Spectroscopic Techniques for Pharmaceutical and Biopharmaceutical Industries
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Lecture 16: Atomic Spectroscopy--4

Hello students, welcome to lecture 16 of this course. Last time I discussed about how does a spectra of alkali metals and alkaline earth metals will look like.

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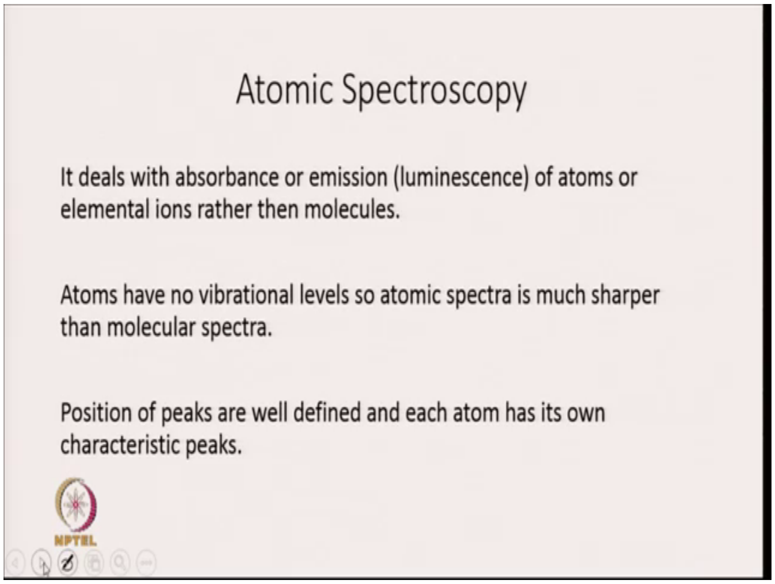

Atomic Spectroscopy

It deals with absorbance or emission (luminescence) of atoms or elemental ions rather then molecules.

Atoms have no vibrational levels so atomic spectra is much sharper than molecular spectra.

Position of peaks are well defined and each atom has its own characteristic peaks.

I will discuss it again and then I will move and show you some application of atomic spectroscopy. As the name suggests a atomic spectroscopy deals with absorbance or emission of atoms or elemental ions rather than molecules. Since atoms have no vibrational levels so atomic spectra is generally much sharper than molecular spectra. Not only that positions of peaks are well defined and each atom has its own characteristic peaks and that is main advantage of atomic spectroscopy.

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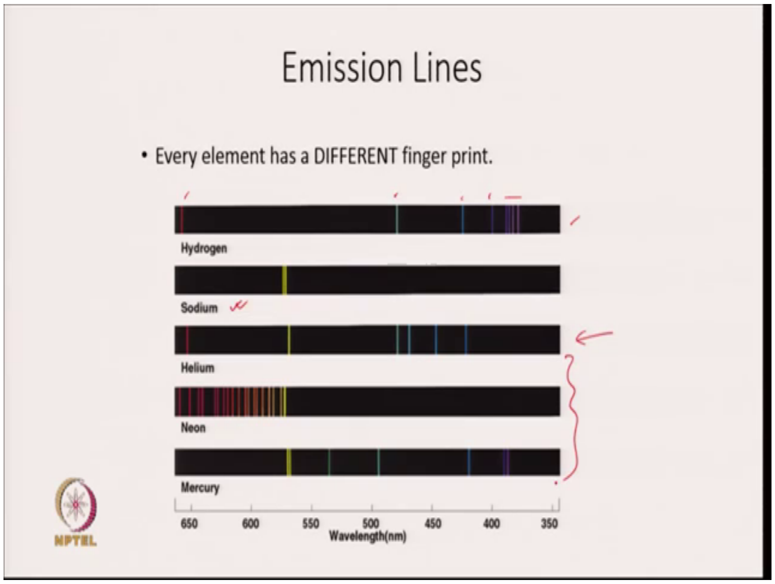

Emission Lines

- Every element has a DIFFERENT finger print.

The emission lines of different elements are peculiar to that element only and hence every element has a different fingerprint. So if you look at hydrogen its line is here at this point and this point, this point and these 4 points, It is quite different then if you look at the spectral lines of sodium atoms. They are not at the same position, they are not at the same position and if you look at the helium it also has quite different spectra comparison to hydrogen and sodium. Similar is the case of all the atoms, all the atoms. And so if we look at atomic spectra of different elements we will be able to figure out which element is the in that particular sample.

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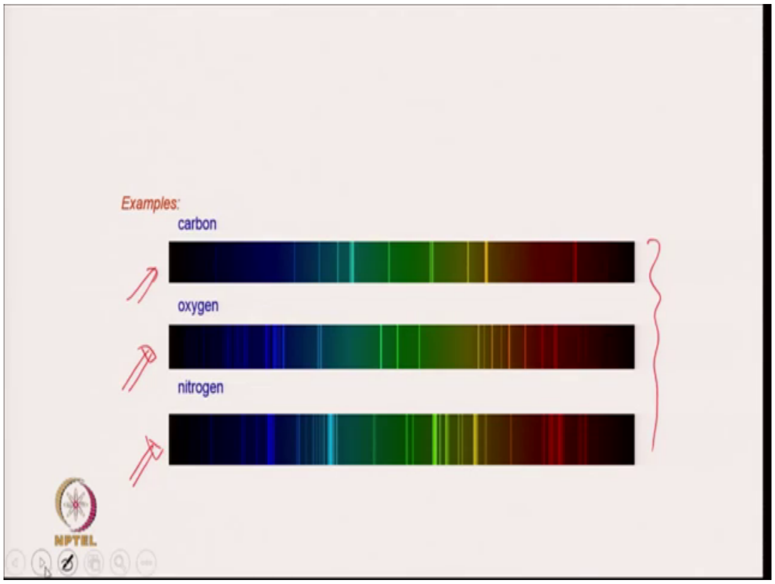

Examples:

carbon

oxygen

nitrogen

Here is some other examples of atomic spectra, this is atomic spectra of carbon, this is atomic spectra of oxygen and this is atomic spectra of nitrogen. So each element has its characteristic atomic spectra. Hence, it is very easy to distinguish between the different atoms using your atomic spectroscopy.

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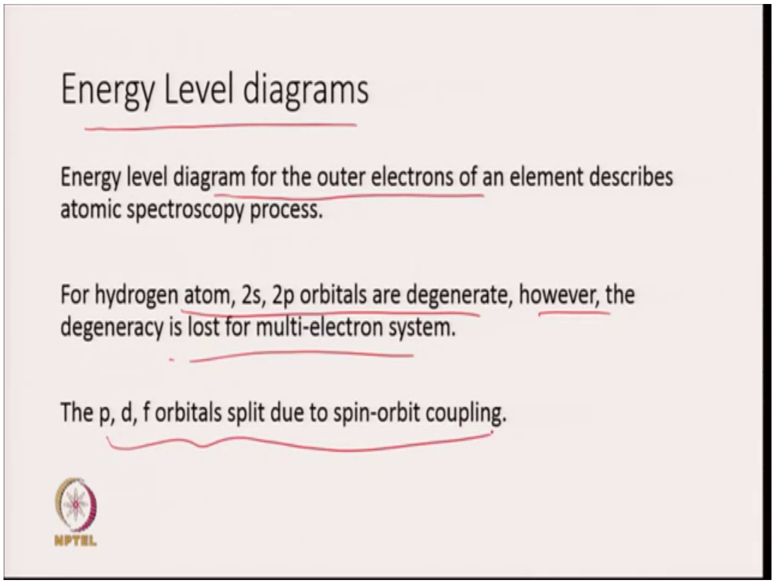

Energy Level diagrams

Energy level diagram for the outer electrons of an element describes atomic spectroscopy process.

For hydrogen atom, 2s, 2p orbitals are degenerate, however, the degeneracy is lost for multi-electron system.

The p, d, f orbitals split due to spin-orbit coupling.

The basis of atomic spectroscopy is the energy level diagrams of different atoms. The energy level diagram for outer electron of an element describes atomic spectroscopy process, so outer electrons are very important. For example alkali metals the outer electrons are in s orbital and so the 1 electron in outermost s orbital basically describes its atomic spectroscopy process. For hydrogen atom 2s 2p orbitals are degenerate that is what we discussed during last lectures however the degeneracy lost for multi-electron system. I am just giving you recap of previous lectures. Again p, d, f orbitals split due to spin-orbit coupling. So these are the few things which already we have discussed in the previous lecture.

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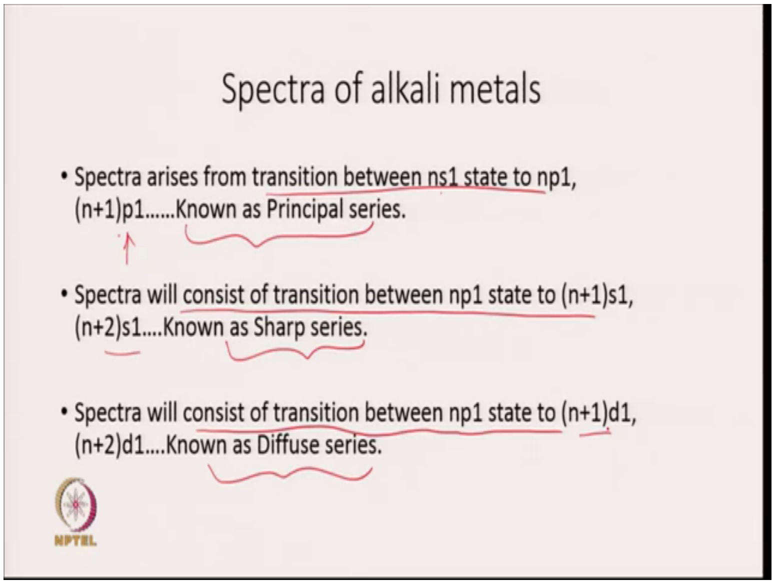

Spectra of alkali metals

- Spectra arises from transition between ns1 state to np1, (n+1)p1……Known as Principal series.
- Spectra will consist of transition between np1 state to (n+1)s1, (n+2)s1….Known as Sharp series.
- Spectra will consist of transition between np1 state to (n+1)d1, (n+2)d1….Known as Diffuse series.

Now let us go back and see again discuss spectra of alkali metals, here spectra arises from transition between ns1 state to np1 state. The transition can happen from ns1 state to n plus 1 p state or ns1 state to n plus 2p 1 state and since the electron is finally ending up in the p level and so the series which arises from these transitions is known as principle series.

The spectra of alkali metal also consist of transition between np1 state to n plus 1 s1 or n plus 2 s1. So, now we are looking at the transition from first excited state or second excited state to n plus 1 s1 state or n plus 2 s1 state because this is also allow transition since delta l is minus 1, delta l is minus 1 and when the final electron the electron which is getting promoted is landing up in the s orbital. The spectra which is due to transition between these states are known as sharp series. Similarly, spectra can also have transition contribution from transition between np1 state to n plus 1 d1 n plus 2 d1 state.

And since electrons are landing up in d state and so it is known as diffuse series, it is known as diffuse series. Transition between ns1 to n plus1 d1 is not allowed since delta l is plus 2. So transition is not allowed between s to d, s state to d state.

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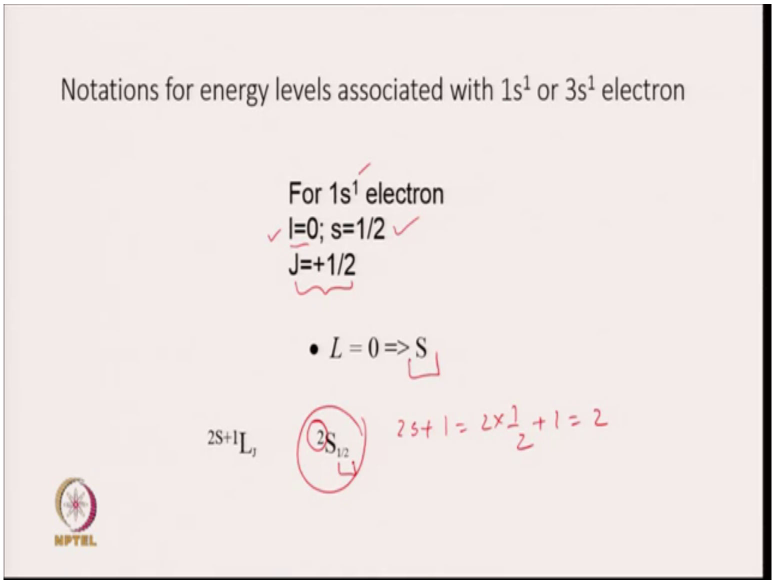

Notations for energy levels associated with $1s^1$ or $3s^1$ electron

For $1s^1$ electron

$l=0$; $s=1/2$

$J=+1/2$

- $L = 0 \Rightarrow S$

${}^{2S+1}L_J$

${}^{2}S_{1/2}$

$2s+1 = 2\times\frac{1}{2}+1 = 2$

Now let us look at what are the energy levels associated with 1 s1 or 3 s1 electron which is basically your ground state of alkali metal. So for s1 electron l is 0 and s is half, s is half. There is only 1 electron and its l value is 0 and s value is half. So J have only 1 value and that is plus half and since this l is equal to 0 corresponds to s state and so the energy level associated with 1s1, 2s1, 3s1 is s and the more specific notation is 2s half.

Now you can see this is your multiplicity which is given by 2s plus 1 and that is 2 into half plus 1 is equal to 2. So multiplicity is 2 and this is your J value and since there is only one J value it means the energy states associated with 1s1 configuration is only one and that is given by 2s half.

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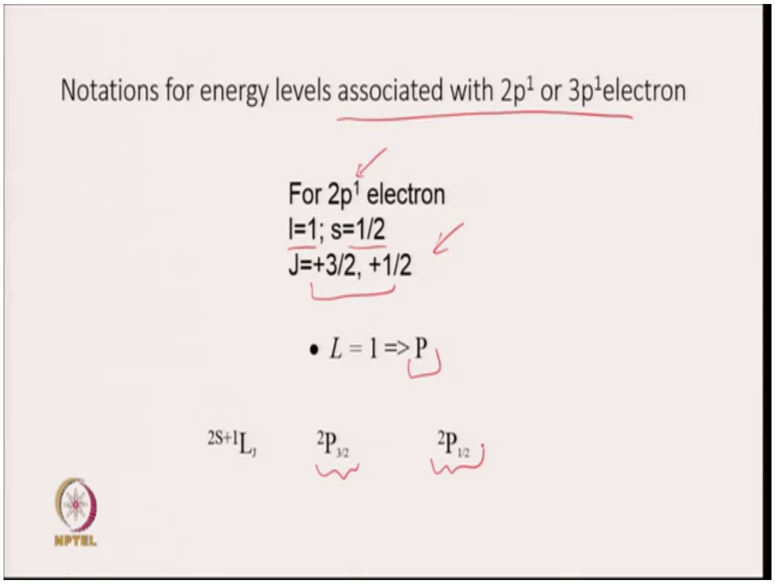

Notations for energy levels associated with $2p^1$ or $3p^1$electron

For $2p^1$ electron

l=1; s=1/2

J=+3/2, +1/2

- $L = 1 \Rightarrow P$

$^{2S+1}L_J$ $^2P_{3/2}$ $^2P_{1/2}$

Now if you want to look at the transition between ns1 to n plus 1 p1 we also need to look at what will be the energy level associated with this p1 electron. So energy level associated with 2p1 or 3p1 electron is so if we look at this electron l value is 1 and s value is half. So J is going to having two values 3 by 2 and half, it means that there will be two energy states associated with 2p1 configuration. Since l is equal to 1, so this corresponds to the level p and since J has two values and so the two terms arising due to spin-orbit coupling will be 2p 3 by 2 and 2p half, 2p 3 by 2, 2p half. So we have seen that only one energy is associated with, only one energy level is associated with 2s1 electron or 3s1 electron whereas there are two energy states associated with the excited state 2p1 or 3p1 electron.

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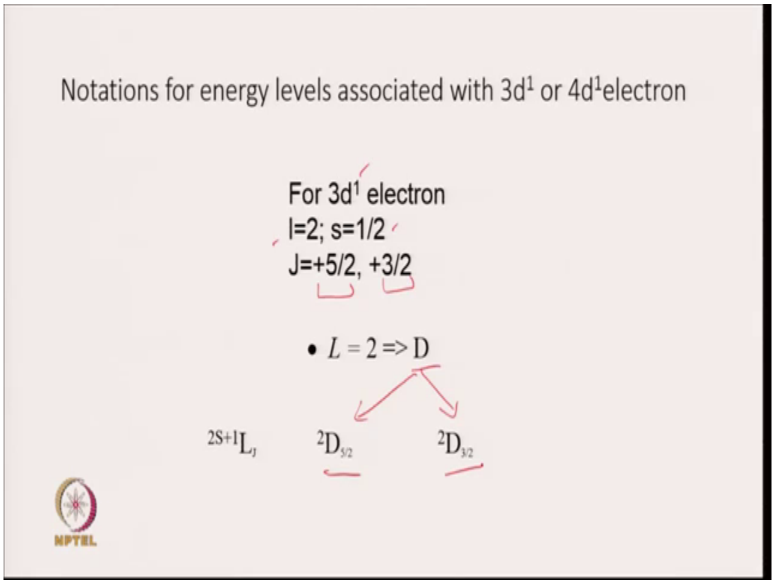

Notations for energy levels associated with $3d^1$ or $4d^1$electron

For $3d^1$ electron

l=2; s=1/2

J=+5/2, +3/2

- $L = 2 \Rightarrow D$

$^{2S+1}L_J$ $\quad$ $^2D_{5/2}$ $\quad$ $^2D_{3/2}$

Now notation for energy level associated with 3d1 or 4d1 electron. So suppose electron is getting promoted from p level to d level. We have already seen what will be the energy, number of energy levels when electron is in the p orbital. But if suppose electron is going from p to d and we want to know what is the energy levels associated with 3d1 electron or nd1 electron. So for d1 electron l is equal to 2, s is equal to half so J is going to have two values, so plus 5 by 2 and plus 3 by 2, so it is going to have two energy levels.

Since l is equal to 2 it means we are dealing with the level d and since there are two J values it will get split into two levels due to spin-orbit coupling and those levels are 2D 5 by 2 and 2D 3 by 2. So now we have looked at, there is only one energy level associated with 1s1 configuration, there are two levels associated with np1 or nd1 electron. Now we will look at the transition.

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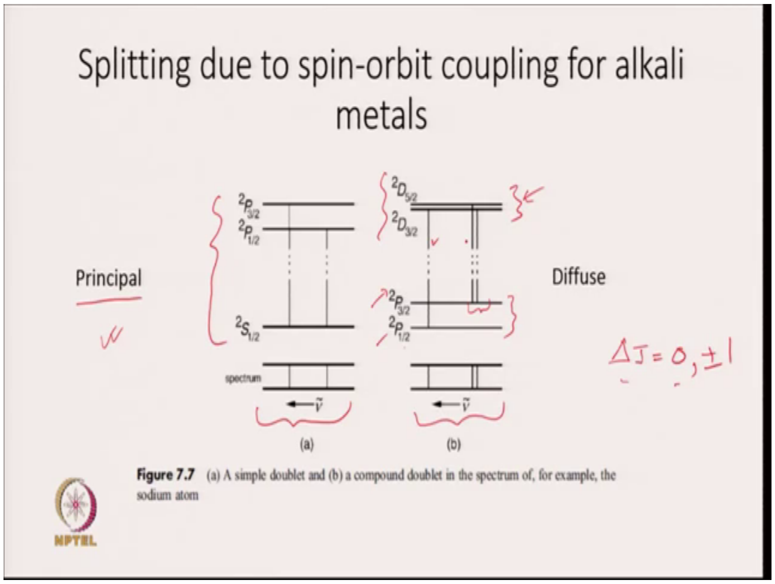

Splitting due to spin-orbit coupling for alkali metals

$\Delta J = 0, \pm 1$

Figure 7.7 (a) A simple doublet and (b) a compound doublet in the spectrum of, for example, the sodium atom

So suppose your electron is going from s to p then we can think of this transition which is called principle transition and the transition which is allowed is 2s half going to 2p 3 by 2 and 2s half going to 2p half.

If you remember the selection rule is delta J is equal 0 and plus-minus 1. So, electron going from 2s half to 2p 3 by 2 is allowed because delta J is 1. Similarly, electron going from 2s half to 2p half is also allowed since delta J will be equal to 0. So this is for the principle series for electron going from s1 configuration to p1 configuration. Now look at the electron going from p1 to d1 which is allowed transition because delta l is plus 1. Now, we have just seen that p level is basically split into 2 levels due to spin-orbit coupling.

Similarly D level is split into two due to spin-orbit coupling and the terms for these 2 energy levels are 2p half and 2p 3 by 2. Similarly the term for your p level splitting is 2D 5 by 2 and 2D 3 by 2. Now, if we look at the transition from p level to d level what we can see is p the transition from 2p half to 2d 3 by 2 is allowed since delta J is 1. But transition from 2p half to 2d 5 by 2 is not allowed since delta J in that case will be your plus 2, so that is not allowed transition. So you see just only one transition from 2p half.

Now look at the transition from 2p 3 by 2, both transitions are allowed it means transition from 2p 3 by 2 to 2d 3 by 2 is the allowed and 2p 3 by 2 to 2d 5 by 2 is allowed since delta J is either 0 or plus 1. So, this leads to a doublet in the principle series of sodium atom whereas there is a compound doublet in the diffused series in the spectrum of sodium atom. Now why compound doublet, why not triplet? That I have already discussed and that is because of the very narrow gap between 2D 3 by 2 and 2D 5 by 2. So what happens that lambda max of these 2 transition is almost at similar position and sometimes it looks like a diffused or it looks like one peak and so triplet is basically known as compound doublet.

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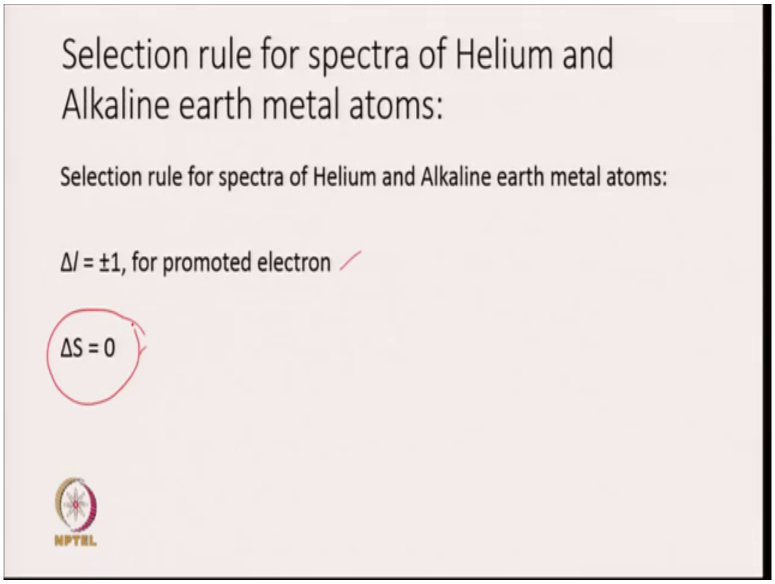

Selection rule for spectra of Helium and Alkaline earth metal atoms:

Selection rule for spectra of Helium and Alkaline earth metal atoms:

$\Delta l = \pm 1$, for promoted electron

$\Delta S = 0$

Now we will go and look at the spectra of helium and alkaline earth metal atoms. For this selection rule is delta l is equal to plus-minus 1 for promoted electron and delta s is equal to 0 and delta n is suddenly unlimited. So here only thing I have added is delta s is equal to 0 and we will discuss why this is important.

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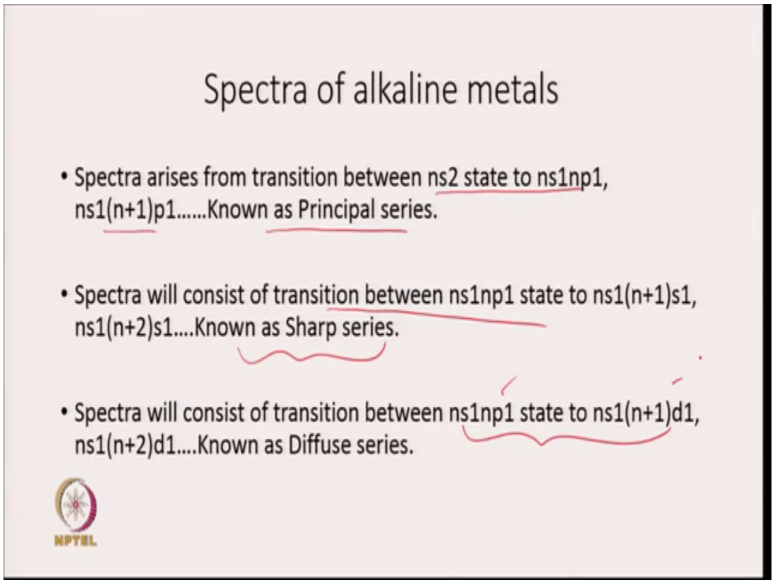

Spectra of alkaline metals

- Spectra arises from transition between ns2 state to ns1np1, ns1(n+1)p1......Known as Principal series.
- Spectra will consist of transition between ns1np1 state to ns1(n+1)s1, ns1(n+2)s1....Known as Sharp series.
- Spectra will consist of transition between ns1np1 state to ns1(n+1)d1, ns1(n+2)d1....Known as Diffuse series.

So, the spectra of alkaline earth metal will arise from transition between ns2 state to ns1 np1 state or ns1 n plus 1 p1 and since the promoted electron lands up in p orbital, so it is known as principle series. The other line will correspond to transition between ns1 np1 state to ns1 n plus 1 s1 or ns1 n plus 2 s1. So it is from the excited state to the s state only and the since now promoted electron is in the s orbital so, it is known as sharp series. Spectra will also consist of transition between these states so p1 to d1. And as I discussed (that) since the promoted electron is now in d orbital and so this is known as diffused series.

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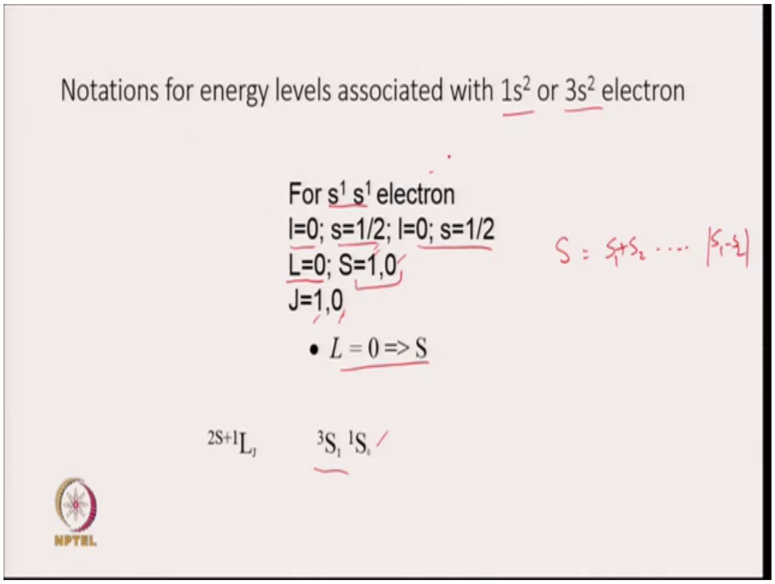

Notations for energy levels associated with $1s^2$ or $3s^2$ electron

For s^1 s^1 electron

l=0; s=1/2; l=0; s=1/2

L=0; S=1,0

J=1,0

- $L = 0 \Rightarrow S$

$^{2S+1}L_J$ $^3S_1$, $^1S_0$

$S = s_1+s_2 \dots |s_1-s_2|$

Now, let us think about the energy level associated with s2 electron, s2 electron of alkali metals, alkaline earth metals, s2 electron of alkaline metals, so 1s2 or 3s2 or 2s2 electron which we are discussing about. We have already discussed about how to calculate the energy levels of or energy of helium orbital. What we used to do is, we used to take 2 electrons as 2 systems, one system consisting of one electron and this nucleus and the second system consisting of electron and nucleus.

So, that is what we are going to take here, will not consider this as a 1s2 electron but we are going to consider this as s1-s1 electron. When we will do it for the first electron l is 0 and s is equal to half, for second electron l is equal to 0 and s is equal to half. So capital L is equal to 0 and capital S is equal to (your) 1 or 0, since if you remember capital S is equal to s1, small s1 plus s2 and going to s1 minus s2 with the this(thing). So when we add this up, we will get 1 and when we subtract this we will get 0.

So we have 2 value of S and 1 value of L and if I calculate J, if I take s if 1 then it is 0 plus 1 1 and for 0 0 there will be 0. So we have two J value, two s value and one L value, L is 0 so it will corresponds to level s and if we go and take s is equal to 1, J is equal to 1 then we will get 3s1 whereas if we take s is equal to 0 and J is equal to 0 then I will get 1s0. So there is 2 terms arising from s1-s1 electrons, 3s1 and 1s0.

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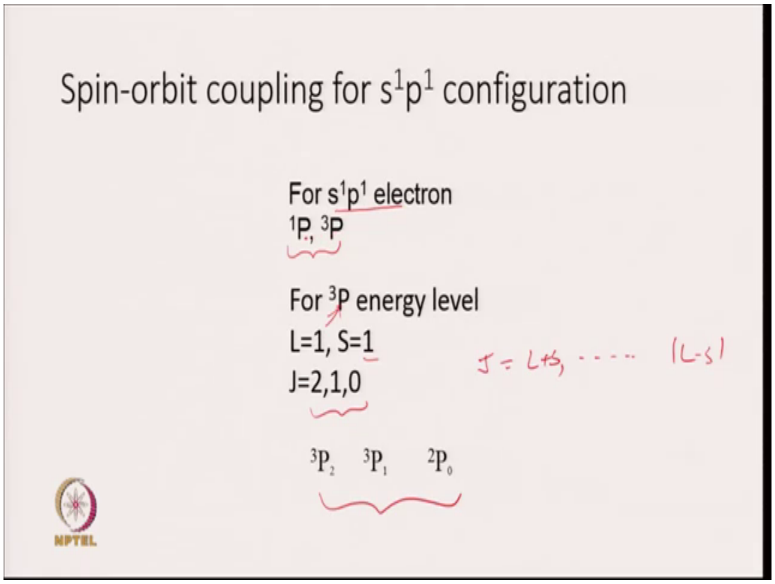

Spin-orbit coupling for s^1p^1 configuration

For s^1p^1 electron

^1P, ^3P

For ^3P energy level

L=1, S=1

J=2,1,0

$J = L+S, \dots |L-S|$

$^3P_2$ $^3P_1$ $^2P_0$

Now we will look at the spin-orbit coupling for s1p1 configuration. So for s1p1 configuration or s1p1 electron we have two different terms 1P, 3P and we can get this term as we have done for s1-s1. Now, let us look at 3P, for 3P energy level L is equal to 1 for this P and S is equal to 1 because multiplicity is 3 and so J value will be your L plus S to L minus S and that means J has 3 values, so (3) 3P energy levels will be split into 3 levels due to spin-orbit coupling. Now, I have just taken 3P not 1P.

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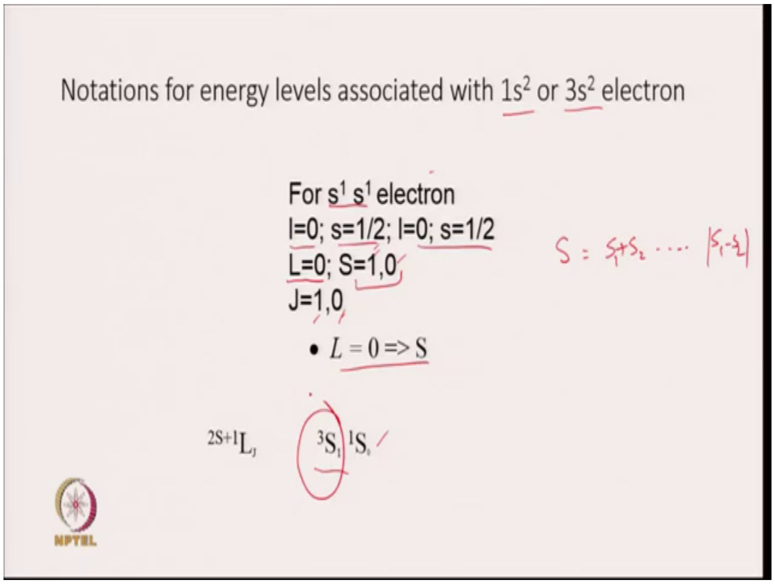

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For s^1 s^1 electron

l=0; s=1/2; l=0; s=1/2

L=0; S=1,0

J=1,0

- $L = 0 \Rightarrow S$

$S = s_1+s_2 \dots |s_1-s_2|$

$^{2S+1}L_J$ $^3S_1$ $^1S_0$

Since what I am going to look at is transition from this state 3S1 to your 3P levels.

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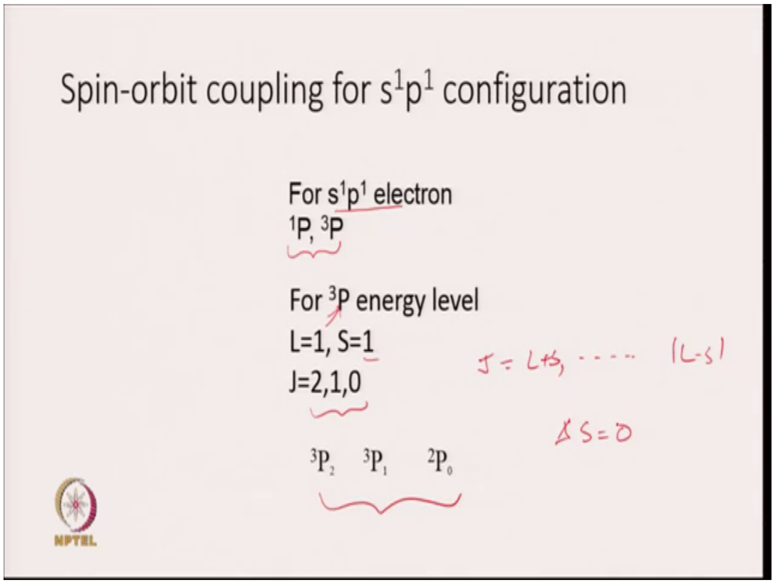

Spin-orbit coupling for s^1p^1 configuration

For s^1p^1 electron

^1P, ^3P

For ^3P energy level

L=1, S=1

J=2,1,0

$J = L+S, \dots |L-S|$

$\Delta S = 0$

$^3P_2$ $^3P_1$ $^2P_0$

3P is 3P level. Why I am taking 3s is because you remember delta s should be 0 for the transition. If delta s is equal to 0 then only we have allow transition. So, if we are looking at the transition from 3s state, the allowed transition will be in the 3P state not in 1P state and that is why I just discussed the splitting of 3P energy levels. So now we know that 3s level.

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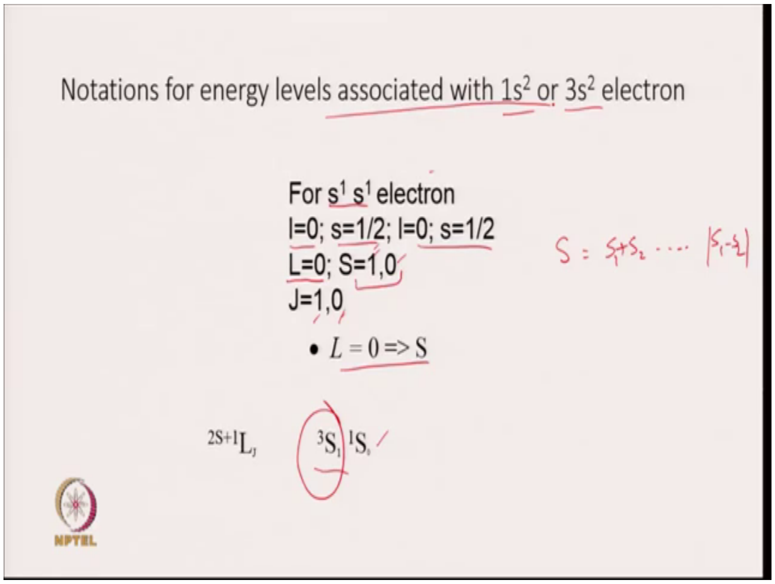

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l=0; s=1/2; l=0; s=1/2

L=0; S=1,0

J=1,0

$S = s_1+s_2 \dots |s_1-s_2|$

- $L = 0 \Rightarrow S$

$^{2S+1}L_J$ $^3S_1$ $^1S_0$

If you look at 3s level you have only one 3s level in if the configuration is 1S2.

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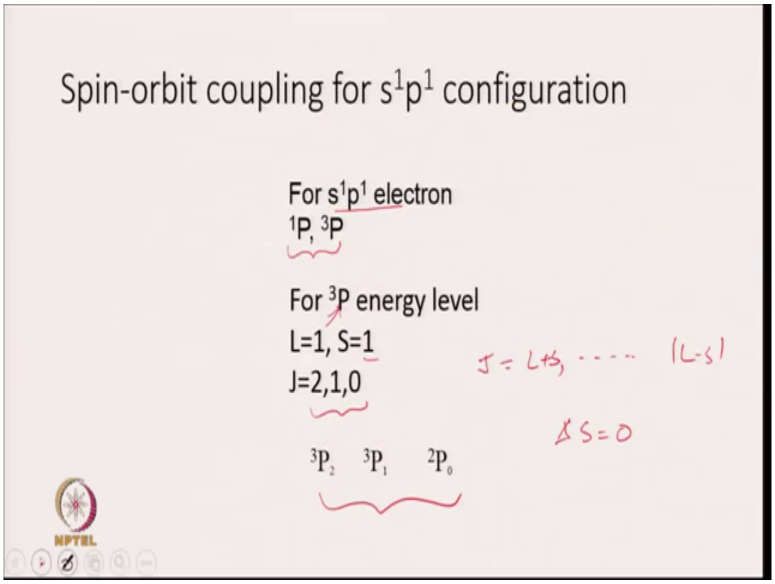

Spin-orbit coupling for s^1p^1 configuration

For s^1p^1 electron

$\underbrace{^1P, ^3P}$

For ^3P energy level

L=1, S=1

J=2,1,0

$J = L+S, \ldots\ldots |L-S|$

$\Delta S = 0$

$\underbrace{^3P_2 \quad ^3P_1 \quad ^2P_0}$

Whereas there are three energy levels so here I have done okay so 3P2, 3P1 so P level goes into three different levels.

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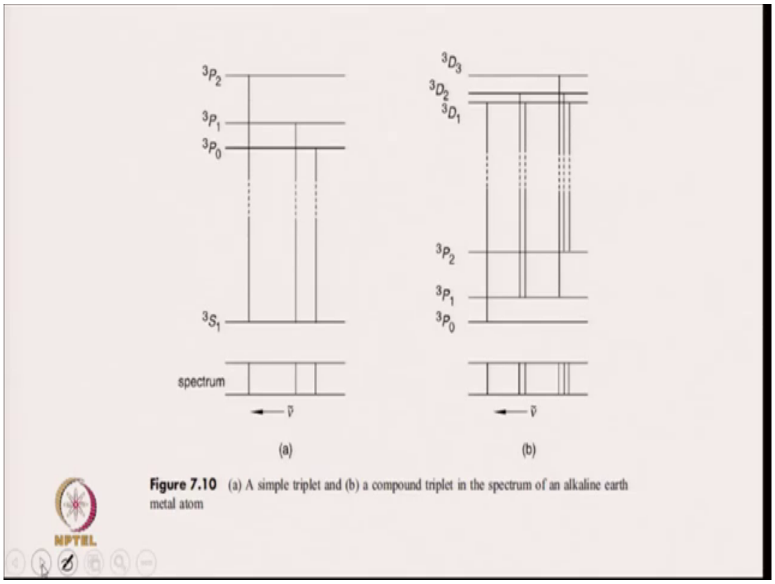

Figure 7.10 (a) A simple triplet and (b) a compound triplet in the spectrum of an alkaline earth metal atom

Now what we will do is.

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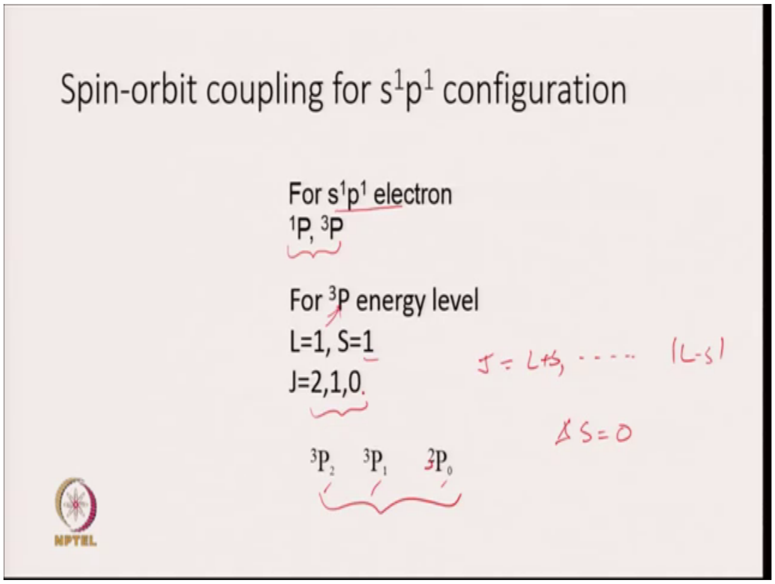

Spin-orbit coupling for s^1p^1 configuration

For s^1p^1 electron

^1P, ^3P

For ^3P energy level

L=1, S=1

J=2,1,0.

$^3P_2$ $^3P_1$ $^3P_0$

$J = L+S, \dots |L-S|$

$\Delta S = 0$

Here I have done wrong this will be 3, this will be 3. So 3P is split into three different levels 3P2, 3P1 and 3P0 and these are the J values 2, 1, 0.

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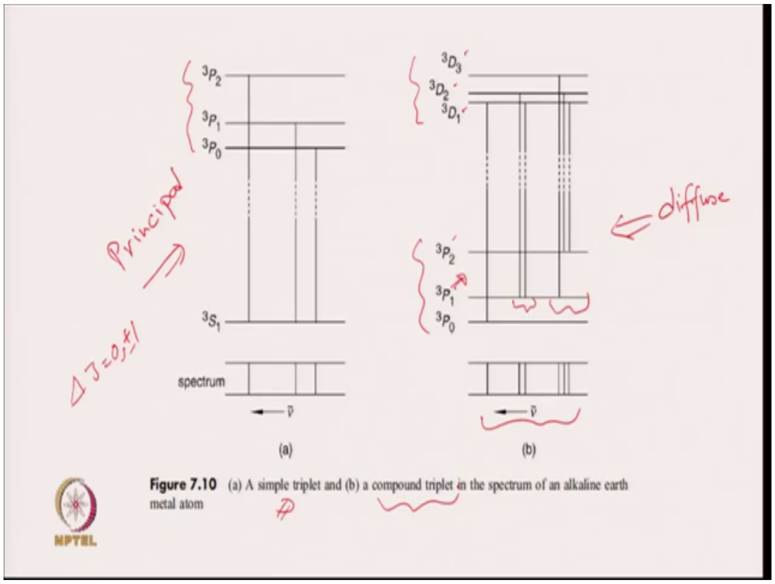

Figure 7.10 (a) A simple triplet and (b) a compound triplet in the spectrum of an alkaline earth metal atom

So now we will look at the transition from the 3s level to the 3p level and since it is ending up electron is ending up in 3p level this will correspond to principle series, principle series. And here we are looking at the transition from P to D and so this will be the diffused series. Now look at this is 3s1 and there are three different states coming out from 3P due to spin-orbital coupling and again delta J will be equal to 0, plus-minus 1 and so the transition is allowed between 3S1 to

3P0 since delta J is minus 1. 3S1 to 3P1 since delta J is equal to 0 and 3S1 to 3P2 since delta j is equal to plus 1, so three transition are allowed and we will get a simple triplet.

And if we look at the transition from 3P to 3D or let us start from 3p0 there is only one transition allowed between 3P0 to 3D1 since delta J is equal to 1. But 3P0 to 3D2 is not allowed because delta J is 2 and 3P2 to 3D3 is not allowed since delta J is equal to 3. From 3p1 only two transitions are allowed 3P1 to 3D1 since delta J is equal to 0, 3P1 to 3D2 since delta J is equal to 1. 3P1 to 3D3 is not allowed since delta J is equal to 2. Transition between 3P2 to 3D3 and 3D2 and 3D1 all are allowed since if we go from 3P2 to 3D1 delta J is minus 1. If you go from 3P2 to 3D2 delta J is 0 and if you go from 3P2 to 3D3 delta J is plus 1. So all 3 transitions are allowed but as we discuss this will come like overlapping peak and this will also come like overlapping peak.

This will not come as 5 peaks but it will be like a compound triplet, so this is the way we discuss or we understand the spectrum of different elements. Here I have shown you the spectrum of alkaline earth metals where we are going from s2 to s1p1 or s1p1 to d1. Now we have discussed atomic spectra we will go to the techniques which is based on atomic spectra. First we will discuss the technique and then we will look at the application.

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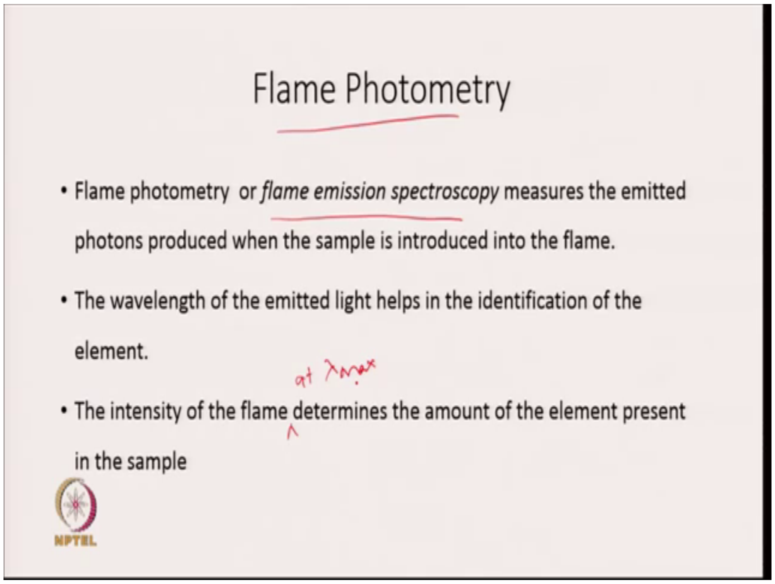

Flame Photometry

- Flame photometry or *flame emission spectroscopy* measures the emitted photons produced when the sample is introduced into the flame.
- The wavelength of the emitted light helps in the identification of the element.
- The intensity of the flame at λ_{max} determines the amount of the element present in the sample

So first technique which is based on atomic spectroscopy is known as Flame Photometry, flame photometry which is also known as flame emission spectroscopy measures the emitted photons produced when the sample is introduced into the flame. The wavelength of emitted light is unique for an atom and that is why it helps in the identification of the element. The intensity of the flame determines the amount of the element present in the sample, here I mean intensity of flame at the lambda max determines the amount of element present in the sample. Flame photometry basically based on the same principle as the flame test using qualitative analysis.

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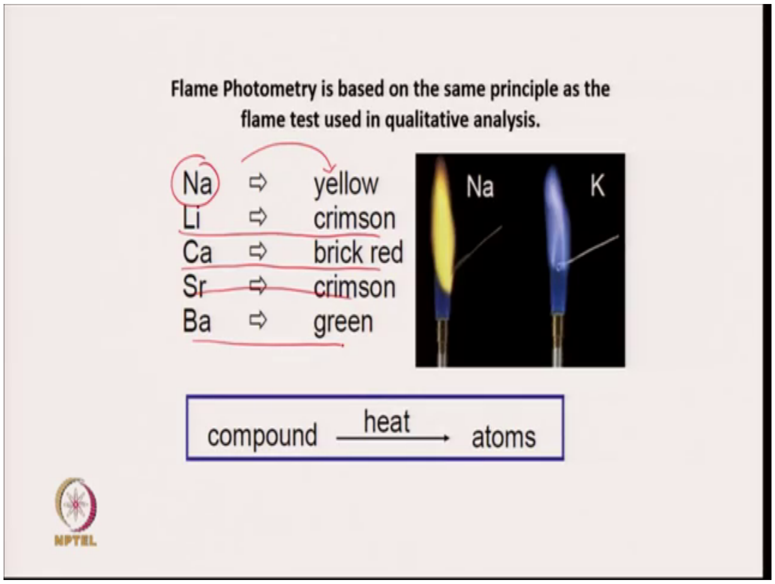

Flame Photometry is based on the same principle as the flame test used in qualitative analysis.

Na ⇨ yellow
Li ⇨ crimson
Ca ⇨ brick red
Sr ⇨ crimson
Ba ⇨ green

compound $\xrightarrow{\text{heat}}$ atoms

If you remember qualitative analysis, if we used to put sodium we used to get a yellow flame, lithium used to give you crimson colour, calcium gives you brick red colour, strontium gives you crimson colour and barium gives you green colour. What is basically happening? As electron is going from ground state to excited state and then it comes back to ground state by emitting light and lambda max will change for different kind of atom and the colour of flame will depend on the lambda max and just by looking at the colour you can know that which atom is present in that particular sample.

This is when atom is put into the flame but you can also put compound in the flame. What happens that if we put compound in flame, compound is broken into atoms and then we can see a spectra due to atoms and that is what is happening here.

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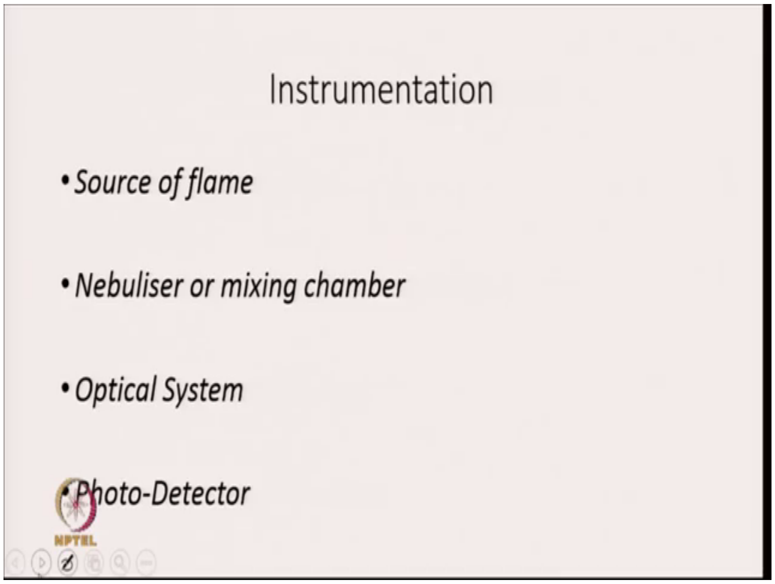

Instrumentation

- *Source of flame*
- *Nebuliser or mixing chamber*
- *Optical System*
- *Photo-Detector*

Now first I will discuss about instrumentation, the instrumentation of flame spectrometer has 4 important components, one is source of flame, the second is nebuliser or mixing chamber and third is optical system and photo detector.

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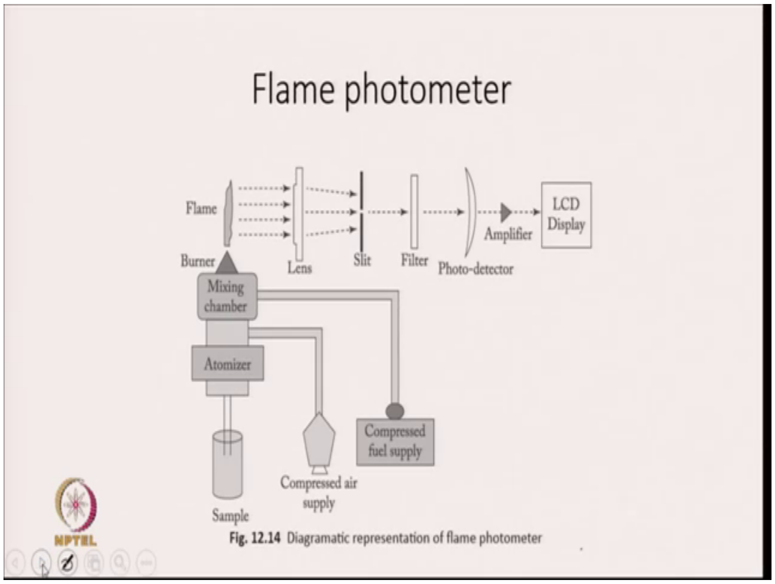

Flame photometer

Fig. 12.14 Diagramatic representation of flame photometer

And a typical representation of flame photometer is given here. So here is sample, here is atomizer and then you are mixing fuel here that is mixing chamber and when it is burnt there is a flame, you pass through lens then through slit, it again goes through filter and then finally here is the amplifier and you see the signal on the LCD display. So it is quite simple representation.

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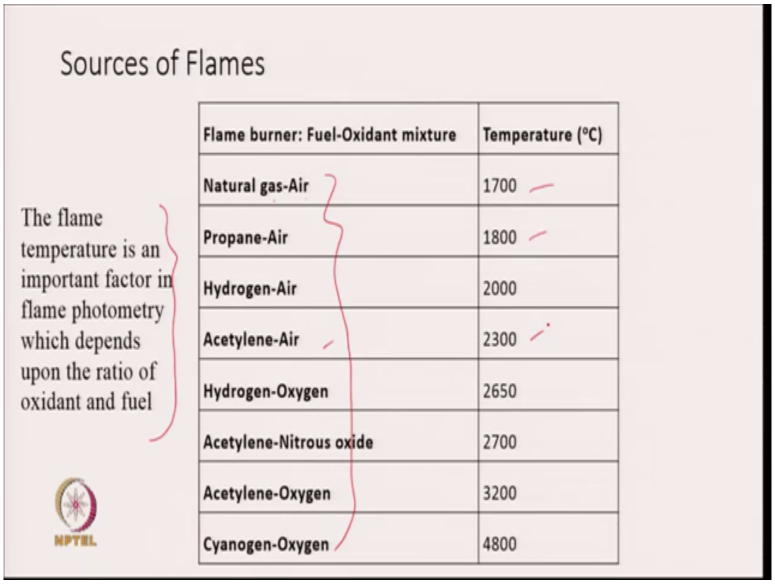

Sources of Flames

The flame temperature is an important factor in flame photometry which depends upon the ratio of oxidant and fuel

Flame burner: Fuel-Oxidant mixture	Temperature (°C)
Natural gas-Air	1700
Propane-Air	1800
Hydrogen-Air	2000
Acetylene-Air	2300
Hydrogen-Oxygen	2650
Acetylene-Nitrous oxide	2700
Acetylene-Oxygen	3200
Cyanogen-Oxygen	4800

Now first we will discuss about source of flame. It is very important to use the right flame if you want to know whether a particular element is present in the sample or not. These are the fuel oxidant mixture used for flame burner. Why we use different fuel oxidant mixture? Because the flame temperature is an important factor in flame photometry. The temperature depends upon the ratio of oxidant and fuel. For example natural gas and air mixture temperature is 1700 degree Celsius, propane air is 1800 degree Celsius. So depending upon the kind of element you are analysing you need to use different kinds of flame. Acetylene air is 2300 degree Celsius.

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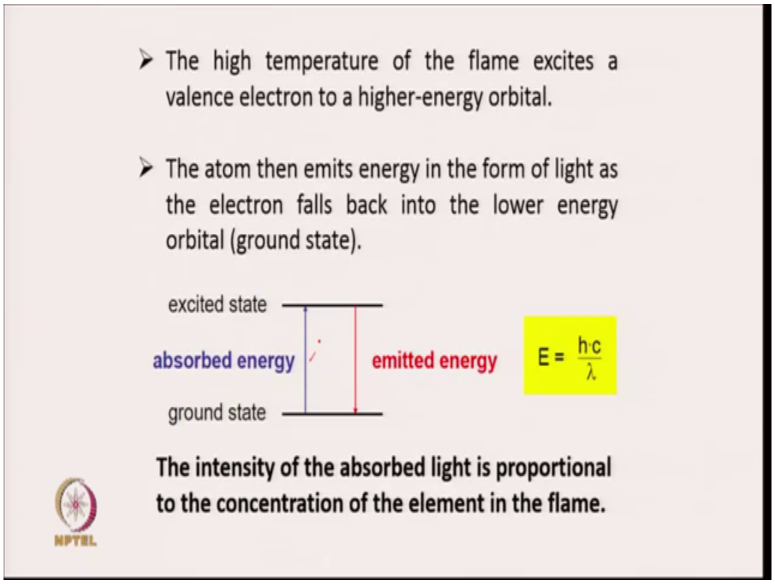

- The high temperature of the flame excites a valence electron to a higher-energy orbital.
- The atom then emits energy in the form of light as the electron falls back into the lower energy orbital (ground state).

excited state

absorbed energy

emitted energy

ground state

$$E = \frac{h \cdot c}{\lambda}$$

The intensity of the absorbed light is proportional to the concentration of the element in the flame.

So, this is about the sources of flame. What does this flame does is that high temperature of flame excites a valence electron to a higher energy orbital and then what happens that atom then emits energy in the form of light as the electron falls back into lower energy orbital. So here you are supplying energy as heat and what you are getting back is the energy in form of light, energy in form of light or electromagnetic radiation.

The intensity of the absorbed light is proportional to the concentration of the element in the flame. So intensity of absorbed light is proportional to concentration of the element in the flame, whereas lambda max will depend on the gap between 2 atomic orbitals or 2 atomic energy states.

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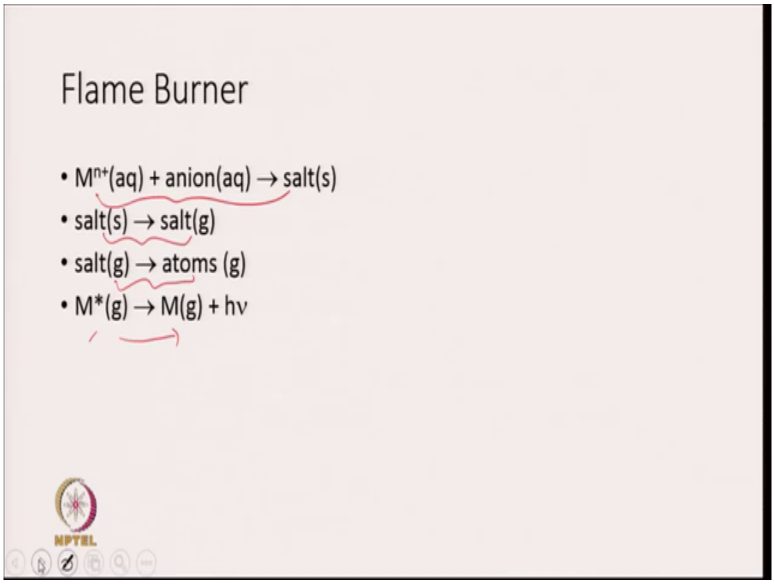

Flame Burner

- $M^{n+}(aq) + anion(aq) \rightarrow salt(s)$
- $salt(s) \rightarrow salt(g)$
- $salt(g) \rightarrow atoms\ (g)$
- $M^*(g) \rightarrow M(g) + h\nu$

So when I put my sample into a burner what will happen is you have this salt, so suppose you have put salt in a flame then first thing will happen is salt will vaporize to gas and then salt will dissociate into atoms. This atom will go to excited state and when it comes back to ground state it will emit light, this is the wave flame your flame emission spectroscopy works.

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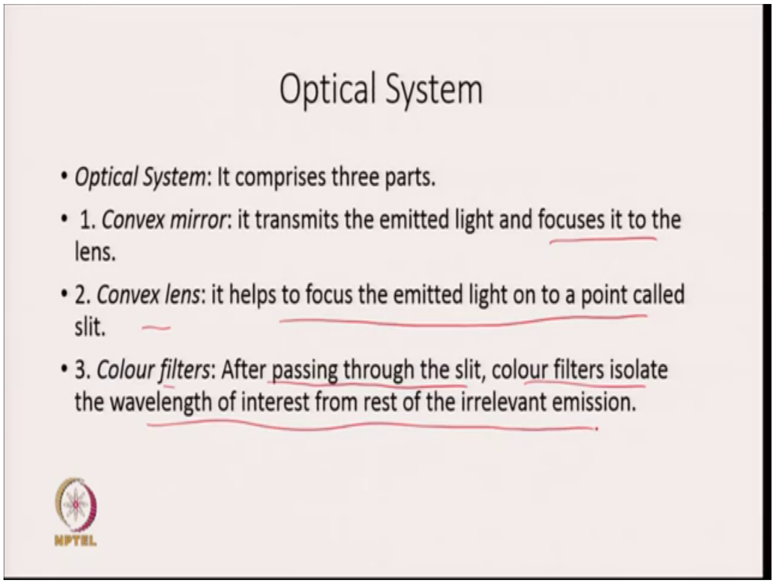

Optical System

- *Optical System*: It comprises three parts.
- 1. *Convex mirror*: it transmits the emitted light and focuses it to the lens.
- 2. *Convex lens*: it helps to focus the emitted light on to a point called slit.
- 3. *Colour filters*: After passing through the slit, colour filters isolate the wavelength of interest from rest of the irrelevant emission.

Now other part of the instrumentation is optical system. It has 3 different parts convex mirror, if you remember the schematic diagram of the flame photometer there was a convex mirror. It basically transmits the emitted light and focuses it to the lens. Now what lens does? It helps to focus the emitted light onto a point called slit and then the third party colour filter. When the emitted light pass through the slit colour filter isolate the wavelength of interest from rest of the irrelevant emission, rest of the irrelevant emission. So these are the part of optical system used in the flame photometer and finally photo detector.

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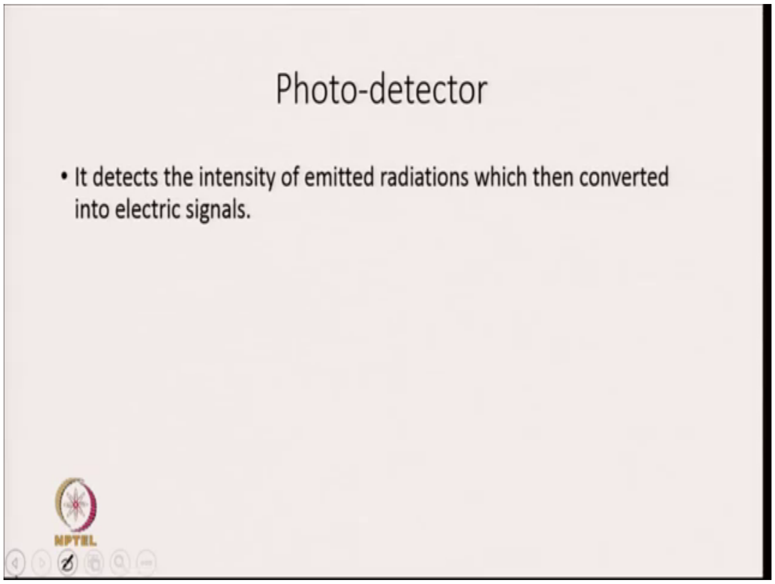

Photo-detector

- It detects the intensity of emitted radiations which then converted into electric signals.

It detects the intensity of emitted radiations which then converted is converted into electric signals, electrical signals.

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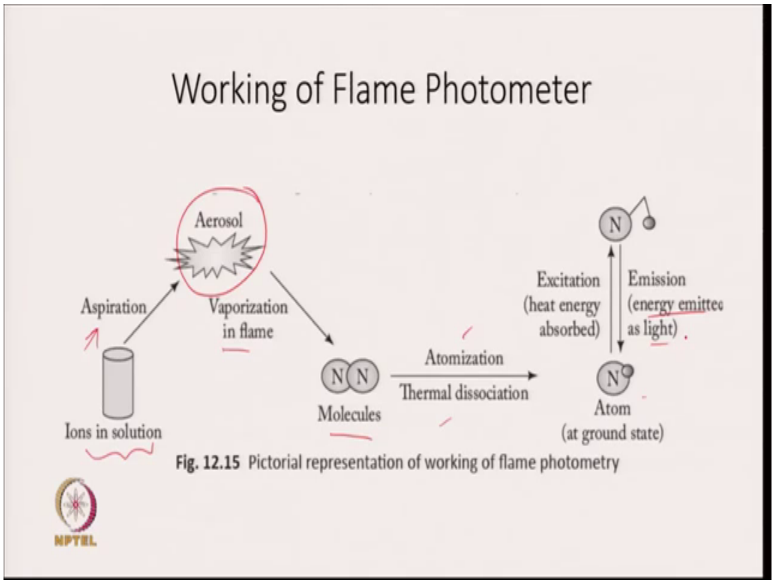

Working of Flame Photometer

Fig. 12.15 Pictorial representation of working of flame photometry

Now this is your working flame, working of flame photometer working of flame photometer. So first thing is ions are taken in solution and when you do aspiration what you will get is aerosol and it will vaporize in the flame to give you molecule in the gas phase and then atomization will takes place. So basically thermal dissociation to atom. Atom has one electron and that will get excited to the excited state on absorption of heat and when it comes back to ground state then energy will be emitted as light. So this is a simple working scheme of a flame photometer.

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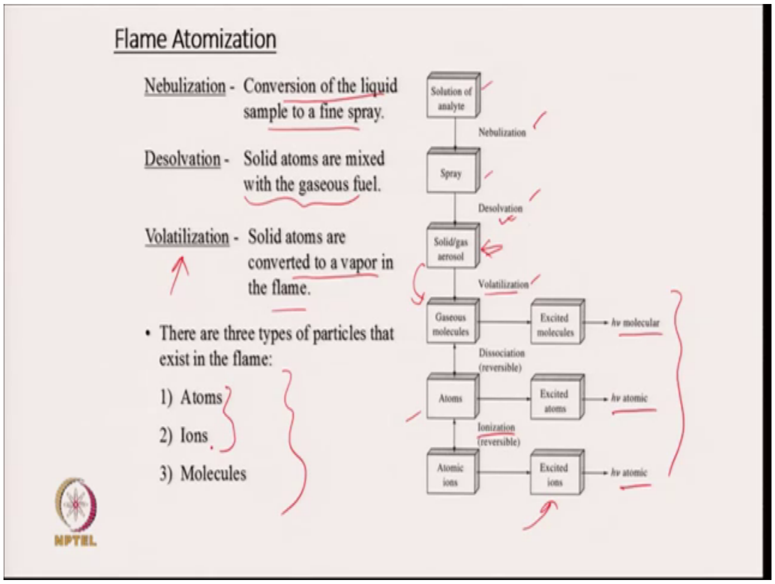

Flame Atomization

Nebulization - Conversion of the liquid sample to a fine spray.

Desolvation - Solid atoms are mixed with the gaseous fuel.

Volatilization - Solid atoms are converted to a vapor in the flame.

- There are three types of particles that exist in the flame:
  1) Atoms
  2) Ions
  3) Molecules

So the whole process has several different steps, first is solution of analyte is nebulized into a spray, nebulized in the spray and then desolvation process happens which forms solid to gas aerosol, that is what we discussed that how solution is going to aerosol. When you put this into a flame then volatilization happens and these aerosols convert into gaseous molecules. Now this molecule can go to excited state since it is being heated and so it can go to excited state, then you will be dealing with molecular spectroscopy. The other thing which can happen is gaseous molecule can dissociate to give atoms and now atoms can go to excited state and then we are dealing with atomic spectroscopy.

The third thing can happen that atoms can get ionized and then it can go to excited state. In that case we are again we are dealing with atomic spectroscopy. So there are 3 important terms we came across nebulisation, desolvation and volatilization. Nebulisation is conversion of liquid sample to a fine spray. So you have started with liquid sample and you want to make it into a spray that process is called nebulisation.

Now in the desolvation , solid atoms are mixed in to the gaseous fuel to make it aerosol. So now the solid atoms in water is mixed with gaseous fuel to give you aerosol and the last step is your volatilization which is basically when solid atoms are converted to a vapor in the flame. So the temperature must be very high so that atom can be converted into vapor. So it is atom need to be converted into vapor. So if you understand this you now know that 3 types of particle can exist in flames atoms, ions and molecules but what we are mainly concerned in atomic spectroscopy is atoms and ions. So this is about flame photometry.

Now we will go to much higher technique called atomic absorption spectrometer. The only difference is now our source will be different, method of atomization will be different and the source of flame will also be different.

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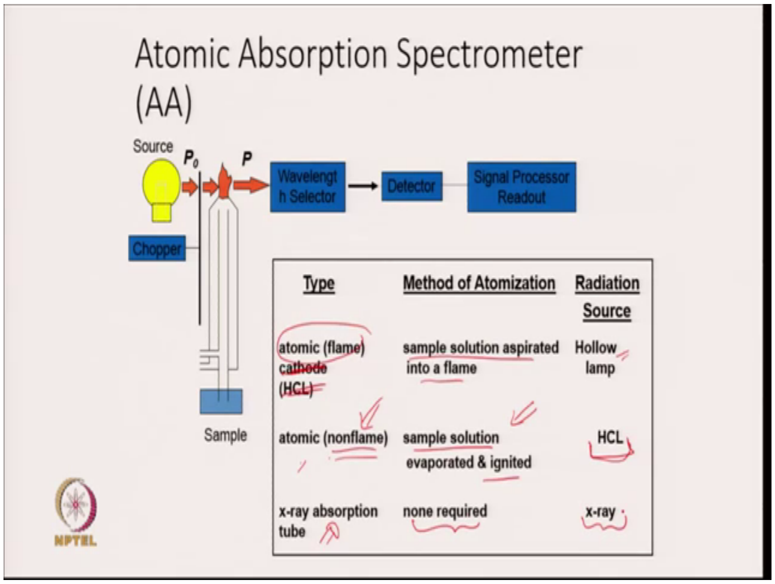

Atomic Absorption Spectrometer (AA)

Type	Method of Atomization	Radiation Source
atomic (flame) ~~cathode (HCL)~~	sample solution aspirated into a flame	Hollow lamp
atomic (nonflame)	sample solution evaporated & ignited	HCL
x-ray absorption tube	none required	x-ray

What we mean? Radiation source is different. So the first thing which we discussed is your atomic flame photometer, sample here, sample solution aspirated into a flame and we use this, for this we use hollow lamp. For atomic spectroscopy which is basically atomic absorption spectrometer when we take a situation where we are now not taking flame, so non-flame condition. In this case what we need to do is, we take sample solution evaporated and ignited, sample solution evaporated and ignited, this is the method of atomisation and for that radiation source is your hollow cathode lamp, hollow cathode lamp.

So, I think this is, this is just cancel this out sorry for this. So, for the second type of atomic absorption spectrometer which is based which is not based on flame is when we use hollow cathode lamp as a radiation source. In this case sample solution gets evaporated and ignited using hollow cathode lamp. In the third kind we have x-ray absorption tube. Here method of atomization not required, our radiation source is x-ray, radiation source is x ray.

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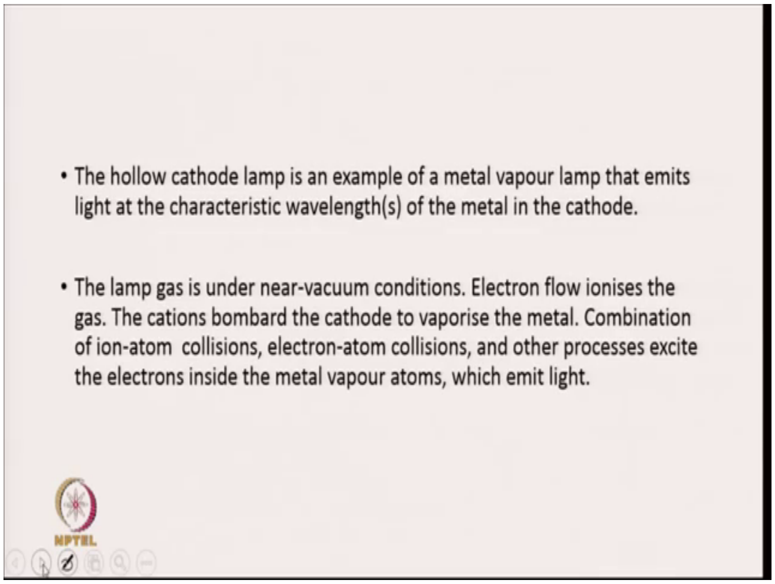

- The hollow cathode lamp is an example of a metal vapour lamp that emits light at the characteristic wavelength(s) of the metal in the cathode.
- The lamp gas is under near-vacuum conditions. Electron flow ionises the gas. The cations bombard the cathode to vaporise the metal. Combination of ion-atom collisions, electron-atom collisions, and other processes excite the electrons inside the metal vapour atoms, which emit light.

What is hollow cathode lamp? It is an example of a metal vapour lamp that emits light at the characteristic wavelength of the metal in the cathode. The lamp gas is under near vacuum condition and electron flow ionizes the gas, the cations bombard the cathode to vaporise the metal. Combination of ion atom collision, electron atom collision and other processes excite the electron inside the metal vapour atoms which emit light, this is the basis of hollow cathode lamp HCL.

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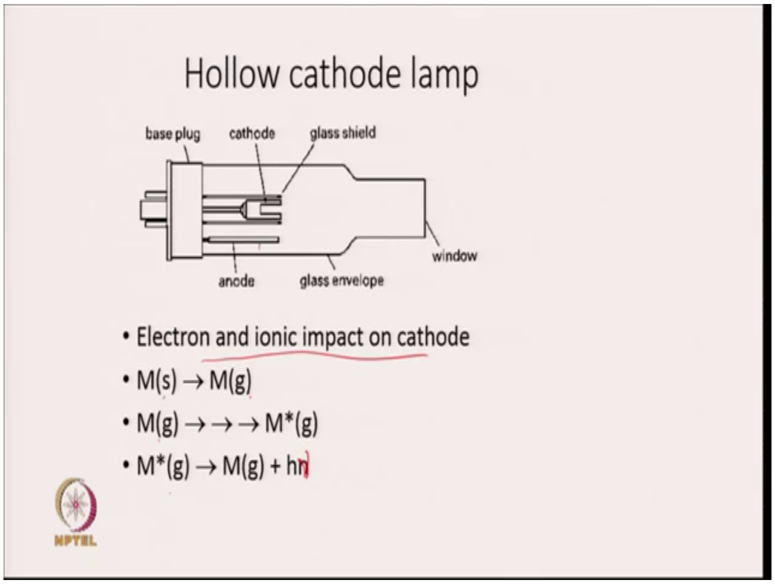

Hollow cathode lamp

- Electron and ionic impact on cathode
- $M(s) \rightarrow M(g)$
- $M(g) \rightarrow \rightarrow \rightarrow M^*(g)$
- $M^*(g) \rightarrow M(g) + hn$

So this is like this is a schematic representation of hollow cathode lamp, this is your cathode and this is shielded by a glass, this is glass envelope, this is window and this is anode and electron and ionic impact on cathode will happen, M s will first go to m gas metal from solid form to metal in gas form. Then this get excited and when excited metal comes back to ground state it will give you light h n, it will give you light.

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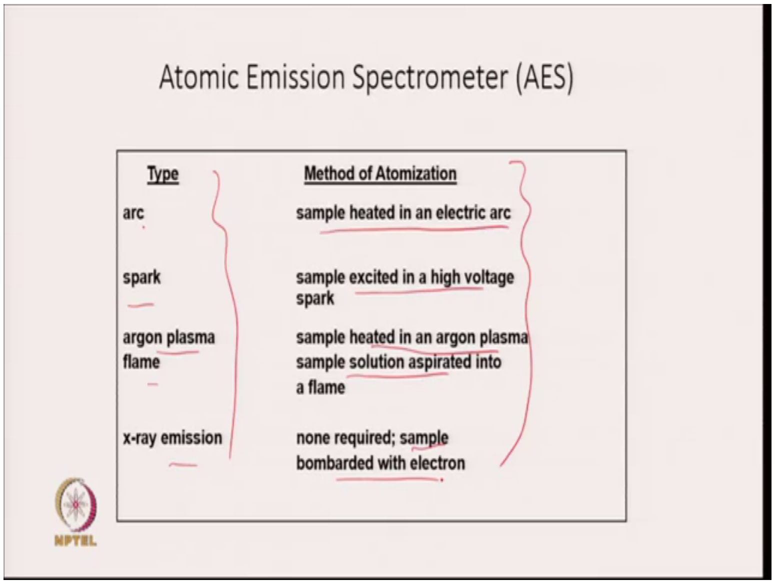

Atomic Emission Spectrometer (AES)

Type	Method of Atomization
arc	sample heated in an electric arc
spark	sample excited in a high voltage spark
argon plasma	sample heated in an argon plasma
flame	sample solution aspirated into a flame
x-ray emission	none required; sample bombarded with electron

Now second kind of spectroscopy based on atomic spectroscopy is atomic emission spectrometer. Here, there can be different types and method of atomization is different. Arc type, method of atomization is sample heated in an electric arc. When the type is spark then sample excited in high voltage spark. Then you have argon plasma flame sample heated in an argon plasma sample solution aspirated into a flame. Then x-ray emission sample bombarded with electron, sample bombarded with electron.

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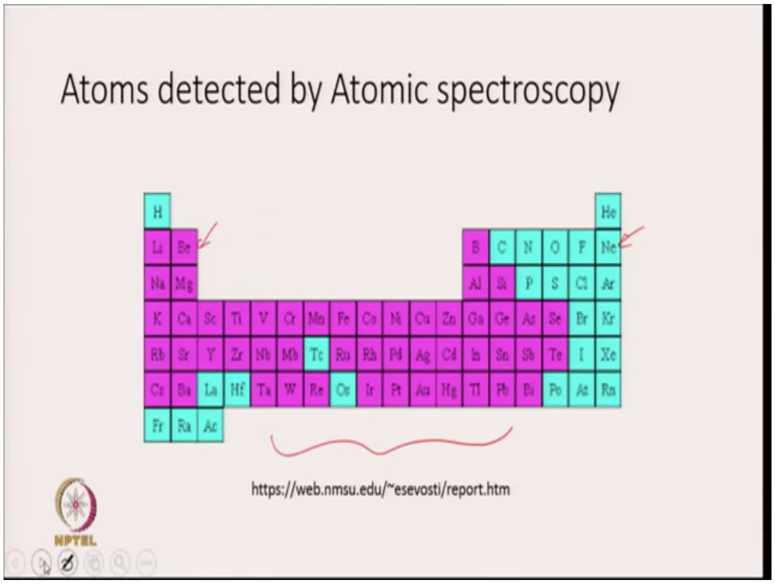

Atoms detected by Atomic spectroscopy

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mb	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac															

https://web.nmsu.edu/~esevosti/report.htm

Now all these 3 methods, flame photometry, atomic absorption spectroscopy and atomic emission spectroscopy helps us to detect the atom and the atoms detected by atomic spectroscopy are quite large and here is the, a list of atoms which can be detected from atomic spectroscopy. So this colour which is pink will tell you that which metals can be detected by atomic spectroscopy. Whereas this metals cannot be detected by atomic spectroscopy. So you can see there are a large number of atoms which can be detected by atomic spectroscopy and that is one of the very important advantage of using atomic spectroscopy.

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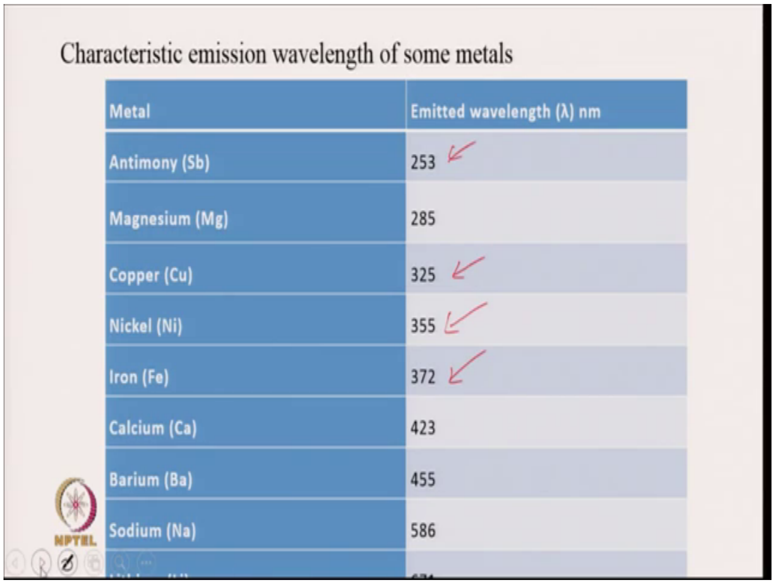

Characteristic emission wavelength of some metals

Metal	Emitted wavelength (λ) nm
Antimony (Sb)	253
Magnesium (Mg)	285
Copper (Cu)	325
Nickel (Ni)	355
Iron (Fe)	372
Calcium (Ca)	423
Barium (Ba)	455
Sodium (Na)	586

There are characteristic emission wavelengths of some metals. For example antimony emitted wavelength comes at around 253 nanometre, copper 325 nanometre, nickel 355 nanometre, iron 372 nanometre. So, if you look at the atomic spectra and if you see these peaks for example (350) peak at 355 nanometre and you cannot say that nickel is present in that sample, nickel is present in that sample.

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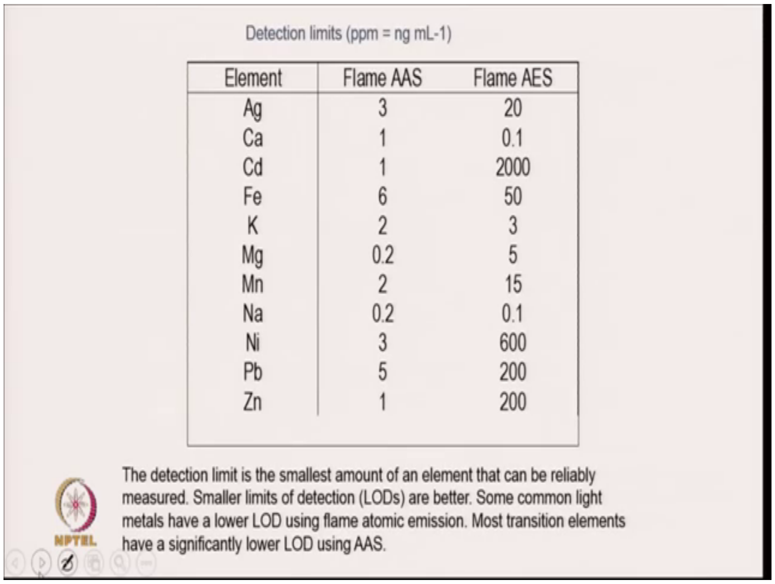

Detection limits (ppm = ng mL-1)

Element	Flame AAS	Flame AES
Ag	3	20
Ca	1	0.1
Cd	1	2000
Fe	6	50
K	2	3
Mg	0.2	5
Mn	2	15
Na	0.2	0.1
Ni	3	600
Pb	5	200
Zn	1	200

The detection limit is the smallest amount of an element that can be reliably measured. Smaller limits of detection (LODs) are better. Some common light metals have a lower LOD using flame atomic emission. Most transition elements have a significantly lower LOD using AAS.

Okay this is some detection limit in ppm, this is the difference between flame AS flame ES. So always your concentration of the metal detected from different spectroscopy is different and this is the list. You can find out this on the on different books. So I am not going to discuss that much.

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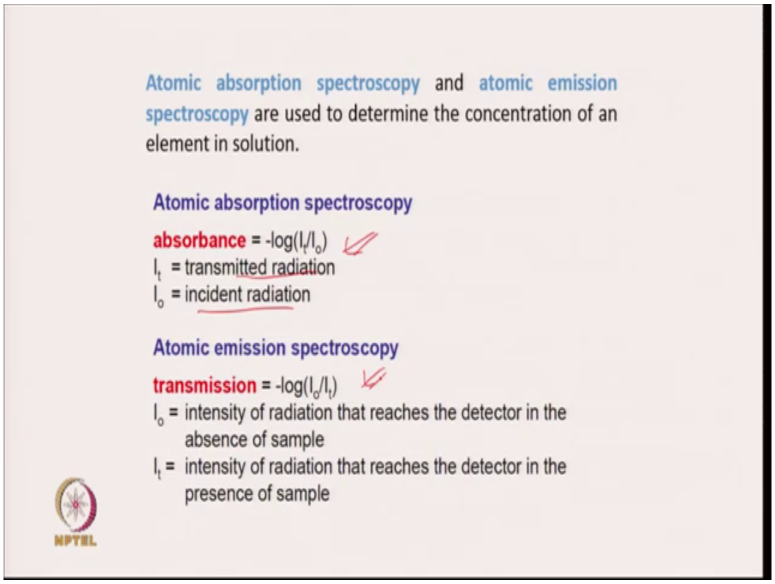

Atomic absorption spectroscopy and atomic emission spectroscopy are used to determine the concentration of an element in solution.

Atomic absorption spectroscopy

absorbance = $-\log(I_t/I_0)$

I_t = transmitted radiation

I_0 = incident radiation

Atomic emission spectroscopy

transmission = $-\log(I_0/I_t)$

I_0 = intensity of radiation that reaches the detector in the absence of sample

I_t = intensity of radiation that reaches the detector in the presence of sample

Now, what is the other use apart from detecting the matter? We can also know the concentration of element in solution using atomic spectroscopy. What we can do is, we can look at the intensity or absorbance at a particle wavelength at which a particular atom absorbs or emits, absorbs and emits. And absorbance we know is related to intensity by this formula which is Beer-Lamberts Law, here I T is transmitted radiation intensity of transmitted radiation and I 0 is intensity of incident radiation. Again in atomic emission we can look at the transmittance, we can look at the transmittance or transmission. Once we know that this absorbance or transmission is proportional to concentration and so we can know the concentration of particular element in the solution.

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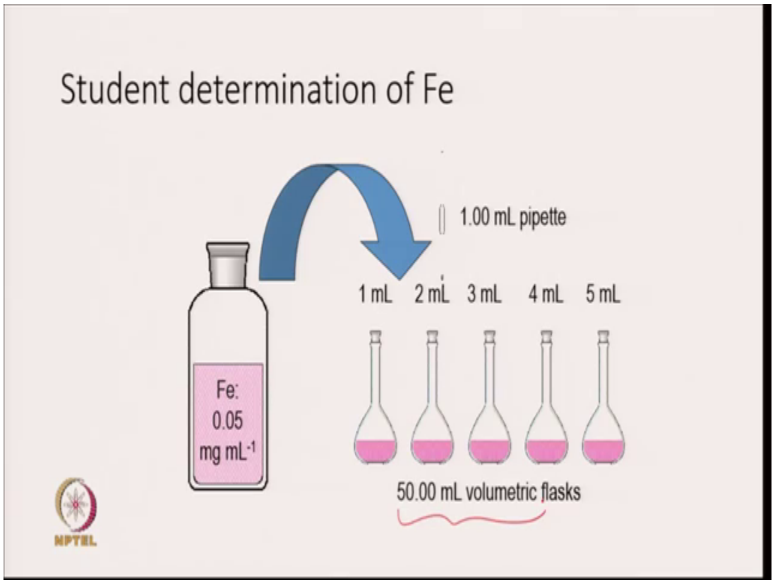

Student determination of Fe

The way we do it is for example if suppose you have iron in a sample, what we do is, so first thing which you need to do suppose I want to calculate the concentration of iron in a particular sample. As you make a standard solution of iron, or for example iron sulphate. Take a particular concentration and make different, make the sample, several samples in 50 ml volumetric flask of different iron concentration, different iron concentration and then what you do is you look at the absorbance of these samples and then you first make a calibration curve, calibration curve.

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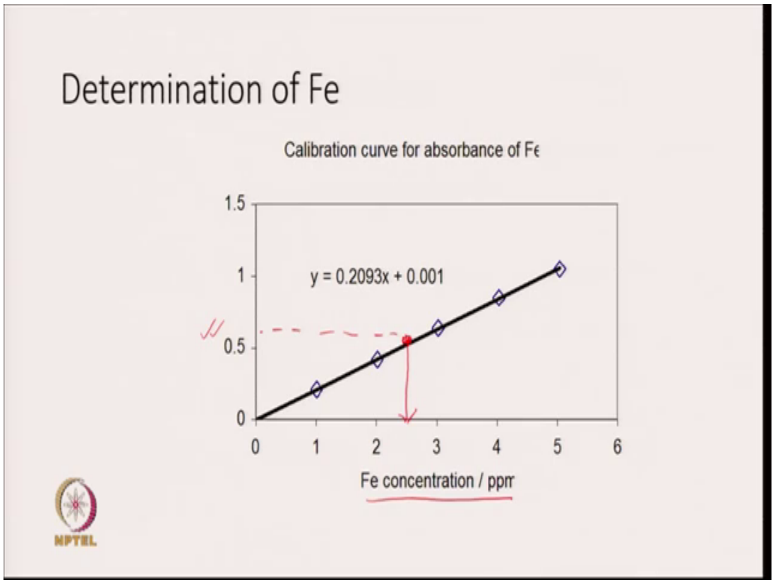

Determination of Fe

So you see here what has been done is, iron concentration in ppm and here is the absorbance. So you are plotting absorbance versus iron concentration in ppm and you make a calibration curve and this is your calibration curve.

Now you take your sample in which you want to know the concentration of iron and then you see where it ends up. For example, it ends up in between then you know what will be the concentration of iron in that sample. So it will be around 2.5 ppm, 2.5 ppm if the absorbance of your sample is around this 0.6 or something like that. So, you can calculate amount of an element in the sample using your flame photometry or atomic absorbance spectroscopy or emission your spectroscopy. First thing you need to do is make calibration curve with the standard sample. Once you do that and it is very easy to know what is the concentration of the element in particular sample, in that particular sample which you want to analyse.

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Application of Atomic Absorption Spectroscopy

Now we will go to look at application of atomic absorption spectroscopy.

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There are several different kind of application of atomic spectroscopy. Here are the different fields in which atomic spectroscopy is atomic spectroscopy is right now being used. First is environmental, forensic science, agriculture, clinical, pharmaceutical, petrochemicals.

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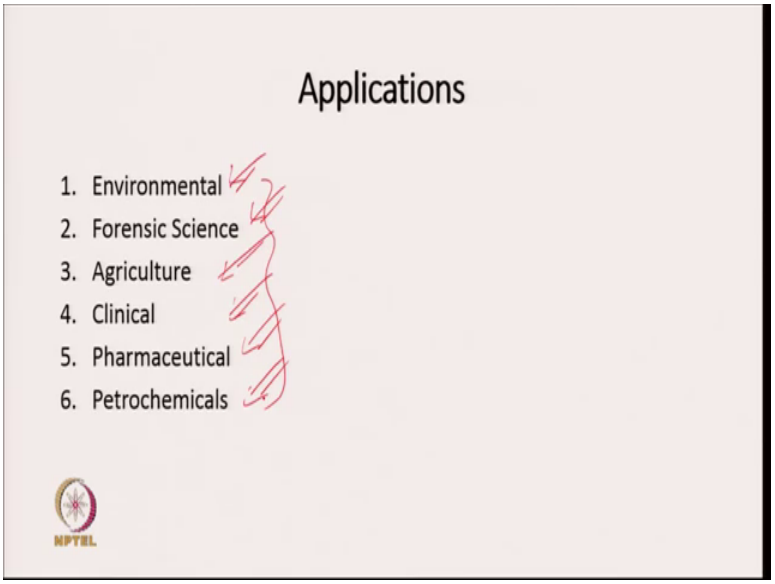

Applications

1. Environmental
2. Forensic Science
3. Agriculture
4. Clinical
5. Pharmaceutical
6. Petrochemicals

Now first we will look at the environmental applications. First is monitoring, studies in sediments. Atomic absorption spectroscopy has been used for the analysis of many elements, sediment samples from surficial to segments extracted from cores. It is applied or application includes qualitative elemental measurements in a wide range of soil and sediment sample to monitor changes in sediment loads and to determine the geochemical processes that alter the chemical spaces of each elements.

So, if suppose any geochemical process is happening that will lead to change in the, change in the composition of the sediment. So you will find different amount of different atoms in the sediment and based on that you can tell which kind of geochemical processes are happening and for that you need to know what is the concentration, what is the amount of different chemical spaces of each element and that is where atomic spectroscopy can be of help to you.

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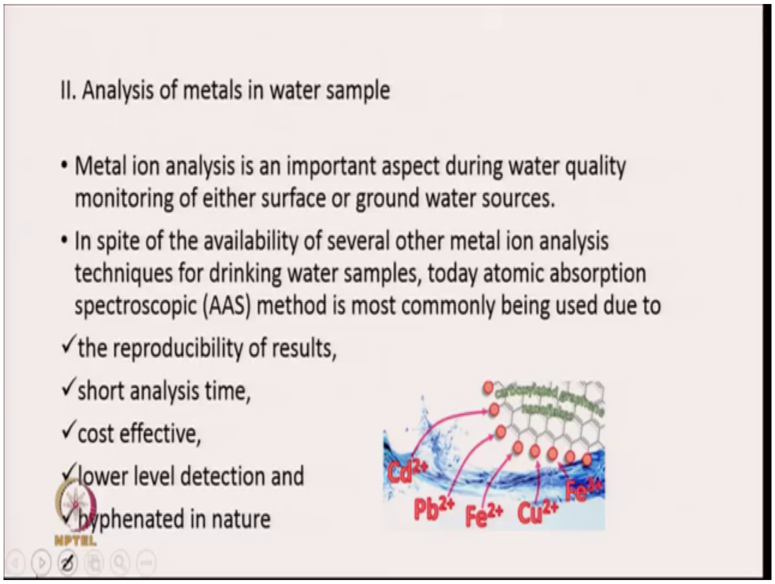

II. Analysis of metals in water sample

- Metal ion analysis is an important aspect during water quality monitoring of either surface or ground water sources.
- In spite of the availability of several other metal ion analysis techniques for drinking water samples, today atomic absorption spectroscopic (AAS) method is most commonly being used due to

✓the reproducibility of results,
✓short analysis time,
✓cost effective,
✓lower level detection and
✓hyphenated in nature

Similarly, you can also look at the analysis of metals in water sample. Metal ion analysis is important aspect during water quality. So water quality depends on kind of metal ion it has. So if you get water from either surface or ground you need to check what are the elements in that water sample and that can tell you whether that water can be used for drinking or not. Although there are several other methods for analysis but atomic absorption spectroscopy is most commonly used to look at the metal in water because of the reproducibility of results, short analysis time, cost effective, lower level detection and hyphenated in nature.

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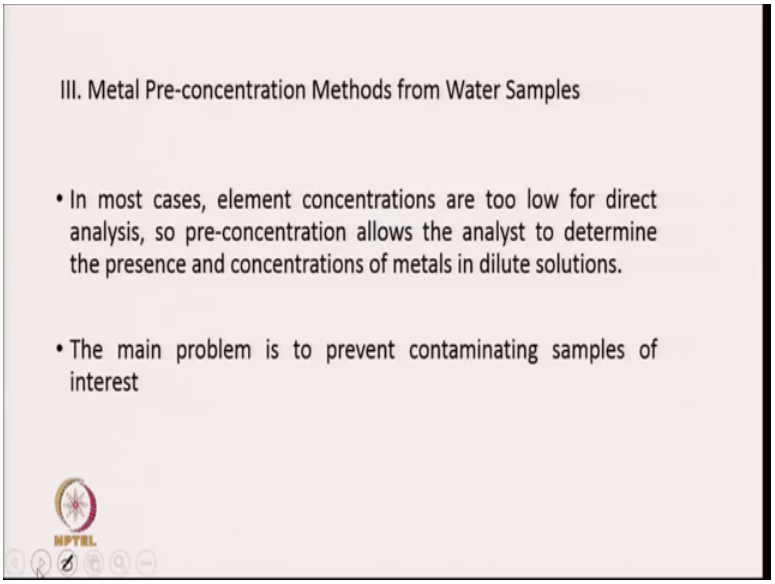

III. Metal Pre-concentration Methods from Water Samples

- In most cases, element concentrations are too low for direct analysis, so pre-concentration allows the analyst to determine the presence and concentrations of metals in dilute solutions.
- The main problem is to prevent contaminating samples of interest

So first what we need to do is, we need to concentrate the metal in the water sample. Since the element concentration are too low for direct analysis. So first thing we need to do is pre-concentration, the main problem is to prevent contaminating sample of interest during your pre-concentration.

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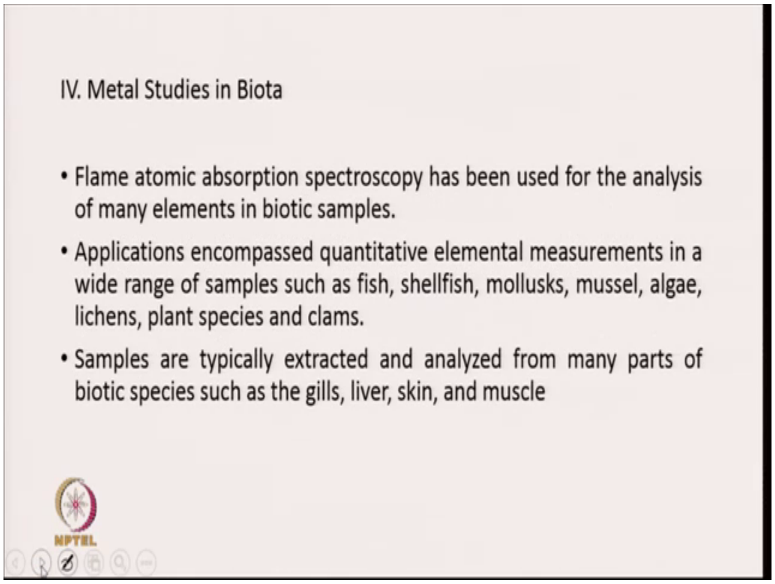

IV. Metal Studies in Biota

- Flame atomic absorption spectroscopy has been used for the analysis of many elements in biotic samples.
- Applications encompassed quantitative elemental measurements in a wide range of samples such as fish, shellfish, mollusks, mussel, algae, lichens, plant species and clams.
- Samples are typically extracted and analyzed from many parts of biotic species such as the gills, liver, skin, and muscle

But once you do that you can know what is the amount of the different element present in the water sample. You can also study the metals presents in biota, means you can look at the biotic samples and see what are the different elements present in that biotic sample? And what is the concentration of that element? The application here includes quantitative elemental measurements in wide range of samples such as fish, shellfish, molluscs, mussel, algae, lichens, plant species and clams. Samples are typically extracted and analysed from many parts of biotic species such as the gills, liver, skin and muscles. So this is the way to know what is the metals present in that biotic sample.

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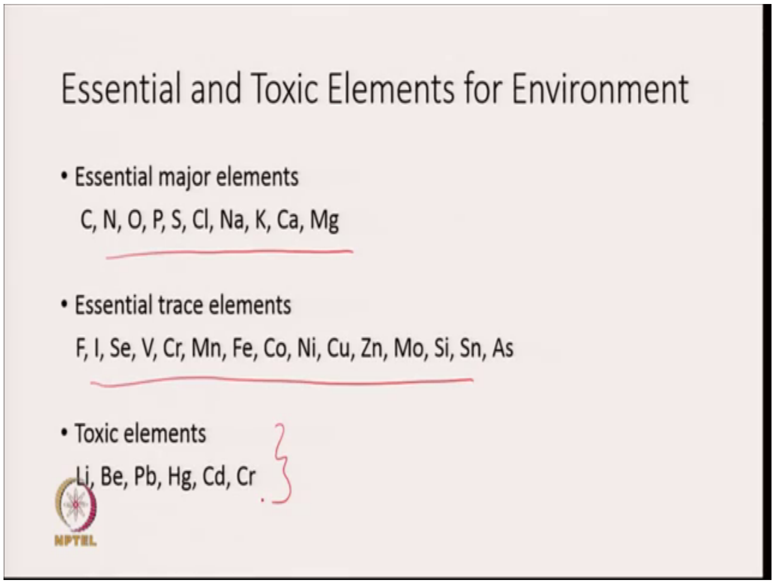

Essential and Toxic Elements for Environment

- Essential major elements
  C, N, O, P, S, Cl, Na, K, Ca, Mg
- Essential trace elements
  F, I, Se, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, Si, Sn, As
- Toxic elements
  Li, Be, Pb, Hg, Cd, Cr

The essential and toxic elements for environment, some metals are essential for the environment and some metals are toxic. What are the essential major elements? It is carbon, nitrogen, oxygen, phosphorus, sulphur, chlorine, sodium, potassium, calcium, magnesium. Essential trace elements are these. while toxic elements are these 6, lithium, beryllium, lead, hg, cadmium, chromium and each one of them can be analysed by atomic absorption spectroscopy or flame photometer.

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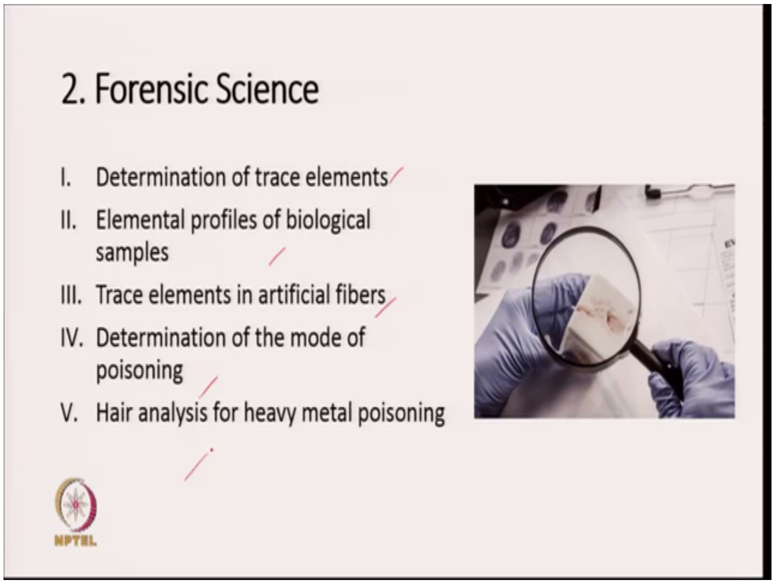

2. Forensic Science

I. Determination of trace elements
II. Elemental profiles of biological samples
III. Trace elements in artificial fibers
IV. Determination of the mode of poisoning
V. Hair analysis for heavy metal poisoning

So next application is in forensic science, in forensic science you can look for trace elements, you can look for elemental profiles of biological samples, you can also look at the trace elements in artificial fibres, you can look at the determination of the mode of poisoning and the hair analysis for heavy metal poisoning. So these are the few different things which can help you in forensic science and hence atomic absorption spectroscopy or spectroscopy method based on atomic spectroscopy is quite often used in the forensic science.

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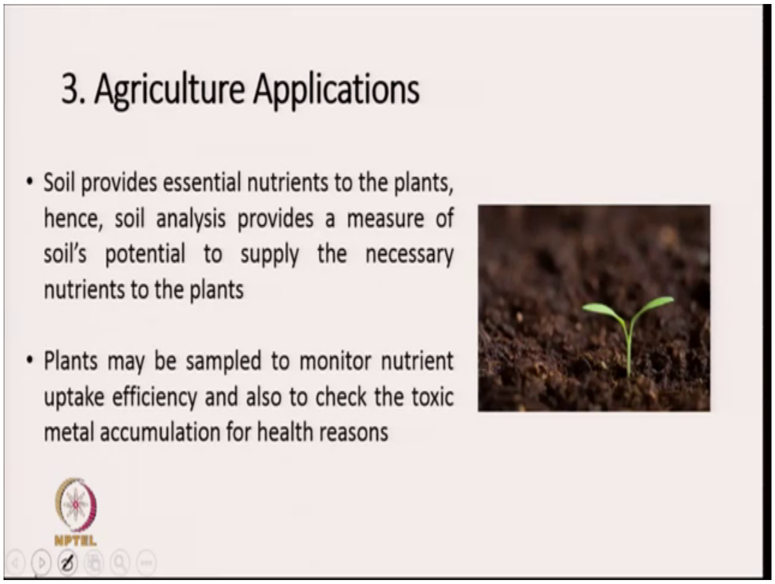

3. Agriculture Applications

- Soil provides essential nutrients to the plants, hence, soil analysis provides a measure of soil's potential to supply the necessary nutrients to the plants
- Plants may be sampled to monitor nutrient uptake efficiency and also to check the toxic metal accumulation for health reasons

So there are other applications but since time is over I will like to stop here.

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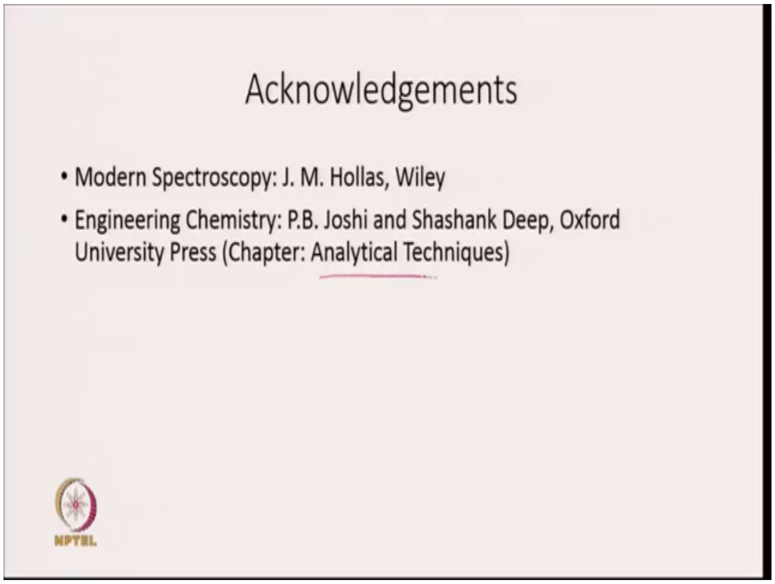

Acknowledgements

- Modern Spectroscopy: J. M. Hollas, Wiley
- Engineering Chemistry: P.B. Joshi and Shashank Deep, Oxford University Press (Chapter: Analytical Techniques)

These are the 2 books which I have referred for making notes which is your Modern Spectroscopy by Hollas and then the second book is my book, the Analytical Techniques chapter has quite analytical technique chapter I had discussed these techniques in details and you can go and look at this chapter. Thank you, thank you for listening.