis sometimes also very much important because whatever salt we take as our table salt, common salt or food material, we all will be getting this as sodium chloride or potassium chloride, we are not taking these in some other salt because we should have that question all the time that why we are not taking any other salt of sodium or any other salt of potassium light for making food and all these things, we know that bi carbo used which is sodium bicarbonate, again you have the corresponding sodium salt but the anion is bicarbonate which we produce in our body also when we bond the food material and we get the carbon dioxide.

Now the other one that means the anionic counterpart that means Cl and this Cl whether we can determine this particular chloride ion concentration, forget about the presence of the corresponding cations like Na + or K +, but if we want to determine the total concentration of Cl – in any fluid whether we take as water or it can be your biological fluid in our body, in serum, in suit, anything. As the know that this Cl – if we can little bit careful about thinking the process of some electrode reaction, what we are discussing for many classes.

So the electrode reaction what we are thinking about, one such half cell reaction we have seen that is AgCl Ag + that means the corresponding 1 and silver ions are there, silver ions are getting so is 2Ag 0, so this silver ion silver 0 as we know the pure silver ion silver 0 electrode we know, but the other one is also that silver chloride electrode and this we all know that a very good RE that means your corresponding reference electrode we know the half cell potential and all this. So in some way if we can have some good idea in any electrochemical method where the system can sense the corresponding chloride ion

concentration because making this half cell what we have seen that certain amount of 0.002 molar chloride concentration was required for making that particular cell.

So you see this particular concentration and the cell potential, the corresponding E 0 value for the half cell is dependent on the corresponding concentration of this chloride, so in any way we can have some idea or clue that we can manipulate the process for tracking the corresponding presence as well as the concentration of the chloride in any fluid, it is possible then. The determination of chloride concentration in any fluid and we will see that if it can be a typical biological fluid so how we can see that, we can go for electrochemical method and that electrochemical method is a typical one where we can consider it as coulometric titration because the chloride can be handled in all different types of titration particularly we know that since we are talking about this Ag +.

So if you have the corresponding unknown chloride concentration which is unknown, we want to determine the unknown chloride concentration, we can have AgCl which precipitate out and we know that one such titrimetric method is the precipitation reaction like the neutralisation reaction or redox reaction or middle ion complexation reaction so this particular precipitation reaction can also be useful to determine this Cl – but why you should go for any electrochemical technique to determine this Cl – that is the most important question to be asked because this concentration because for a meaningful precipitate if you want to have it, if you want to see or locate it by addition of some indicator, what we should know that we should know that this concentration this is also a very low concentration so this concentration are 0.2 or 0.02 something like that.

So this higher level of concentration so which is 10 order or 100 order of magnitude higher concentration than that concentration what we find in the corresponding electrochemical cell or what we can apply for any electrochemical method. So when your concentration is high, what you can do you can go for this corresponding precipitation type titration, but if the concentration is low we cannot go for this. The thing is that as we go down to a concentration because we know that 10 to the – 3 molar to 10 to the power – 5 molar concentration is good and very easy to handle not for your typical analytical method using different iterations so these are useful for your spectrochemical methods, what we have seen earlier, so when spectrochemical methods.

Now if we go down further than means 10 to the power – 5 molar to 10 to the power – 7 molar what we should do, we should go for some time this spectrochemical method using UV

visible spectrometer we can go here simply the fluorometric technique the fluorescent we can measure. At the same time also this concentration we can handle for Electrochemical methods of analysis, so we now that dream titrimetric method which is based on coulometric that means we can measure the corresponding coulomb count or electrical charge around for a typical titration when chloride is the anion in any biological fluid.

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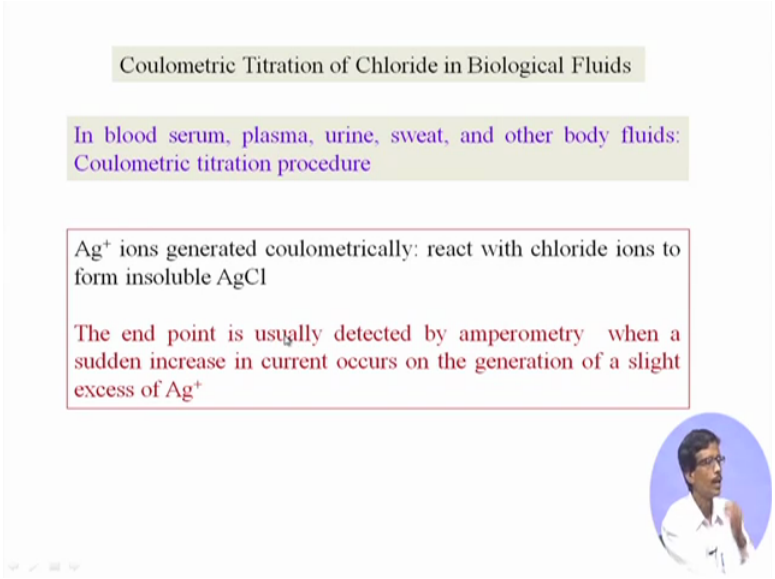

So that will be a very good example for utilisation of electrochemical method because this is typically introductory class for you where we can introduce the thing that how we can move from a typical electrochemical method or electrochemistry to a bio-electrochemistrycal process that means how we can apply 2 different biological problems or determination of the corresponding concentration in different biological fluids so starting from blood serum to plasma to sweat, urine and any other body fluids if we had because always we have either sodium chloride or potassium chloride, we get it from direct salt or we get it from any food material so anion, the most prevalent anion apart from the sulphur-based or the nitrogen-based other anion chloride is the typical anion.

So the suitable procedure is your electrochemical method and that electrochemical method not by voltammetry, not by potentiometry, it would be on coulometric method. So coulometric titration procedure would be useful in that way so how we do that, again we can do that the Silver ions application that means this is the fundamental information, the fundamental knowledge, it should always have that whenever is problem is with silver ion you think of chloride, whenever it is for chloride ion you think of the corresponding silver ion. So silver ion is generated coulometrically.

So if we generate silver iron coulometrically that means the number of electron transfer taking place for the required number of silver ion to be produced in solution is known by the coulometric charge count or the coulomb which can react with the available chloride ions such that it can immediately react to give you the silver chloride precipitation or electrical sense because these 2 are combining for a half cell reaction which is your Ag + Ag cell half cell electron because we know the potential also we can find out the corresponding change in the concentration with respect to your chloride concentration. So when we go for amperometry, so this is the new terminology what you write now you come listen and try to remember it because it is related to ampere, related to coulomb is coulometric titration, if it is related to ampere it will be amperometric titration.

So in amperometric titrations as known from the name itself that it is ampere that means the current, so if we can measure the corresponding current during the titration what we measure for potentiometric method the change in the potential values during titration, now we can measure the corresponding change in the current in terms of several amperes because it is not several amperes, it is several milliamperes, microamperes or nanoamperes as we go down down. So what that electrical sense mechanism that electrical sense in mechanism is known to us from 10 to the – 3 to 10 to the – 5 then 10 to the – 5 to 10 to the – 7 and then again 10 to the – 7 to 10 to the – 9 molar can be handled in terms of the corresponding current ampere.

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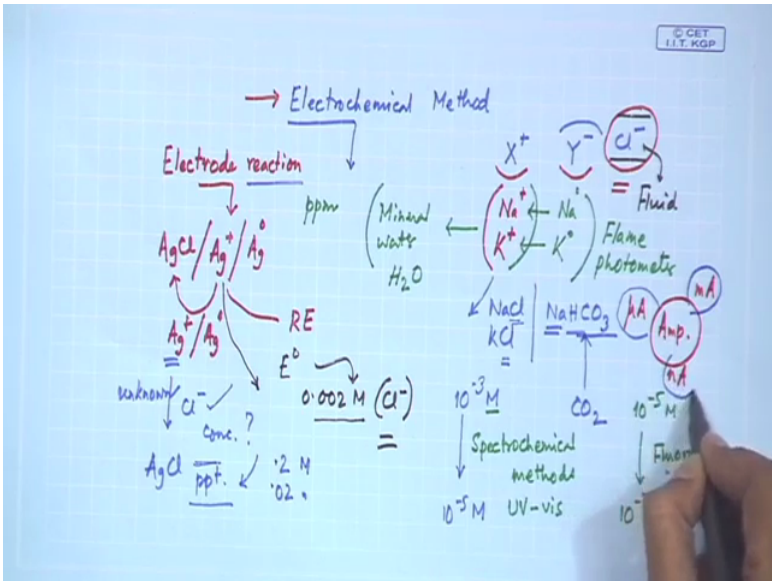

So this ampere we will that routinely we can use as microampere, we can use it as the milliampere or we can use it as nanoampere. So as we go down we can have some information or the corresponding electrochemical transducer which is amplifying the signal

what is coming out from the electrode reaction because we have the electrode and that electrode is responsible for giving you the corresponding reading in terms of either voltage or in terms of corresponding current. So milliampere to microampere and then microampere to nanoampere you can tackle or you can handle because these are all concentration dependent, at a certain concentration you get a current of milliampere range, in other case you get current in the microampere range, in other case you get all you can go down to nano level which is a nano ampere range.

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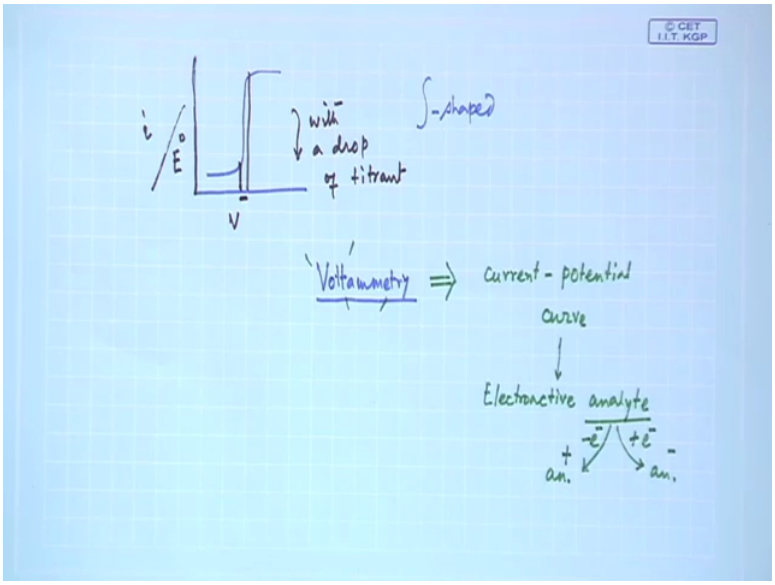

So the detection of this current by this amperometric method is useful when a sudden increase in current occurs that we have seen also earlier that what is there that is sudden change during the endpoint we get certain change in case of your potentiometric titerations what we have seen that the potential is changing and there is a sudden jump, so this staircase like or the integral type sometimes we call it as the integral step that integral step curve so this integral step curve will tell us that sudden change so you see that this particular change only few drops only, so this is your change so this is your E 0 axis and this is your volume. So this volume is very small, this volume is very small.

So as we always know that with a drop of titrant when it is coulometric, a drop of titrant at the endpoint there is a colour change certain colour change from say colour to colourless species or one colour to the other colour so this particular one will also give you the idea that you have a sudden change so sudden increase in now we are talking in terms of sudden increase in current I. So it can be in any unit, it can be milliampere it can be microampere or it can be nanoampere, but we should be able to plot it. So this plot will tell you that there will

be a sudden increase in current occurs on the generation of the corresponding species like your silver ion.

That means generation of slight access of silver ion there will be that particular current change that will affect your corresponding potential as well as the current which is being traverse because why you have the slight access of silver ion in the medium because your chloride has all been exhausted. Whatever chloride ions you had earlier in this biological fluid has all been consumed so that is the typical process what we follow for any titration or titrimetric method is that the silver ion will be now access because we are titrating everything with the silver ion so chloride concentration is 0 because all the chloride has been consumed to form the silver chloride and therefore, you have the corresponding sudden increase in current in terms of the corresponding ampere values and can be detected by the typical amperometric titration.

So the required amount of silver ion that you need for this sort of titration can be found out so which we are quantitatively with the Cl – is found from the Faraday's law how much you require depending upon the corresponding charge and the current we can use that can be useful from the well-established Faraday's law. So that basically tells us that how you can go for the typical technique which is your voltammetry. So as we have seen that earlier we used corresponding one that Faraday's law for the typical reactions where we can find out the corresponding charge in the coulometric process, now we can go for the voltamatric method.

So voltammetry like not like your potentiometry but you have now voltammetry or voltammetric methods of analysis. So you should immediately know that we are talking about something where these 2 terms are there, one is volt and another is ampere. Voltage versus ampere is there therefore, we have always we have if we get the plot the current potential curve what we are looking for. So the output of this particular technique the voltammetry method of analysis will give rise to a corresponding current potential curve for any electro active analyte. So the analyte should be electroactive that means that species or the analyte what is there, it can go for oxidation or it can go for reduction that means analyte, if you consider it can be oxidised or analyte it can be reduced by taking electron or by using electron okay.

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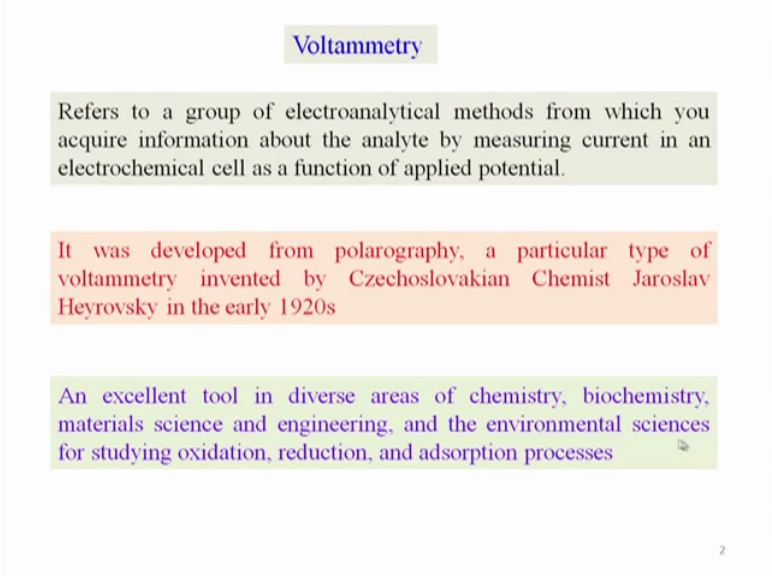

So if it is there we can get a particular methodology what will be called as the voltammetry methods of analysis and there are different things that means we will not find any time for discussing once again the corresponding electrodes, but the basic idea behind changing or the corresponding improvement of the electrodes compared to your potentiometric method that we will discuss. So a group of analytical methods so we are jumping on somewhere where not only a single method of analysis but a group of methods we can have and when we can get the information by measuring the current in an electrochemical cell, so we will still with that electrochemical cell now we try to measure away from your potential measurement, away from your coulomb charge measurement.

Now we consider to measure the current as a function of applied potential that means you are polite potential will not be now fixed, it will now be variable and with that variation in the applied potential to the analyte, we will find out the corresponding current change with that particular process and we will try to plot the current versus potential plot which is your typical voltammetric plot, but the discovery the historical discovery has been made by Professor Hetrovsky of Czechoslovakian origin basically started all these things during 1920, for that later on he got Noble prize also for that. And that particular time this is a different one is not considering as a voltammetric type of thing but it is a special type of voltammetry which is known as polarography.

So we have the electrode, on the electrode surface you see either oxidation reduction and that can be monitored nicely with respect to the unknown concentration of analyte which is giving

rise to the corresponding response of electron transfer. So is basically an excellent tool in diverse areas of chemistry, not only chemistry when it apply to chemistry we call it as analytical chemistry as well as the electro analytical chemistry. When we will apply to biochemistry, it will be analytical biochemistry or electro biochemistry or bio electrochemistry. For material science as well engineering and then the environmental sciences because in any case wherever we try to understand or try to find out the processes like oxidation, processes like reduction or sometimes the absorption processes.

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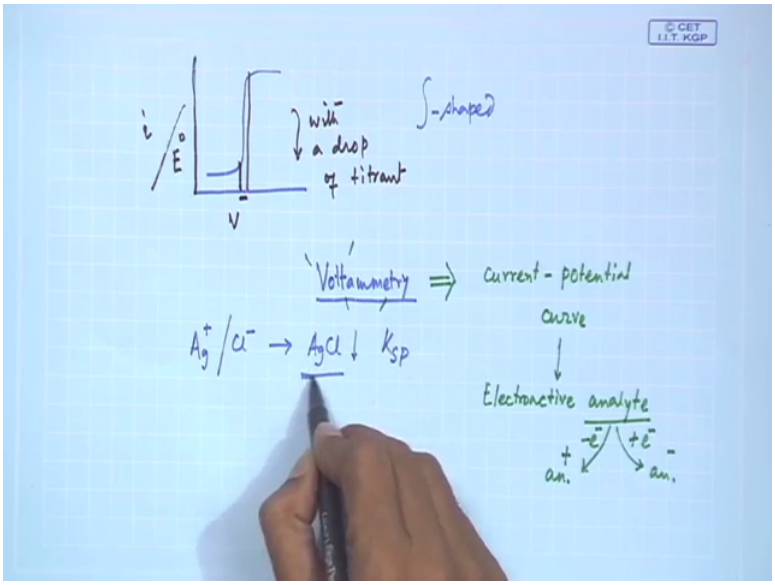

So these 3 things basically together initially we will discuss about the oxidation or the reduction reaction then finally we can think of the corresponding absorption processes because we know now that why you have the absorption related to these sorts of processes because we can have just now we have seen that you can get silver 0 to silver ion and when it combines with chloride ion you get the corresponding formation of silver chloride which is a precipitate we know it is insoluble medium having a certain magnitude of solubility product. So if you exceed the solubility product that means the individual multiplication of the concentration of these 2 ions you get the corresponding precipitation.

So this when initially form when it is very low concentration it is forming, it can form a film like material and as we know that this film like material and we are talking about something where you have the thing that you can have that corresponding one is the electrode. So we are talking about electron transfer on electrode and we are talking about some solution and this is forming in the electrochemical cell, so it is surrounded by this particular electrode so you can

have a very thin film of this materials can be deposited, so once they are deposited as a film on this electrode and if these are considered for the corresponding absorption.

So we can study the absorption processes as well and the very simple idea how you apply your idea for that because if you know the corresponding the position as you know that the coulometric deposition on the electrode surface of the metallic state that means when copper is deposited from copper 2 + or cadmium is deposited from cadmium 2 + as the metallic species, we know that that the deposition will increase the weight of the electrode and it takes the corresponding weight and we find out the corresponding weight difference that means the Delta w for the amount of deposition related to the charge transfer.

Now, if any other material is also deposited on the film that we can find out and also this species that means what is being deposited on the electrode as a film is also electro active because you can go back again to your silver 0 because it is starting from silver 0. So if we can go back to silver 0 or any other species like that that means during that particular electron transfer reaction the material can be leased out can be removed can be eliminated from the electrode surface that means this particular type of absorption as well as the dissolution process from the electrode surface can also be monitored. So this oxidation, reduction and absorption processes can be monitored by means of this polagraphic technique or the most advanced one is your voltammetry technique.

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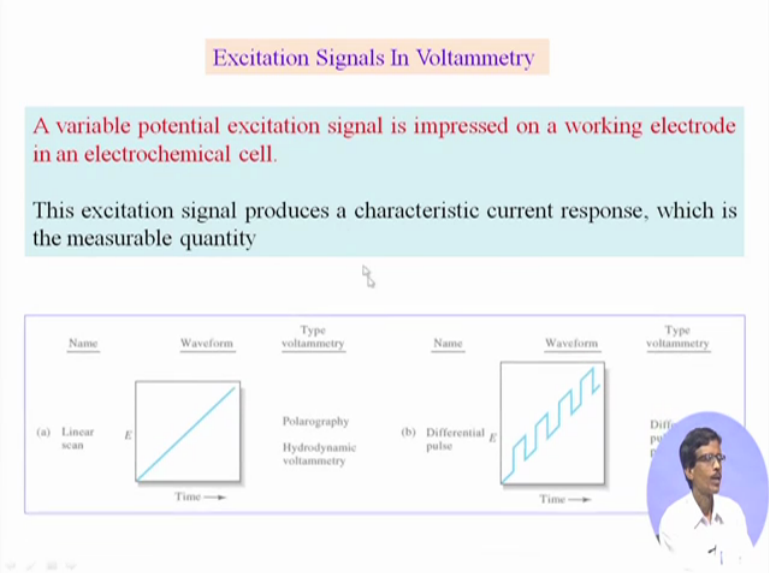

So during this particular process that means the voltammetry process what we use different excitation signal because why we get because we will be doing towards something the

process is known as cyclic voltammetry, why we are doing another term which is cyclic one is not a linear sweep safe cyclic sweep or linear sweep all these things are related to those things but particularly you should know what are the excitation signals that means the excitation signals how you put the corresponding potential. So a variable potential which is used for your excitation that means for your electro activity is allowed to get on the working electrode that means W we call in an electrochemical cell.

These excitation signal produces characteristic current response, so when you put the potential depending upon the signal because nowadays most advance instrumental technique and the computer control instruments also can give rise to all these advantages because most of these advantages are based on the development for the different computers and the corresponding instrumental parts basically which is the measurable quantity. So the current response we measure as we put the corresponding voltage as ramp say. So if you have a typical waveform how we call it so is the linear scan so some will be transferred as the corresponding cyclic one as I told you so if you have the linear scan 1 so this linear scan voltammetric process is that now we will be considering with respect to time.

So how your potential is changing with respect to time so E is linearly increasing, so waveform looks like this so we get them for a linear scan voltammetric of thing so you have the corresponding polarography, it is a technique what we get from linear scan waveform is polarography and hydrodynamic voltammetry. So these are the 2 processes so that is why polarography is the oldest technique is almost 100 years old, so this 100 years old technique but it has the original for that type of waveform. Now, once you know that the linear sweep voltammetry or the linear sweep polarographic method can be useful for this sort of analysis.

You can apply that to a chain in the corresponding waveforms if you have a differential pulse that means the differential pulse is your corresponding Delta E versus time Delta E Delta T, d by dt that particular form so it looks like this so you have the this particular point you have the corresponding pulse and this corresponding one that is also linearly increasing and the when it is coming back to this level this is also increasing linearly but the waveform is little bit different from that of (())(28:05) so at this point you have the corresponding pulse is the differential pulse. So if you give the differential pulse to the system, your nature of this plot will be different so the type of voltammetry what we get in your DPP is the differential pulse polarography.

So originally when it is linear one, you have polarography and when it is non-linear one or differential type of thing we get the differential pulse polarography. So in the same fashion when I will be seeing the voltammetric technique, it can be cyclic one also and this can also be at that point will be differential pulse voltammetry which we call as the DPV because nowadays these are all very routine because the oldest one historically these are all important but the improvement the technique is for is getting improved and the convenience of the process is increasing day by day, it should be very useful and the size of the electrode particularly, the electrode which are going through the micrometre size we call that microelectrodes but earlier we call the smaller electrode as the micro electrode.

So the development not only in terms of the electrode development but the electronic instrumental part as well as the ease of doing the operation that how quickly you can do or how quickly you can measure because sometimes we can call is as NS2 orXC2 that means you can do immediately if you have a solution you give the electrode and measure it. So these 2 are not useful nowadays because the polarographic technique is useful for the electrode type is the corresponding hanging marker electrode which is HME that means dropping marker electrode.

So that dropping marker electrode had some early advantages which has now been removed but handling a dropping marker electrode is not very much useful not very much handy because from the environment concern also the hanging dropping electrode is discarded that is why we are slowly moving from one technique to the other and remove to the voltammetry technique.

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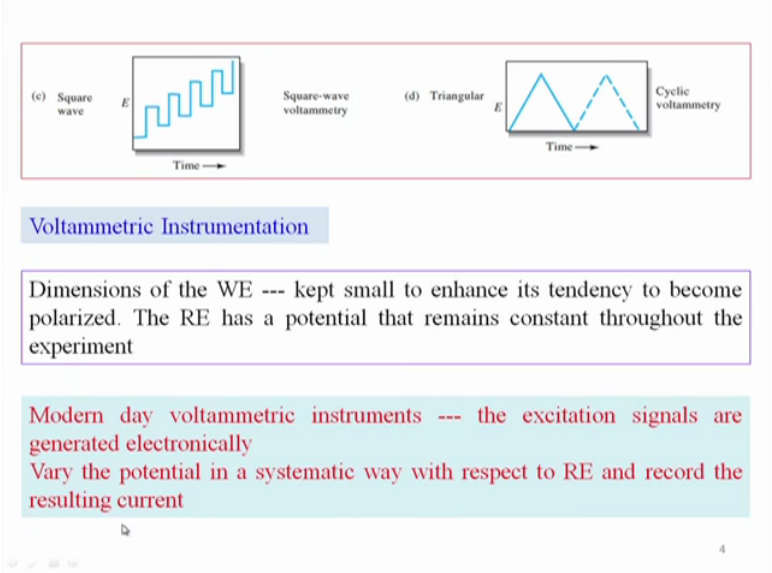

So when you have the square wave one the previously what we see is the differential + but is linearly increasing from say like this linear scan but when you get where wave, square wave is also changing but the wave is square or this type and the nature of this wave is different and we get the corresponding one is known as square wave voltammetry. So depending upon the waveform what you have, the name of the technique is also levelled with respect to that so if your waveform is square wave, it will be termed as square wave voltammetry.

If it is triangular and cyclic one it will be cyclic voltammetry because the triangular waveform what we get potential is moving from here is reaching some point and then it is coming back again to the original level but your time has elapse that means this part is not coming to here. So with respect to E so with a time cycle that means with second if you are able to scan a corresponding potential that means certain amount of millivolts say 500 millivolts if you are able to scan within a second, so you have a scan rate for that. So 500 or 100 or 50 millivolts which is the slowest possible scan rate so you have with time. So this is if this is a second scan, so what you do that means if it is 50 millivolts per second so half of the second it goes to 0 to 25 millivolts and then again it is turning back to the corresponding voltage again to 0.

So this triangular waveform is giving rise to the birth of cyclic voltammetric technique and that we will see how is full this technique is and is most convenient one so these waveforms should be generated by different voltammetric instrumentations and these instrumentations are depending on the working electrode, their dimensions as I told now just that you can have the microelectrodes, the smaller electrodes and they all kept small to enhance the tendency to become polarised that we have seen earlier that the polarisation effects are there when the

size of the electrode is more and RE in the corresponding reference electrode and it has a potential that remains constant throughout the experiment.

So how should I do that because since we are considering some reference, the reference electrode can be considered as a reference material and with respect to that reference we are measuring something? We will be measuring the working electrode potential also and if something else is also there which can also be monitored with respect to that reference electrode so this should be constant and how you get that constant reference electrode potential if you do not allow to pass any current through this reference electrode so we must have some alternative arrangement that we saw not allow to pass any electron through this reference electrode and this will remain constant throughout the experiment that means throughout the time period within which you are doing all these experiments for your measurements.

So the most latest type of this instrumentation that there is voltammetric instrumentation, the excitation signal these signals which generate electrochemically and definitely these are all computer-controlled that is why and this computer-controlled and electrochemically generated waveforms will give rise to corresponding measurements only and what we do is that the potential in a systematic way will vary or will change and with respect to the reference electrode we record the resulting current so that is the most important thing that how you follow the thing that you bring the reference electrode.

And the local electrode will say us and will give us the values what we can put on the working electrode and with respect to that we now record the corresponding current what is being passed through the electrochemical film for your plot of your current potential plot so that we will see in our next class that how we can continue with that how we measure and how we get the corresponding current potential curve for its measurement. Okay, thank you very much.