Trace and ultra trace analysis of metals Using atomic absorption spectrometry

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Lecture – 29

Mercury cold vapour technique, FAES and Electrothermal AAS

In the last class we were discussing about the interferences in hydride generation atomic absorption spectrometric. So, what we said that there are virtually no spectral interferences in the determination of mercury.

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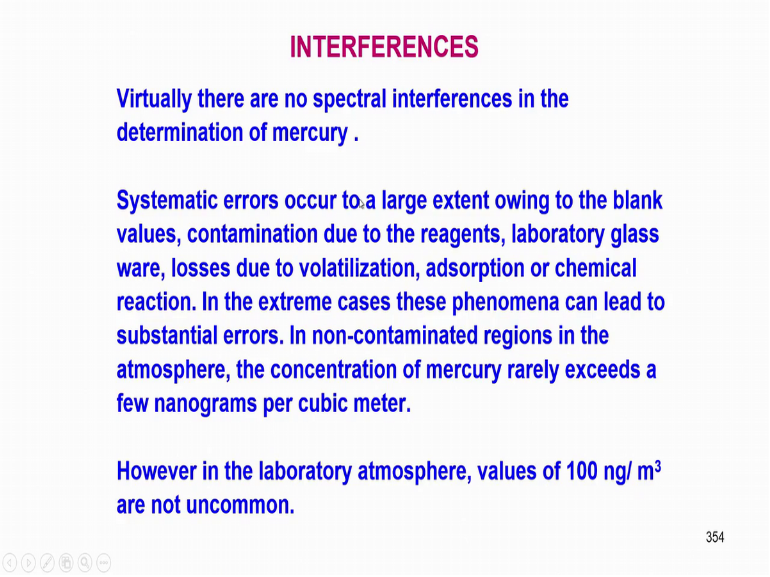

INTERFERENCES

Virtually there are no spectral interferences in the determination of mercury .

Systematic errors occur to a large extent owing to the blank values, contamination due to the reagents, laboratory glass ware, losses due to volatilization, adsorption or chemical reaction. In the extreme cases these phenomena can lead to substantial errors. In non-contaminated regions in the atmosphere, the concentration of mercury rarely exceeds a few nanograms per cubic meter.

However in the laboratory atmosphere, values of 100 ng/ m^3 are not uncommon.

So, basically because we measure the atomic absorption of mercury only around 253 nanometer or something like that. And then there are not many spectral interferences are known, because most of this spectral interferences have already been tabulated, and available in the databases all over the world.

So, what we have to understand is whenever we want to determine mercury, there are no spectral interferences and systematic, but systematic errors occur to a larger extent owing to the blank values. Because mercury contamination is almost everywhere in the air everywhere in the whole world, even air we breathe contains some amount of mercury. And the laboratories definitely yes, and then coal burning definitely yes, automobiles not much, but any air cities urban areas do have lot of mercury in the air which we normally breathe.

So, this systematic errors always occur to a large extent, owing to the blank value itself having some certain amount of mercury. So, apart from that we have laboratory glassware losses due to volatilization, adsorption or chemical reaction also can occur. So, in the extreme cases this phenomena can lead to substantial errors. Basically any environment normally atomic absorption instruments are not kept in ac rooms. They are kept in a open atmosphere. And sometimes air itself can be contaminated; there may be volatilization of mercury from previous experiments in the laboratory etc.

So, in extreme cases this can lead to substantial errors that is the statement we want to make. So, in non contaminated areas regions in the atmosphere the concentration of the mercury is there, but it rarely exceeds a few nanograms per cubic meter that you need to understand; that means, if the concentration of mercury is less than few nanograms per cubic meter in the air we breathe, we can call it as noncontaminated area, but in the laboratory atmosphere values of even 100 nanograms per meter cube are not uncommon. That is 100 ppm ppb sorry, 100 ppb are not uncommon at all in the laboratory atmosphere ok.

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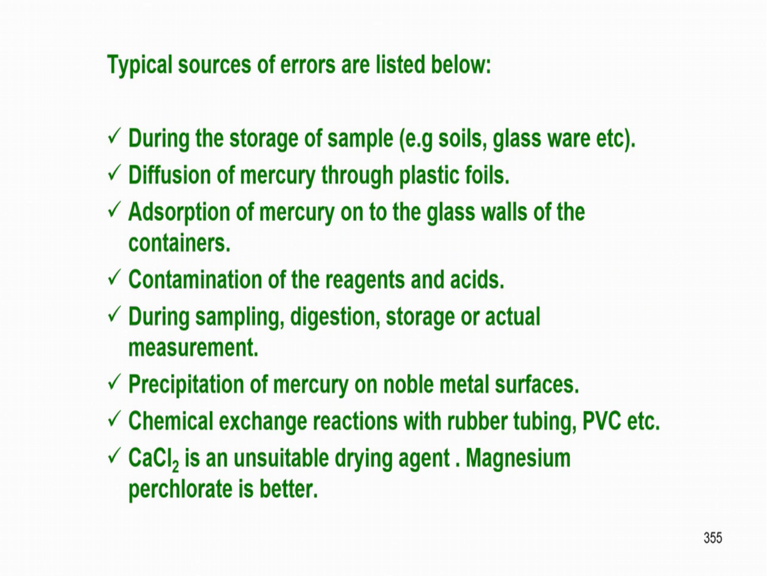

Typical sources of errors are listed below:

- ✓ During the storage of sample (e.g soils, glass ware etc).
- ✓ Diffusion of mercury through plastic foils.
- ✓ Adsorption of mercury on to the glass walls of the containers.
- ✓ Contamination of the reagents and acids.
- ✓ During sampling, digestion, storage or actual measurement.
- ✓ Precipitation of mercury on noble metal surfaces.
- ✓ Chemical exchange reactions with rubber tubing, PVC etc.
- ✓ $CaCl_2$ is an unsuitable drying agent . Magnesium perchlorate is better.

So, what are the typical sources of errors? Normally 99 percent of the cases whenever we have to handle mercury, the storage of the sample plays a very important role the soils for example, if you want to analyse soil, there is certain amount of mercury contamination can occur from anywhere. And then glassware definitely yes, because quite often we keep the mercury in the glassware handle them etc. And then suppose there is mercury in a plastic foil in a bag plastic bag, then again there is diffusion of mercury because of the possibility of vapour pressure. I had already told you that mercury has got a very high vapour pressure 0.0003 at room temperature.

So, whatever is the air containing mercury if it is in a plastic bag, can diffuse outside from the plastic bag itself. So, we have to be very careful regarding the diffusion of the mercury through the plastic foils. And then adsorption of the mercury onto the glass wall definitely yes, of the containers and then the contamination of the reagents if you are determining mercury day in and day out in a given laboratory, then there is a possibility contamination of reagents and acids occur quite often. It is the experience of all the people who work on mercury for long periods.

So, the reagents itself if it gets contaminated definitely you will get very high blank value so; obviously, blank value will be subtracted in the final estimation, but still there will be contamination and we have to be very careful how we keep our reagent on and acids, that is also very important. Most of our acids need to be free from mercury. So, during sampling, digestion, storage or actual measurement also contamination can occur. Where then precipitation of mercury on noble metal surfaces whenever you have platinum or something like that in the laboratory or elsewhere mercury can form amalgam and it mercury vapour can get deposited from an amalgam, or if it comes in contact with mercury salts then the mercury can get reduced on the noble metal surfaces and get contaminated. So, that is another source of error we normally recognize on metal surfaces.

So, then what else? The chemical exchange reactions for example, if you are passing the mercury vapour or the sample through a rubber tube or a PVC tube. The PVC tube and rubber itself may be having certain amount of contamination. Or mercury can get exchanged from rubber to the air or air to the rubber tubing or PVC tubing. And then sometimes we find that calcium chloride is also an unsuitable drying agent. It may have an impurity of mercury, leading to high blank values. So, the other one is magnesium perchlorate. That is a better drying agent, and what we want to say from this slide is these are the different kinds of contamination, possible contamination in the normal determination of the mercury at parts per billion level, you please remember that, only when we determine mercury we go to parts per billion and parts per trillion level. And cold vapour mercury is the best method to determine mercury in ppb levels, but whenever you are doing estimation in parts per billion level you have to be PVC careful with respect to the contamination.

So, if there is contamination from the sample, you can change the sample if there is acid. You can change the acid, if it is plastic foil you can change them and, but during sampling digestion storage and actual measurement they are not under your control. So, one has to be very careful with respect to blank values, in this and then we have to make sure that noble metals are not around exposed into the atmosphere, and then rubber tubing if it gets contaminated you have to change it, and calcium chloride if it is not convenient and if it gives you blank values you should be able to change it to magnesium perchlorate.

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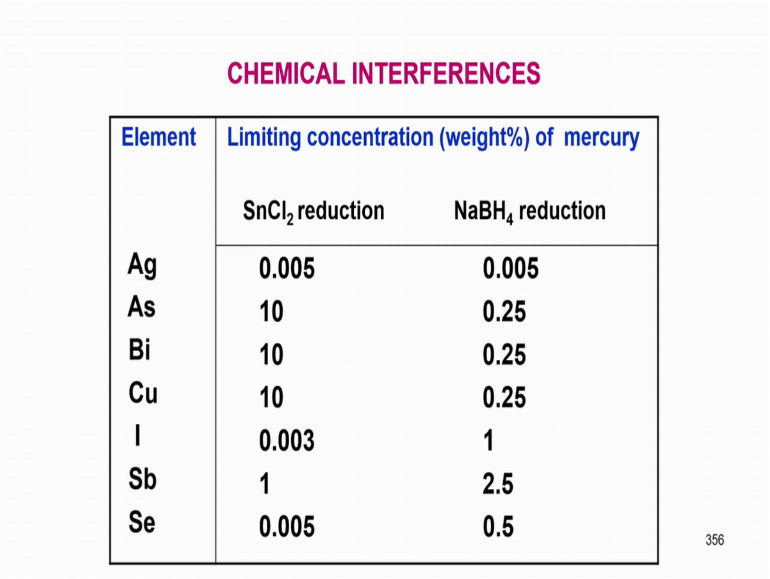

CHEMICAL INTERFERENCES

Element	Limiting concentration (weight%) of mercury	
	$SnCl_2$ reduction	$NaBH_4$ reduction
Ag	0.005	0.005
As	10	0.25
Bi	10	0.25
Cu	10	0.25
I	0.003	1
Sb	1	2.5
Se	0.005	0.5

So, what are the other interferences of in the determination of the mercury? We did say that it is almost specific, but there is a certain possibility of interferences from some other source it is nonspecific absorption. And these I have tabulated them here and by both methods and then for example, there is silver along with SnCl 2 it may interfere in the reduction of mercury to elemental state. So, this kind of interferences can occur it is not the atomic absorption measurement, but it is the interference which will in reduce the conversion of the mercury salt into mercury element. In the solution, because in all this samples mercury we have to generate anyway by either by stannous chloride method or sodium borohydride method, they have to be acidic and we have to add sodium borohydride or SnCl 2 reduce mercury and then we are passing nitrogen to bubble the to dry out the mercury vapour.

So, if there is silver then SnCl 2 stannous chloride reduction method, if you are employing for the determination of the mercury. The interference level will be 0.005 ppm or weight percent. And then same thing is true even with NaBH 4 reduction and then arsenic stannous chloride it is about 10 percent of the mercury. So, if you are determining about 1, ppb 0.1 ppb of arsenic can interfere in the reaction. That is reduction of mercury to vapour. Same thing is, but with NaBH 4 reduction slightly alkaline conditions it is 0.25. So, always we say that NaBH 4 reduction is preferable compared to stannous chloride reduction.

But ninety percent of the analysis were being conducted up to 1990s using stannous chloride, even now lot of people do that, but the switching over to NaBH 4 is always preferable. Sodium borohydride tablet cost around 800 to 1000 rupees per 100 gram whereas; stannous chloride is much more cheaper. So, because of that reason also people prefer stannous chloride only because of the cost. Now there are other elements which I have listed here one is bismuth that is about 10 percent of mercury copper is also around 10 iodine is you should be PVC careful, because 0.0003 percent mercury forms an iodide complex. HgI, HgI 2 HgI 3 minus and HgI 4 2 minus, all kinds of possibilities are there with iodine. And therefore, one has to be very careful if there is iodine. And if the iodine is it is there we have to find out a way to get rid of this iodine ok.

There are very simple methods, because we know that most of the iodides can be precipitated as chloride or bromide or iodide whose solubilities are very less. Silver bromide for example, silver iodide silver chloride their solubilities are very less. So, if there is any if you suspect any amount of iodine in the sample, what you will do? Normal, what you should be doing is you have to add a little bit of silver chloride solution, and then iodine will precipitate as silver iodide and then that will not interfere, but again you should be very careful because the quantity of iodine is very less. Similarly antimony 1 ppm or one percent of weight per one weight percent of mercury interferes in stannous chloride this is 2.5, selenium is 0.005, as bad as iodine.

And on the other side in sodium borohydride reduction it is 0.5. So, if I ask you to compare the 2 methods the method what you choose should be sodium borohydride, if both are available.

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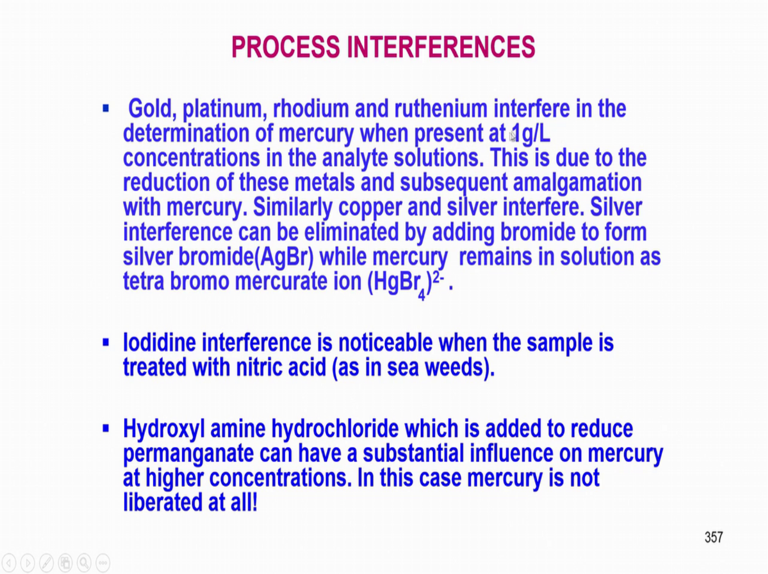

PROCESS INTERFERENCES

- Gold, platinum, rhodium and ruthenium interfere in the determination of mercury when present at 1g/L concentrations in the analyte solutions. This is due to the reduction of these metals and subsequent amalgamation with mercury. Similarly copper and silver interfere. Silver interference can be eliminated by adding bromide to form silver bromide(AgBr) while mercury remains in solution as tetra bromo mercurate ion $(HgBr_4)^{2-}$.
- Iodidine interference is noticeable when the sample is treated with nitric acid (as in sea weeds).
- Hydroxyl amine hydrochloride which is added to reduce permanganate can have a substantial influence on mercury at higher concentrations. In this case mercury is not liberated at all!

So, sodium borohydride method has gained wide popularity in the determination of mercury. So, then there are process interferences this I have already told you gold, platinum, rhodium, ruthenium etc they interfere in the determination of mercury, when present at 1 gram per liter of the solution. That is 1 ppm that is no not 1 ppm, 1 gram per liter is 1 milligram per ml, yes that is 1 ppm. So, around 1 ppm levels all these noble metals gold silver platinum rhodium ruthenium, all these things interfere in the if they are present in the analyte solutions.

So, this is due to the reduction of these metals and subsequent amalgamation with mercury. I think I have explained to you enough regarding the amalgamation problem with mercury if any of these metals are around you should be always expecting some sort of amalgamation. Similarly copper and silver. Silver interferences can be eliminated we can eliminate as I had already told you, that we if we add bromine bromide potassium bromide or sodium bromide it will form silver bromide and when whereas, mercury remains in solution as the HgBr 4 2 minus. So, same thing is true with respect to other element that is copper and silver, they also form iodides, and we have to convert them into least soluble salt with respect to bromide, with respect to mercury.

So, iodine interferences is noticeable when the sample is treated with nitric acid. For example, if you want to determine iodine in seawater, where there are seaweeds then they do have lot they do concentrate iodine, iodide iodine as iodide and whenever you want to determine in organic substances it is important that we oxidize the organic substance into with nitric acid to convert it into inorganic salt solution and then analyze. So, use of nitric acid is very common in almost all chemical analysis, of real samples for example, in seaweed in food in agriculture in plants materials etc nitric acid is always used for the dissolution of the sample. Similarly sometimes hydroxylamine hydrochloride it is added to reduce permanganate.

Normally it has a substantial influence on mercury at higher concentrations. So, you have to be very careful if there is permanganate and hydroxylamine hydrochloride because in this case mercury is not liberated at all.

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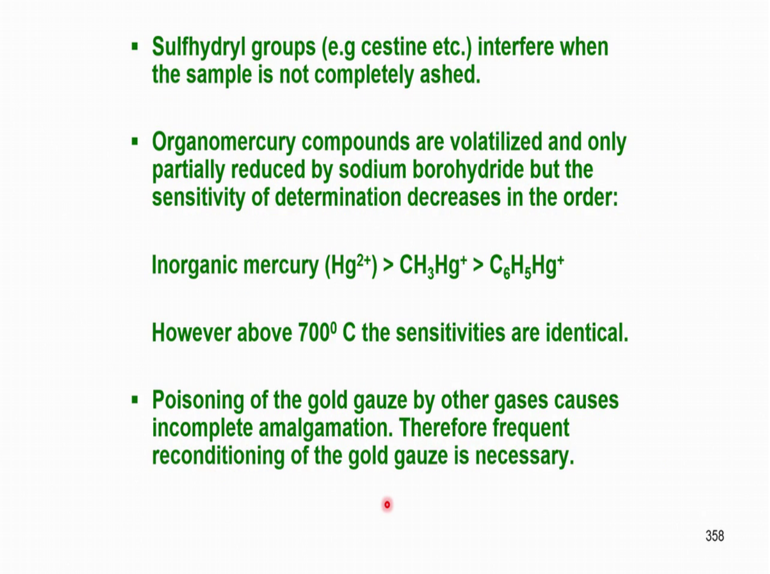

- Sulfhydryl groups (e.g cestine etc.) interfere when the sample is not completely ashed.
- Organomercury compounds are volatilized and only partially reduced by sodium borohydride but the sensitivity of determination decreases in the order:

  Inorganic mercury (Hg^{2+}) > CH_3Hg^+ > $C_6H_5Hg^+$

  However above 700^0 C the sensitivities are identical.
- Poisoning of the gold gauze by other gases causes incomplete amalgamation. Therefore frequent reconditioning of the gold gauze is necessary.

So, you may conclude that mercury may not be there whereas; it could be there in the sample. Then there are other organic compounds like sulfhydryl groups, these are present in amino acids. So, if you want to determine mercury in the body fluids amino acids may be there with sulfhydryl groups and they interfere when the sample is not completely ashed, the treatment of the sample with nitric acid is called ashing, and we also had little bit of magnesium and other things during ashing process.

The details of analysis you can find out from the textbooks or prescribed AOAC methods association of analytical chemists, they produce a number of a monographs and other literature, which will give you typical procedures for the determination of for ashing and other aspects of analytical chemistry. So, organometallic compounds quite often they are volatilized and only partially reduced by sodium borohydride, sodium borohydride works only for inorganic compounds not organic compounds so, but in that in that case you should go for stannous chloride method. So, organometallic compounds are volatilized, but only and only slightly partially reduced, but the sensitive therefore, the sensitive of the determination decreases, and the order of decrease of the absorbance reading for inorganic mercury is inorganic mercury is very high, methyl mercury it is lower compared to inorganic mercury is lower, and if it is phenyl mercury then it is still lower.

So, if I do the determination of the mercury, I use a 700 degrees or 1000 degree then there is no problem. That is because I have already told you that most of the mercury liberated from the environment goes to a gold foil on which mercury deposit is and then amalgam is formed. This amalgam decomposes above 500 degrees or even sometimes even 3 fifty degree centigrade you can collect your mercury. In fact, earlier most of the jewelers used to collect small quantities of gold using mercury, forming mercury amalgam and then you operating the mercury and then collect the gold, which is having higher by economic value.

So, they used to generate about 600, 700 degree centigrade in the normal skills. Jeweler skills, but in atomic absorption if I use 700 centigrade the sensitivity of methyl mercury the phenyl mercury and inorganic mercury. All of them would be essentially same. But if you use lower temperature inorganic mercury will give you higher reading compared to methyl mercury, and methyl mercury will give you higher reading than phenyl mercury owing to the decomposition potential of this, these compounds. Sometimes there maybe other elements in the vapour they may cause poisoning of the gold gauze. Platinum poisoning we are all quite aware because platinum can form sulphur. Hydrogen sulphide can get deposited on platinum and forming platinum sulphyte and then it will the top surface may not be available for amalgamation at all.

So, poisoning of the gold gauze by other gases causes incomplete amalgamation. So, frequent reconditioning of the gold gauze is necessary. How do we increase? The how do we recondition the gold? That is very simple all you have to do is take out the gold piece heat it around 1000 degree centigrade and then gold piece is ready for action once again. It is a very simple process, but we should be aware of the complications that is why I am suggesting that the gold we have to why people use gold is because gold is least resistant to poisoning. Even though we have written here there maybe other gases that cause incomplete amalgamation surface and changes. Platinum and palladium are the most prone to poisoning, but gold also to some extent can happen because gold can do can and does form sulphur compounds on the surface.

So, frequent reconditioning of the gold gauze is necessary and you should be doing it if you want to determine gold in number of samples over a period of time. So, if you are regularly doing gold either we say why do not you recondition the gold piece put it in a flame and see that most of the sulphur is gone or simply heat it to 1000 degrees do not make any measurement, but put it back and then do the analytical determination of the gold.

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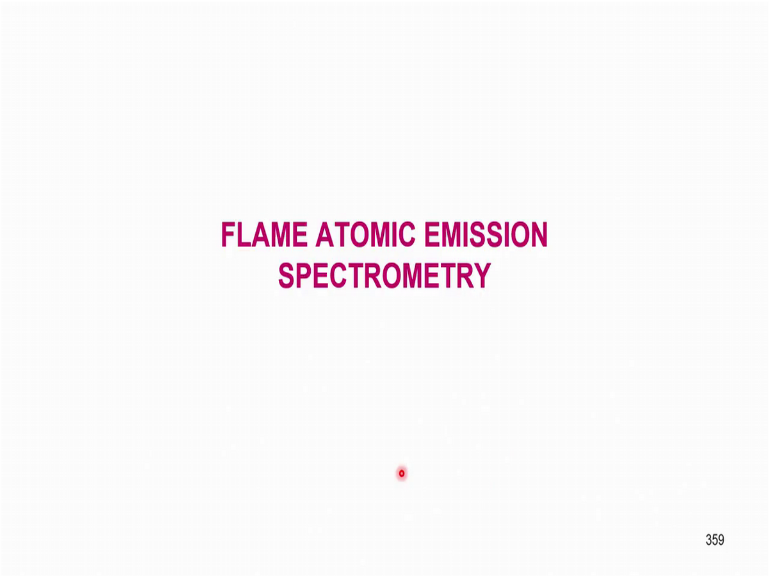

FLAME ATOMIC EMISSION
SPECTROMETRY

Now, that is all I wanted to tell you about the mercury determination. So, far we have discussed the hydride generation technique as a modular attachment. And also we have discussed cold vapour mercury as an attachment. In cold vapour mercury what we need is only a small alpha violet lamp, with a small filter which will give you a 253 nanometer wavelength and you can determine the gold sorry, mercury in as a modular attachment.

So, nowadays there are some dedicated instruments available for the determination of the mercury by cold vapour method.

You do not need an atomic absorption at all. So but whenever you buy an atomic absorption it makes sense to buy cold vapour mercury determination modular attachment also. Same thing is true with the respect to hydride generation. Now I want to introduce you to another technique that is flame atomic emission spectrometry. Now you may be wondering why I am teaching you flame atomic emission spectrometry whereas, we are talking about flame atomic absorption spectrometry. And the reason is some elements can be determined by flame atomic emission rather than flame atomic absorption.

But they possibility of using the same optics, same instrument as atomic absorption, makes the flame atomic emission also possible to for the determination of some elements. What are those elements? I think most of you already know about it that is lithium sodium potassium etc this are alkali metals, and there are alkaline earth metals, that is calcium, strontium, barium etc.

So, before I proceed I want to simply tell you that atomic absorption instrument can be used as an emission spectrometer atomic emission spectrometer for some for some elements only. Alkali and alkaline earth metals, but the, but the possibility of using atomic absorption instrument as an emission spectrometer is quite there at just at the flick of a button we can change from absorption to emission to absorption. So, there is a possibility that whenever you buy an atomic absorption instrument the atomic the instrument will have a switch which tells you whether you would like to do atomic absorption or atomic emission anyone of these 2 you can measure.

That is why we should know a little bit of atomic emission spectrometry. Rather flame atomic emission spectrometry, that is why we want to discuss flame atomic emission spectrometry. There is not much to discuss except to recapitulate some of the things what we have said earlier.

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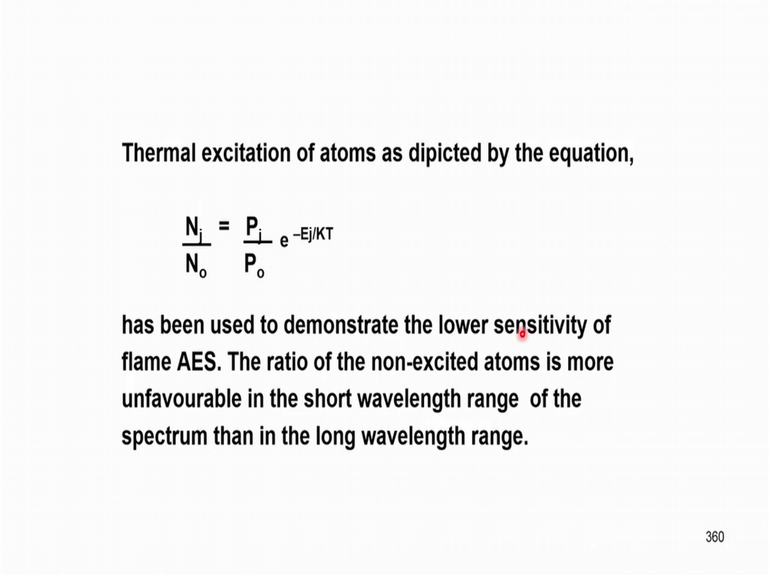

Thermal excitation of atoms as dipicted by the equation,

$$\frac{N_j}{N_o} = \frac{P_j}{P_o} e^{-Ej/KT}$$

has been used to demonstrate the lower sensitivity of flame AES. The ratio of the non-excited atoms is more unfavourable in the short wavelength range of the spectrum than in the long wavelength range.

So, thermal excitation of the atoms as depicted by this equation I think all of you are familiar with this equation, that is N j by N 0 is equal to P j by P 0 into E to the power of minus E j E j by KT. This is the number of atoms if you for your convenience I am telling you that N j represents the number of atoms in the excited state, number of atoms in the ground state P j is the probability function of the E j excited state.

P 0 is the probability function of the ground state, E is the you know, what E is the and E j is the energy difference, and KT, K is known as Boltzmann constant, T is the temperature this equation we have discussed earlier in the theoretical aspects of atomic emission. So, this equation has been used to demonstrate the lower sensitivity of flame atomic absorption, atomic absorption correct.

So, the ratio of the non excited atoms is always more unfavorable in the short wavelength range of the spectrum than the long wavelength range. What we are essentially saying here is at any temperature the number of atoms in the ground state are more than the number of atoms in the excited state, that is the bottom line. And I have written the same thing in a textbook style that is the ratio of the non excited atoms is more unfavorable in the short wavelength range of the spectrum than in the long wavelength range; that means, the atomic emission occurs in the long wavelength range that is above 500, 600 range not in the UV or visible range of course, it is visible range, but not in the UV definitely.

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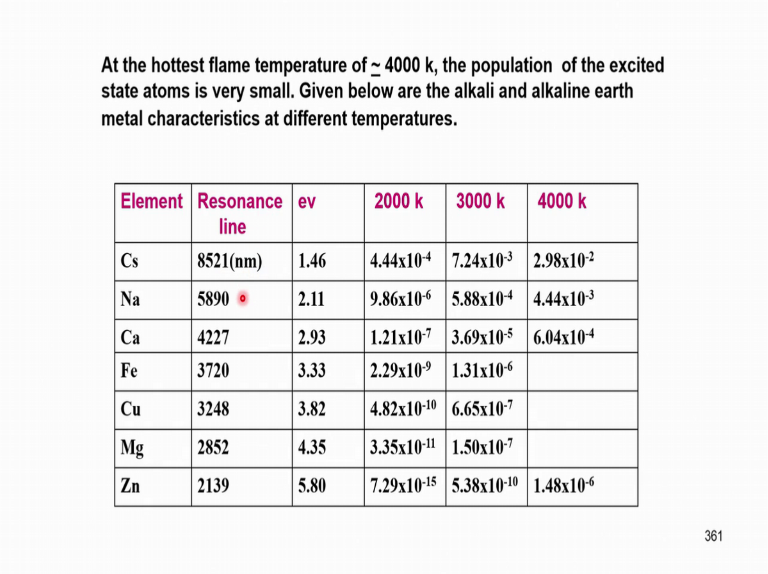

At the hottest flame temperature of ~ 4000 k, the population of the excited state atoms is very small. Given below are the alkali and alkaline earth metal characteristics at different temperatures.

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

So, I had shown you this figure this table also at the as we increase the temperature if the temperature is low, then the concentration of the atoms in the excited state and ground state would be different, but if I increase the temperature from 2000 to 3000, 3000 to 4000 the concentration of the atoms would be more. Now we can look at this table this table I had shown you earlier also. And what we want to say at this point of time is, as the hottest flame temperature of around 4000 degrees the population of the atoms is still very small they are all in the range of minus 2 to minus 3; that means, one out of 100 one out of 1000 1 out of 10000 and if it is zinc it is 1 out of a 1 million.

So, but the elements concentration that is atom concentration I have given the this table I had shown you earlier, and this cesium the resonance line is 852 that is nanometers that is in the visible range, and the energy required is 0.46 and 2000 concentration of the atoms is one in 10 to 4 in 10000 at 3000 it is 17000 and at 4000 to in 100; that means, only 2 atoms are in the excited state to 0.98 you can say almost 3. Only 3 atoms are in the excited state compared to 100 atoms, out of 100 only 3 will be in the excited state.

Same thing is true with sodium it is emission line is 589 and then electron volt energy required to excite is 2.11 at 2000 it is about 10 atoms in one million, and 3008 is about 6 in 10000, and at 4000 it is about 4 atoms in 1000 atoms in the ground state. Same similarly you can read the other numbers and you can see that as we pass through alkaline earth metals iron cobalt magnesium zinc etc they are all in millions that is few atoms per million. So, that is not very convenient for us.

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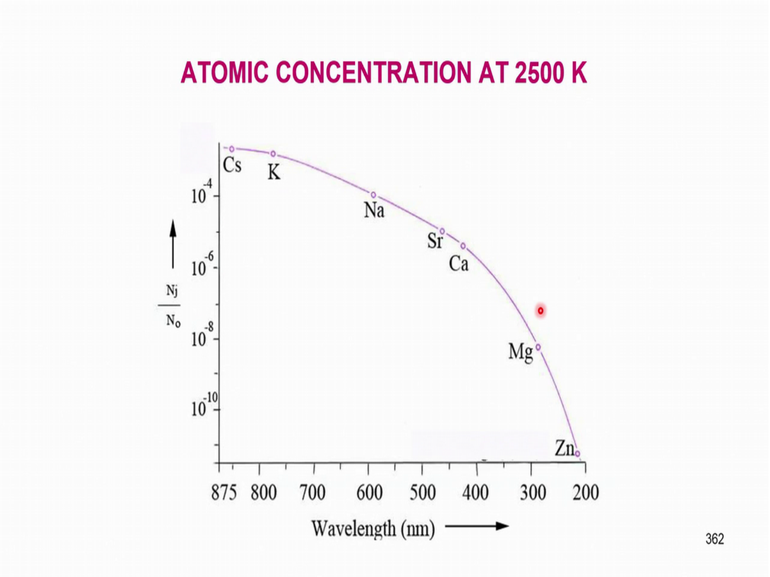

ATOMIC CONCENTRATION AT 2500 K

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Ah, but these numbers can be very significant as we can see now. So, the atomic concentration where I have plotted here N j by N 0 this is the wavelength and so, cesium it is highest potassium is lowest sodium is still lower strontium etc, but concentration of atoms like this zinc and other things they all are in the range of 10 raise to minus 10 range. That is N j by N 0 it is not the total number of atoms, but it is the ratio. So, this figure is very convenient to determine which sort of elements we can determine by flame atomic emission.

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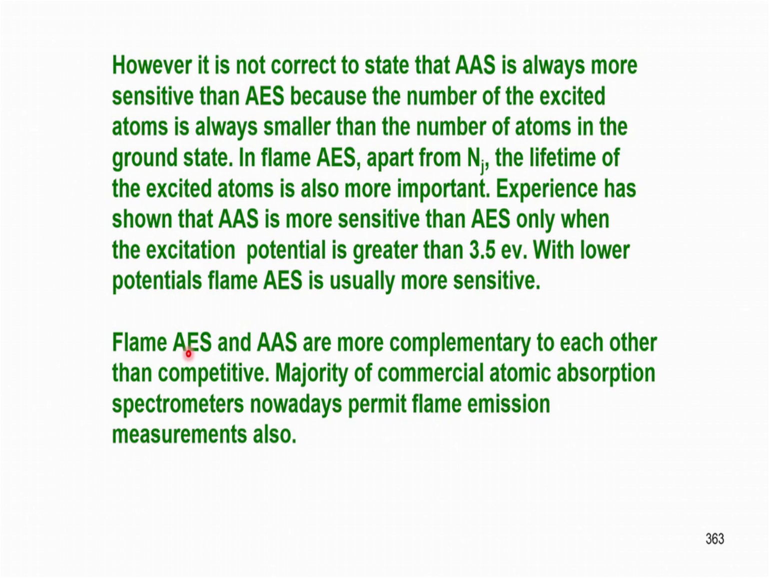

However it is not correct to state that AAS is always more sensitive than AES because the number of the excited atoms is always smaller than the number of atoms in the ground state. In flame AES, apart from N_j, the lifetime of the excited atoms is also more important. Experience has shown that AAS is more sensitive than AES only when the excitation potential is greater than 3.5 ev. With lower potentials flame AES is usually more sensitive.

Flame AES and AAS are more complementary to each other than competitive. Majority of commercial atomic absorption spectrometers nowadays permit flame emission measurements also.

So, what we want to say at this point of time is that, it is not correct to state that atomic absorption is always more sensitive than atomic emission. That is wrong because the number of excited atoms is always smaller than the number of atoms in the ground state that is what we have been saying all the way in flame atomic emission apart from the N j, that is the number of atoms in the excited state the lifetime of the excited state is also more important.

So, assume that at any time 4 atoms are in the excited state, but if the excited state remains in the flame for longer time, then the atomic emission can occur very easily so the lifetime of the excited atoms is more also more important during atomic emission. So, experience have shown that atomic absorption is more sensitive than AES only when the excitation potentials is more than 3.5 electron volts, with lower potentials flame AES atomic absorption it is usually more sensitive. So, again as I was telling you atomic emission and atomic absorption are complementary to each other which can be measured with the same instrument with the flick of a button.

So, majority of the commercial atomic absorption spectrometers nowadays permit flame emission measurement also. So, this what I have been telling you, but nowadays the flame atomic emission spectrometers are available independently. Also you they cost very less approximately about 50 to 60000 rupees for the for sodium potassium lithium etc. They are known as flame atomic emission spectrometers, but because we are studying atomic absorption we will study a little bit more about the flame atomic emission also. We will continue our discussion.