Trace and ultra trace analysis of metals Using atomic absorption spectrometry
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Lecture – 23
Background correction on flame AAS I

Greetings to you. In the last class I had discussed about the interferences in atomic absorption. And I had told you that they even though atomic absorption is a specific element phenomenon there will be interferences because we are going to generate free atoms in the flame atmosphere.

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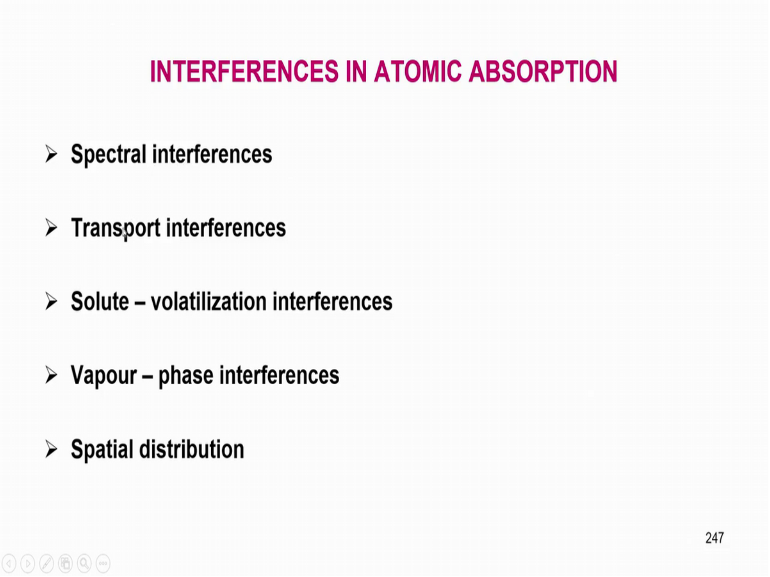

INTERFERENCES IN ATOMIC ABSORPTION

- Spectral interferences
- Transport interferences
- Solute – volatilization interferences
- Vapour – phase interferences
- Spatial distribution

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So, the different types of interferences are spectral interferences, where there resonance line match transport interference. There may be different height different other different heights. There will be vapour phase transport vapour phase reaction etcetera, are there in the transport interferences.

Solute volatilization interference are basically the something to do with the viscosity surface tension etcetera. And then vapour phase in track interference that is once the vapours are there in the flame. They will be interacting with each other to produce molecular species such as CHOOH carbon and NH radicals and spatial distribution we have already discussed; depending upon the vapour concentration the spatial distribution of the atoms will be different. So, there will be change in the absorbance, because that is the one which we normally measure.

So, if the absorbance is different from what is expected, then we call it spatial interference. Then we have discussed in detail about all these things.

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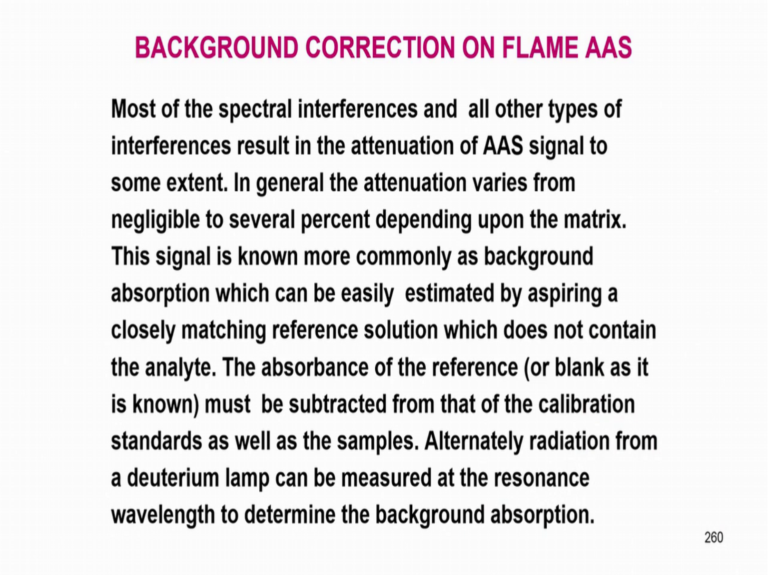

BACKGROUND CORRECTION ON FLAME AAS

Most of the spectral interferences and all other types of interferences result in the attenuation of AAS signal to some extent. In general the attenuation varies from negligible to several percent depending upon the matrix. This signal is known more commonly as background absorption which can be easily estimated by aspiring a closely matching reference solution which does not contain the analyte. The absorbance of the reference (or blank as it is known) must be subtracted from that of the calibration standards as well as the samples. Alternately radiation from a deuterium lamp can be measured at the resonance wavelength to determine the background absorption.

And now, we will consider how to correct some of the interferences that occur in atomic absorption this is called background correction on flame atomic absorption spectrometry. So, what is required is whenever there is, a change in the absorbance due to any extraneous factor we correct those extraneous factors in such a way that the signal remains intact.

So, most of the spectral interferences and all other types of interferences, result in the attenuation of atomic absorption signal to some extent, this is what we have already told I said I any reduction in the absorbance or increase in the absorbance is interference. More than 10 percent absorbance increase or decrease is called as interference. So, in general so, in general the attenuation means reduction in the signal. So, in general this reduction in the signal varies from negligible levels up to several percent maybe, 5 percent 10 percent sometimes you may not even get a signal. So, it all depends upon the matrix elements.

So, this signal is known more commonly as background absorption which can be easily estimated by aspirating a closely matching reference solution, which does not contain the analyte; that means, we are doing aspirating a solution which contains water as a blank. Now what we want to do is, if there are extraneous elements then we try to match the extraneous elements apart from the analyte. So, that becomes the matrix solution.

So, here the absorbance of the reference or blank as it is known it must be subtracted from that of the calibration standard as well as the samples. Because in the blank there will be some amount of absorbance that maybe molecular absorbance spectral interference whatever it is and that needs to be subtracted to get the correct analytical result. Alternately radiation from a deuterium lamp can be measured at the resonance wavelength. This is a very important aspect of background correction. What we do is apart from hollow cathode lamp, apart from hollow cathode lamp a we use a deuterium lamp. So, what is the deuterium lamp we have discussed in spectrophotometry a deuterium lamp is a lamp made of hydrogen atoms, and then it gives you absorbance in all frequency ranges.

So, the analytic absorbance at the analytical wavelength also is part of the hydrogen lamp. So, that a difference between the hydrogen lamp and the atomic absorption lamp hollow cathode lamp we can subtract that from the deuterium lamp. So, this can be measured at the resonance wavelength to determine the background absorption. So, what we do is we take the sample and aspirated, measure the absorbance in the deuterium lamp and measure the absorbance in the hollow cathode lamp subtract that and that is the correction due to other extraneous matters.

So, background correction in flame atomic absorption is always a slightly tricky business and most of the atomic absorption spectrometers have the hydrogen lamp or deuterium lamp as it is known, along with the hollow cathode lamp and other EDL or whatever it is vapour discharge lamps etcetera, all these things are there along with hydrogen lamp deuterium lamp. So, radiation from the deuterium lamp also passes through the flame and radiation from the hollow cathode lamp also passes through the flame.

So, whatever is whatever absorption occurs at the hollow cathode lamp is the sum of those two. So, if we subtract the background from hydrogen lamp then we get the actual atomic absorption signal ok.

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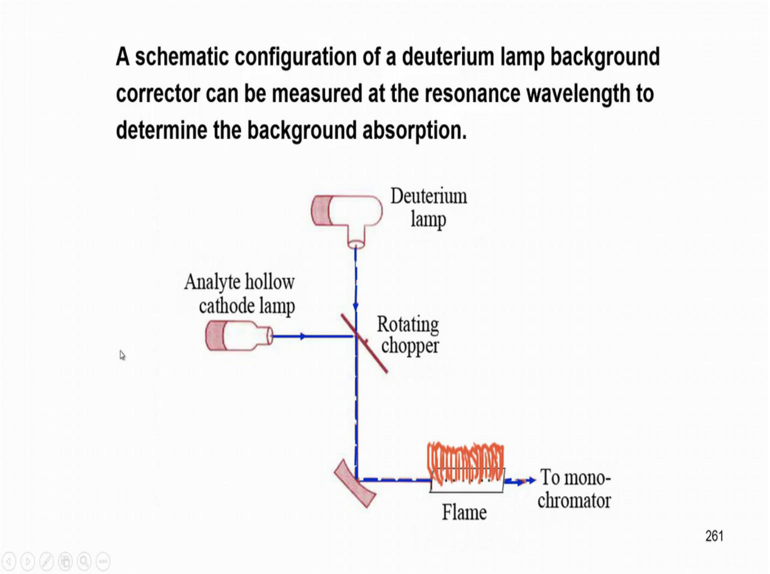

A schematic configuration of a deuterium lamp background corrector can be measured at the resonance wavelength to determine the background absorption.

So, this is how the schematic configuration of a deuterium lamp, background character can be measured at the resonance wavelength to determine the background absorption. What happened? I have a hollow cathode lamp here, and then deuterium lamp here, are both of them I have a rotating chopper. And then this is the observed radiation from the hollow cathode lamp, and this is the radiation from deuterium lamp.

So, this rotating chap chopper once allows the radiation, as it rotates it allows alternately the radiation from deuterium lamp and hollow cathode lamp. Once it allows deuterium lamp as the chopper cuts the this thing hollow cathode lamp radiation will pass through there. So, I have a optics and other things remain the same, in the atomic absorption spectrometer.

So, the radiation from deuterium lamp and hollow cathode pass through the same optics. So, I have a concave mirror here and then it passes through the flame. And in the flame I have the aspirated sample and then this radiation passes through to the monochromator. So, when the radiation from deuterium lamp passes through at the same wavelength, whatever is the absorbance without this hollow cathode lamp absorbance is measured. And with the when analyte is falling analyte chopper clears analyte wavelength then, the absorbance from the atomic absorption is measured. The difference is what corresponds to the lamp.

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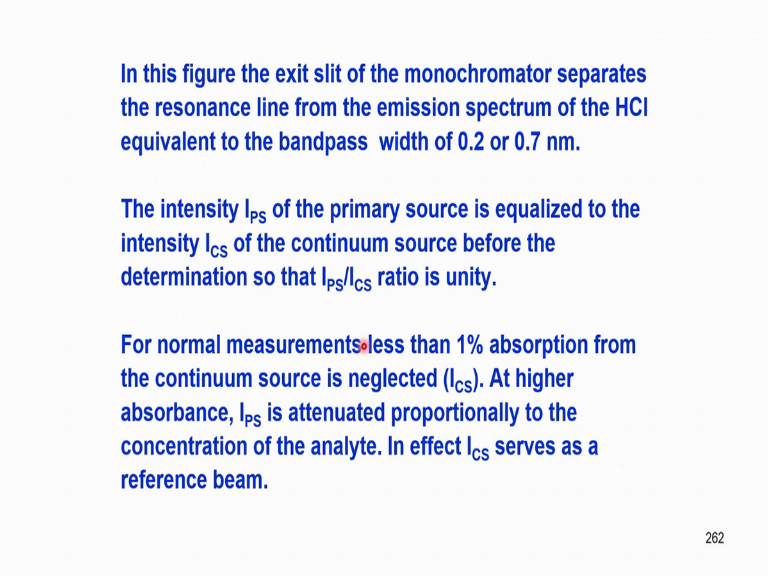

In this figure the exit slit of the monochromator separates the resonance line from the emission spectrum of the HCl equivalent to the bandpass width of 0.2 or 0.7 nm.

The intensity I_{PS} of the primary source is equalized to the intensity I_{CS} of the continuum source before the determination so that I_{PS}/I_{CS} ratio is unity.

For normal measurements less than 1% absorption from the continuum source is neglected (I_{CS}). At higher absorbance, I_{PS} is attenuated proportionally to the concentration of the analyte. In effect I_{CS} serves as a reference beam.

So, the exit is in this in this figure, exit it of the monochromator separates the resonance line from the emission spectrum of the hollow cathode lamp to the band pass width of 0.2 to 0.7 nanometers. Because that is the band pass width normally is present in almost all atomic absorption spectrometers. So, the intensity I PS I will be there, in a little bit of a notations here, but nothing to be worried about not too much mathematics also. The intensity I PS of the primary source is equalized to the intensity I CS of the continuum source before the determination So that the ratio of I PS and I CS is unity.

Initially whatever is the flame absorbents and I PS the ratio is set to unity; that means, there is both of them match. So, for normal measurement less than 1 percent absorption from the continuous source is neglected for the I CS; that means, normal measurement less than 1 percent, if it is it is absorbance I CS is neglected, we do not need that. At higher absorbance I PS is attenuated proportionally to the concentration of the analyte; that means, at higher pay suppose it is 5 percent I PS is also adjusted to 5 percent.

So, that the analyte concentration is not affected by the background. So, in effect I CS this is a sample survey as a reference beam ok.

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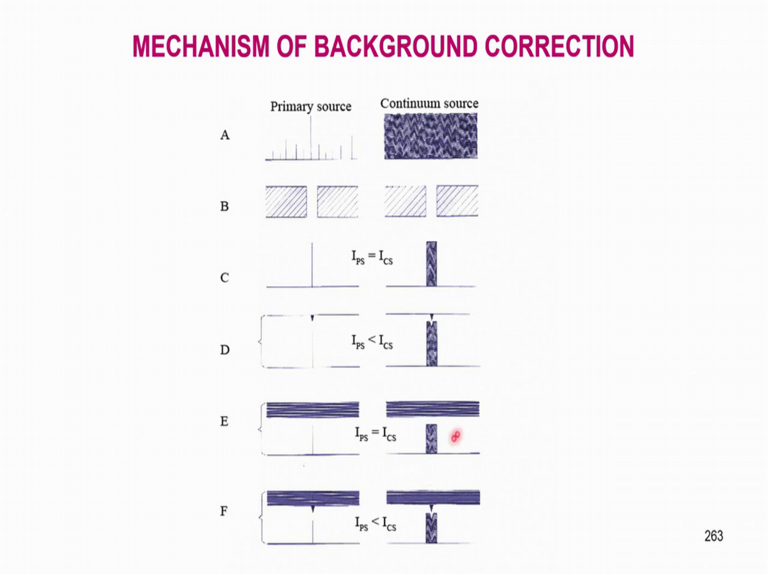

MECHANISM OF BACKGROUND CORRECTION

So, this is the mechanism of background correction. What I have here? I have shown you 2 series here one on the left side primary source etcetera, I have written here it is a continuum source. So, he is this is my analyte line this is the monochromator.

So, only this line is selected and it passes through a look at them a pointer it passes through this and then this is here both I PS and I CS signal, this is the analyte signal I CS and this is the I PS . So, if I PS is less than 1 percent or something like that we neglect the ratio otherwise both of them are made equal; that means, the radiation coming from this, and radiation coming from this, this is the continuum source that is hydro deuterium lamp ok.

So, both these are matched. So, total absorbance corresponding to this without the sample is converted into this I PS is less than I CS. So, this much signal is attenuated. And then what we do we do this I PS is equal to I PS. This is by done electronically you do not have to do much regarding this background correction because it is automatically automated. The electronics and the operations are designed. So, if I PS is less than I CS then it is neglected and So much is you see the small triangle here, this small triangle corresponds to the background absorbance.

So, this a absorbance at this wavelength is subtracted corresponding to deuterium lamp absorption, whenever there is no hollow cathode lamp. So that means, it is the absorbance of the total background without it is not the atomic absorption, it is a background absolution that way we have to subtract anyway. So, this is how the mechanism of background connection works and what we normally say is they you do not have to do much along with the hollow cathode lamp you switch on a deuterium lamp.

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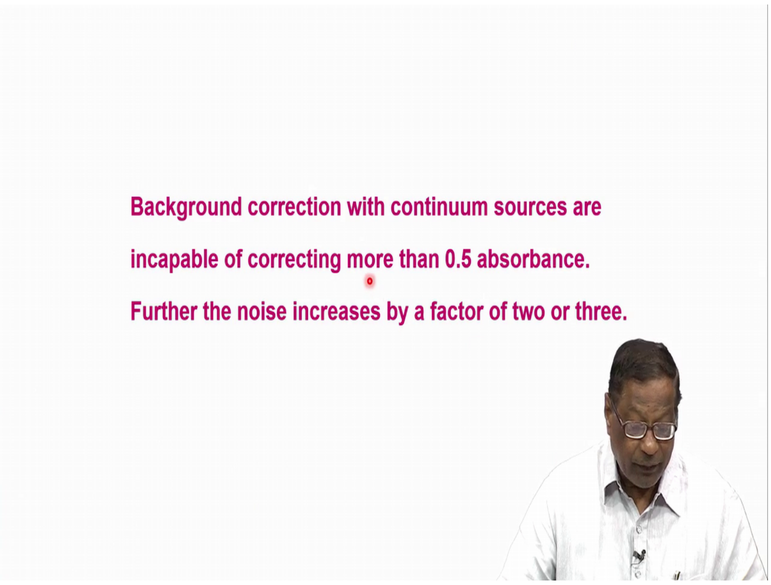

Background correction with continuum sources are incapable of correcting more than 0.5 absorbance.

Further the noise increases by a factor of two or three.

So, electronics and other things we will take care of the background. So, background correction normally are with continuum sources that is like, hydrogen lamp you can also use a xenon lamp also does not matter, but you have to choose the wavelength at which we are measuring that is for copper if you are using 224.7 for background also you have to adjust and select only that portion corresponding 224.7 nanometer plus or minus 0.2 nano band pass width whatever is that comes.

So, if the background correction is background absorbance is more than 0.5 in observance units. Whatever what are the normal units for absorbance in a in the atomic absorption, in the hole of atomic absorption the absorbance is measured between 0 and log 2. 2 is the log negative, log of absorbance that is 0 percent is a 100 percent transmittance, to absorbance 2 is 100 percent transmittance. So, the units of measurement in atomic absorption are between 0 and 0.2.

So, if it is more than 0.5 for the background then it is a little difficult to adjust, to correct the background coming from the sample, that is blank.

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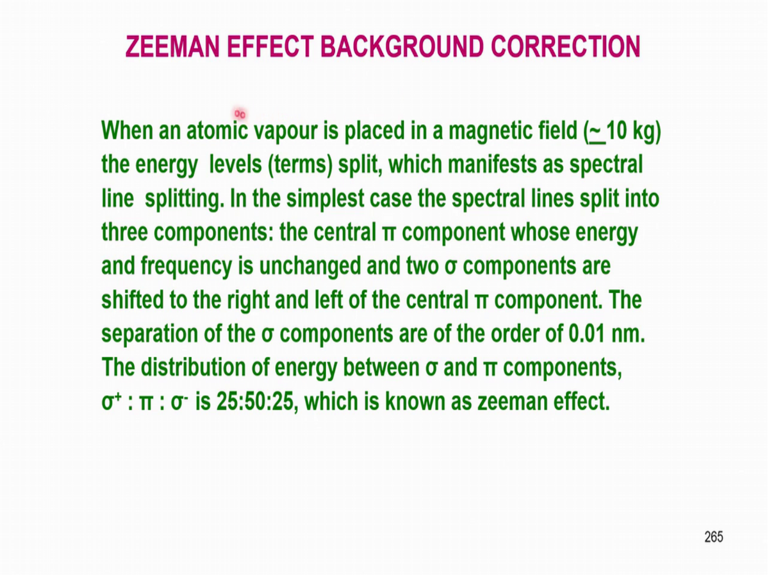

ZEEMAN EFFECT BACKGROUND CORRECTION

When an atomic vapour is placed in a magnetic field (~10 kg) the energy levels (terms) split, which manifests as spectral line splitting. In the simplest case the spectral lines split into three components: the central π component whose energy and frequency is unchanged and two σ components are shifted to the right and left of the central π component. The separation of the σ components are of the order of 0.01 nm. The distribution of energy between σ and π components, $\sigma^+ : \pi : \sigma^-$ is 25:50:25, which is known as zeeman effect.

So, the noise also increases by a factor of 2 or 3; that means, the signal noise that is some amount certain amount of electrical noise and other things which we have already discussed that also increases by a factor of 2 or 3. This means the signal to noise ratio decreases, actually what we need we need the signal to noise ratio to increase for atomic absorption, but if the background is more than 0.5 that is the blank analyte shows the absorbance of more than 0.5 then it is difficult to correct.

So, we try to keep the background absorption less than 0.5 as far as possible which is to be subtracted from the hollow cathode lamp signal, that is atomic absorption signal. So, we also have another way of handling background correction. Here the mechanism is entirely different. So, when and atomic absorption vapour is placed in a magnetic field, that is atomic vapour that; that means, what I do is, I want to put the flame around the flame I want to put 2 magnets. So, the I am putting the atomic vapour in a magnetic field that is of the order of about 10 kilogoss levels ok.

So, in 10 kilogoss levels you put me in the corner, my photo yeah. So, when these terms the energy levels split I had already explain to you earlier that sodium lamp in whenever I put it has got 2 lines 589.6 and 589.0 nanometers. So, the if it is not there are 2 lines similarly, all the energy levels split, whenever I put a magnetic field. So, in the simplest case the spectral lines split into 3 components. One is the central pi component another is 2 or 3 sigma components ok.

So, the energy of the total energy of pi and sigma components are same. Sum of the energies are same, but they are split into 2 different levels. And this sigma and pi components are not to be confused with the atomic structure pi or pi bonding and sigma bonding etcetera, these are energy levels split and the symbols are unfortunately are same, but we call them sigma and pi. So, sigma components are shifted to the right and left of the central pi component.

So, the separation of the sigma components are of the order of about 0.01 nanometer. Both the all the energies signals are separated and the distribution of energy between sigma and pi components is approximately 25 to 50 to 25 that is 50 percent for pi and 25 percent for 2 sigma 1 is sigma plus another is sigma minus sigma plus and sigma minus occur along the central wavelength along the frequency or to the left and right of the signal. This effect is known as Zeeman Effect ok.

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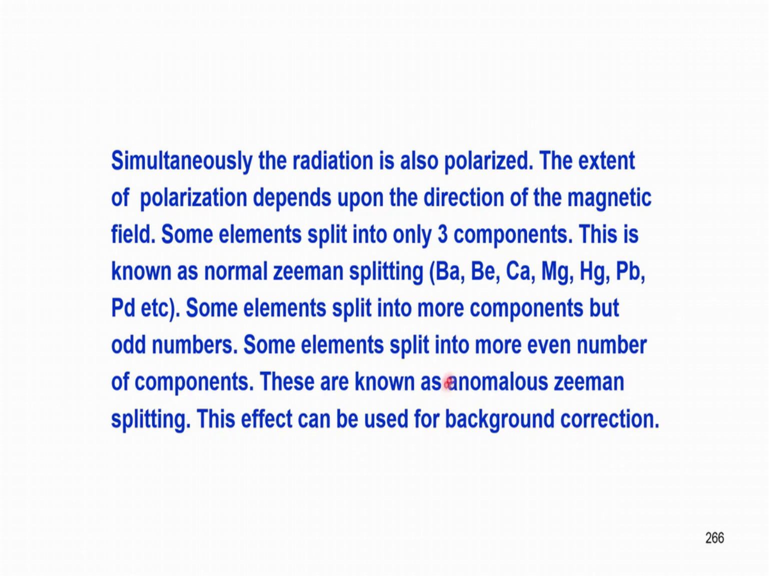

Simultaneously the radiation is also polarized. The extent of polarization depends upon the direction of the magnetic field. Some elements split into only 3 components. This is known as normal zeeman splitting (Ba, Be, Ca, Mg, Hg, Pb, Pd etc). Some elements split into more components but odd numbers. Some elements split into more even number of components. These are known as anomalous zeeman splitting. This effect can be used for background correction.

So, simultaneously what happens? The signal also is polarized; that means, the only one component will reach the detector. Now we have sigma and pi components right. So, pi component if the if the magnet is not is operating that is polarized. So, sigma components are pi components are perpendicular to each other. So, that you should imagine. So, only one component is aligned along with the detector. So, some elements what happened they split into only 3 components this is known as normal Zeeman splitting and this occurs in barium, beryllium, calcium, magnesium, mercury, led, palladium etcetera.

Some elements split into more than one component, more than 3 components, but in odd numbers 3, 5, 7 like that, they split under the effect of magnetic field. Some elements split into even more components, these are known as anomalous Zeeman Effect. So, this effect can be used Zeeman Effect can be used for background correction. So, what we have said is that we conduct place a magnetic field around and then in the magnetic field the hollow cathode lamp line is split into pi and sigma components.

So, and it is polarized at a time either pi component will reach the detector or sigma component will reach the detector. So, when I have the sigma only when I have the magnetic field on only the pi component will reach when I do not have the magnetic field that is when it is off all the absorbance will be taken place. So, the difference between the 2 gives you the background correction. So, this effect is known as a Zeeman Effect and Zeeman Effect can occur normal Zeeman Effect or anomalous Zeeman Effect ok.

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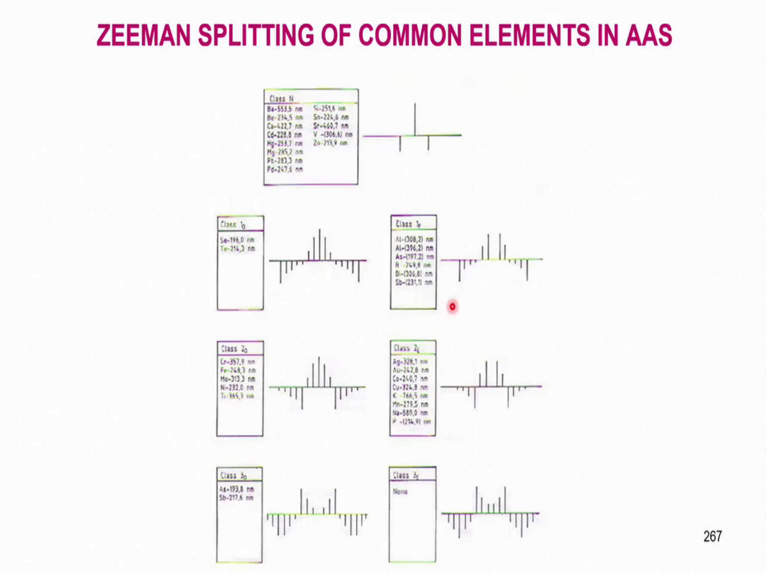

ZEEMAN SPLITTING OF COMMON ELEMENTS IN AAS

So, here I am showing you the splitting of common elements in atomic absorption. We will study this a little later in the next class.

Thank you.