Trace and ultra trace analysis of metals Using atomic absorption spectrometry

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Lecture – 10

Theoretical basis of AAS I

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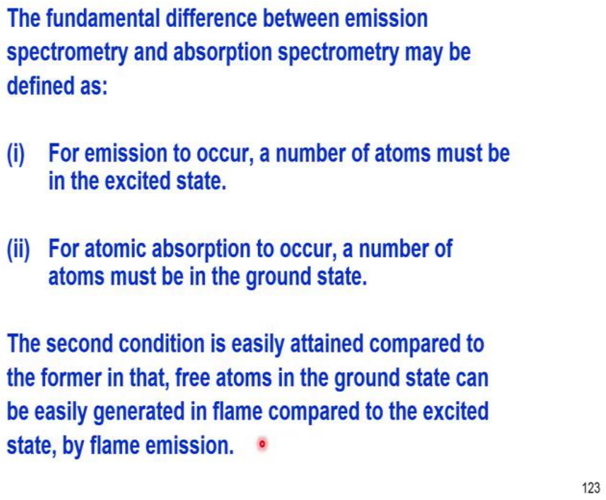

The fundamental difference between emission spectrometry and absorption spectrometry may be defined as:

(i) For emission to occur, a number of atoms must be in the excited state.

(ii) For atomic absorption to occur, a number of atoms must be in the ground state.

The second condition is easily attained compared to the former in that, free atoms in the ground state can be easily generated in flame compared to the excited state, by flame emission.

So, the fundamental difference between an emission spectrometry and absorption spectrometry may be defined; we can define it like this for emission to occurs a number of atoms must be in the excited state I want you to understand when an emission occurs when an absorption occurs if I have lot of atoms; atoms at the excited state just like in sunset solar atmosphere then the emission can occur when those an atoms at higher energy level come down to the ground level for that a number of atoms must be in the excited state then only we can see some amount of darkness, is not it. Whenever they emit certain amount of energy is lost and that energy is available and for atomic absorption to occur lot of atoms must be in the ground state the opposite also should be true.

So, what we are saying is the; for emission to occur I must have lot of an atoms at the higher energy level for absorption to occur I must have lot of atoms in the grounds state. So, from ground state absorb energy goes to the higher energy state from higher energy state emits the radiation comes down to ground state. So, which is more easier I want to pose you a question which is more easier to have atoms in the ground state or at the excited state in normal circumstances ponder over this there is certain lot of energy around as electromagnetic radiation is available, but all of it will be not absorb by the atoms from the objects around us, but it because it has to be quantized only the quantized amount of energy is it is able to absorb right. So, the maximum no of atoms in a given system if I am not supplying any additional energy would be in the ground state if I supply energy they will be higher energy level.

So, the second condition is easily attained compare compared to the former that is electrons will be in the grounds state. That means, free atoms in the ground state can be easily generated in the flame compared to the excited state by flame emission I do not know how to say this for atomic absorption and emission to occur it will not occur in a material which is which I am holding here for example, there is a metal tip here the atoms in this metal tip are not free atoms they are free to move they are all fixed in a matrix if I take any metal or a key chain for example, I have a key chain here and this key chin is made of steel. That means iron atoms are there may be some chromium manganese etcetera they are all there.

So, the atoms in this key chain are not ready to absorb the radiation because they are all bound electrically neutral the radiation around this around me is not enough to absorb the radiations for the atoms to promote them to the next higher energy level this is what I was trying to tell you since last 5-10 minutes what it means is most of the atoms in the at room temperature are bound they are not free atoms if I have a free atom then it can absorb or emit radiation. Now how we generate a free atom in the laboratory even if I give you this key chain you may not be able to generate free atoms from this key chain for that what I do is the free atoms I have to generate from a system which is to be melted and vaporized.

So, that is the trick I will have to employ I have to find out how I can make a substance melt vaporize the atom atoms will be there in the vapor state even than the atom will be in the neutral they will be in ground state they will not be even in the vapor form if I take for example, mercury you take mercury is liquid at room temperature right. So, if I heat mercury it will boil and then it will become vapor similarly if I take led around 200, 300 degrees if I heat led will become liquid and then it will start vaporizing sodium around thousand degrees like that they form vapor in the given atmosphere and in the vapors also electrons are there in the ground state not at excited state atoms I mean atoms are in the ground state because the radiation around it is not quantized.

So, it is free atoms I can generate by heating it in the flame and in the flame if the concentration increase etcetera they can emit radiation also for example, you must have studied in your high school level that or collage level that if you take sodium metal and burn it in the air it gives out yellow light put it in a flame it will give yellow light if you take potassium it will give a violet light. So, that is emission because, but if there is note; that means, there are lots of potassium atoms in the flame which can get excited and emit the radiation when they come back. So, in the flame I have atoms in the ground state which can be excited to higher energy levels and if the higher energy level is attained without emission then it is absorption and once the higher energy level atoms come down to the ground state then it emits radiation that is how you see.

So, yellow light from sodium and then red light from potassium etcetera you just study your flam test in qualitative analysis in your college level you will see that there are number elements which will give characteristics emission lights in the flame that is known as borax beat test if any of you have they remember I suggest you take a look. So, what we are saying essentially is what we are saying essentially is you take a metal system heat it convert it in to vapor state and in the vapor state you will see that atoms are in the ground state there are very few elements in the periodic table which have higher concentration in the flame in the vapor state in a flame they are sodium potassium nitrate they emit the light. So, both emission and absorption occur in the flames. So, if you understand this much we will proceed to be next slide.

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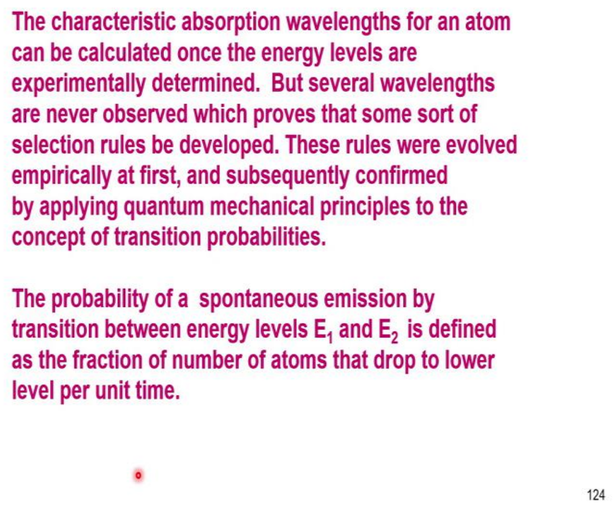

The characteristic absorption wavelengths for an atom can be calculated once the energy levels are experimentally determined. But several wavelengths are never observed which proves that some sort of selection rules be developed. These rules were evolved empirically at first, and subsequently confirmed by applying quantum mechanical principles to the concept of transition probabilities.

The probability of a spontaneous emission by transition between energy levels E_1 and E_2 is defined as the fraction of number of atoms that drop to lower level per unit time.

So, the next slide is can we determined the characteristics wavelength for an atom once the energy levels are experimentally determined I have shown you Gaussian diagram in the Gaussian diagram I had shown you that different energy levels are there were determined by the lines I had shown you that corresponding to particular frequency and particular wavelength.

So, the characteristic wavelength that is resonance wavelength for an atom can be calculated once we know the energy, but several wave lengths are not observed at all it is not that you will see every line in a spectrum whenever you take a spectrums some of them are not observed which proves that there is some sort of selection rules are there which permit a particular transition and which forbid particular transition. So, these rules were evolved empirically at first, but looking at number of spectrums which particular frequency line appear which did not appear like that and subsequently they were conform by applying quantum mechanical principles to concept of transition probability. So, the possibility of a spontaneous emission by transition between energy levels and e; E 1 and E 2 what I am saying is possibility of transition.

Now, I am talking about the probabilities. So, so the probability of transferring from one energy level to another energy level is defined as the number of atoms that are in the ground state and to the higher energy state. So, fraction of no of atoms that drop to the lower level per unit time of course, you were introduce a parameter known as unit time.

So, this unit time we can determine the probability of a spontaneous emission like sodium and potassium.

Mathematically what I do is I write an expression something like this.

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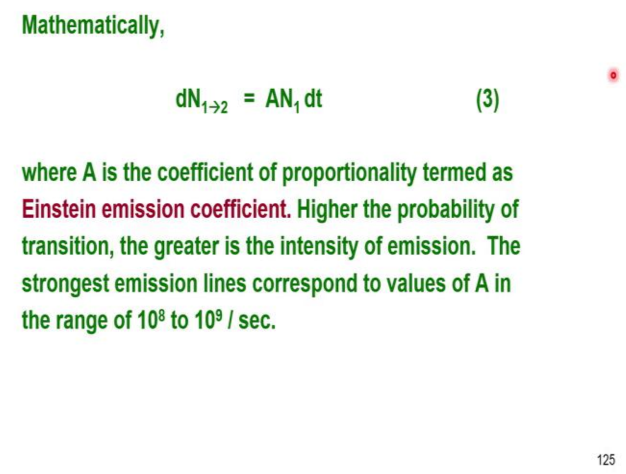

Mathematically,

$$dN_{1\rightarrow2} = AN_1\,dt \qquad (3)$$

where A is the coefficient of proportionality termed as **Einstein emission coefficient.** Higher the probability of transition, the greater is the intensity of emission. The strongest emission lines correspond to values of A in the range of 10^8 to 10^9 / sec.

D; this is the probability one is 2 is the transition that is AN 1; A is the coefficient of proportionality termed as Einstein emission coefficient higher the probability of transition the greater is the intensity of emission the strongest emission lines correspond to values of a in the range of 10 raise to 8 to 10 raise to 9 per second what I am going to teach you now is to derive an expression for this spontaneous probability of transition from one level to high another level that is level 1 and 2, I am going to derive in small expression mathematical expression.

And this you will not find in any text books, but this is the fundamental basis of all atomic absorption try to understand it is not very important that to become a good analytical scientists you must understand this, but if you are aware of this it makes lot of difference to your scientific career. So, what I am saying is try to understand the derivation at least the logic behind it and then we will see how we can quantify the emission or absorption.

So, what we are saying is the d N; the transition one is to 2 is a function of Einstein emission coefficient multiplied by the number of atoms there and with respect to time and the time range is 10 raise to 8 to 10 raise to 9.

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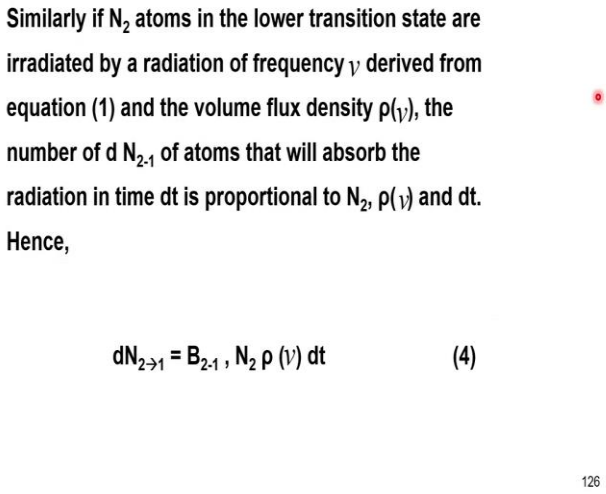

Similarly if N_2 atoms in the lower transition state are irradiated by a radiation of frequency ν derived from equation (1) and the volume flux density $\rho(\nu)$, the number of d $N_{2\text{-}1}$ of atoms that will absorb the radiation in time dt is proportional to N_2, $\rho(\nu)$ and dt. Hence,

$$dN_{2\to1} = B_{2\text{-}1}\,,\ N_2\,\rho\,(\nu)\,dt \qquad (4)$$

Similarly, is N 2 number of atoms in the lower transition state r at the lower transition state are irradiated by transition frequency that is quantum mechanized frequency mu derived from equation one and the volume flux density is row v the number of d atoms n 2 to one of atoms that will absorb the radiation in time d t is proportional to n 2 rho v and d t these are the 3 parameters one is flux another is number of atoms and t is the time fraction. So, I am going to write d N 2 to 1 is equal to B 2 to 1 that is another proportionality constant and N 2 is the number of atoms rho v is the flux. So, what do you mean by flux total number of atoms in the in a given space.

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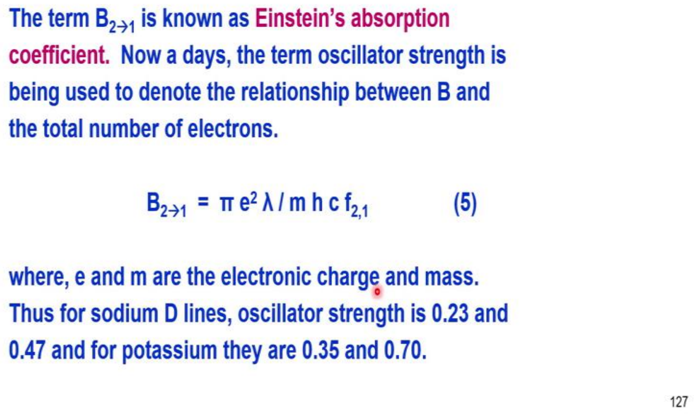

The term $B_{2\rightarrow1}$ is known as **Einstein's absorption coefficient.** Now a days, the term oscillator strength is being used to denote the relationship between B and the total number of electrons.

$$B_{2\rightarrow1} = \pi e^2 \lambda / m h c f_{2,1} \qquad (5)$$

where, e and m are the electronic charge and mass. Thus for sodium D lines, oscillator strength is 0.23 and 0.47 and for potassium they are 0.35 and 0.70.

So, the B 2 to 1 is known as Einstein absorption coefficient earlier we had written a similar expression as emission coefficient.

So, now I am going to introduce this is from 1 to 2 and from 2 to 1; it is known as absorption it is essentially the same thing quantification higher to a higher energy level lower energy level higher to lower is emission lower to higher is absorption. So, nowadays what is important is the term if an electron is going up and down up and down up and down we call it an oscillator. So, how many times it happens is known as oscillator strength.

So, we use the a term what is oscillator strength in all our expression the between b and the total number of atoms and this can be quantified by this expression pi into e square into lambda divided by mass into Planck's constant into velocity of light and frequency where e and m are the electronic charge and mass here this is e and this is m for sodium d lines oscillator strength is 0.23 if I put all these numbers for sodium it is I get a number what is known as what a approximately 0.23 and 0.47 for 2 resonance lines and for potassium they are 0.35 and 0.70. So, oscillator strength is an important parameter in atomic absorption spectrometry it does not appear in your day to day analysis or anything like that, but still it is a parameter to be known.

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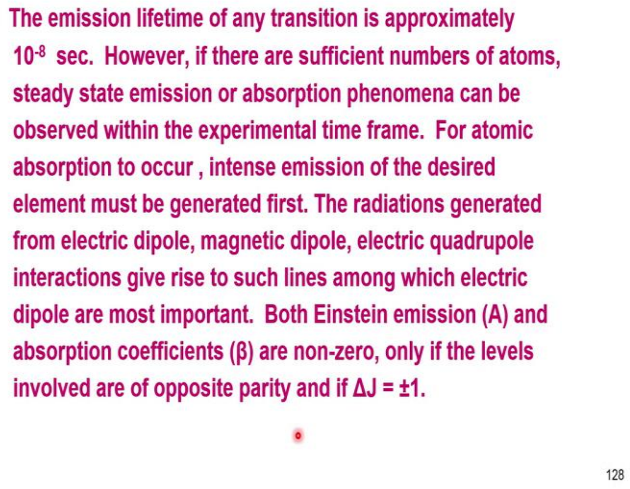

The emission lifetime of any transition is approximately 10^{-8} sec. However, if there are sufficient numbers of atoms, steady state emission or absorption phenomena can be observed within the experimental time frame. For atomic absorption to occur , intense emission of the desired element must be generated first. The radiations generated from electric dipole, magnetic dipole, electric quadrupole interactions give rise to such lines among which electric dipole are most important. Both Einstein emission (A) and absorption coefficients (β) are non-zero, only if the levels involved are of opposite parity and if $\Delta J = \pm 1$.

So, the emission life time of any transaction is approximately 10 rise to minus 8 seconds this I have already I have also told you in this spectrophotometric course in NPTEL that 10 raise to minus 8 is the emission life time of any transaction.

So, if there are sufficient numbers of atoms study state emission or absorption there will be equilibrium between absorption and emission absorption and emission. So, this study state absorption phenomena can be observed within the experimental time frame. So, say within few minutes, few seconds etcetera after some time you will not see any change we it will remain steady because it will be in equilibrium state. So, for atomic absorption to occur in tens emission of the desired element must be generated first; that means, I have to provide radiation which is to be absorbed by the free atoms.

So, I need to provide intense emission of the corresponding wavelength energy electromagnetic radiation of the resonance value whatever is the resonance wavelength I have to produce radiation of that wavelength in very high intensity you get it so high intensity of same wavelength that is resonance wavelength that we have to generate first. So, radiations generated from electric dipole magnetic dipole electric quadruple interactions give rise to such in lines among the which electrical dipole is the most important what do you mean to say in this is how do I produce an intense radiation corresponding to one particular wavelength for sodium that is 589 how am I going to produce. So, there are 3 methods one is electrical dipole magnetic dipole and electrical quadruple interactions.

So, how do I generate this thing using electrical dipole is the best way. So, both Einstein emission and absorption coefficients are non-zero only if the levels involved r of opposite parity and if delta j that is the different between the 2 is plus or minus 1; that means, energy level must be in resonance.

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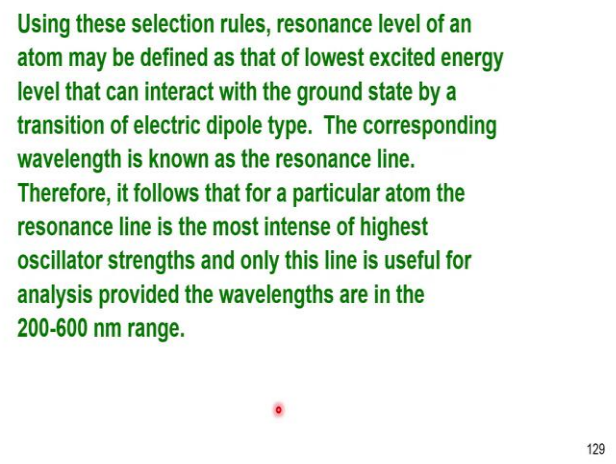

Using these selection rules, resonance level of an atom may be defined as that of lowest excited energy level that can interact with the ground state by a transition of electric dipole type. The corresponding wavelength is known as the resonance line. Therefore, it follows that for a particular atom the resonance line is the most intense of highest oscillator strengths and only this line is useful for analysis provided the wavelengths are in the 200-600 nm range.

So, under this caller using the selection this election; this is one of the selection rule only if delta j is plus or minus 1. So, if it is plus or minus 2 definitely it would not work. So, using such selection rules which are available from the literature resonance level of an atom may be determined of element for that matter may be determined as that of the lowest excited energy level that can interact with the ground state by a transaction of electrical dipole type.

So, what we are saying is methane electrical dipole type given a selection rule the resonance line of an any element can be determined; that means, we have number of data which can already in our computer in our data base in our Google or whatever it is the resonance levels of the energy of almost all the elements of the periodic table; they are already calculated and available information is available to us and the corresponding wavelength is known as resonance line. So, this you should understand. So, it is very common practice in most of the atomic absorption spectrometers what is a resonance line.

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So, many time you will come a across technical term the resonance line of iron is. So, much the resonance line of resonance line of chromium copper is 324 per 2.7 like that also what you will understand by that we mean that the lowest energy level corresponding to the transition is a resonance line. Therefore, it follows that a particular atom for a particular atom the resonance line is the most intense line that is why we are shown it as a thick line. So, that is the highest oscillator strength and only this line is useful for analysis provided the wavelengths are in the 200 to 600 nanometer range the resonance line must be 200 to 600 nanometer range that covers UV and visible range.

Thank you, we will continue our class in the next meeting.