Trace and ultra trace analysis of metals Using atomic absorption spectrometry

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Lecture – 26
Hydride Generation AAS I

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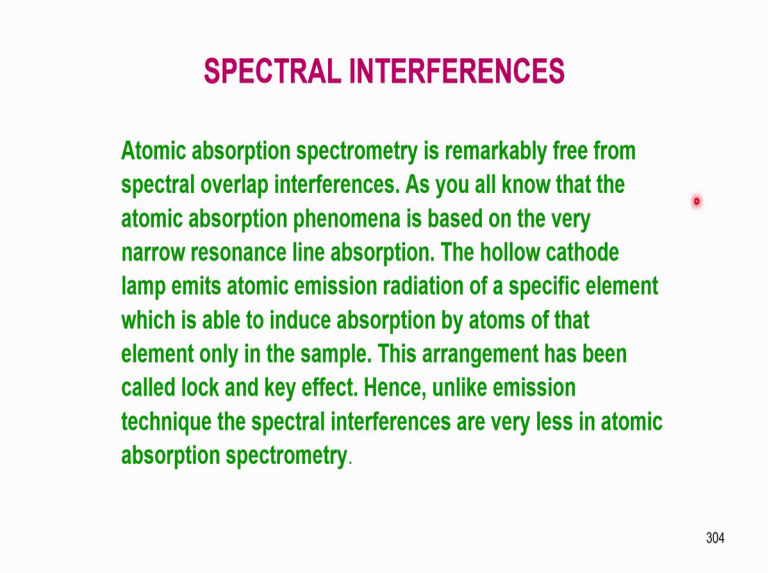

We have been discussing atomic absorption and the spectral interferences in the last slide I had shown you that the resonance lines are most important in this thing when does AS is specific for each element because of the resonance line. But quite often the resonance line not quite often sometimes the resonance lines of two different elements are almost similar are all exactly they match in terms of frequency and wavelength. So, when they match the monochromator is not able to distinguish between two different atoms resonance lines. So, there will be enhancement of the signal whenever there is spectral interference and if the sample contains both the elements there will be definitely enhancement of the signal and if it is not there it does not make a difference anyway.

So, the hollow cathode lamp basically emits the atomic emission radiation of a specific element that is able to induce absorption of atoms yeah. So, these are invent is called as lock and key effect; that means, hollow cathode lamp should emit the radiation and a free atom should absorb data. So, it is like a lock and key as for as spectral resonance measurement is concerned. So, unlike emission technique spectral interferences are very

less in atomic absorption spectrometry why because emission lines there are quite a few maybe several hundreds, but resonance lines are very few one or two maybe not more than that.

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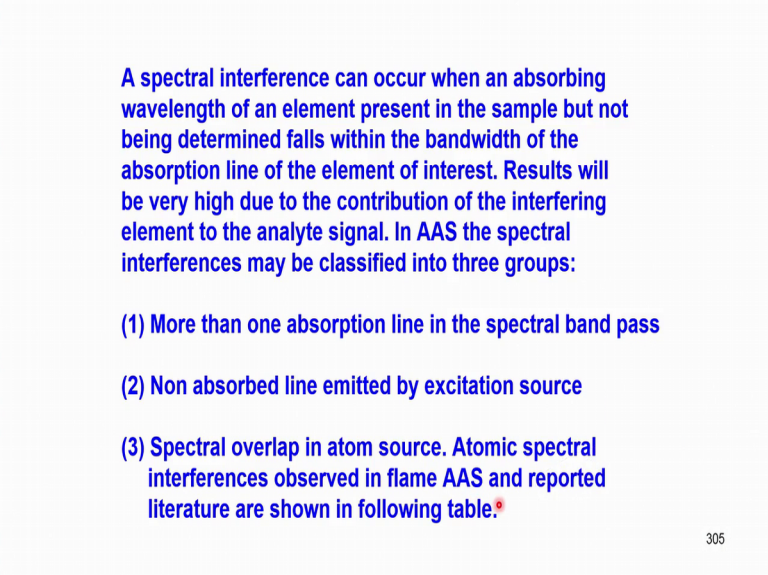

So, the spectral interference can occur when an absorbing wavelength of an element present in the sample, but not being determined, but it is a resonance line falls within the bandwidth of the absorption line of the element of interest this is the technical definition of spectral interference the first sentence in this slide is the definition a spectral interference can occur when an absorbing wavelength of an element or analyte present in the sample, but not being determined falls within the bandwidth of the absorption line. That means, monochromator is unable to distinguish between the resonance lines of two different elements which falls within the bandwidth of the absorption line.

So, the results will be very high due to the contribution of the interfering element this way I have explained to you time and again that spectral interference means enhancement of the signal rather than reduction in the signal attenuation in atomic absorption spectrometry the spectral interferences may be classified into three groups we normally do that. So, what are the different classes that we classify? So, suppose there are there is more than one absorption line in this spectral band pass from the same element, suppose there are two absorption line within plus or minus 0.003 to 0.005 nanometers range monochromator cannot distinguish and some non absorbed line

emitted by excitation source within that band push band pass width the hollow cathode lamp gives you some additional absorbance.

So, that also cannot be separated; that means, it is the non absorbing radiation emitted by the excitation source which cannot be separated from the by the monochromator. So, third type is spectral overlap in the atoms source. So, in the atomic source that is in the flame atomic spectral interferences observed can be observed in the flame AAS and reported literatures are shown in the next table I want to show you some of the spectral overlaps in the atomic atom source. So, we will I do not know where is the table, but we will try to insert it in the next class or later.

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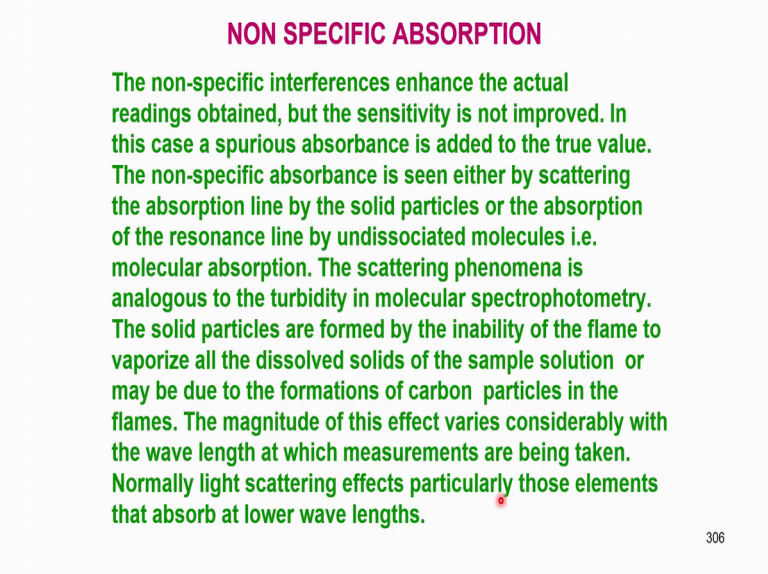

Now, we will discuss about the nonspecific absorption. We have already discussed a little bit about the nonspecific absorber absorption from different matrix components like chloride bromide. So, sulfate phosphate etcetera, but the these interferences if they are spectral in nature the nonspecific interferences also enhance the actual reading; that means, absorbance will be higher, but the sensitivity is not improved because nonspecific absorbance normally it means that the absorbance is not continuous all the time it would not be there nonspecific absorbent means nonspecific. It may be there in one matrix it may not be there in another matrix or if you want to analyze led in their blood there may be nonspecific absorbance may be more, but if you want to analyze led in the air it may be different because the air components are different compared to blood the components

like that there are in water seawater, so many places the nonspecific absorbance is always there that we have seen in the interferences section and I had shown you the table containing sodium chloride potassium, phosphate, silica, alumina and all those things.

So, what do we want to tell you is that the nonspecific absorbance is seen either by scattering the absorption line by the solid particles of the absorption of the resonance line by undissociated molecules that is molecular absorption basically what we want to tell you is it is a molecular absorption may not be exactly same in all matrix. So, the scattering phenomena is essentially analogous to turbidity in spectrophotometry. So, if you have taken the course you know that in atomic absorption or in spectrophotometry we measure the transmittance of the sample is very important.

So, even in spectrophotometry if the sample is turbid absorbance reading will be very high because of the scattering phenomena. So, just like molecular spectroscopymeter the solid particles if they are in the flame in atomic absorption they tend to broaden the absorption line or the resonance line by the undissociated molecules. So, actually any broadening of the absorption line, any broadening of the absorption line ready results in the general reduction in the sensitivity of the sample analyte. So, the solid sometimes the solid particles are formed by the inability of the flame to vaporize everything if the flame temperature is low; obviously, it can to vaporize all the solid particles this we have seen earlier in the determination of chromium in presence of molybdenum and iron because the temperature of the acetylene flame is only 2400 and we recommended 3000 using nitrous oxide.

So, same cases is I am telling you here that solid particles formed by the inability of the flame to vaporize all the dissolve semi solids of the sample solution, others not emulate and apart from analyte all the dissolved solids or it may be due to the formation of carbon particles in the flame. Now this requires a little bit of consideration. So, what I want to tell you in atomic absorption is that the solid particles whenever they vaporize the spectral interference occurs when the emission of the solid particles occurs in the resonance line range that is been band pass width.

So, that is why we call it spectral interference. If it is somewhere else the monochromator does not pick it up, but it will definitely pick up that portion of the radiation in the in spectral band pass width if there are a lot of solids in the sample even

though it is nonspecific sometimes what happens is there will be lot of carbon atoms and carbon when it burns it gives you continuous emission that will cover the resonance line also. So, that portion of the radiation coming from carbon particles burning or scattering and emission lines we will be picked up by the monochromator whatever is there within the band pass width of the sample.

So, that is what we mean here. So, the within the band pass width of the sample radiation whatever is the radiation within that range apart from the analyte we will be picked up and it gives you additional absorbance. So, the magnitude of this effect varies considerably depending upon the wavelength at which measurements are being taken if it is in the visible range carbon interference will be quite high and if it is in UV may be a little less normally light scattering element effects particularly those elements that absorb at lower wavelengths this is an important aspect.

Normally light scattering affects the elements it affects; that means, it decreases increases the absorbance at lower wavelengths.

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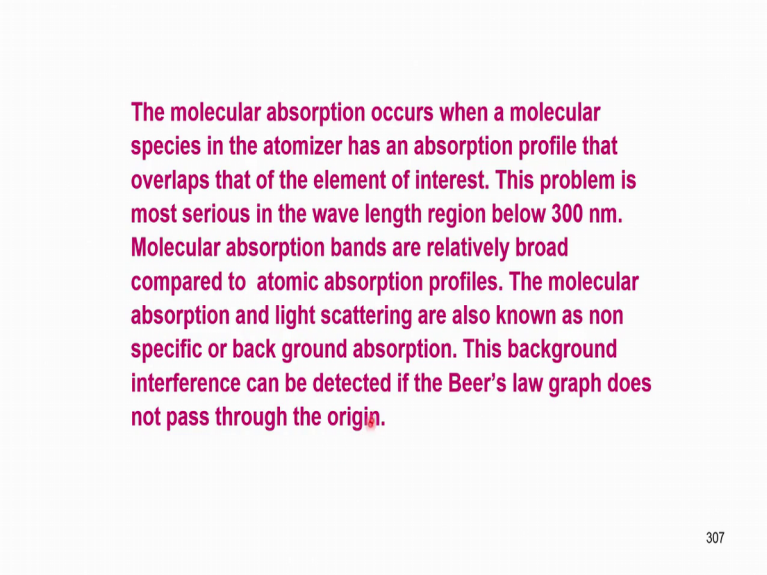

So, the molecular absorption when does it occur when a molecular species even has an atomic absorption has an absorption profile that overlaps the element of the interest, this problem is most serious in the wavelength region below 300 nanometers. So, molecular absorption bands are relatively broad compared to atomic absorption profiles and the

molecular absorption and light scattering are also known as nonspecific or background absorption the molecular adsorption both and light scattering due to solid particles they are also known as nonspecific or background carry absorption this background interference we can detect if the Beer Lambert's law does not pass through the origin this is the bottom line.

That means, whenever you do a calibration curve in atomic absorption what you do is you take standard solutions 1 ppm, 2 ppm, 3 ppm, 5 ppm etcetera measure the atomic absorption by a aspirating into the sample that absorbance in it will be 0 to 2 absorbance. So, if you plot absorbance versus concentration calibration line if it does not pass through the origin then it means that there can be there is some amount of background interference that is only you know only way we can determine whether there is background absorbance or not. So, this point you should remember especially whenever you are doing atomic absorption, sometimes you will be baffled why it is not passing through the origin whenever I even though I do not put the sample in the analyte in the blank or reference because I need a zero reading still it does not read show some more certain amount of absorbance. So, it does not pass through the origin, but it passes for cuts the y axis somewhere above or below. So, that difference is what is background absorbance, but it can happen due to molecular species or it can happen due to scattering.

So, the nonspecific absorbance absorption was initially we attributed it to salt particles that is which do not vaporize. But a strong evidence is there to indicate that scattering is often insignificant by comparison with molecular absorption; that means, there are two reasons why there will be there is enhancement due to background.

So, one is scattering by the solid particles another is by the absorption of the molecular species like CH NH 2 OH etcetera carbon, CN cyanogens radicals etcetera and these have got absorption peak starts starting from 300 to 600. So, part of it will cover the resonance line also. So, among the two that is molecular absorption and scattering the scattering is almost insignificant compared to molecular absorption in both flame and non flame both situation. So, the background absorption basically plays a vital role in the determination of trace elements in different composite matrix – blood, plasma and environmental sample drugs air any environmental any sample you take background absorption is always certain amount of it will be there and if the length of maximum portion comes from scattering from the molecular absorption rather than scattering.

Because normally we ensure that whenever we prepare a standard solution or even the sample solution there should not be any unresolved particles in the sample even in atomic absorption analysis the sample should be free from suspended impurities because suspended impurities also get aspirated into the flame and scattering takes place. So, what do we do we use a pre filtration step to remove all the suspended particles then only we allow it to into the flame. Suppose we do not do that then what happens? Many of the particles present in the sample they clog the burner holes because burner hole is not at such a high temperature, but it is fairly high temperature because the flame is 2300 and the base of the flame it may be around 12 it may be around the 1600 to 1800 degree centigrade many of the solid particles do not vaporize.

So, they clog, they go and sit there in small holes and block the airflow or acetylene flow. So, this means that the material will not be fuel and oxidant will not be burning continuously and there will be pressure back pressure will be there. So, I keep on passing the gas it does not get out. So, there is a pressure block and the flame may backfire. So, this is what happens especially in atomic absorption.

So, the contribution of the scattering in atomic absorption is always much less because we take care to see that suspended particles are very less, but if the matrix component itself contains certain amount of solids like sodium chloride in seawater they do clog and it is important for us to keep the atomic absorption system and that a burner cleaning using a metal plate or something they bleed something like that. So, that the holes are kept clean all the time just like what you do in your Bunsen burner or in your home at LPG gas.

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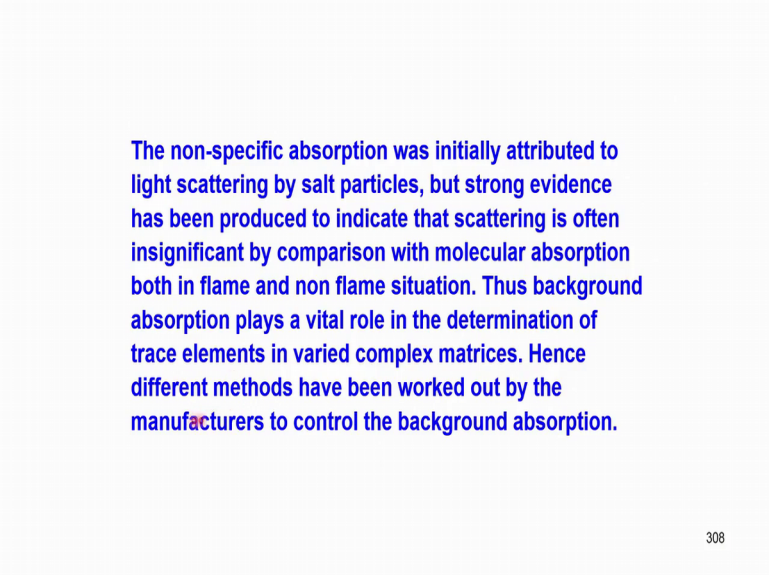

So, different methods have been worked out by the manufacturers to control the background absorption. So, I wanted you to see this slide and understand the interference of salt particles as well as and the contribution from the molecular species.

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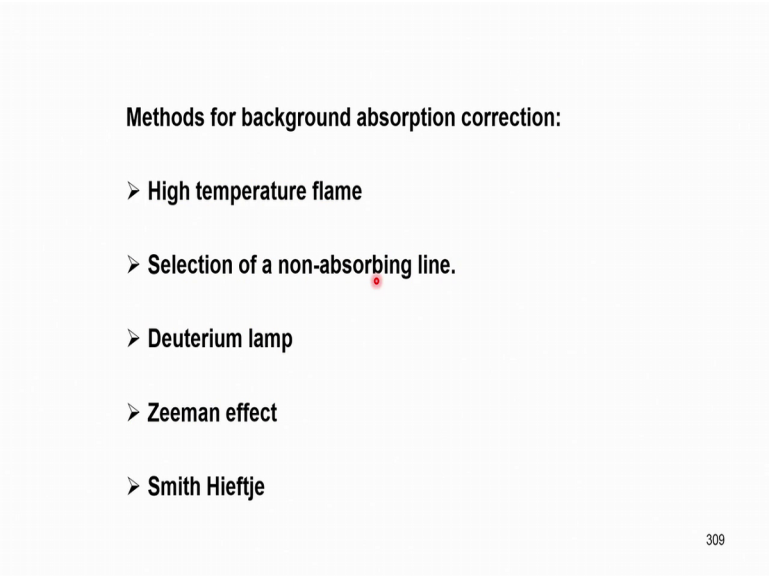

What are the different methods for background correction? Now you are imagine that we are discussing the background absorption it is an interference in atomic absorption and background absorption must be corrected before we actually take the absorbance from the analyte.

So, background absorption if at all if it is there it can be reduced it can be reduced by flame conditions that is number 1. Number 2 we can reduce it by selection of non absorbing another resonance line where absorbance is very less that also is possible then I can use a deuterium lamp measure the whatever is the deuterium lamp and blank. So, whatever blank is giving you absorbance you measure that and assume that contribution of the sample background is almost same in this analyte this is known as deuterium background correction. So, it measures all other absorbance within the band pass width of the hollow cathode lamp and then corrects that absorbance.

And then Zeeman effect we have already seen yesterday or about two classes before that whenever I place a magnetic field the Zeeman splitting will take place there it will lead to pi and sigma components sigma components are 25, 25 and pi is 50 and if I put a rotating polygraph, rotating if I put a polarizer if I put a rotating polarizer then whenever the pi component is turned out of the path I get only the background and then that background can be corrected or I can use Smith Hieftje correction also. So, all these things are possible for the background correction.

Now, look at this slide this is what I have listed here one is high temperature flame to burn everything selection of non absorbing line, this is in the ultimate case then you cannot do anything better than you cannot avoid absorption at all interference deuterium lamp normally it measures and Zeeman effect yes, Smith Hieftje effect yes. So, these are these are the different kinds of background absorption systems and whenever you buy an atomic absorption you will have to select one of these as the background absorption system depending upon the purpose for which you buy atomic absorption system.

So, if you want to do very high level research then Zeeman effect would be ideal, but the disadvantage is Zeeman effect will give you reduced sensitivity. Deuterium lamp cannot correct for spectral interference and non absorbing line if you choose they may it may not match with the matrix. High temperature flame not always possible and the Smith Hieftje is again something to do only with the hollow cathode lamp ok.

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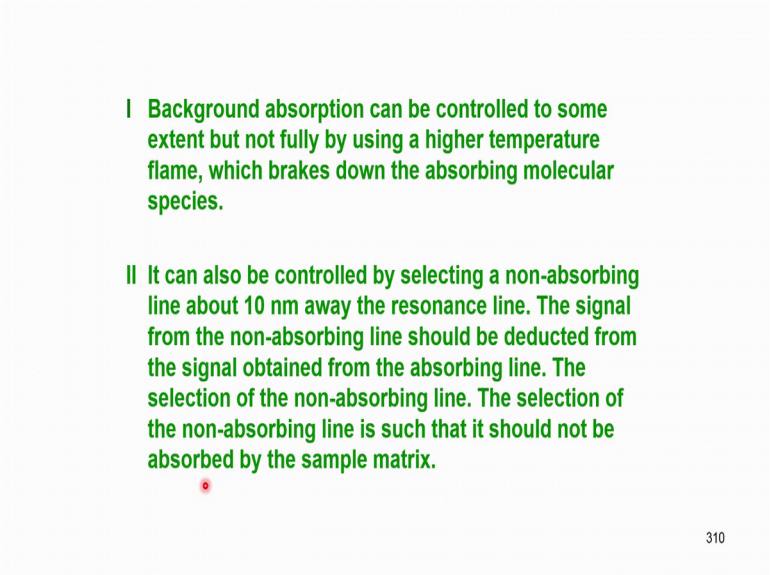

So, it can be controlled to some extent, but not fully by using a higher temperature, it cannot do a correction fully. It breaks down the absorbing molecular species that is remember that is, but it does not do justice to the background absorption correction it can also be controlled by selecting a non absorbing line about 10 nanometer away from the resonance line. What we normally do is we assume that we assume at the spectral wavelength resonance wavelength you measure the absorbance and measure the absorbance about 10 nanometer away that is not that resonance line, but 10 nanometers away we assume that absorbance is uniform within plus or minus 10 nanometers ok.

So, if we does not change much within plus or minus 10 nanometers it also will not change much and on the spectral resonance line. So, with that assumption we can measure the absorbance about 10 nanometers or whatever it is. So, subtract that much it is a crude method actually, what you should do is measure the background absorptions only at the resonance line, but 10 nanometers away whenever you are in faced with difficulties and the accuracy is more important you can take a look at this aspect also. So, the signal from the non absorbing line should be directed from the signal obtained from the absorbing line that is what we do.

So, the selection of the non absorbing line is such that it should not be absorbed by the sample matrix where this is important because sample matrix also should not be absorbing it should only be the background ok.

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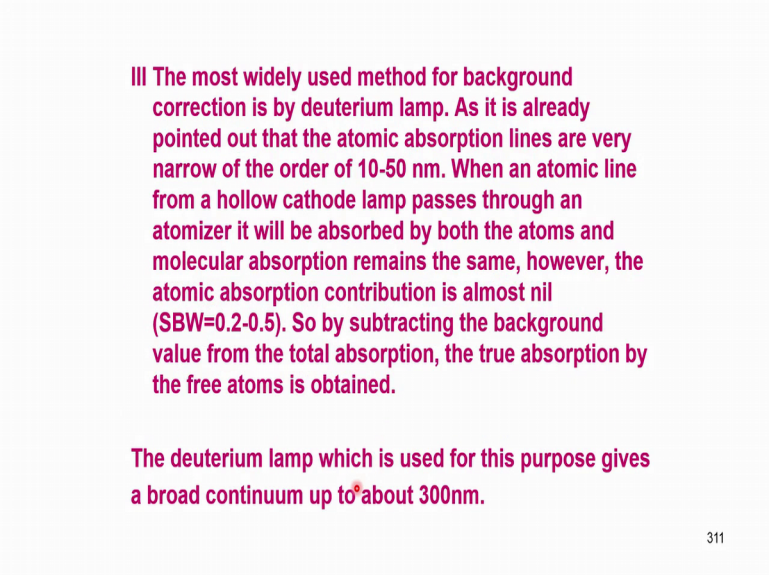

So, the instrument manufacturers give you a deuterium lamp 99 percent of the instrument manufacturers do give you deuterium lamp for background correction. So, I have explained to you the logic of background correction using deuterium lamp it has got a continuous absorption line covering the resonance line. So, within the normal band pass width when the hollow cathode lamp is on deuterium lamp irradiation is also on they are ratioed and then that much is subtracted from the absorbance line electronically.

So, as we have already pointed out that the atomic absorption lines are very narrow and there when an atomic absorption of a hollow cathode lamp passes through an atomizer it will be absorbed by both the atoms and molecular absorption remains the same. However, atomic absorption contribution is almost nil due to it to the background. So, by subtracting the background value from the total absorption through absorption by the free atoms is obtained standard by band pass width this is SBW is standard band pass width and the molecular absorption in this range is what is picked up because our slit width is between 0.2 and 0.5 nanometers in any instrument.

So, the deuterium lamp used for this purpose gives a broad continuum spectrum about up to about 300 nanometers ok.

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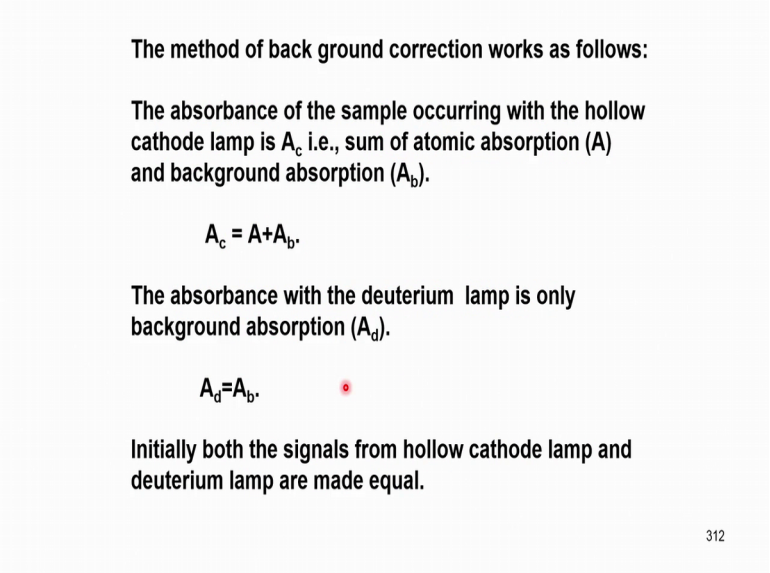

So, the method of background correction works like this the absorbance of the sample occurring with the hollow cathode lamp that is ac that is some of the absorption and background absorption atomic absorption A and A b, A is the atomic absorption contribution from background is A b. So, the absorbance with deuterium lamp is there the background only background correct absorption that is A d is equal to A b.

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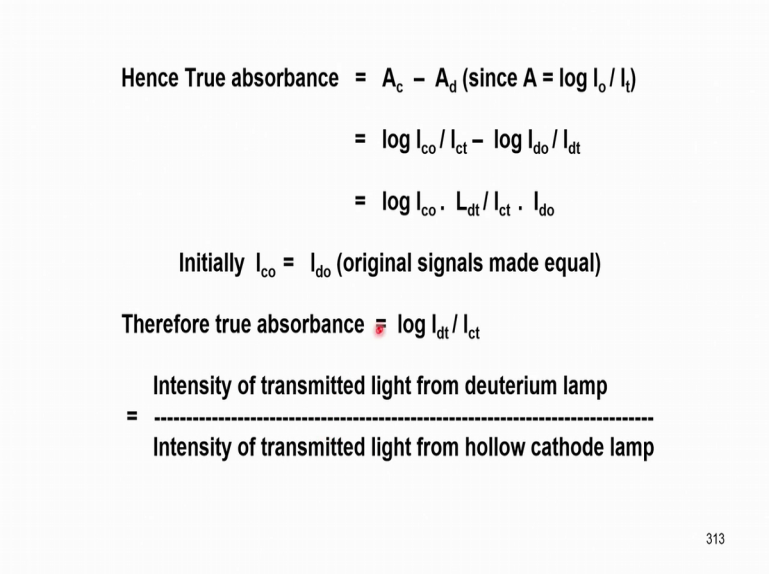

So, initially both the signals from the hollow cathode lamp and deuterium lamp are made equal and then true absorbance would be A c minus A d that is equalized and this is in the

log scale. So, in the log scale the actual absorbance would be log of co minus ct that is intensity subtracted by dy dt this is for the deuterium lamp, this is for a total chemical lamp, chemical as well as this thing. So, from the chemical lamp what I have is that it is a function of the initial concentration the do and from the both and then ratio we have to apply a correction ratio and, initially what I do is I see your intensity of the chemical species he is made equal to the deuterium lamp signal.

So, the true absorbance is log of dt by I say log of I dt by I ct; that means, intensity of the transmitted light from the deuterium lamp divided by intensity of the transmitted light from the hollow cathode lamp this is the true absorbance.

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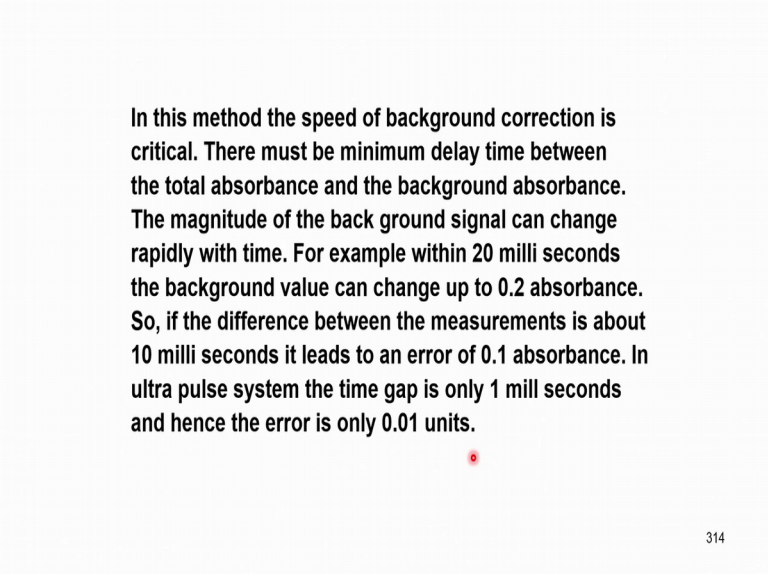

So, in this method the speed of background correction is critical we have to do it as we measure. So, there must be a minimum delay time between the total absorbance and background measured absorbance there should not be any delay in the measurement not even a few microseconds.

So, if we measure the absorbance without delay then I can apply the correction. So, the magnitude of the why because magnitude of the background correction background signal it may change rapidly with time also, if you plot a graph like this. So, when the graph goes like this very slowly it is a different matter, but if there is there are spikes in the background it has to be corrected as and when they occur. So, that has to occur within

a few microseconds that is the challenge. So, normally within 20 milliseconds the background value can change by 0.2 absorbance also 0.2 absorbance is quite high.

So, 20 milliseconds it can change your background itself can change from 0 to 0.2 absorbance. So, if the difference between the measurements is about 10 milliseconds it leads to an error of about 0.1 absorbance 20 milliseconds 0.2 absorbance. So, our measurement is every 10 milliseconds; that means, if the error can occur up to 0.1 absorbance right. So, the ultrapulse system the time gap in the ultrapulse system the time gap is only 1 millisecond that is a correction and if even if you use 0.1 millisecond the absorbance error is about 0.01 unit understood.

So, this is very important because what we are saying essentially is we say that background absorbance is all that there all the time it can be corrected by deuterium lamp, but it can change very fast. So, we need a very fast data acquisition system in atomic absorption because within 20 milliseconds the absorption changes of can change up to 0.2 absorbance in it. So, if I make a measurement at 10 milliseconds 0.1 absorbance 1 millisecond 0.01 absorbance unit that is also very significant. So, we have to have a very quick background correction system less than 1 millisecond.

So, electronically it is possible and the since last 20 25 years there are systems which can do even up to 0.1 milli seconds, but in atomic absorption spectrometry 0.1 millisecond is more than sufficient. We need not go to 0.01 milliseconds or correction data acquisition system may not be necessary.

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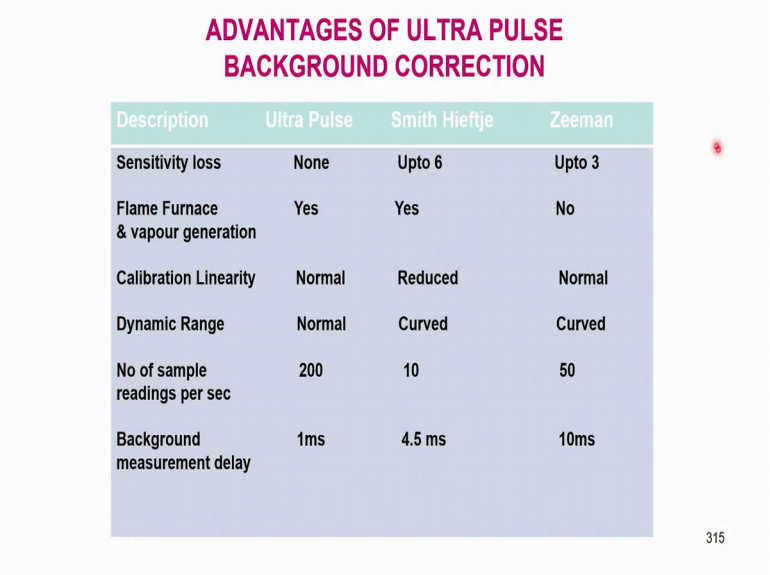

So, now here I have listed the advantages of ultra pulse background system. So, what I am comparing three systems, one is ultra pulse that is I keep on giving a pulse wave all the absorption is taken care of at within milliseconds Smith Hieftje I am putting a in this system, I am increasing the current of the hollow cathode lamp and here in Zeeman I am just putting a magnet. So, these are the three different systems I want to compare now.

So, the sensitivity loss in ultra pulse is almost nil; that means, the signal will not be affected by atomic absorption, but in Smith Hieftje I can lose up to six times the sensitivity; that means, if the absorbency is about 0.3 I end up with about 0.05 absorbance 6 times. And here it can be up to three times the sensitivity loss this is mainly because the sigma and pi lines of these Zeeman atomic absorption themselves split. So, the actual absorbance what you get in Zeeman is about 50 percent maximum. So, suppose I use flame furnace and vapor generation. So, in vapor generation flame furnace ultra pulse I can use Smith Hieftje I can use and Zeeman you cannot use there is no system that you can use it for flame furnace and vapor generation vapor generation is a little difficult, but the dynamic range calibration linearity is normal this is reduced this is normal in Zeeman.

So, it is not does not get affected dynamic range and this is also normal this is curve this is curved because of this signal acquisition problem. So, number of sample readings I can take 200 times I can pass ultra pulse take the reading, here in Smith Hieftje I can do

it 10 times per second or something like that and reading and here I can do up to 50 times. So, whenever I do 200 times the reading will be more reliable than 10 times or 50 times, so 50, 200 is better than 50 that is better than 10. So, background measurement delay also can happen in the of about 1 microsecond here it is about 4 micro seconds and here it is about 10 microseconds.

So, among the three if you have a choice whenever you are buying an atomic absorption spectrometer what you should be doing is do it ultra pulse if possible otherwise Zeeman otherwise Smith Hieftje depending upon the requirement of the quality of research what you would like to do ok.

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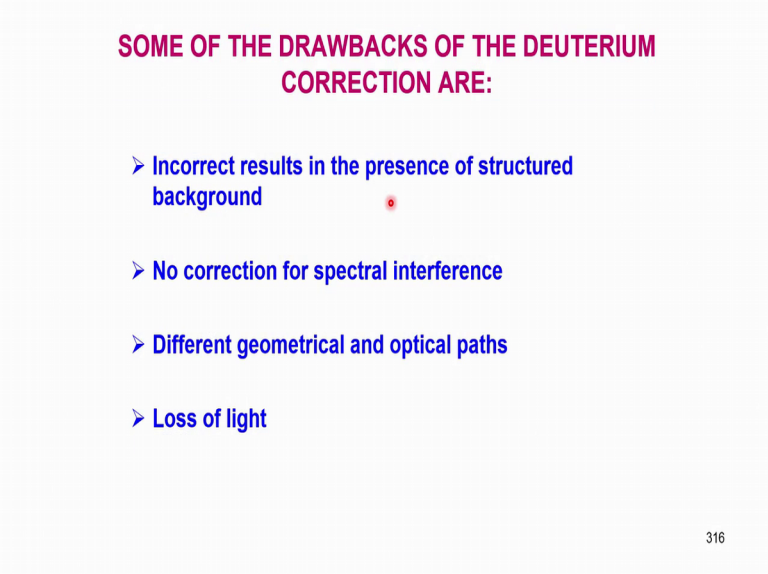

So, now deuterium correction background there are advantages and disadvantages. So, the drawbacks include incorrect results in the presence of structured background occurs and then no correction for spectral interference nothing can be done and different I accept go for some other resonance line here in the second one.

So, in the third one different geometrical and optical paths are there. So, there will be certain amount of loss of sensitivity and there is certain amount of loss of intensity of the light signal also. So, these are the typical problems with a deuterium background, in spite of this 90 percent of the atomic absorption spectrometers where use of the as is very

routine and minimal routine is more important routine then the people do go for deuterium correction.

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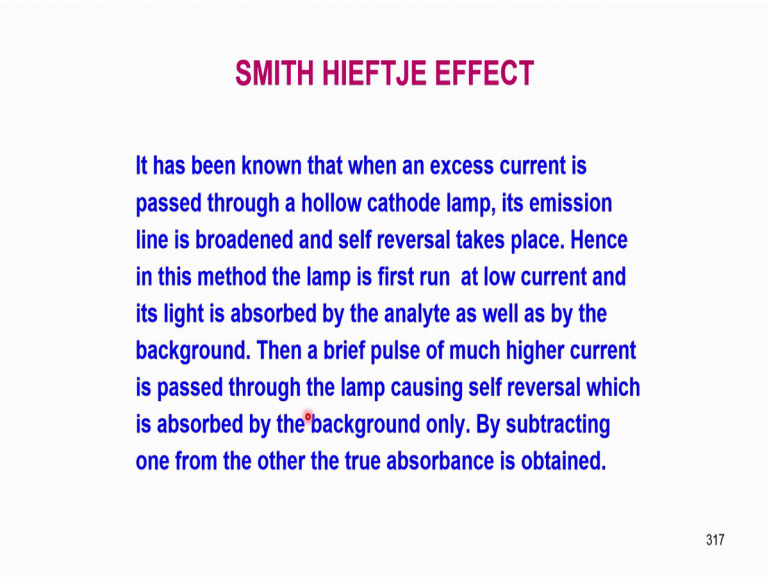

In Smith Hieftje self reversal takes place and lamp is first run at low current and then a high current. So, whenever there is high current there is no absorbance and only the background will be checked and a brief pulse of much higher current is passed through and we subtract the sample from the background.

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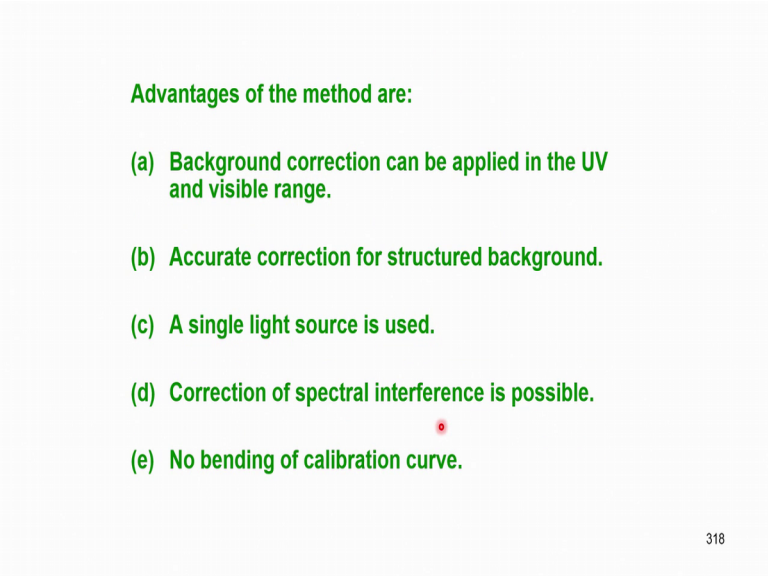

So, advantages of this method include background correction can be applied in UV and visible range both of them in Smith Hieftje accurate correction for this structure background they will. So, what I was trying to tell you that if the background keeps on changing very fast then accurate correction is possible with respect to this Smith Hieftje. And single light source is required I do not need a deuterium lamp or I do not need any other equipment to provide ultra pulse, I do not need any magnet for this single hollow cathode lamp same thing can be used, let us say one advantage now.

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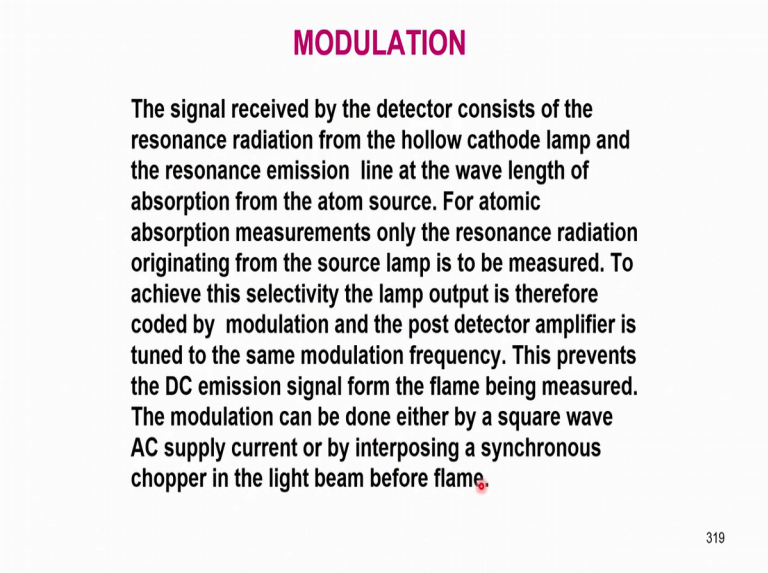

So, correction of spectral interference is definitely possible and no bending of the calibration curve; that means, the calibration curve will be passing through the origin and we do not have to worry about the accuracy of the analysis. So, we will discuss about the modulation of the atomic absorption signal in our next class.

Thank you very much.