Atomic and Molecular Absorption Spectrometry for Pollution Monitoring

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Lecture – 11

Woodword Fieser rules, structure - property relationship

We will continue our discussion on Woodward fieser rules for dienes, dienones, ketones, dia etcetera. And I had explained to you yesterday that Woodward fieser rules.

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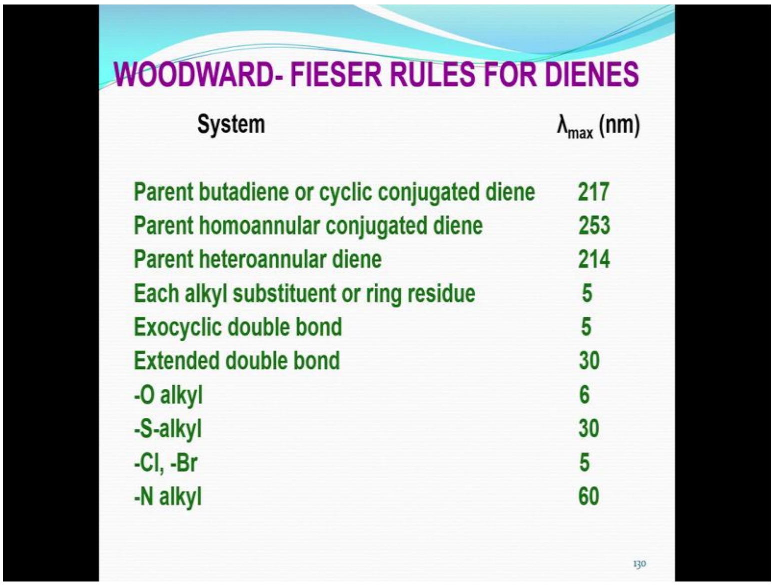

WOODWARD- FIESER RULES FOR DIENES

System	λ_{max} (nm)
Parent butadiene or cyclic conjugated diene	217
Parent homoannular conjugated diene	253
Parent heteroannular diene	214
Each alkyl substituent or ring residue	5
Exocyclic double bond	5
Extended double bond	30
-O alkyl	6
-S-alkyl	30
-Cl, -Br	5
-N alkyl	60

Basically describe where a best peak has to be form can be decided. And then all other functional groups including conjugated dienes etcetera contribute to the shifting of the lambda max, and we can estimate where the UV visible peak can appear. So, these are the basic rules like we will just to remind you, that butadiene or etcetera co conjugated dienes 217 and 250 homoannular dine is 253 like that best peak etcetera.

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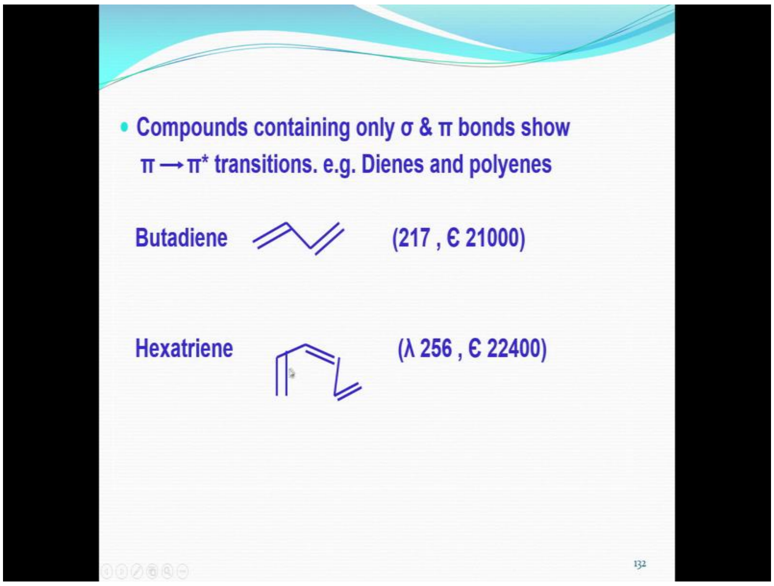

- Compounds containing only σ & π bonds show π → π* transitions. e.g. Dienes and polyenes

Butadiene (217 , Є 21000)

Hexatriene (λ 256 , Є 22400)

We were trying to do couple of examples. This is the conjugated diene. Double bond single bond double bond double bond single bond double bond single bound etcetera.

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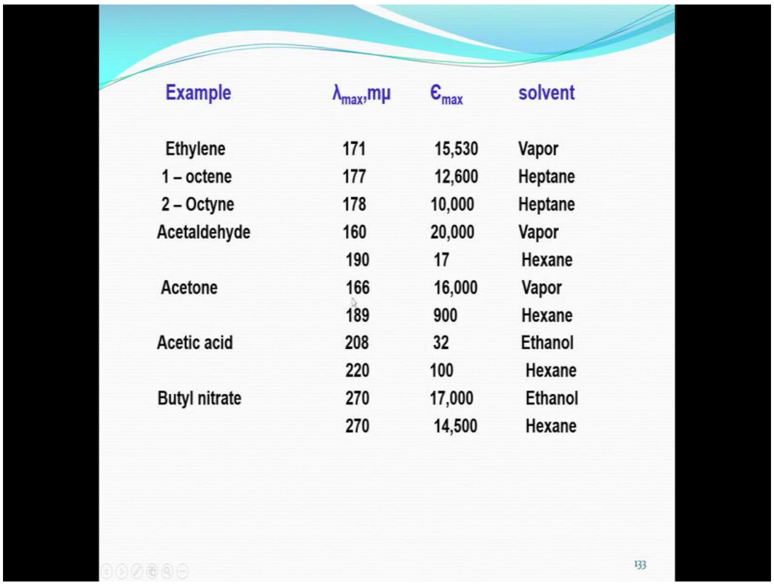

Example	λ_{max}, mμ	$Є_{max}$	solvent
Ethylene	171	15,530	Vapor
1 – octene	177	12,600	Heptane
2 – Octyne	178	10,000	Heptane
Acetaldehyde	160	20,000	Vapor
	190	17	Hexane
Acetone	166	16,000	Vapor
	189	900	Hexane
Acetic acid	208	32	Ethanol
	220	100	Hexane
Butyl nitrate	270	17,000	Ethanol
	270	14,500	Hexane

And then we had added explain to you, how we can estimate the lambda max, which corresponds to what type of transition. So, for example, whether it is n to pi star or pi to pi star depending upon the intensity of the transition as well as the wavelength.

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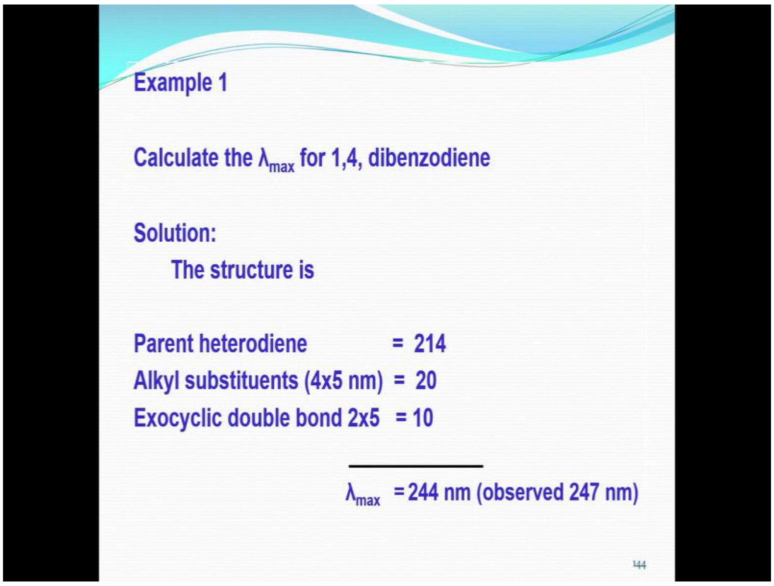

Example 1

Calculate the λ_{max} for 1,4, dibenzodiene

Solution:

The structure is

Parent heterodiene = 214
Alkyl substituents (4x5 nm) = 20
Exocyclic double bond 2x5 = 10

λ_{max} = 244 nm (observed 247 nm)

So, based on that we I had explain to you that we can estimate now this is the simplest example one for dibenzodiene the structure is here and parent diene is 214 there are 4 into 5 alkyl substituents exocyclic double bond is 2 into 5.

So, that the x the lambda max expected is 244 nanometers and observed is 247 nanometers. So, we can see how closely we come to the prediction of the wavelengths. In general I had to tell you that at there want be much difference between the absorption peak between if they lambda max is 244 and observed is 247. It comes within the experimental error purview. So, plus or minus 3 nanometers we can always expect depending upon the instrument.

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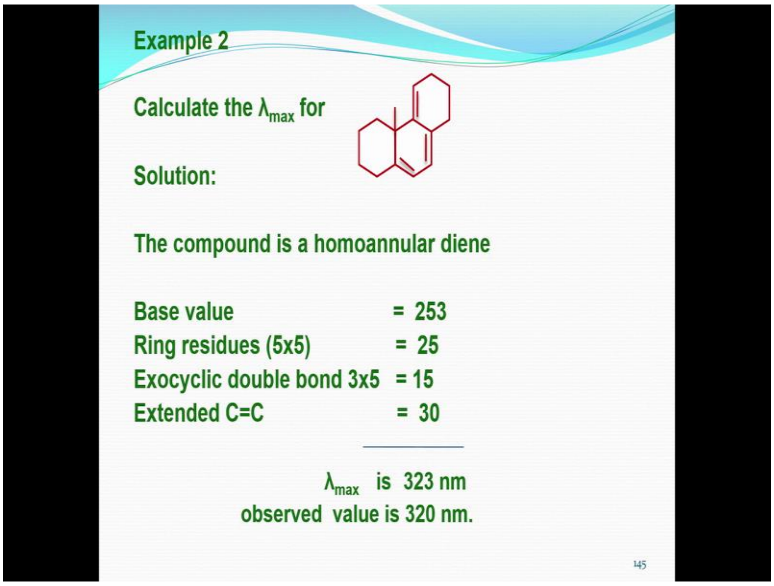

Example 2

Calculate the λ_{max} for

Solution:

The compound is a homoannular diene

Base value = 253
Ring residues (5x5) = 25
Exocyclic double bond 3x5 = 15
Extended C=C = 30

λ_{max} is 323 nm
observed value is 320 nm.

So, that is the kind of thing. Now I want you to look at the next example that is this compound. You can see that they this compound has got 3 cyclohexane rings and there are 2 double bonds and their one double bond outside the ring 2 double bonds inside the ring and there is one I alkyl substituent somewhere here. So, what do we do is we when we want to calculate where the lambda max is we take a base value of 253 because it is known as because it is a homoannular diene, the what do we mean by homoannular there are 2 double conjugated double bond system is located inside a ring.

So, this is double bond single bond double bond and all these are inside the ring. So, we take that the way we take it that the best peak should be at 253 nanometers. Now you can calculate the ring residue this is one, this is a one residue this is second residue this is third substituent and forth substituent and fifth substituent. All the bonds attached to double bond or you can take it as ring residue. So, you can see that if I start from the left, I can see inside the ring there is 1 2 and then 3 then 4 this is 5. 5 alkyls substituents are there ring residues.

So, actually these are ring residues and alkyl substituent means there will be 1 C s 3 group or something like that. So, we know that alkyl substituent that is about 5 nanometers to the base peak. So, this is contributes 25 nanometers. And then you can see that this double bond on the top of on the top of the 2 rings is attached to a ring inside in the middle. So, this double bond is known as exocyclic double bond. So, in exocyclic double bond this double bond is exocyclic to this ring and this double bond is exocyclic to this ring and this double bond is exocyclic to top ring.

So, ring at double bonds attached outside the rings there are 3. So, 3 each exocyclic bond contributes about 5 nanometers that is 15. So, there is also one extended double bond because this is homoannular then single bond and double bond attached extending the conjugation. So, extended double bond contributes about 30 nanometers. So, lambda max is if you had up all these the lambda max is 323 nanometers where we should get a peak and what is the observed value observed value is 320 nanometers. Again you can see the closeness of the prediction, how accurate the empirical rules work in the ultraviolet region.

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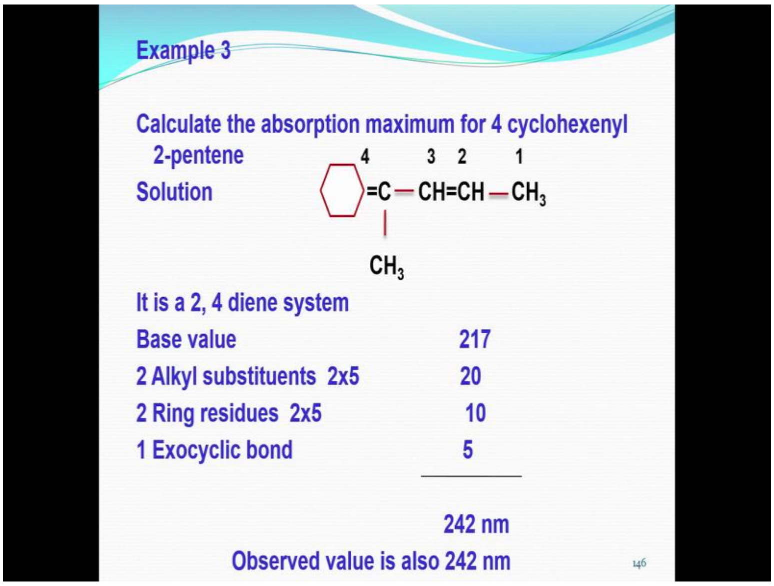

Example 3

Calculate the absorption maximum for 4 cyclohexenyl 2-pentene

Solution

It is a 2, 4 diene system

Base value	217
2 Alkyl substituents 2x5	20
2 Ring residues 2x5	10
1 Exocyclic bond	5
	242 nm

Observed value is also 242 nm

Now, look at this example. This is known as cycle 4 cyclohexenyl 2 pentene. So, we I want you to find out where is the expected peak. Now here we can see that it is the cyclohexenyl ring. It is not a benzene ring. So, the structure diene this is the diene structure, double bond single bond double bond single bond. And then there are substituents all over. So, if I start from here the single bond 1 CH 3 and then there is a CH CH double bond. And then on the second carbonatom third carbonatom there is one CH 3. And another double bond attached to a ring. So, this is a 2 4 diene system. So, it may be 1 3 diene or it may be 2 4 diene either way we get conjugation. For example, this double bond can be here this double, then these become single bond this becomes double bond. These become single bond it would be one of the resonance structures.

So, if I take this compound and try to determine where it is the base value is 217. It is not 253 because both double bonds are not inside a ring. 6 membered ring or 5 membered ring carbon rings it is not there, base values 217 there are 2 ring residues. One is this and another is this. So, 2 alkyl substituents are there 1 2. So, that is 2 that is 5, 10 and 2 ring residues. That is another 10, one exocyclic double bond attached to this ring. That is if you add up all this then it will be 242 nanometers and observed value is 242 nanometer matching exactly what we are observing.

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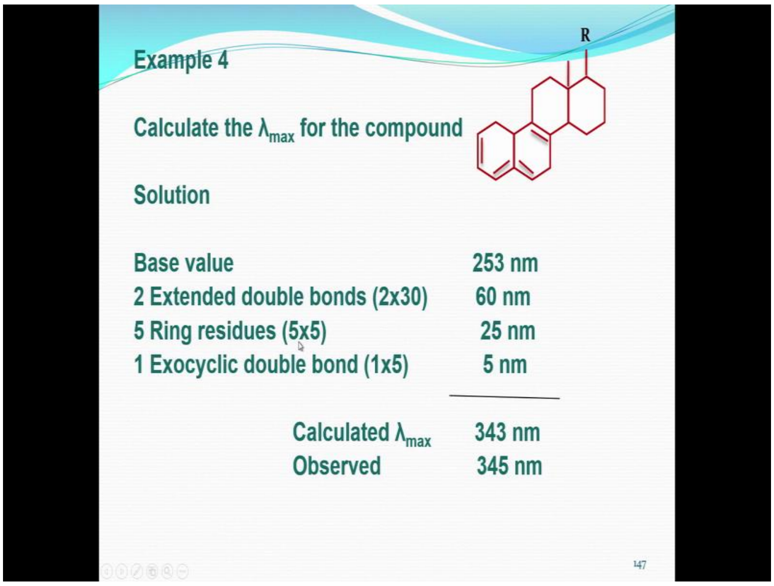

Example 4

Calculate the λ_{max} for the compound

Solution

Base value	253 nm
2 Extended double bonds (2x30)	60 nm
5 Ring residues (5x5)	25 nm
1 Exocyclic double bond (1x5)	5 nm
Calculated λ_{max}	343 nm
Observed	345 nm

So, now you look at this compound like this.

Now, these are all I want to tell you that most of the compounds what we are dealing with here in this class is are the natural products, derived from bark of the trees or flowers or fruit is or medicinal trees or something like that. So, these are all something like we know very fragrant compounds, tasty compound sometimes acids lemon etcetera they all have these all natural products. So, the structure has to be determined quite often whenever we extract something with the structure needs to be determined and if this structure needs to be determined do you want to know where the bonds are etcetera. And once the structure is determined we can expect where the peak is there.

So, for this compound the lambda max base value is 253, because I see a double bond here inside a ring. This is the conjugation system double bond single bond double bond and then single bond double bond and then single bond single bond. So, this double bond is not in conjugation with these systems. So, the only thing we are considering is a double bond in this structure. Here I see a head homoannular diene, 2 double bonds inside one ring. So, here it is now the even though they are inside the inside one ring, but they are separated by 2 single bonds. So, I cannot take it has an extended double bond or homoannular diene, but as far as this ring is concerned it is a homoannular diene base value is 2 5 3.

So, there are extended double bonds. So, 2 extended double bonds are there. So, the; obviously, it is 60 5 ring residues 25 nanometers one exocyclic double bond 5 nanometer and calculated value and observed values are matching almost perfectly to 343 and 345. Here I think I have made a mistake, this double bond also should have been here actually it is there is a typographical error. So, I hear that is why I have taken 2 extended double bonds instead of one extended double bond as I had explained to you earlier.

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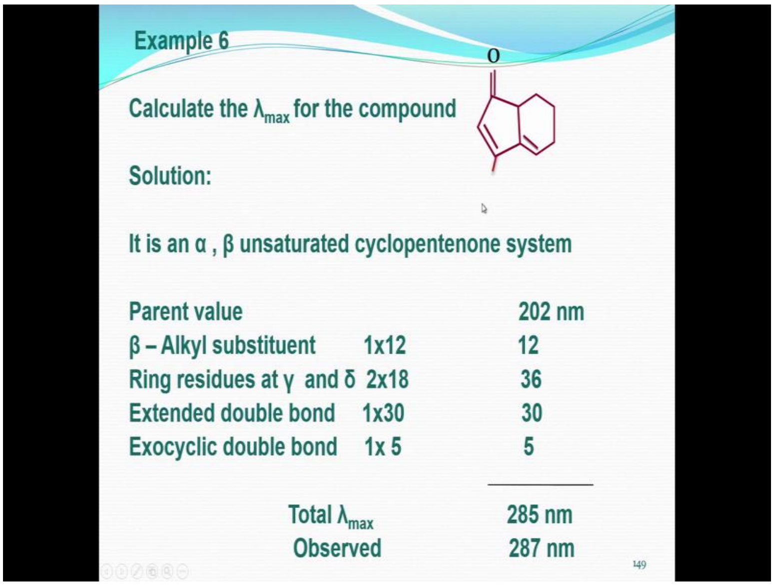

Example 6

Calculate the λ_{max} for the compound

Solution:

It is an α , β unsaturated cyclopentenone system

Parent value		202 nm
β – Alkyl substituent	1x12	12
Ring residues at γ and δ	2x18	36
Extended double bond	1x30	30
Exocyclic double bond	1x 5	5
Total λ_{max}		285 nm
Observed		287 nm

So, typographical error if you correct it. It the double bond should be here. In conjugation with this single double bond single bond double bond. So, let us look at another example this is a compound.

Here it is a 5 membered ring. And then double bond single bond double bond single bond and double bond single bond double bond, but we cannot take this as a conjugated diene, but as a conjugated ketone. So, this is cyclopentenone on system parent value is 2 not 2. If you look at the rules what I have given your earlier, and they are all there and there is on beta I will this is the alkyl sub if I take this double bond single bond double bond single bond. So, this is alpha beta gamma delta this is the functional group. So, from the functional group you say one this is alpha this is beta this is gamma this is delta. So, there is one beta alkyl substituent and for this there is one substituent here, and another substituent here there are 2 this is alpha beta gamma. And the gamma carbonatom there is there are 2 residues.

So, each gamma contributes about 18 nanometers that makes it 30 extended double bond is the one extended double is another addition of 30 nanometers. And then exocyclic double bond which one is that this double bond is exocyclic to this 5 membered ring. It is attached outside immediately through a one of the corner carbonatoms. So, that is exocyclic double bond. Lambda max expected is 285 and observed is 287 nanometers. Again see the closeness of the expected and calculated peak.

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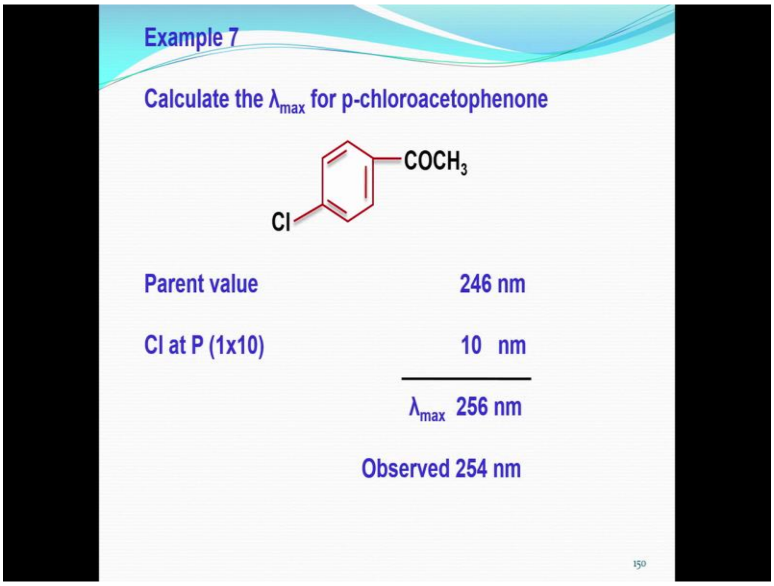

Example 7

Calculate the λ_{max} for p-chloroacetophenone

Parent value 246 nm

Cl at P (1x10) 10 nm

λ_{max} 256 nm

Observed 254 nm

Now, look at another example this is parachloroacetophenone. This is the benzene ring. So, but there is COCH 3 C double bond O 1 2 double bond single bond single bond and double bond.

So, parent value is 246. And there is chlorine at the para position. So, expected is 10 if you look at the table you will see that the observed value would be 256 sorry calculated value is 256 and the observed value is 254 nanometers within the experimental error.

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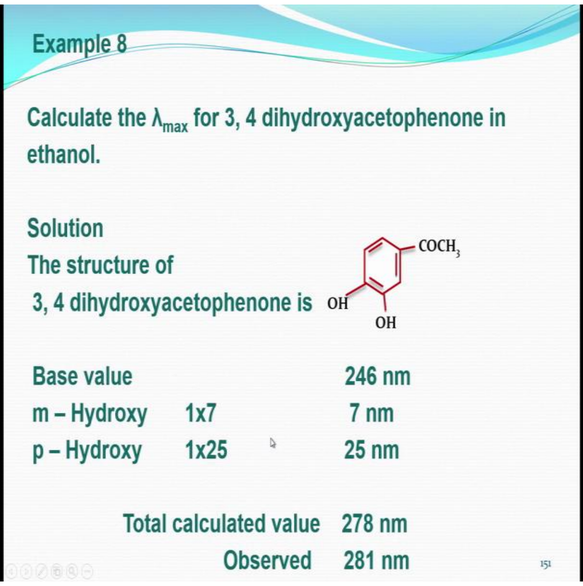

Example 8

Calculate the λ_{max} for 3, 4 dihydroxyacetophenone in ethanol.

Solution

The structure of 3, 4 dihydroxyacetophenone is

Base value		246 nm
m – Hydroxy	1x7	7 nm
p – Hydroxy	1x25	25 nm
	Total calculated value	278 nm
	Observed	281 nm

Now, another example this is 3 4 dihydroxyacetophenone. Again the similar structure what you have drawn, but it is in ethanol. So, the structure is this. Benzene ring COCH 3 group 2 4 3 4 dihydroxy with respect to this he we 3 1 2 3 this is 3 and this is 4.

So, there are 2 hydroxyl groups on this structure. So, base value is again 246 meta hydroxy is approximately 7, and then para hydroxy is 25 calculated is 278 and observed is 281 nanometers beautiful is not it.

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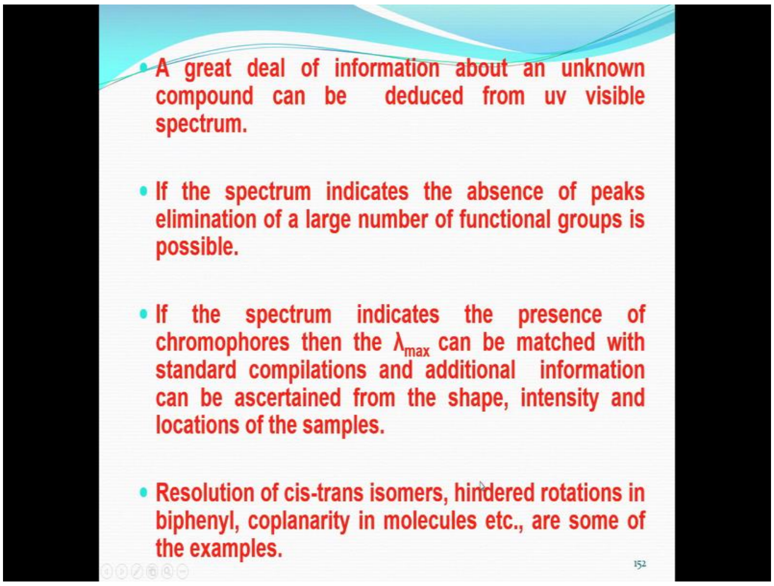

- A great deal of information about an unknown compound can be deduced from uv visible spectrum.
- If the spectrum indicates the absence of peaks elimination of a large number of functional groups is possible.
- If the spectrum indicates the presence of chromophores then the λ_{max} can be matched with standard compilations and additional information can be ascertained from the shape, intensity and locations of the samples.
- Resolution of cis-trans isomers, hindered rotations in biphenyl, coplanarity in molecules etc., are some of the examples.

So, this is the specialty of the Woodward fieser rules. This I had already covered in the last class. So, we can draw information about you visible. So, absence of peaks eliminates a large number of functional groups, is suppose we have to see very less number of peaks. Then you can say that there are not many functional groups in this compound. So, if there if there are peaks then you can say between let us say between 180 and 300.

If you see number of peaks you can always say it could be an aromatic structure or it may not be an aromatic structure. If you see only one out of peaks how many peaks. So, we expect normally sigma to sigma star sigma to n to sigma pi to pi star n to pi star only 4 peaks. So, if there are no peaks like that, then we can say that it could be something like a hydrocarbon or something like that. So, we can always conclude that absence of from the absence of peaks we can always say that. So, many functional groups are not there. Then if the spectrum indicates the absence of peaks elimination of large number of functional groups is possible it follows is not it.

So, then if the there are some peaks then we say that that is a chromophore and the chromophore means it has to give some sort of a peak and you we and visible region. Now we can say that you can match them with standard compounds compilations and there are number of compendiums available for number of organic compounds the peaks have been recorded and if the peaks match simply with respect to wavelength and intensity you can say that this peak has been matched in such a compound. So, they unknown compound what we are dealing with you could be this compound.

Therefore, we can always saying by comparison of this spectrum, we can always say yes this can be done. Then I can simply confer or reject the presence of a particular compound just by looking at the spectrum your visible spectrum. So, resolution of sometimes cis transformer for isomers also is possible. This also I have covered a little bit in the last class.

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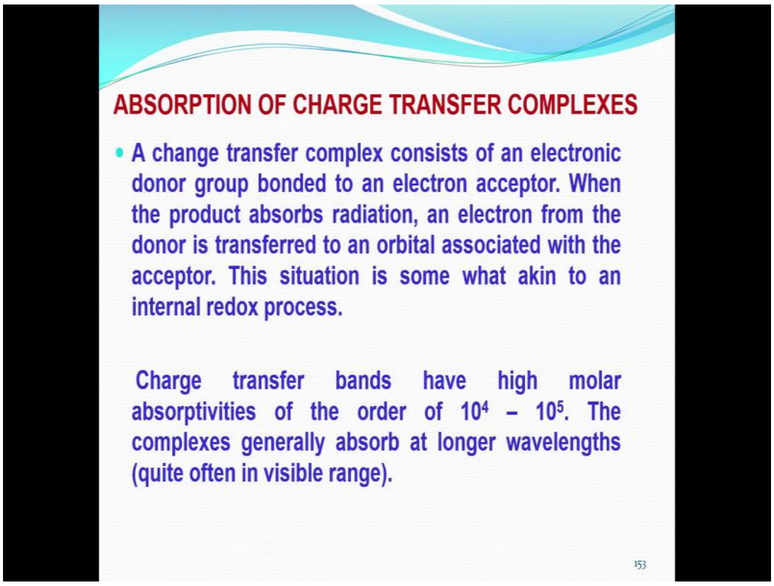

ABSORPTION OF CHARGE TRANSFER COMPLEXES

- A change transfer complex consists of an electronic donor group bonded to an electron acceptor. When the product absorbs radiation, an electron from the donor is transferred to an orbital associated with the acceptor. This situation is some what akin to an internal redox process.

Charge transfer bands have high molar absorptivities of the order of 10^4 – 10^5. The complexes generally absorb at longer wavelengths (quite often in visible range).

So, sometimes what happens is it charge transfer complex. It means some part of some electrons of a functional group; I transferred to a parent molecule parent group or to a metal item etcetera. And then some certain amount of transaction takes place, but it is not an allow transition it. It need not be refer to the sigma to sigma star or rent to pi star pi to pi star etcetera.

So, such a compound it is big forms a coloured compound. Not exactly known as a transition compound, that is electronic excitation, but some amount of an electric electron acceptor would be there. So, when an electron acceptance acceptor is the compound could be coloured to some extent. So, such a compound is known as charge transfer complex. So, the charge transfer complex normally is coloured. So, the there is a donor atom donor functional group and there is an acceptor functional group. So, what happens here is when the product absorbs radiation that is if I allow the light to fall on the material, then only the transition takes place. So, that the compound becomes coloured only when the electrons are transferred.

So, it may be just a routine regular sunlight or it may be specific wavelength radiation also. So, is this situation is somewhat likening to an internal redox process. Because basically an electron transfers means reduction or oxygen. So, there it there has to be one receptor and there has to be one acceptor. So, basically it is a redox transfer. So, charge transfer bands normally it shows a peak. So, the peak corresponds to very high molar absorptivity. You remember I had discussed that absorbance is equal to epsilon b c. So, epsilon represents the molar absorptivity. So, most of the charge transfer complex is have high molar absorptivities. So, the complex is generally absorbing at higher wavelengths that are lower energy. And this higher wavelength can quite often extend into visible range; that means, with an ordinary spectrophotometer. You can see the kal charge transfer complexes, displaying colour can be determined by spectrophotometer.

So, your visible range varies from 350 to 800 nanometers. So, you can if the there is a peak if it is coloured and like any rainbow. Any of the rainbow colors you can we can visually see that. So, charge transfer complex is for many important part of spectrophotometry because many of the in a organic materials and any once form charge transfer complexes with variety of organic compounds. So, that itself is a big part of a research which has been going on since la 1920’s or 1930’s. And we can see that a large number of publications have been done have been published on charge transfer complex determination of the metals and the onions.

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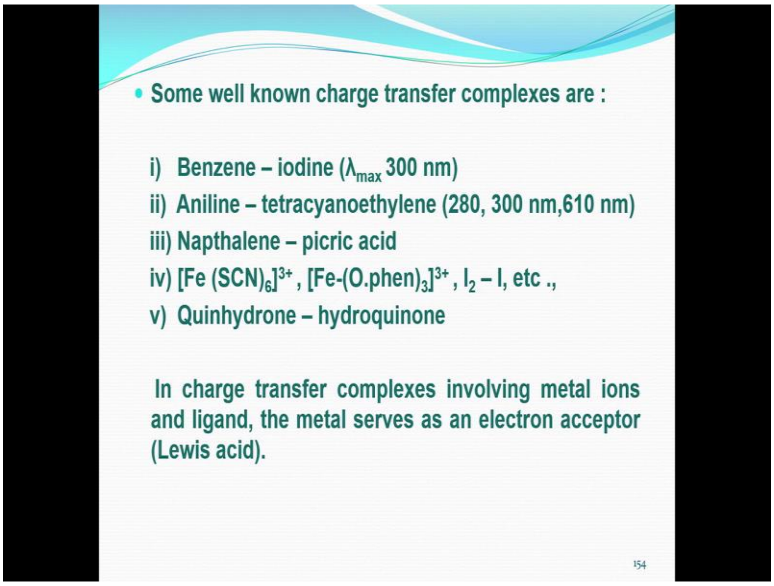

- Some well known charge transfer complexes are :

i) Benzene – iodine (λ_{max} 300 nm)
ii) Aniline – tetracyanoethylene (280, 300 nm,610 nm)
iii) Napthalene – picric acid
iv) $[Fe(SCN)_6]^{3+}$, $[Fe\text{-}(O.phen)_3]^{3+}$, $I_2 - I$, etc .,
v) Quinhydrone – hydroquinone

In charge transfer complexes involving metal ions and ligand, the metal serves as an electron acceptor (Lewis acid).

Now, here some well-known charge transfers complexes. What are they for example, if I take benzene add a little bit of iodine to that you will see a violet colour. And this violet colour corresponds coloured substance solution exhibit is a lambda max around 300 nanometers; that means, it is coloured.

So, similarly you take aniline at tetracyanoethylene compound you will see 3 peaks on at 280 on at 300 and on at 610. Remember the charge transfer complex is not electronic transitions. It is only the it is a big molecule is which charge is concentrating on one side of the molecule giving rise to an impression of colour colour compound being formed, but nevertheless the charge transfer complexes can be use for spectrophotometry, naptheline picric acid is another one and then there are a several inorganic may metals reacting with ligands. For example, this ferric iron reacts with thiocyanate to give you ferric thiocyanate and ferrous ion will react with ortho phenanthroline to give you another charge transfer complex. Iodine if you had iodine to iodide solution that also will give your coloured solution.

That is also a charged complex charge transfer complex and 4th example or fifth exam what I am giving is quinhydrone and hydroquinone. This is the yellow coloured substance which is in equilibrium with each other.

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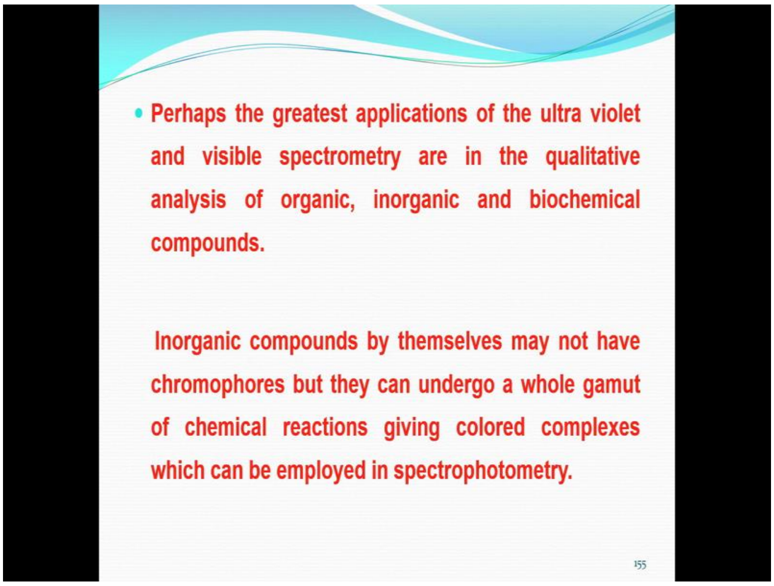

- Perhaps the greatest applications of the ultra violet and visible spectrometry are in the qualitative analysis of organic, inorganic and biochemical compounds.

Inorganic compounds by themselves may not have chromophores but they can undergo a whole gamut of chemical reactions giving colored complexes which can be employed in spectrophotometry.

So, in charge transfer complexes, involving metal ions and ligand the metal serve as an electron acceptor this is a very simple rule, because most of the metals are known as Lewis acids. Lewis acids have the property of acting as electron deficient compounds. So, any electron cloud coming near the metal it tries to attract. So, the leaves acid is a very simple known definition. Now what I want to tell you is about the application, so of this UV visible spectrophotometer.

Now I had told you that several organic compounds exhibit n to pi star sigma to sigma star pi to pi star and n to pi star transitions. Then charge transfer complexes can form with any of the organic and inorganic complexes therefore, the greatest applications of ultraviolet and visible spectrophotometry are in the quantitative analysis of organic inorganic and bio chemical compounds why because I can either form a specific compound or a charge transfer compound. And these are unable to buy a Beer Lambert's law that is molar absorptivity is equal to epsilon b c apply b c which is proportional to concentration.

Therefore, it follows that the concentration of a substance is proportional to it is molar absorptivity or absorption. So, inorganic compounds by themselves do not may not have chromo, for what metal ion will have chromo for nothing. It is a just an ion insulation zinc insulation there all colour less basically maybe some of them are coloured like chromium etcetera, but not all 90 percent of inorganic ions are colour less so, but they can undergo a whole gamut of chemical reactions which will give you coloured complexes or coloured onions and charge coloured charge transfer complexes. All these can be employed in spectrophotometric.

So, the applications of UV visible spectrophotometer especially with respect to pollution control normally involve determination of inorganic compounds determination of organic compounds determination of bio chemical compounds, because quite often we always talk of equally and several other pathogens which are involved in this things.

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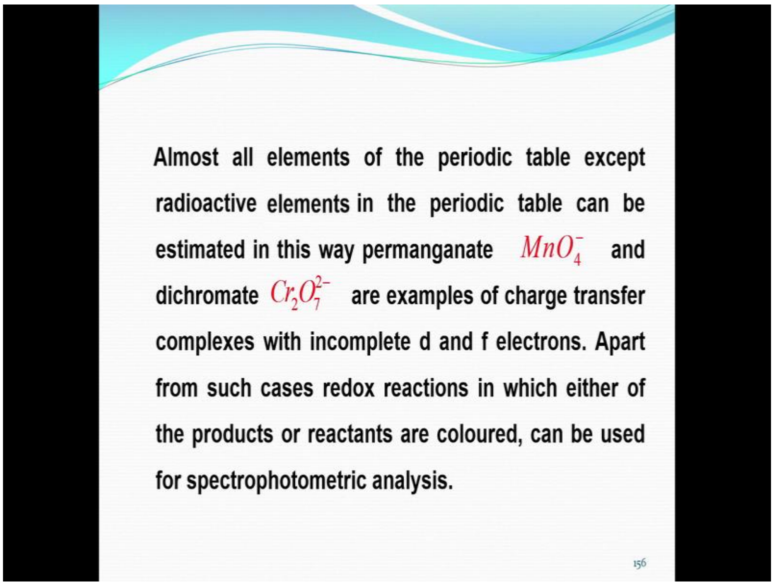

Almost all elements of the periodic table except radioactive elements in the periodic table can be estimated in this way permanganate MnO_4^- and dichromate $Cr_2O_7^{2-}$ are examples of charge transfer complexes with incomplete d and f electrons. Apart from such cases redox reactions in which either of the products or reactants are coloured, can be used for spectrophotometric analysis.

So, the applications all are always like this. And then almost all elements of the periodic table except radioactive element can be determined in this way. Almost every element in the periodic table may be even sometimes we assume that sodium potassium etcetera they are all colour less, but still there are organically reagents which will give coloured complexes, with sodium and potassium also. So, many of them can be determined by spectrophotometry, but what happened says except radio active compounds, normally would not handle radio active compounds in day to day analysis nor do they enter our environment in discernible concentrations.

So, some ions like manganese and potassium permanganate that is a MnO 4 what I have shown you here and dichromate potassium dichromate the any on is C r 2 O 7 2 minus. These example are all colored substances, but they are all charge transfer complexes. So, most of the charge transfer complexes have incomplete d and f electrons. Apart from such cases redox reactions several other kinds of reactions can be can produce a coloured product or they can reduce the colour by forming a non-coloured product. So, all such things can be used in spectrophotometric analysis.

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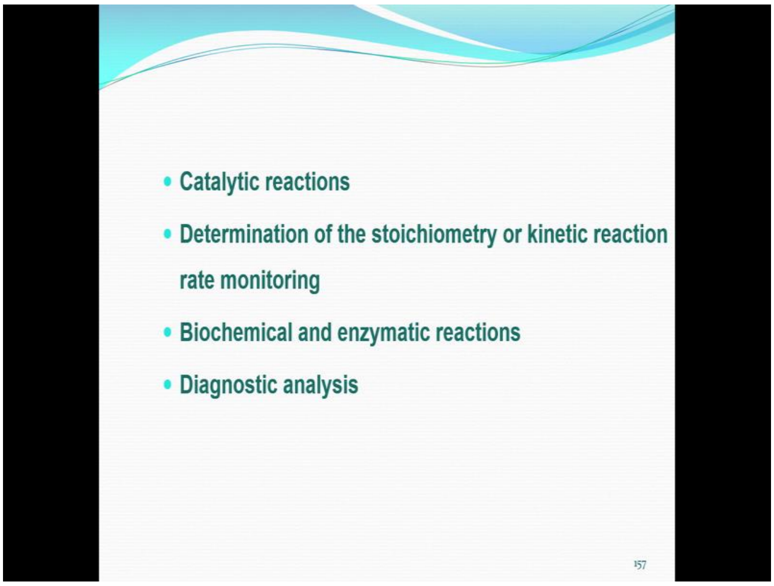

- Catalytic reactions
- Determination of the stoichiometry or kinetic reaction rate monitoring
- Biochemical and enzymatic reactions
- Diagnostic analysis

Now, what type of reactions, we can follow using spectrophotometer. One is catalytic reactions number 2 is determination of stoichiometry. I can find is there is a coloured compound being formed in a chemical reaction. I can always say that you can determine the composition, how much of the metal is there how much of the organic compound is there. Sometimes it is very important for us to determine the stoichiometry of a chemical reaction.

Sometimes these reactions can proceed in a rate determining step involving several steps therefore, it is also possible for us to determine the kinetic reaction rate that also we can monitor then biochemical and enzymatic reactions, I have already explained to you that these things are important in day to day life and diagnostic analysis in clinical chemistry and pollution control and in several other organic and inorganic reactions are possible and that is the duty of spectrophotometry.

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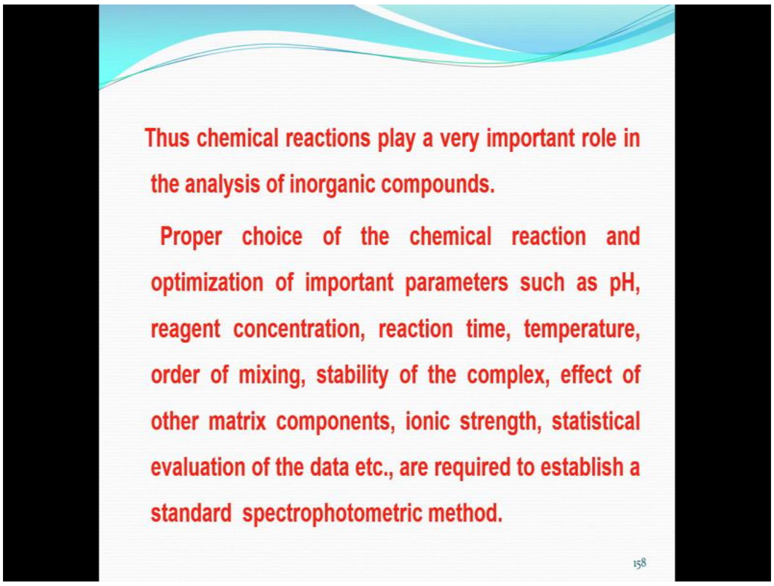

Thus chemical reactions play a very important role in the analysis of inorganic compounds.

Proper choice of the chemical reaction and optimization of important parameters such as pH, reagent concentration, reaction time, temperature, order of mixing, stability of the complex, effect of other matrix components, ionic strength, statistical evaluation of the data etc., are required to establish a standard spectrophotometric method.

So, chemical reactions basically play an important role in the analysis of inorganic compounds. So, only thing is we need to have a proper choice of a chemical reaction and optimize the reaction conditions. What are the parameters one is pH, another is reagent concentration, reaction time I have to optimize temperature order of mixing stability of the complex effect of other matrix components, ionic strength, statistical evaluation of data I required to establish a standard spectrophotometric method?

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Once a method is standardized, spectrophotometry provides an easy, sensitive, rapid and cost effective method to determine minute quantities of substances in microgram or sub-microgram levels. Further improvements can be brought about by pre-concentration, solvent extraction, chromatographic separations and a host of other related techniques.

So, once a method is standardized, the spectrophotometry provides an easy sensitive rapid and cost effective method to determine minute quantities of substances in microgram or sub microgram levels.

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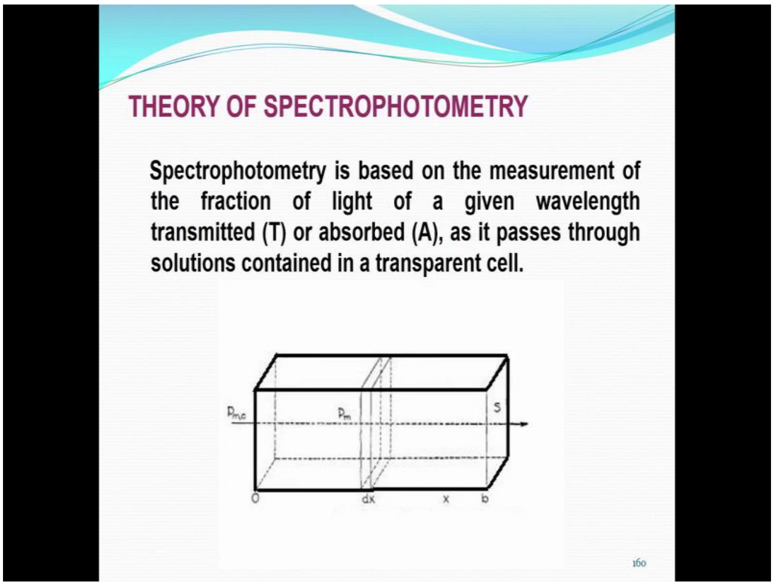

THEORY OF SPECTROPHOTOMETRY

Spectrophotometry is based on the measurement of the fraction of light of a given wavelength transmitted (T) or absorbed (A), as it passes through solutions contained in a transparent cell.

Further improvements we can always bring by about by solvent extraction chromatographic separation and host of other related techniques, which are the tricks of the trade as far as chemistry is cancelled. So, we will continue our discussion on the theory of spectrophotometer in the next module.

Thank you very much.