Analytical Chemistry
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Module 10
Lecture No 50
Electrochemical Methods-II (Continued)

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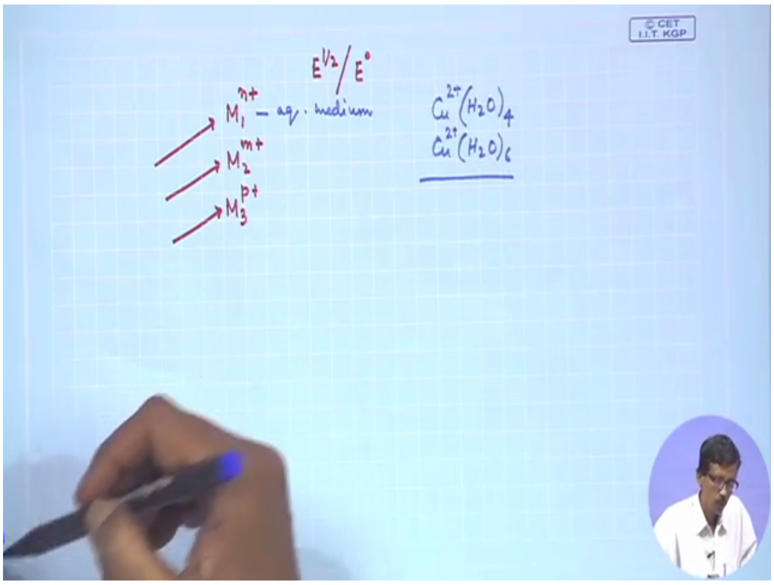

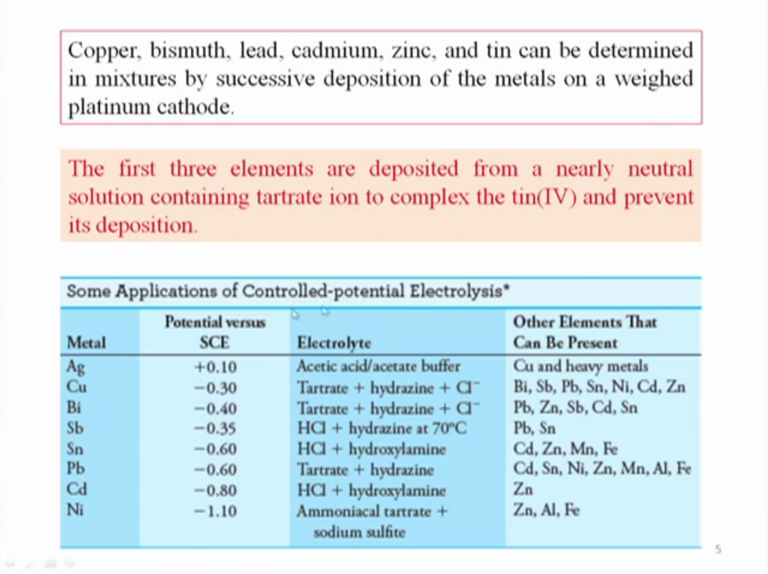

Copper, bismuth, lead, cadmium, zinc, and tin can be determined in mixtures by successive deposition of the metals on a weighed platinum cathode.

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

Some Applications of Controlled-potential Electrolysis*

Metal	Potential versus SCE	Electrolyte	Other Elements That Can Be Present
Ag	+0.10	Acetic acid/acetate buffer	Cu and heavy metals
Cu	−0.30	Tartrate + hydrazine + Cl^-	Bi, Sb, Pb, Sn, Ni, Cd, Zn
Bi	−0.40	Tartrate + hydrazine + Cl^-	Pb, Zn, Sb, Cd, Sn
Sb	−0.35	HCl + hydrazine at 70°C	Pb, Sn
Sn	−0.60	HCl + hydroxylamine	Cd, Zn, Mn, Fe
Pb	−0.60	Tartrate + hydrazine	Cd, Sn, Ni, Zn, Mn, Al, Fe
Cd	−0.80	HCl + hydroxylamine	Zn
Ni	−1.10	Ammoniacal tartrate + sodium sulfite	Zn, Al, Fe

Ok welcome back where we were discussing about that deposition for one after another metal ions, if you have a metal ion say M1, you can have a metal ion M2 or you can have a metal ion M3 of certain charge that is M +, M + or P +. So all will receive electrons for their reduction and only thing that you have to monitor the corresponding E half or E0 values for their electro deposition. So how much you have the corresponding selectivity and we all know that if it is binding to some other groups that means all these species if you have a solvent like water that means in aqueous medium, suppose we are talking in terms of the corresponding deposition of copper2 +.

So it is not that you have the copper2 + it will be bound to say 4 water molecules. So this aqueous species, it can be 4 or sometime we can find that it can be hexaco also this retract one the hexaco species, can copper2 + and bound to these water molecules, can be deposited. So this aqua species can have some E half values or the E0 values for this electro deposition. So just now for binding the tin what we have seen that the tartrate ion the tartrate ion is a chelating species that it can bind more than one positions for these metal ions in the tetravalent state of tin.

So if we go for typical control potential electrolysis for several metal ions, thing is that we will have only the corresponding deposition. Potentials are different these are not exactly your half cell potential values for silver ion to silver copper ion to copper but something else. As we discuss earlier that you have the ohmic potential, you have the corresponding IR drop and all these things and we can have other elements that can be present. That means the selectivity for this particular species is so good that once you fix the potential at say + 0.1 volt. In acetic acid acetate buffer because most of these cases we get in the neutral medium but others are in slightly acetic condition.

So this is the corresponding one for silver deposition that means acetic acid acetate buffer, we know the corresponding pH value for the acetic acid acetate buffer. And copper like and copper other metal ion cannot interfere there can be present, so selectively we can reduce silver at this particular potential value. Similarly copper, bismuth as I told you that is copper to zinc and tin basically, so you see all these cases such as that of your tin and all you have a different potential values for all these things. So these potential values and sometimes you see that the corresponding interfering metal ions are present.

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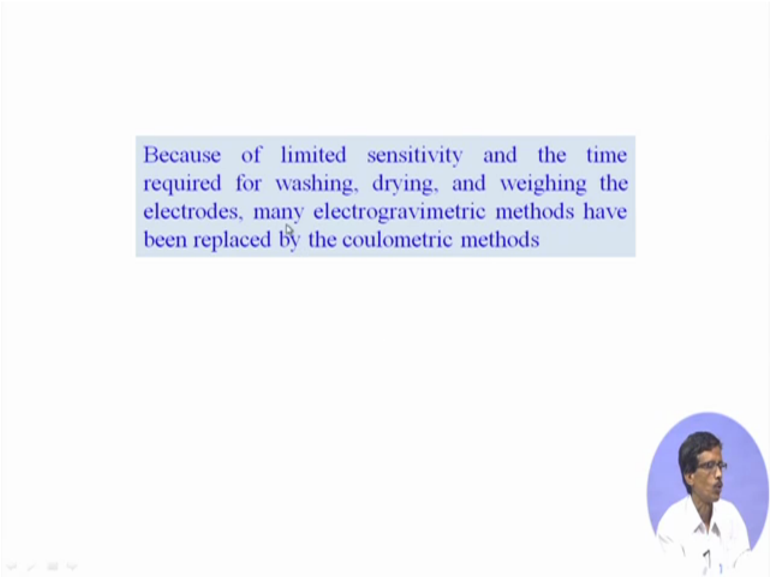

Because of limited sensitivity and the time required for washing, drying, and weighing the electrodes, many electrogravimetric methods have been replaced by the coulometric methods

So in presence of all these things basically we can reduce the corresponding metal ion selectively if we fix the corresponding potential at this value. So what we get therefore that your corresponding sensitivity and selectivity is very good. So if we have that sometimes this you can have also the selectivity, if the selectivity is not so high and the time required for washing, drying and weighing of the electrode, because it has several complicated steps you see that you have the electrode, it has been deposited by some other metal ion say platinum has been deposited by copper.

You wash it from the solution then dry it and then take the weight of the electrode to find your delta W. As I told you to find the delta W that means it will tell you that how much metal ion as copper has been deposited as metallic copper on the platinum electrode. So many of these electrogravimetric method that is why is taking some time. And if the selectivity is not so high it is therefore a little bit cumbersome procedure. So which can be replaced by more useful and more functional form of the method which is known as the coulometric methods.

So now we will see what this coulometric method is and how the coulometry can be utilized for your deposition or for the complete electrolysis in terms of the amount of charge which is being passed through the solution. So in this previous case that means electrogravimetric analysis what we have seen that you have to physically deposit the material on the electrode surface, then you take the weight of that material which has been deposited on the electrode surface. But instead of that if we go for the other one that means the amount of charge during electrolysis, if we are able to determine or calculate or measure the coulomb count or the coulombic charges which is being passed through the solution.

And if we can go for exhaustive electrolysis that means the amount of charge which is being passed at that particular potential is basically decaying to 0 as we have seen, then the current is decaying from certain value to a 0 value. So basically this particular method is very much useful to determine exactly the charge which is being passed through the solution.

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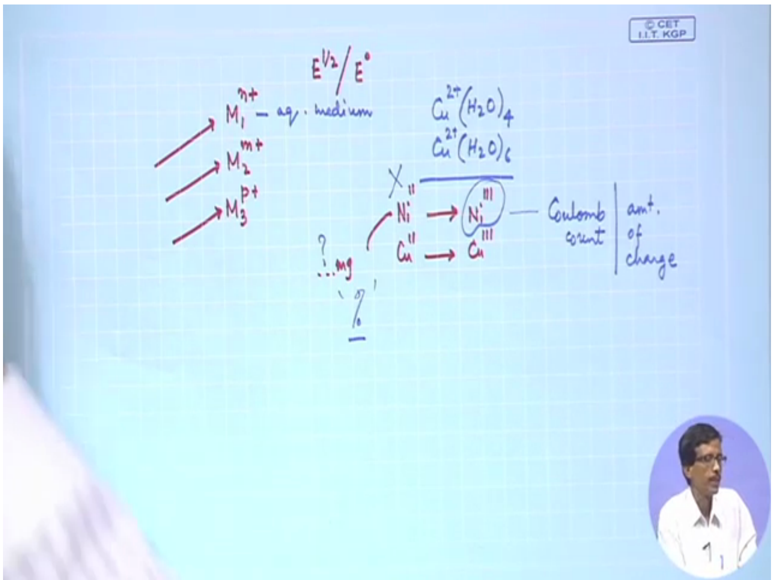

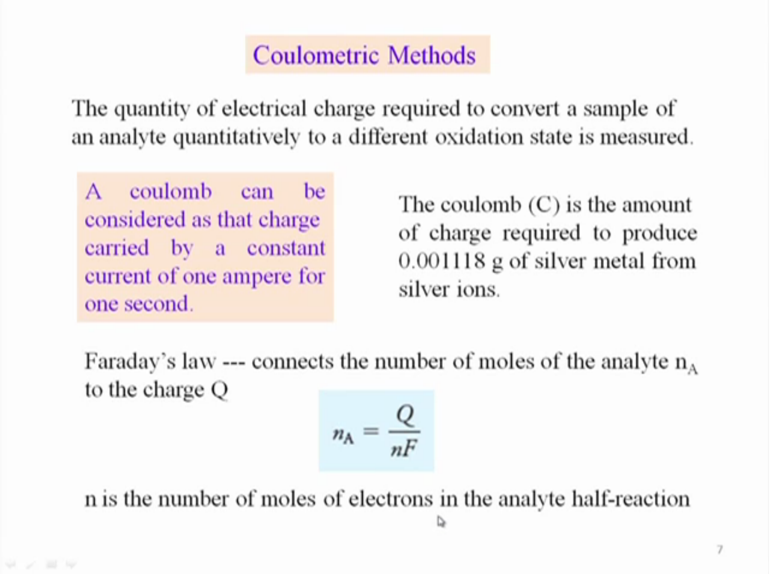

Coulometric Methods

The quantity of electrical charge required to convert a sample of an analyte quantitatively to a different oxidation state is measured.

A coulomb can be considered as that charge carried by a constant current of one ampere for one second.

The coulomb (C) is the amount of charge required to produce 0.001118 g of silver metal from silver ions.

Faraday's law --- connects the number of moles of the analyte n_A to the charge Q

$$n_A = \frac{Q}{nF}$$

n is the number of moles of electrons in the analyte half-reaction

So what we see that coulometric method that coulomb we have to calculate or we have to form. Coulomb is in terms of the capital C we all know so this coulomb can be found as the quantity of electrical charge required so we will be now measuring the corresponding amount of electrical charge, which will be required to convert a sample of an analyte quantitatively to a different oxidation state is measured.

As I told in our previous h paper that you have these oxidation of some nickel compound or some copper compound, both of them are in the bivalent state that means the nickel in +2 and copper in +2 also and if we can oxidize this compound it can be a metal ion complex to nickel3 or copper3 then knowing the corresponding amount of the compound what we are taking in milligram, say we can calculate out the corresponding charge which will be required for complete oxidation of these compounds to its corresponding oxidized form. That means the coulomb count you can calculate theoretically, so you know the amount of charge which is required for complete oxidation of the nickel complex to nickel in the trivalent state.

So this basically so when you go for complete oxidation that means this will not be there in the solution so no more bivalent nickel complex in the present in the solution, so exhaustive electrolysis that means solution will have only the trivalent nickel. And the amount of charge which is being passed as knowing the corresponding coulomb count will also give you how much nickel is present as its corresponding nickel compound.

So by knowing the corresponding amount of charge you can find out the amount originally present as well as its purity that means percentage of that particular sample if it is present with other species within the solution or in the powder form which is has been taken to this solution. So the charge required to convert from one oxidation state to the other that means whether you are going for a oxidation or reduction that is known. So it is the charge which is carried at a constant current of 1 ampere for 1 second this is the corresponding definition of 1 coulomb we know.

And a typical coulomb charge is the amount of charge required then again in terms of an indirect way of this defining this is that electrochemical equivalent we know that electrochemical equivalent of the silver metal from the silver ions is known and that is basically, by definition it is the ampere multiplied by the time is giving you the corresponding coulomb charge but it is also for a standard process for deposition of silver metal from silver ion.

And if the deposition is 0.201118 gram off silver the charge will be passed is 1 coulomb. So you have to go for the corresponding use of Faraday’s laws to find out the corresponding coulombic charge what is being passed through the solution. So as we know that the Faraday’s law can connect the number of moulds of the analyte, basically now we are looking for just now what we have seen for your milligram concentration, so this milligram concentration will now be converted to the corresponding moles of your analyte because this is your unknown thing which can be correlated to your corresponding coulomb count for your coulometric methods of analysis.

So now two things will now correlated is nA is the moles of analyte and the charge which is Q or C in the units of C which is there. So the moles of analyte because is the coulomb is the corresponding Faraday charge, Faraday charge is for 1 mole so you have the nA that means the number of moles of analyte and the charge if you know these two things so you will get the number of moles of electrons in analyte half reaction. So we can find out this and not nA this n is the number of moles of electrons basically h in the analyte half reaction. So this particular formulation can give you the corresponding amount of charge as well as the corresponding amount of electricity what is passed through the solution.

And when we see that the both the potential as well as the current is decreasing with time so the whole amount we can go for determining in this way, that if we integrate over sometime is 0 to 20 minutes or something. So the integration for that whole path or the whole time will give you the corresponding total charge for that, so not only the current which is a variable quantity but also the corresponding time also. So this basically give you the corresponding coulombic charge so for that particular integration over the time period will give you the total coulomb charge which is being passed through the solution.

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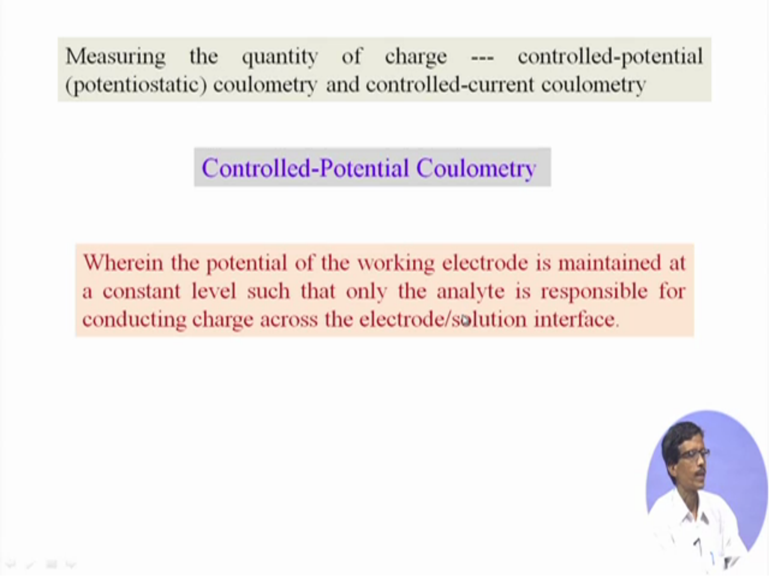
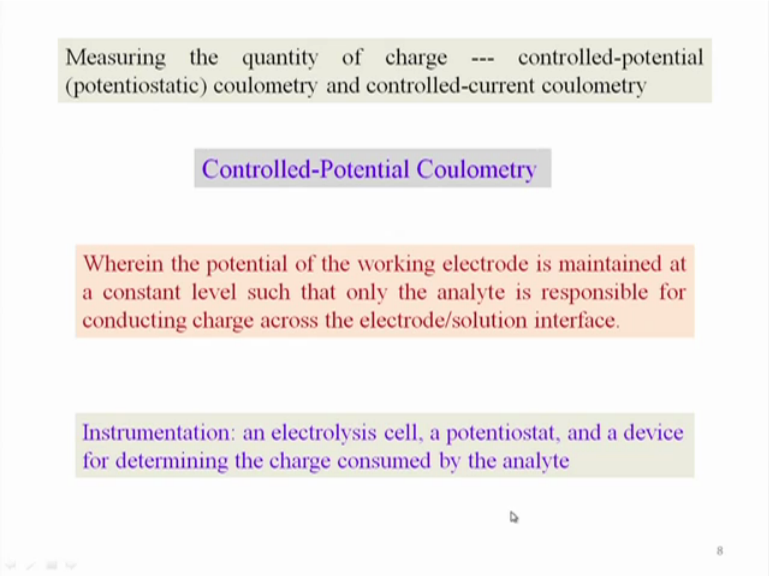


Measuring the quantity of charge --- controlled-potential (potentiostatic) coulometry and controlled-current coulometry

Controlled-Potential Coulometry

Wherein the potential of the working electrode is maintained at a constant level such that only the analyte is responsible for conducting charge across the electrode/solution interface.



Measuring the quantity of charge --- controlled-potential (potentiostatic) coulometry and controlled-current coulometry

Controlled-Potential Coulometry

Wherein the potential of the working electrode is maintained at a constant level such that only the analyte is responsible for conducting charge across the electrode/solution interface.

Instrumentation: an electrolysis cell, a potentiostat, and a device for determining the charge consumed by the analyte

So we basically go for some automatic instrumental techniques that means how to measure the quantity of charge which is being passed. So control potential coulometry or constant current coulometry. So these are the two basic processes or techniques we can have. So just now what we are discussing is the corresponding control potential or fixed potential which is known as also potentiostatic, because this control we are controlling the potential for coulometry. So at a particular potential you go for a coulometric oxidation or reduction and in other case you can have the control current that means the current can also change and you get the corresponding coulometric charge from there.

So we are in one case we do not bother about the corresponding current in other case we do not bother about the corresponding potential, but you are able to measure the corresponding charge. So the first technique is your that control potential coulometry where we get that the potential at the working electrode is maintain at a constant level. That means whatever we have seen that whether you have a + 0.1 volt of potential or - 0.6 volt of potential for two different analytes for two different metal ions to be reduced on the platinum cathode. So what we see here for this definition that only the analyte is responsible for conduction charge.

So it is the analyte so we are pin pointing that particular analyte which is electrode active that means which is say going for reduction is responsible for conducting the charge. That means whatever charge we are measuring by this coulometer is due to that particular analyte across the electrode or that solution electrode interface. So this solution electrode interface is giving us that particular analyte which was there in the solution as ditching the electrode and then electrode is giving the electrons required number of electrons at that potential for the reduction of that your analyte.

So automatic instrumentation now-a-days is available so you do not have to bother about what you can do with the instrumentation so what you have the most important thing is your beaker or the electrolytic cell so which you consider as an electrolysis cell. Then you have what we are measuring is that the controlling the potential a potentiostatic unit, a potentiostat, a device for determine the charge consumed by the analyte, that means you have the corresponding coulometer over there which can automatically calculate out a digital coulometer we all know. So digital coulometer can also calculate out the total amount of coulomb to be passed for exhaustive electrolysis in the coulometric cell.

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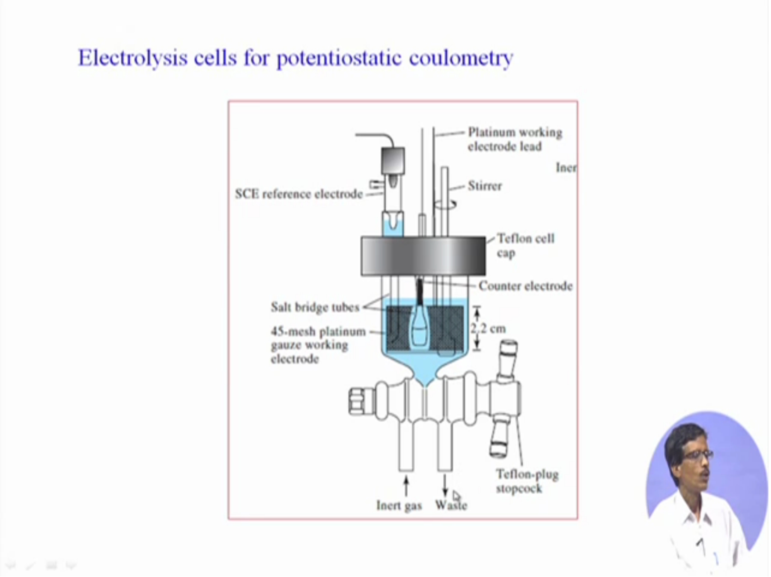

Electrolysis cells for potentiostatic coulometry

So if you have the electrolysis cell for potentiostatic coulometry how it looks like and what is the corresponding formation of these things. So we have introduced something that you can have a number of electrodes and that electrodes can have your reference with that of your corresponding reference electrode. So when you go for this electrolysis and we are basically looking for a coulometric measurement, that means we are going to measure with the help of a coulometer at a fixed potential what we find by the use of that particular coulometer.

So you have the cell this is the corresponding cell you have in your hand, so this cell basically you have and this particular cell can have the corresponding electrodes. So you have the standard reference electrodes as a saturated calamine electrode, you have the corresponding platinum working electrode is, so this is the platinum working electrode and you have the corresponding counter electrode. And also you have the corresponding salt bridge tubes are available, so counter electrode is there and the corresponding platinum electrode. So this is the cell and the corresponding placement of the different electrode so you have the reference working as well as the counter electrode.

So this is basically the same thing what we have seen earlier that is a three electrode system in the block diagram what we have seen, that particular three electrode system is there stop and this particular thing that means what you have these working electrode so platinum working electrode or platinum working electrode lead basically, so that is basically the corresponding not that thing this is the connector and this is the corresponding wire gauze. So it is 45 mesh platinum wire gauze ties your working electrodes.

That means you are covering the entire area because this thing will be a very first process only a few minutes you take for exhaustive or the complete electrolysis of the solution. And you see that there will be a colour change if you go for a electrolysis or complete electrolysis from this particular wire gauze is known a simple disc type of electrode or wet type of electrode as we do for potentiometric measurements or we will see in our next class as the voltametric measurement.

But the coulometric measurement you have to go for the corresponding surface area of the electrode is very hig. H so you have the corresponding platinum wire gauze that is there that means it has less adsorption, also so is a fine mesh wire gauze system and then you have the corresponding stirrer, the magnetic stirrer from the top, the motor is over here. So motor is connected to this stirrer and stirrer is giving you the corresponding stirring condition. So this particular stirring condition is very useful also because the coulometry we do under stirring condition also, because the whole solution to be stirred because if there is something which is diffusion controlled and on the surface of the electrode if it is not stirred that means for an unstirred solution the solution or the analyte which is very close to your electrode mesh or the electrode wire gauze will be reduced.

So the solution over here or the analyte concentration over here will not immediately reaching your electrode surface that means you do not have a homogenous solution in terms of its decrease in concentration that means the concentration that means the depleting concentration of the solution should be homogenized or mixed uniformly by a magnetic stirrer which can be over head, that means motor is over here.

So overhead magnetic starrer will stir this particular solution, so that is basically a blade type of thing, so that blade is moving very fast way and giving you this particular one and in sometime also you go for this over, if it is not from the top through this Teflon cell cap, we can have some other arrangements, such that you can go for the gas that inert gas nitrogen, argon and helium. And you have them stopcock arrangement for drain out the corresponding material which you get through oxidation or reduction, that means you do not need to open up the cap and remove the solution.

If you have this arrangement for this so the stop cock is basically the Teflon plug stopcock is for one way it is moving the solution is covered with that inert gas of nitrogen and another way when the electrolysis is finished you can drain out in that particular material that means the oxidized form of the solution through this waste pipeline or waste outlet.

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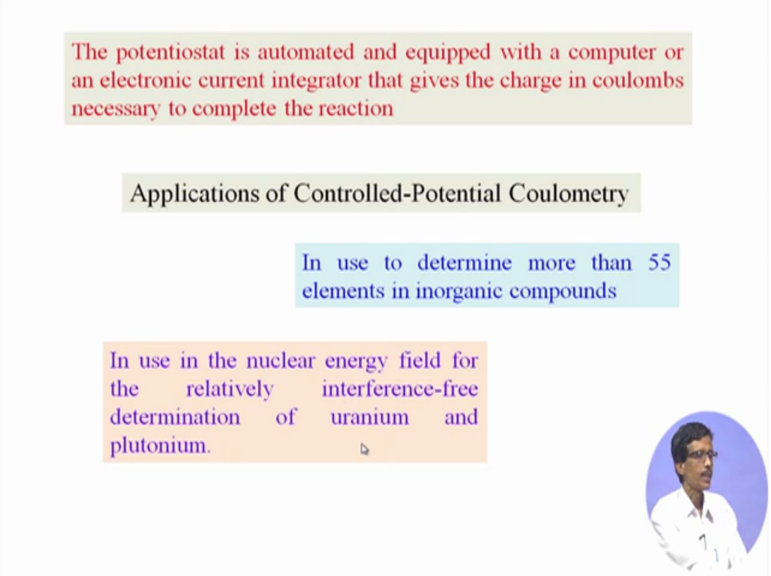

The potentiostat is automated and equipped with a computer or an electronic current integrator that gives the charge in coulombs necessary to complete the reaction

Applications of Controlled-Potential Coulometry

In use to determine more than 55 elements in inorganic compounds

In use in the nuclear energy field for the relatively interference-free determination of uranium and plutonium.

So this automatic instrument or the automated potentiostat how it is useful to us is that is automated and equipped with a computer, because now-a-days is the microprocessor controlled and the computer controlled thing, can give rise to your automatic change in the potential value as well as the recording of the current. So this potentiostat which we consider is that is automated one and is equipped with a computer or electric electronic current integrator that means how much current that means as I told you that mathematically we go for the integration for the charge transfer that gives a charge in coulomb necessary to complete the reaction.

That means that how much current that current indicator will give you the total calculation for the coulombic charge because the coulometer recording in the digital display will show you that how much current has to be passed for complete electrolysis, whether you are going for oxidation or reduction. So there are many number of your control potential coulometric things, that means these are very useful also in terms of determining any unknown analyte concentration. So your analytical technique that electroanalytical technique is very much useful in terms of your coulometric estimation and one such technique is your control potential not the control current one.

Which is most frequently used technique is your control potential coulometric method for the analysis and we can have large number of elements in inorganic compounds such as 55 numbers it can have. So experimentally people have determined 55 elements in inorganic compounds that means the species which are getting reduced or which are getting oxidized also, because the corresponding anions the corresponding non-metallic anions can be oxidized like that of your metallic cations which can be reduced. Then in the area of nuclear chemistry or the corresponding nuclear programme we can have uranium and plutonium.

So the in the energy field because in the all the nuclear reactors we use this particular as the corresponding fuel. So the relatively interference free determination of uranium and plutonium is required. So these two if the corresponding concentration as a fuel of plutonium and plutonium can be determined, so coulometric technique is also useful for the determination of these radio active species like uranium and plutonium for their relative percentages present in this nuclear fuel which is to be introduced for the nuclear energy production.

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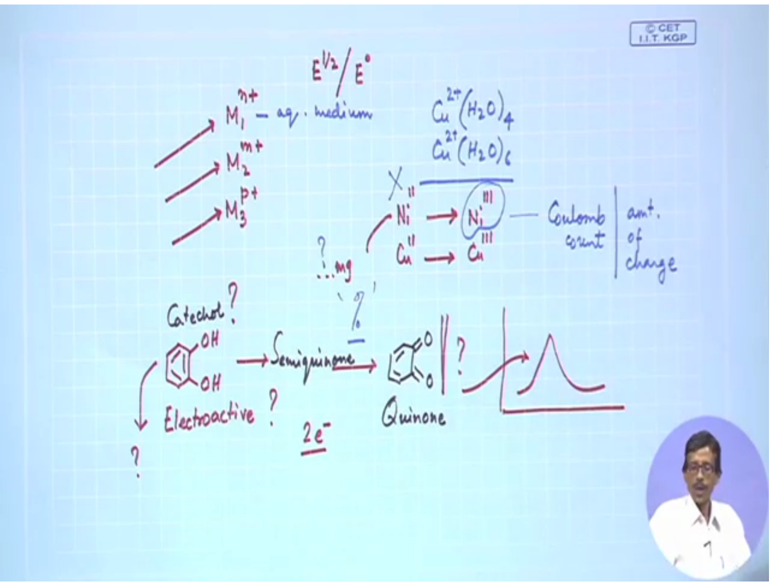

And one very useful example can be that electrolytic determination of organic compounds so what you find that you have seen that metal ions can be reduced copper ions can be reduced to give you the corresponding copper as your copper metallic deposition on the electrode, but some good organic compounds you can have. So electrolytic determination so once you have that means your species that organic compound is electroactive, such as there is simple compound of example is your h the corresponding catechol, we can take the 1,2 dihydroxybenzene it should be electro active.

That means it should go for electron transfer, so if we go for this that means this can be oxidized and you can get the oxidized product as your Quinone, this is Quinone this was your catechol. So this particular reaction is very useful also for this particular type of electro analysis or electrochemical determination because it goes through the intermediate also which is semi quinone. So these things basically, the number of electron transfer because this whole process, if it is a two electron transfer we can measure that and sometime we want to determine the unknown concentration of catechol in any species.

Because biologically also this is important, catechol oxidizes are there which are a normal one and for different biological species, important biological species such as your neuron transmitter formation or neuron transmitter generation in our body also, in the human body, so the catechol oxidizes are there and oxidizes are useful for oxidizing the catechol. But if we want to know the corresponding concentration of this catechol which is your analyte, so you go for this corresponding Quinone.

And if we can measure only the charged transfer or you can detect the corresponding presence of Quinone in terms of his corresponding other property, you can have the corresponding electron transition that means the electronic absorption, for this Quinone which is very much is very much specific. So electronic charge which can be correlated for the corresponding concentration of Quinone as you measure or as you determine in terms of its corresponding formed amount of this Quinone.

So organic compounds so different such organic compounds are very much useful for its determination that means the amount present like that of your Quinone and the catechol thing. And sometime the synthesis also because the electron transfer what you can give that means either you oxidized or reduced because we know that these are the typical chemical reactions what we can perform in some substrate. So if we have a substrate like A and if we want to oxidize it to a product B what we do we add some oxidizing agent to convert A to B.

Similarly if we convert A to C by reduction we use some reducing agent. So these all we do chemically, so chemically we go can go for oxidation as well as reduction for the production or the synthesis of a new organic compound. But here we will take two examples of these types of electron transfer reaction on organic molecule. One is your trichloroacetic acid and another is picric acid because these are very useful also chemically and also in some different techniques what we use based on your chloroacetic acid and picric acid.

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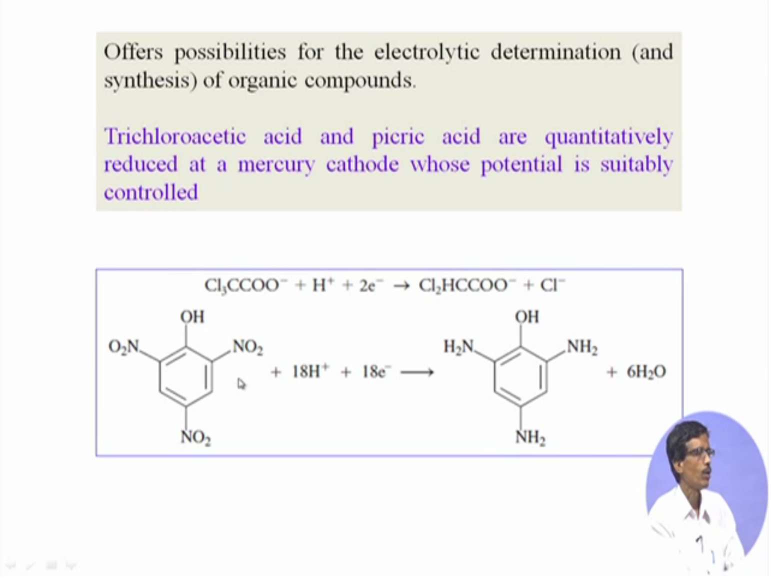

Offers possibilities for the electrolytic determination (and synthesis) of organic compounds.

Trichloroacetic acid and picric acid are quantitatively reduced at a mercury cathode whose potential is suitably controlled

$$Cl_3CCOO^- + H^+ + 2e^- \rightarrow Cl_2HCCOO^- + Cl^-$$

So at a mercury cathode now you take a mercury cathode because mercury will not react with all these two species. And sometimes we use dropping mercury electrode the DME we call the dropping mercury electrode. But if you have a pool of mercury that means some amount of mercury on the bottom of the cell or the beaker and whose potential is given for some conversion that means a known potential is given to that particular thing that means if you have a substrate like trichloroacetic acid.

This is the substrate and which should be reduced by 2 electron 1 proton transfer which will give you a corresponding species as your dihloroacetic acid. So this dichloroacetic acid is produced due to the corresponding breakage of your CCl bond. So CCl bond is being removed as chloride is coming out from this trichloroacetic acid. So this reduction process in other ways is very useful technique, that not only we are synthesizing that means is a typical process for your electro synthesis and this electrosynthesis is giving rise to a new compound which is your dichloroacetic acid.

But at the same time you are producing chloride, anion in the reaction medium. That means you see some organic chlorinated compound because we know that chlorinated because we call as a halogen derivative so halogenated organic compounds are not all the time very useful. But if we go in this manner that means if we are able to take out all the chlorine that means removal of chlorine in a step wise manner from this molecule ultimately we will produce something where we have the corresponding thing that is you have the corresponding one as your CH then CH2 then CH3 will be your acetic acid itself.

So whether we can go for this step wise removal of chloride ions from trichloroacetic acid but at least the first step is operating over here very nicely. So this operation will tell you that you can remove chlorine that means that the carbon chlorine bond can be cleaved. And the heterolytic cleavage will give you chlorine as the chloride ion and proton will be attached to your molecule to giving you the corresponding dichloroacetic acid. And is a typically two electron single proton transfer reaction which is also useful to know because in organic chemistry we do some conversion but we do not care about the number of electron transfer which is being taken over there for this conversion. So another example is trinitrophenol we know which is a picric acid which is a very strong acid compared to phenol itself.

So this picric acid can be reduced nicely electrochemically. Because chemically it can also be possible to reduce your nitro function to amine function, but here three nitro groups are present and these three nitro groups can be reduced to three amine functions, it will be then triaminophenol. So this triaminophenol can be obtained from there and this is also a very interesting reaction to study, that there also that NO2 can be converted to your NH2 function and you see that all these, that means you have three nitro group and these three nitro groups are being converted that means if you have any substrate that also give rise to some indication for number of electron transfer for NH2 to NH3.

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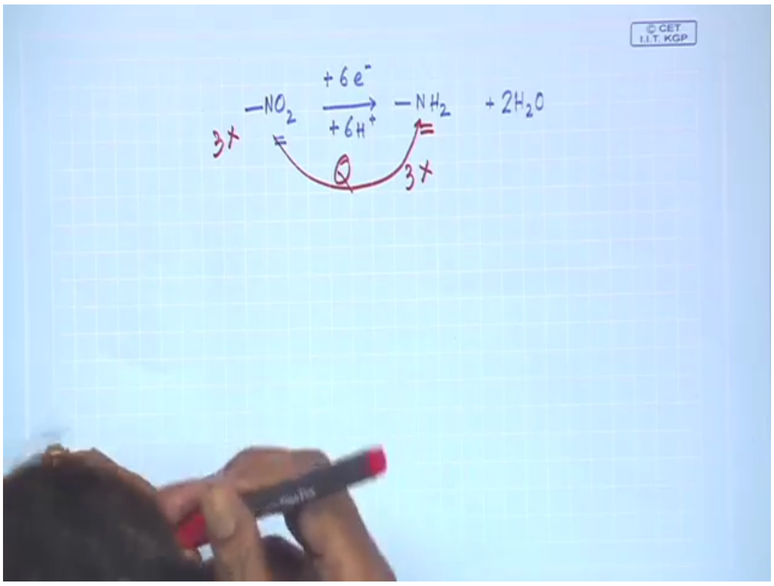

So will be you have to give 18 by 3 you have 3 nitro groups in it, so 18 by 3 is your 6 electron transfer reaction. So not only you have the corresponding 6 electron transfer reaction but also at the same time you get 6 proton transfer reaction. Because for these you have to produce the corresponding one that means you have to produce the corresponding water molecule over there. So if you take out both the oxygen atoms over there so you require to have to balance it in this fashion, that means 4, 6 protons are going 6 protons 2 of them are utilized for your production of ammonia, that amine function and 4 other are required to trap this particular water production.

So this thing that means if you just simple write in this way because while doing this organic chemistry if this we know that the conversion is your typical functional group conversion and nitro can be reduced by so many reducing agents chemically available reducing agents can be used for your conversion. But when you go for typical electro chemical reaction we should precisely know that how many number of electrons are getting transferred because we are talking in terms of not only this particular thing that you have to have the corresponding number of electron transfer for direct conversion of this nitro group to your amine function.

And also the number because in picric acid your 3 number so whether all three will be reduced to your amine function or not. That means whether you have a partial reduction or a complete reduction and that also you can find out not only identifying the product but also by knowing the corresponding charge in from the coulometer ok. Thank you very much.