Trace and ultra trace analysis of metals Using atomic absorption spectrometry

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Lecture – 14
Instrumentation in AAS I

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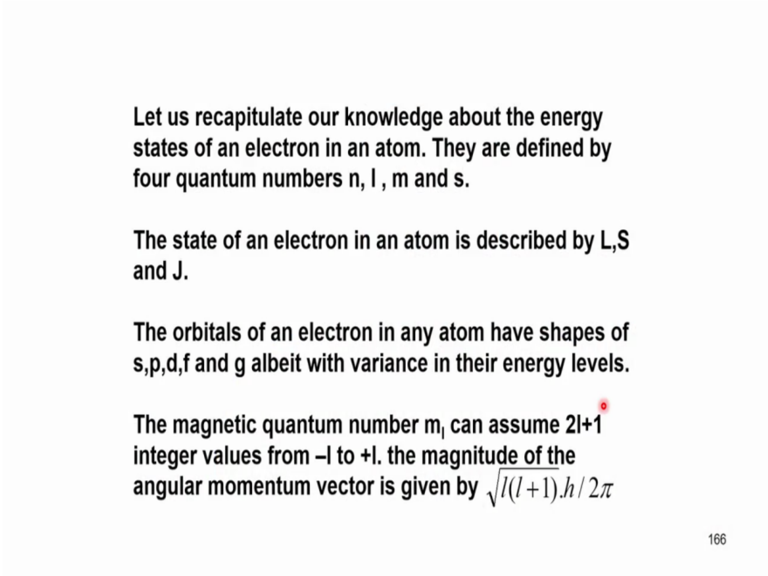

Continuing our discussion about the excitation of the electrons, let us recapitulate what we had discussed so far. So, what we want to say is all elements have electrons in the free state which can be absorbed to form free atoms. So, the electron in any element can be defined by four quantum numbers n, l, m and s; and the state of an electron in an atom is defined by L, S, and J, these are the different combination terms for the energy. So, the energy states of an electron I described by combined spectroscopic terms known as L, S and J, these are known as couplings. So, the orbitals of an electron in any atom have shapes of s, p, d, f and g albeit a variance with their energy level this we already know. So, the magnetic quantum number m can assume 2 l plus 1 integer values, they range from minus l to plus l, and the magnitude of the angular momentum vector is given by square root l into l plus 1 into h by 2 pi, this is I have already taught you earlier.

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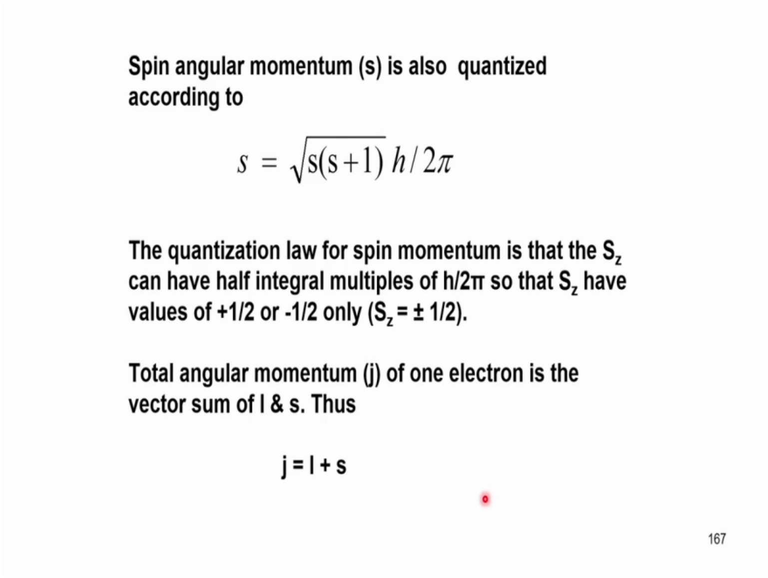

Now, spin angular momentum is also quantized according to this S into S plus 1 square root that is in the square root into h by 2 pi. So, the quantization law for spin momentum is that S z can have only half integral values of h by 2 pi, so that the values are plus half or minus half that is all. So, the angular momentum can have any numbers, but the angular momentum of the spin as well as the orbitals can be combined to give you total angular momentum j that is the vector sum of l and s. So, j is defined as the vector sum of l and s that is what I have written here.

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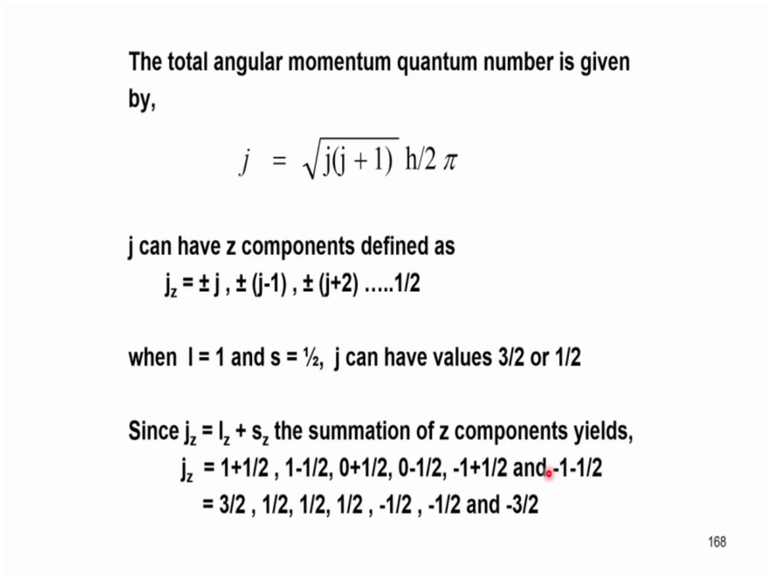

And the total angular momentum quantum number quantum number is given by a square root of j into j plus 1 by h by 2 pi and j also can have just like angular momentum just like angular momentum j z is equal to plus or minus j plus or minus j minus 1 etcetera like that. And when l is equal to 1, and s is equal to half, j can have values l plus s that is 3 by 2 or l minus s that is half. Since j z is equal to l z plus s z that is a summation of z components gives you one plus 1 and half 1 minus 1 and half 0 plus half 0 like that for different states energy states it gives you. So, for 3 by 2, we get 3 by 2, 1 by 2, 1 by 2, 1 by 2, minus 1 by 2 minus 1 by 2 and minus 3 by 2.

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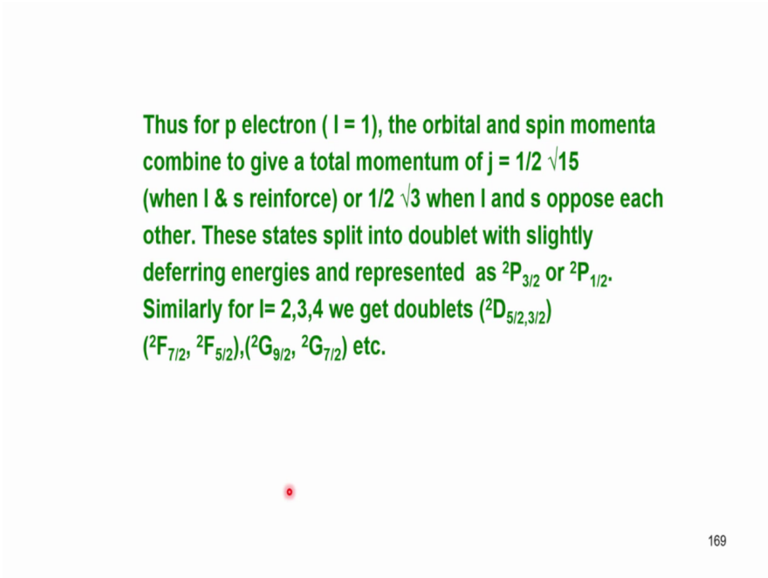

So, for p electron the orbital and spin momentum combined to give a total momentum of j that is 1 by 2 into square root of 15 and when they are reinforcing or 1 by 2 into square root of 3 when l and s oppose each other in terms of their spins. So, these states split into doublet because one is 3 by 2, another is half, so there are 2 states. So, they split into doublet with slightly deferring energies and this is what we get for sodium and many other single electron systems. So, we get doublets 2 D 3 by 2, 5 by 2, 3 by 2 this I have already shown you earlier.

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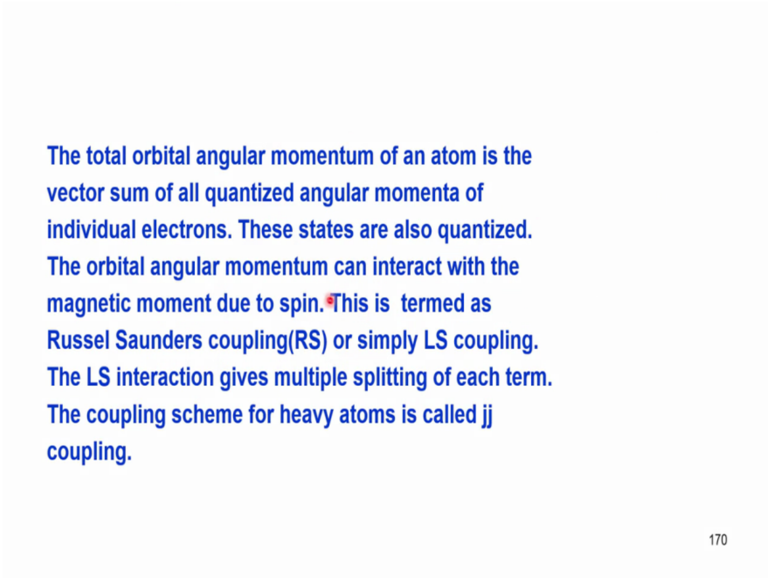

So, the total angular momentum of an atom is the vector sum of all quantized angular momentum of all individual electrons these state for a this is now I am talking about an atom in a free cell in a free cell that is in the vapor form. So, all atoms can have each atom can have quantized angular momentum. So, these states are also quantized. So, the orbital angular momentum can interact with the magnetic moment due to spin. So, this is termed as Russell Saunders coupling or simply LS coupling. So, LS interaction gives multiple splitting of each other which we have already discussed earlier.

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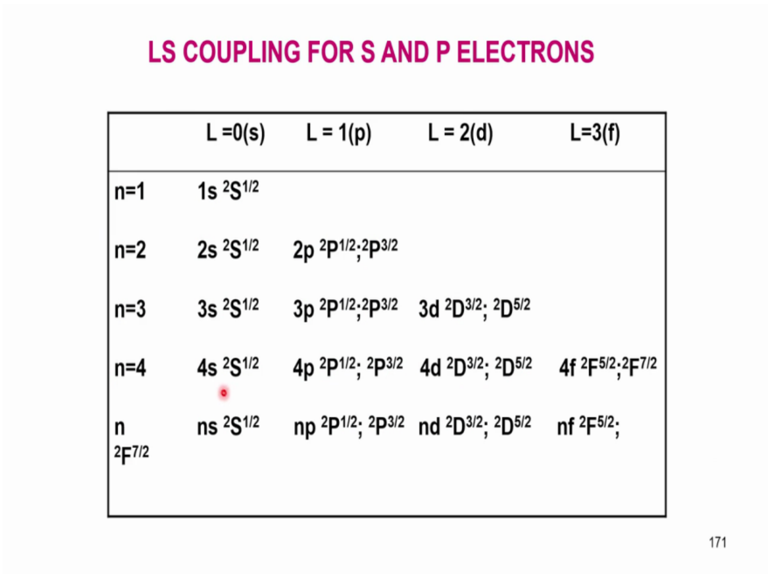

	L =0(s)	L = 1(p)	L = 2(d)	L=3(f)
n=1	1s $^2S^{1/2}$			
n=2	2s $^2S^{1/2}$	2p $^2P^{1/2}$;$^2P^{3/2}$		
n=3	3s $^2S^{1/2}$	3p $^2P^{1/2}$;$^2P^{3/2}$	3d $^2D^{3/2}$; $^2D^{5/2}$	
n=4	4s $^2S^{1/2}$	4p $^2P^{1/2}$; $^2P^{3/2}$	4d $^2D^{3/2}$; $^2D^{5/2}$	4f $^2F^{5/2}$;$^2F^{7/2}$
n $^2F^{7/2}$	ns $^2S^{1/2}$	np $^2P^{1/2}$; $^2P^{3/2}$	nd $^2D^{3/2}$; $^2D^{5/2}$	nf $^2F^{5/2}$;

So, LS coupling for S and P electrons, so, n is 1, l is 0. So, this is 2 S half n is equal to 2, 2 s S 2 half and 2 p to the 1 by 2, 2 p 3 by 2 this we have seen happening in this case of sodium Gaussian diagram. So, n is equal to 3, I can have this; and then n l is equal to 1 it is plus 1 minus 1 and 0 plus l to minus l. So, it is 3 p and minus 2 p, and then 3 D again a doublets. So, n is equal to 4 and we get the s p d; and then f is equal to 7 by 2, we get several other systems also. So, this is known as sp coupling LS coupling.

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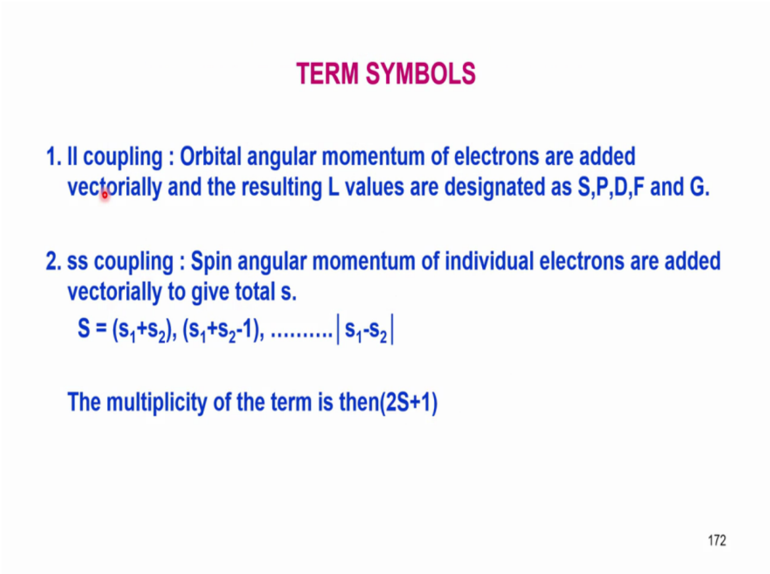

So, the term symbols what we are talking about is the ll coupling and ss coupling. Orbital angular momentum of electrons are added vectorially resulting in capital L. Now, we are talking about the vectorial combination of only angular momentum. And ss coupling it is spin angular momentum, again it will have the; it is known as multiplicity. So, multiplicity is 2 S plus 1.

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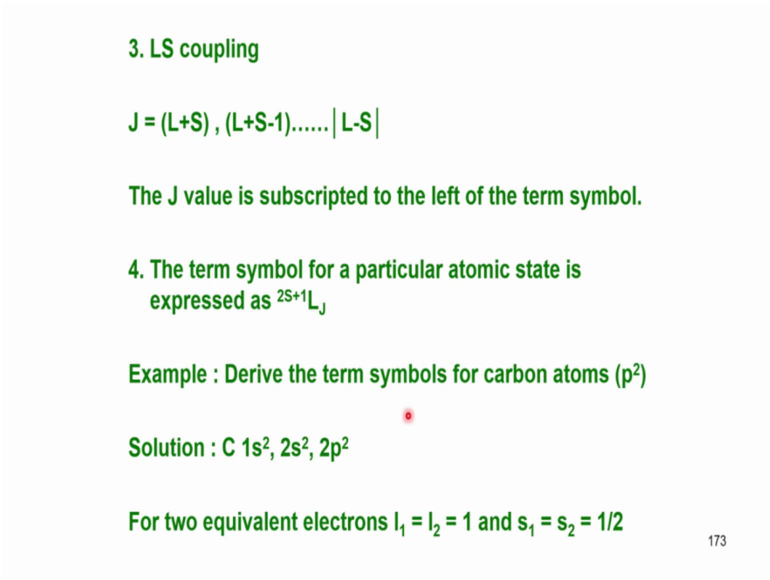

So, in LS coupling, we have capital J; earlier we are talking about small j. Now, capital J corresponds to all electrons in the given system where LS coupling is occurs. So, l plus s is same rules L plus S, L plus S minus 1 until it reaches L minus S. So, the j value is subscripted to the left of the term symbol, and the terms symbol something like this 2 s plus 1 L, I write j at the bottom and it is capital L please note. So, we can derive the terms involves for carbon atoms for example, solution is if I ask you to give you an exercise what are the term symbols for carbon. It is electronic structure is 1 s 2, 2 s 2, 2 p 2; for 2 equivalent electrons the 2 p 2 these 2 are electro equally electrons occupying 2 p orbitals. So, l 1 is equal to l 2 is equal to 1; and s 1 is equal to s 2 is equal to half.

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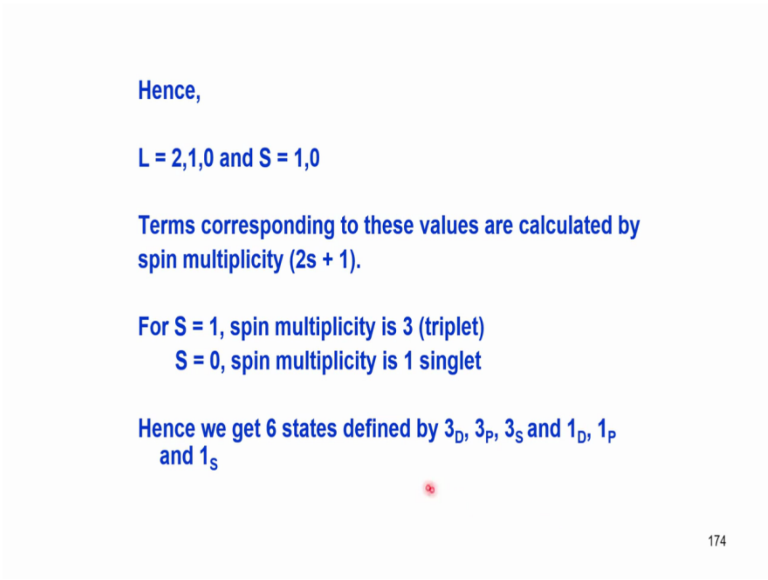

So, l is equal to 2, 1 and 0; s is 1 and 0. So, the terms corresponding to these values are calculated by spin multiplicity. And for S is equal to 1, it is 3; and S is equal to 0, it is single 1 that is known as singlet. So, we get six states correspondingly 3 D, 3 P, 3 S, 1 D, 1 p and 1 S.

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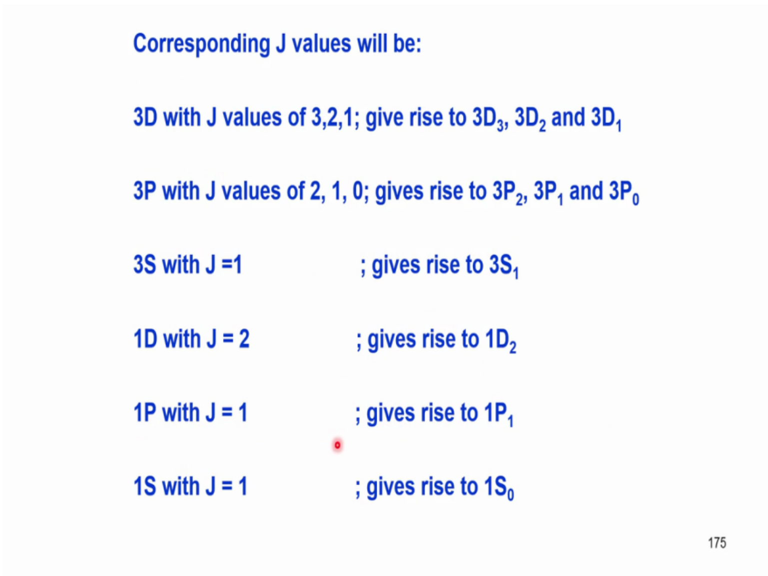

So, corresponding J values would be l plus s again. So, 3 D with J values will be 3, 2 and 1, these gives rise to 3 D 3, 3 D 2 and 3 D 1. And 3 P values will give you with J values will be having 2, 1 and 0 giving rise to 3 P 2, 3 P 1 and 3 P 0. So, 3 S with J 1 will give you 3 S 1, and 1 D with J 2 is will give you 1 D 2, 1 P with J is equal to 1 P, this is for P electron that is known as 1 P 1, and 1 S would give you 1 S 0.

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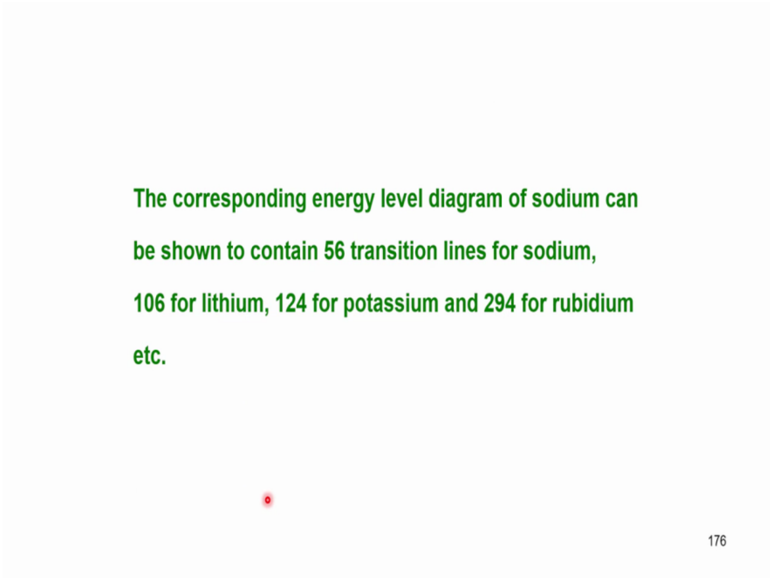

So, the corresponding energy level diagram of sodium can be shown to contain 56 transition lines for sodium, 106 for lithium, 124 for sodium and 294 for rubidium. These are the lines, you will see in the Gaussian diagram. So, for a simple sodium atom, you will see 56 transition lines because of LS coupling and then capital L, capital S coupling and what are the different energy levels like that there are 56 transition lines for sodium, 106 for lithium, 124 for potassium and 294 lines for rubidium. So, all these are not resonance lines.

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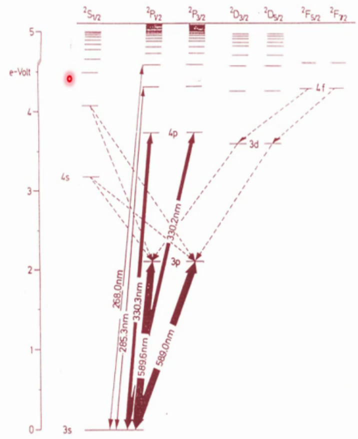
SPECTROSCOPIC CONSIDERATIONS



The energy level diagram for sodium is shown here.
Each line represents an energy level.

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So, based on this thing see this figure now, these are the different lines 56 for sodium, etcetera.

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At the hottest flame temperature of ~ 4000 k, the population of the excited state atoms is very small. Given below are the alkali and alkaline earth metal characteristics at different temperatures.

Element	Resonance line	ev	2000 k	3000 k	4000 k
Cs	8521(nm)	1.46	4.44×10^{-4}	7.24×10^{-3}	2.98×10^{-2}
Na	5890	2.11	9.86×10^{-6}	5.88×10^{-4}	4.44×10^{-3}
Ca	4227	2.93	1.21×10^{-7}	3.69×10^{-5}	6.04×10^{-4}
Fe	3720	3.33	2.29×10^{-9}	1.31×10^{-6}	
Cu	3248	3.82	4.82×10^{-10}	6.65×10^{-7}	
Mg	2852	4.35	3.35×10^{-11}	1.50×10^{-7}	
Zn	2139	5.80	7.29×10^{-15}	5.38×10^{-10}	1.48×10^{-6}

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And you would see that all these things are in these we were discussing. Why so many lines, resonance lines etcetera with this kind of elemental free atom concentration in the excited states. Now, I have explained to you that the based on these structures, we give a schematic diagram because we are interested only in the resonance line one frequency.

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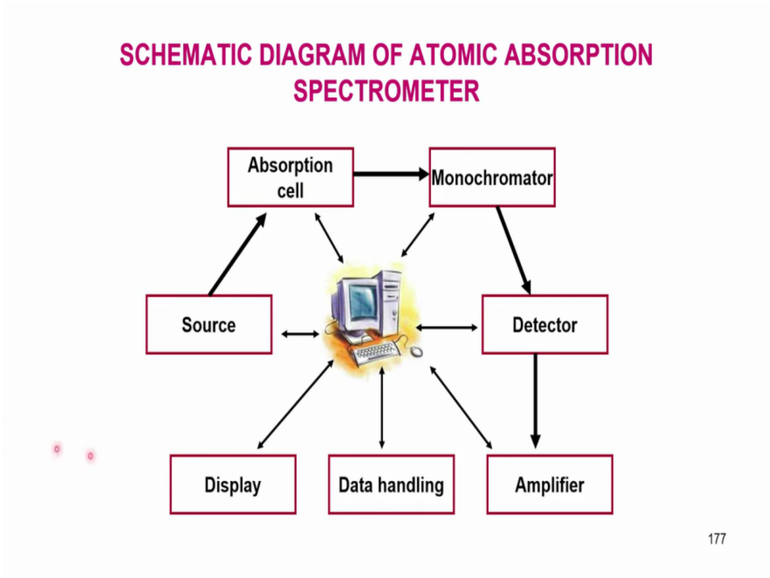

So, what we need is whenever we want to make atomic absorption spectrometer, we need one source, one absorption cell, one monochromator and detector followed by amplifier etcetera, etcetera. This I have shown you in the last class also. I am trying to put you on a firm basis regarding the atomic theory, theory of atomic absorption.

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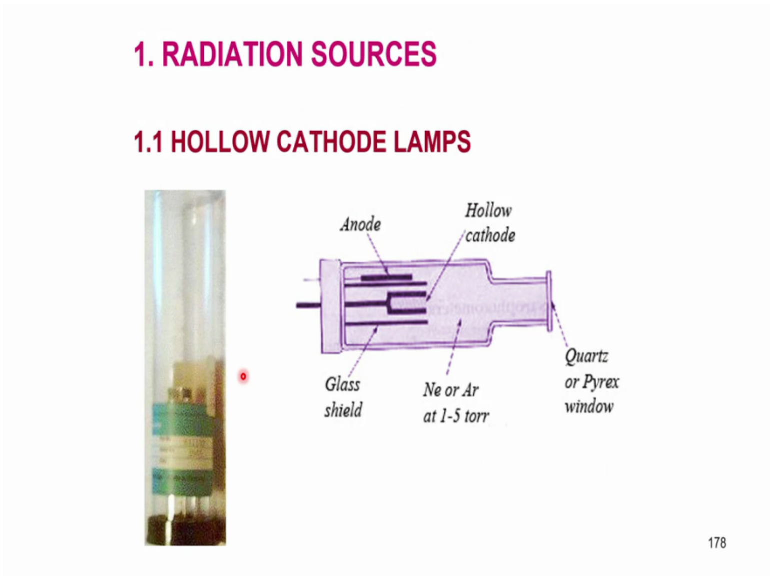

Now, we will continue our discussion on the instrumentation. Now, I am talking about this source now. What are the sources, in sources the Watt Ellen Walsh did was he made a lamp Alan Walsh in 1955 made in hollow cathode lamp, and this hollow cathode lamp he made of the same element which was to be analyzed. So, what is a hollow cathode lamp. So, a hollow cathode lamp, it consists of a glass cylinder filled with an inert gas.

So, go back to this figure this is a hollow cathode lamp. This is the cylinder hollow cathode cylinder this cylinder is evacuated. And we have an cathode made of a cylindrical u type you can see this is hollow cathode. And it is in the form of a circle let us say it is in a cone, it is not u, it is not a frequency instrument, but it is a cylinder whole cylinder I draw shown it to you in the form of projection diagram. And here is the another cylinder surrounding it with space in between that is anode. This is the glass shield. And the whole thing is filled with neon or argon that is at pressure of 1 to 5 torrs.

What is the atmospheric pressure our normal atmospheric pressure is 760 mm pressure that is 760 torrs. So, this is almost of the order of about 10 raise to minus 3 or 10 raise to minus 4 to atmospheric pressures. And the edge of this is made of glass like this, but this edge on the end at the end is quartz or Pyrex window that means, I take a round circular Pyrex plate and fuse it with the glass after putting all these things together. And then I have a power input here for anode and connector, so that these 2 electrodes can be hooked on just like you to just like you fit a any bulb. So, this is the actual photograph of a hollow cathode lamp. We can see that these are all conical and circular, and you can see some glow here. So, this is current hollow cathode lamp used in atomic absorption spectrometry.

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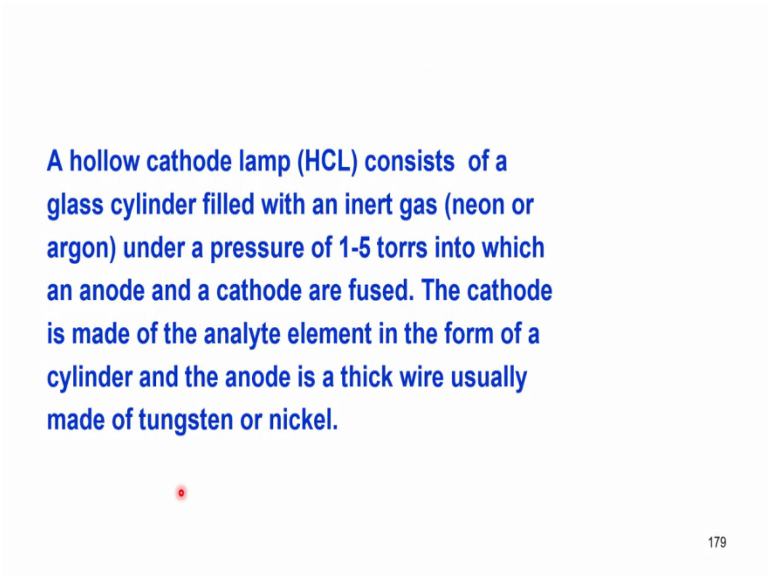

So, what it consists of a glass cylinder filled with an inert gas under pressure of 1 is to 5 torrs into which and anode and cathode are fused. You can see that back again, this anode and this cathode are fused into the glass, and whole thing is evacuated. And then the cathode is made of the analyte element in the form of a cylinder and the anode is a thick wire usually made of tungsten or a steel. So, to make any bulb, you need a cathode and anode. So, anode is tungsten or nickel, but cathode is made of a thin film of the metal which you want to determine, so that is how a hollow cathode lamp is made.

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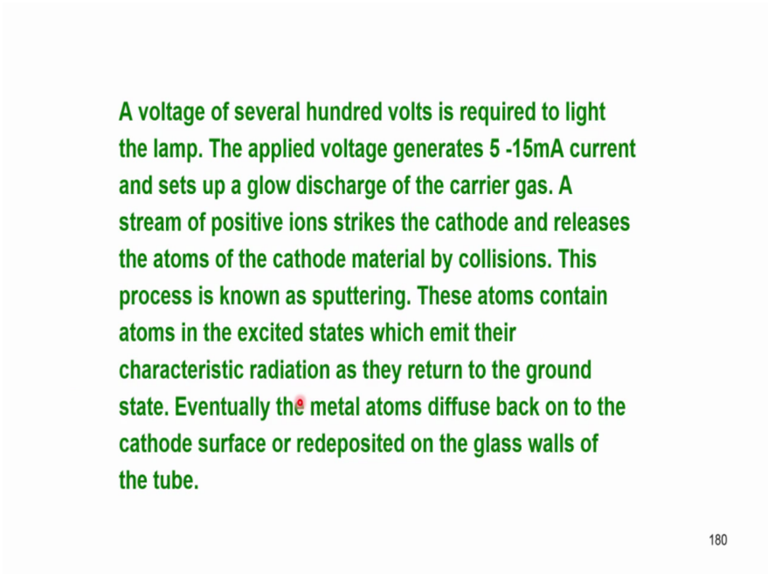

So, what do we do? Suppose, you make the hollow cathode lamp, we apply a voltage of several hundred volts to make this operate. How many volts are required for day to day in your house, it is about 230 volts for normal applications and 400 volts for industrial applications 15 amps etcetera, etcetera there, they are the currents it is not the voltage. So, to operate a hollow cathode lamp, you need several hundred volts that is 700, 800 volts is required to light the lamp. So, the applied voltage how am I need to generate a current of 5 to 16 milli amperes 5 to 15 milli amperes current is generated and this current sets up a glow discharge of the carrier gas.*

So, what do we mean carrier gas it is with hall neon or argon, this is the gas here, and it sets up a glow discharge like this. You see the green color in this hollow cathode lamp. Now, this glow discharge makes the lot of electrons available for the cathode that means, the electrons strike the cathode and releases the atoms of the cathode by collisions. That means, free atoms are generated inside the cylinder by collisions of the electrons generated from neon or argon which heat the cylinder of the made of cathode and releases the metals in a confined space only. And this they do not get out of the system that means, they do not come out of the cylinder there only they keep on sputtering, there only the electron will keep on sputtering, but they do not come out of the cone metallic cylinder that they will be there only, but excited. And sometimes what happens is when the temperature becomes too high they do come out, and deposit at the end of the hollow cathode lamp you which you will see as a thin film which will be silvery basically. So, as you keep on using a hollow cathode lamp, it becomes older and the amount of energy required also will become higher. So, the electrode part of some amount of the material will vaporize and recondense as a thin film on the glass or Pyrex piece, so anyway.

So, this process in which the electron metal atoms are released from the cylinder is known as sputtering. So, because of sputtering, these atoms contain atoms in the excited state, but in the same metal matrix. So, if you imagine a metal piece like this, the electrons on the top layer atoms on the top layer would be sputtering like this, but they do not come out. So, sometimes at high temperature, they do come out some small some small quantity settle somewhere else, where in the temperature is not high. So, these atoms contain electrons in the excited states which emit characteristic radiation as they return to the ground state because electrons are sputtering, the atoms are sputtering as they return to the ground state characteristic radiation keeps on coming out.

Now, I want you to understand now there are 2 radiations one is inside the hollow cathode lamp one is from argon or neon which you have already filled in and that is a glow discharge which we have seen as a blue or green light in the hollow cathode lamp. But there is another type of radiation now that is coming out from the cathode because we are applying high voltage a 15 to 16 milli amperes of current is generated. And these atoms when they return to the ground state, they emit the radiation. So, there are 2 radiation; one is from the cathode another is from the glow discharge, they of the neon or argon. And glow discharge from the neon or organ, you are all very familiar all over the town, you will be seeing neon signs etcetera, but in the hollow cathode lamp after some time what happens is as the temperature of the cathode rises, the discharge from the hollow cathode becomes much more, hundred times more than the glow discharge. So, it will be completely masked and only the radiation that will be coming out would be of the cathode - hollow cathode.

So, now what we have achieved is a radiation - monochromatic radiation coming from cathode material which is much more than the glow discharge. Eventually, so what happens the radiation coming from a metal is always characteristic of metal. So, resonance lines also will be there. So, eventually the metal atoms diffuse back into the cathodes surface or re-deposited on the glass walls to some extent in the tube. So, the cylindrical configuration of the atom of the cathode concentrates the emitted radiation. So, why we need a cylindrical concentration, it is like a tube.

If you have seen a pipe you cut it into a small piece, you will see a cylindrical hollow cathode. So, the free electrons will diffuse back into the metal surface and the cathode concentrates the emitted rate concentrates the emitted radiation and enhances the possibility of re-deposition of the atoms on the cathode rather than on the glass walls that is why we need a cylindrical cathode which is connected at the back to the power source.

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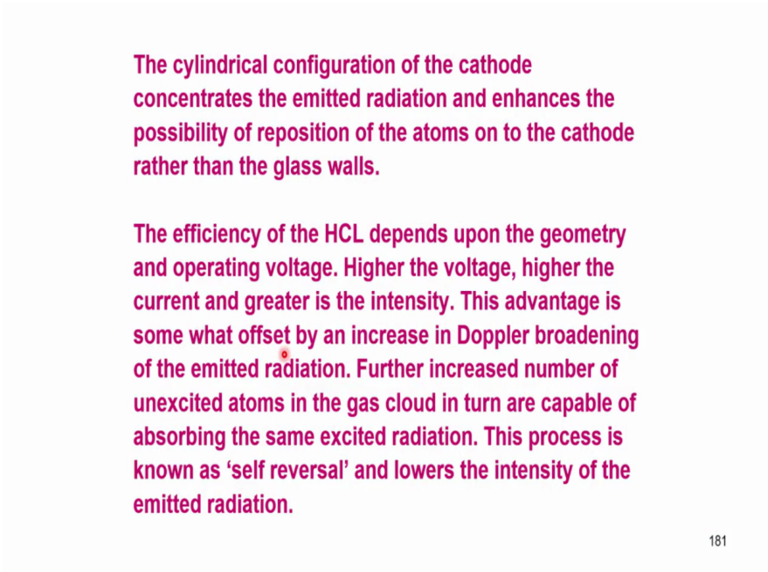

So, the efficiency of hydrochloric acid of the sorry efficiency of hollow cathode lamp that is designated as HCL that is why the confusion efficiency of the hollow cathode lamp depends upon the geometry, and operating voltage. Higher the voltage more is the radiation; higher the current and greater is the intensity. So, to get high intensity relation, we have to apply higher voltage. So, this advantage is somewhat offset, we cannot keep on increasing the voltage to a hollow cathode lamp. Why, because this advantage of supplying higher voltage getting high intensity is somewhat offset by the Doppler broadening.

We remember what we had discussed earlier the Doppler broadening of the spectral line reduces the sensitivity of the determination in the end. So, we do not want to apply too much higher voltage also. Further, increasing the number of unexcited atoms in the gas cloud that are capable of absorbing the same radiation, you remember I had talked to you about sodium lamps in your town which seem to be flickering because there's same elements which get excited can also absorb the same radiation coming from other atoms. So, same system problem happens here also.

So, if I increase the voltage to very high level then what happens? The atoms excited atoms can reabsorb our ground state atoms can reabsorb before it comes out of the hollow cathode lamp the radiation. So, there is a intensity of the radiation coming out of the hollow cathode lamp decreases. So, these are all part of the engineering aspects of hollow cathode lamp. So, what essentially we mean is a sort of self reversal takes place whenever I increase the voltage and current also to that extent that is why we do not want to use very high voltage in hollow cathode lamp even though it leads to increased sensitivity. Increase intensity of the radiation because increase intensity of the radiation increases the Doppler effect and makes the signal weak that is number one, number 2 there is self reversal also just like sodium items sodium lamps in your street.

So, you can take a look at this slide what I have written exactly the same thing. The efficiency of the hydro plates hollow cathode lamp depends upon the geometry higher the voltage higher the current higher the intensity, but the disadvantage is offset by the Doppler broadening and self reversal. This self reversal is a phenomenon which is again used in the instrumentation to our advantage also; how, we will see later. Whenever we try to maybe in the next 2-3 slides I will be able to show you, but the thing is the higher voltage is usually not preferred because it reduces the lifetime of the hollow cathode lamp also. The radiation usually hollow cathode lamps cost somewhere upwards of 25 to 30,000 rupees in India. And it has got a normal hollow cathode lamp has got a life of about two-three years even if you do not use still it goes bad that is the tragedy of hollow cathode atomic absorption hollow cathode lamps, but that means, you have to use the instrument otherwise shelf life is fixed. So, you have to buy anyway.

So, it is a buying a radiation source of each element is a costly process because it caused it one cost around 30,000 rupees you want to buy iron lamp 30,000 rupees cobalt lamp 30,000 rupees, nickel lamps at a 30,000 rupees like that. The cost of the radiation hollow cathode lamp itself may be much more than the atomic absorption spectrometer itself. So, a variety of hollow cathode lamps for most of the elements are available commercially they are available in the market not made in India of course. Where recently somebody in BRC had made one of my colleagues in BRC, Kalpakkam had made the hollow cathode lamps, but I do not know how far the hollow cathode lamps have become commercially in India.

There is a company called as electro ECIL in Hyderabad, Electronic Corporation of India limited they make these analytical instruments atomic absorptions instruments are also made, but the hollow cathode lamps are made by ECIL, but no by nobody else. Right now I do not remember the condition of the instrument. Usually what people do is they make the hollow cathode lamp, they configure it in such a way that a one a hollow cathode lamp made by one company for their instrument it does not fit to be hollow cathode lamp does not fit another instrument and another model that is their business tactic.

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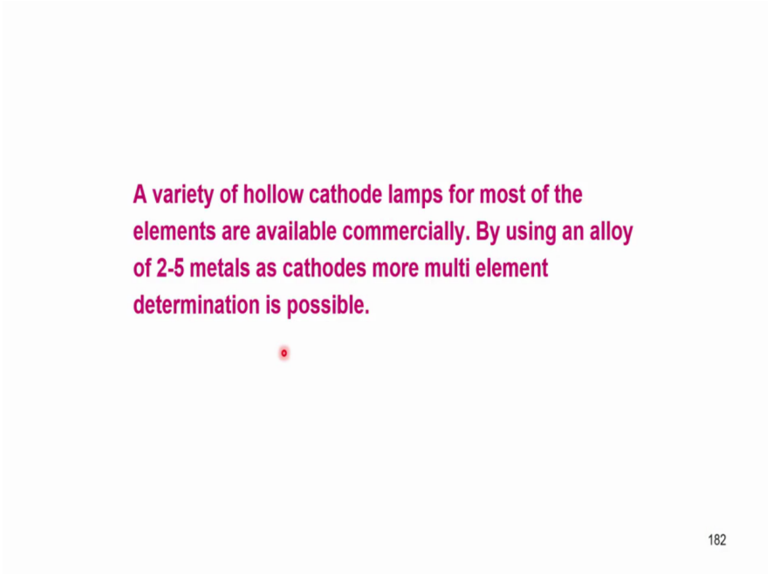

So, you are forced to buy hollow cathode lamps from the same manufacturers. So, a variety of hollow cathode lamps are of course available commercially. And I can use a hollow cathode lamp made of an alloy. Now, what is an alloy, alloy is a metal composition containing 2 or three metal I think many of you are aware what is in alloy. But if I make a conical cylinder or a cathode of the alloy then what happens is I can get the all the components of the alloy, I can use only one lamp because if I use for example, stainless steel, there will be chromium, iron, manganese. So, if I make a hollow cathode lamp cathode made of the stainless steel then I can determine iron, chromium as well as manganese. So, I can use many other alloys are available in the market which can be used for the hollow cathode lamp material. So, these hollow cathode lamps materials can be used for multi element analysis using the same hollow cathode we can determine number of elements, but they should be of in the cathode that is important.

So, I would stop here discussion about the hollow cathode lamp, obviously the self reversal aspect is not here in this, but we will discuss it about during background correction.