Trace and ultra trace analysis of metals Using atomic absorption spectrometry

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Lecture - 28
Cold Vapor HG AAS Flame Emission

So, we are discussing about the hydride generation atomic absorption. What I had told you is that it is a simple modular attachment. We take the chemistry to atomic absorption, convert the metals into hydride, take it into the flame and do the analysis. So, in the flame, most of the hydrides have got a property to decompose, produce metal atoms. Once these metal atoms are produced, all other mechanisms remain the same because they absorb the radiation, go to next higher energy level during that process. They need absorption and that absorption comes from the hollow cathode lamp.

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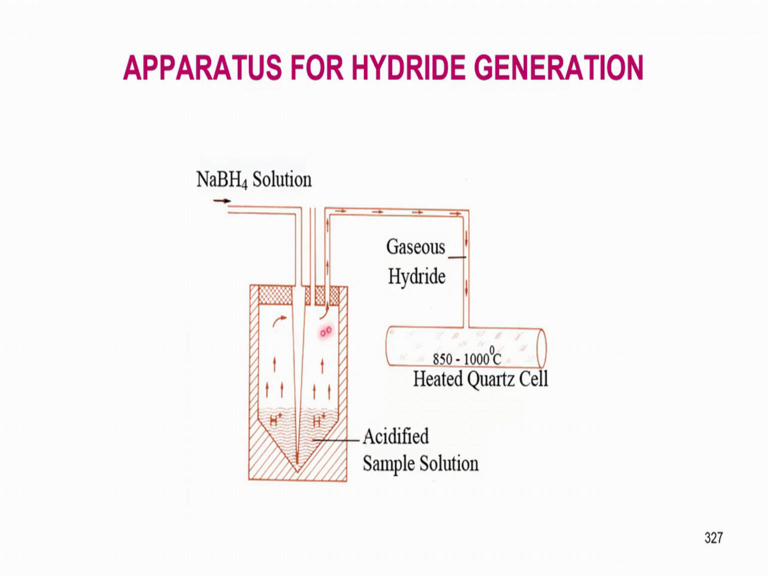

APPARATUS FOR HYDRIDE GENERATION

So, we have discussed this and this is the hydride generation system. It is a closed system with sample, acidified sample solution and sodium borohydride and this is the norm. Now a days instead of zinc and hydrochloric acid and then, the sample is transferred to the heated quartz tube here and then, there it gets decomposed and the chemical analysis gets completed because we measure the transmissions, ok.

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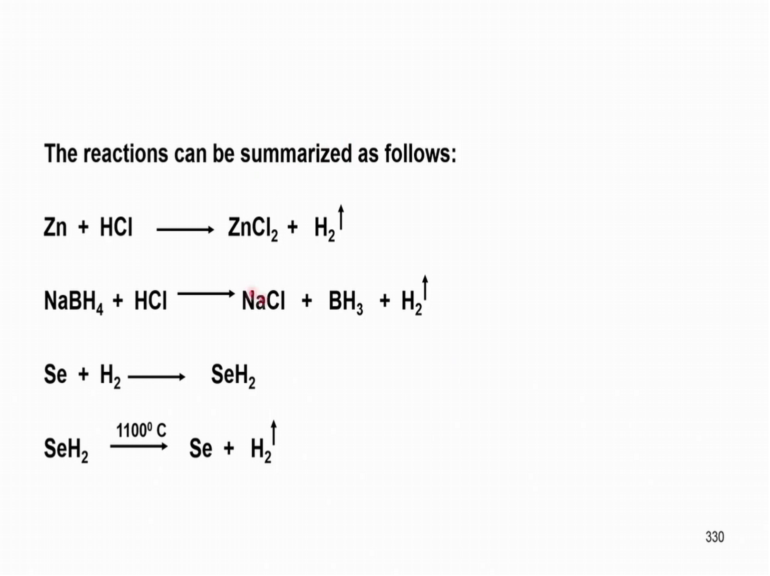

The reactions can be summarized as follows:

$Zn + HCl \longrightarrow ZnCl_2 + H_2\uparrow$

$NaBH_4 + HCl \longrightarrow NaCl + BH_3 + H_2\uparrow$

$Se + H_2 \longrightarrow SeH_2$

$SeH_2 \xrightarrow{1100^0\ C} Se + H_2\uparrow$

So, I have given you the reaction the of Zinc Hydrochloride as well as Sodium Borohydride. In both cases, there is nascent hydrogen generated. So, this nascent hydrogen will react with selenium, tellurium, bismuth, arsenic, antimony, lead, mercury etcetera, all those germanium also.

So, these six elements form hydrides just like SeH2, selenium hydride, tellurium hydride, bismuth hydride, lead hydride etcetera and once into the flame it gets decomposed giving you selenium and hydrogen. So, this selenium will undergo an oxidation reduction process and then, forming free atoms and the free atoms are measured in the absorbance.

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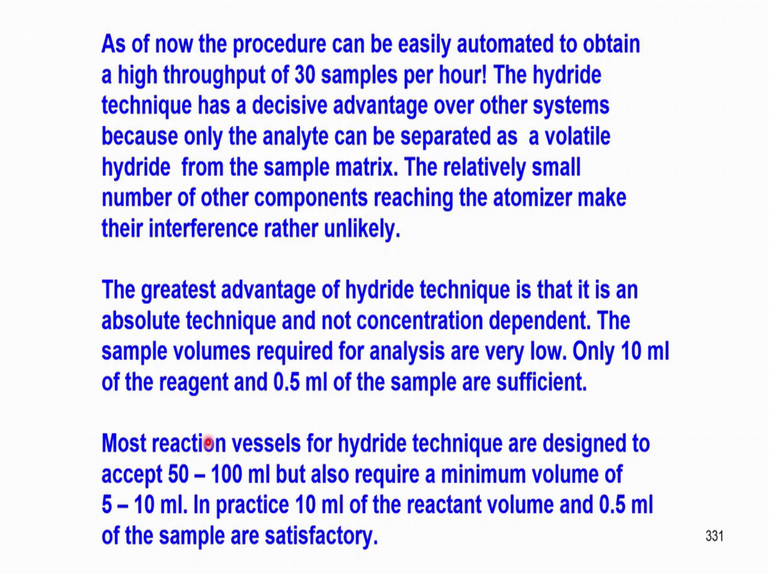

As of now the procedure can be easily automated to obtain a high throughput of 30 samples per hour! The hydride technique has a decisive advantage over other systems because only the analyte can be separated as a volatile hydride from the sample matrix. The relatively small number of other components reaching the atomizer make their interference rather unlikely.

The greatest advantage of hydride technique is that it is an absolute technique and not concentration dependent. The sample volumes required for analysis are very low. Only 10 ml of the reagent and 0.5 ml of the sample are sufficient.

Most reaction vessels for hydride technique are designed to accept 50 – 100 ml but also require a minimum volume of 5 – 10 ml. In practice 10 ml of the reactant volume and 0.5 ml of the sample are satisfactory.

So, I have also told you that the most important part of it is you can use about 0.5 ml of the sample and you can dilute the sample 0.5 ml. Suppose you dilute it 1000 times, then what happens because it is an absolute technique, the detection limit will reach parts per million or parts per billion level. Even parts per trillion level instruments are nowadays available which makes it one of the most powerful technique for the determination of arsenic, antimony, selenium etcetera and these elements are the most toxic elements we have ever known and the requirement of chemical analysis is that sometimes we want to detect arsenic in the blood and then, selenium in the bouyan.

This thing sometimes selenium in the brain and all of these things and most of you must have heard that Napoleon Bonaparte was poisoned with arsenic. Even now we are trying to determine how much of arsenic is there in his hair. So, it does not go away. So, absolute detection limits of 0.5 ppt are possible using hydride generation technique. That is why I am teaching you this thing and the beauty is you can have a throughput of 30 samples per hour. That means, you can have any number of samples and then, to keep on doing the analysis very fast, we are discussing about the interference, the mechanism.

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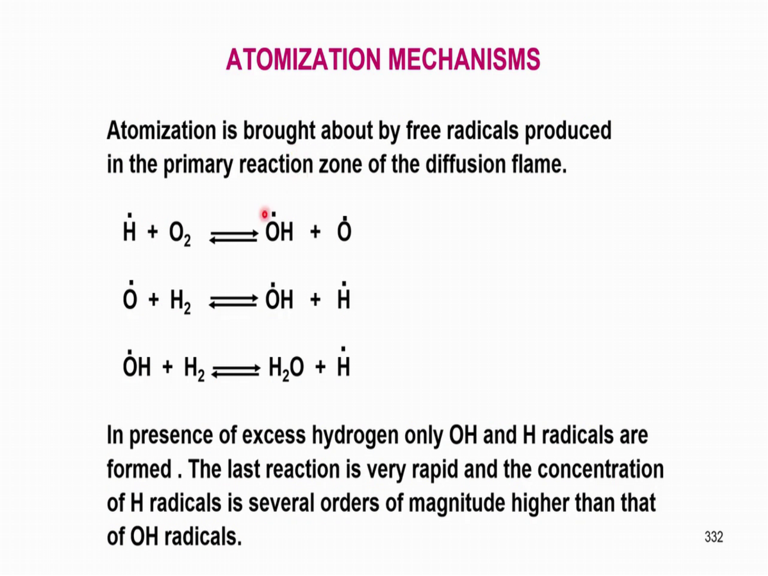

ATOMIZATION MECHANISMS

Atomization is brought about by free radicals produced in the primary reaction zone of the diffusion flame.

$$\dot{H} + O_2 \rightleftharpoons \dot{O}H + \dot{O}$$

$$\dot{O} + H_2 \rightleftharpoons \dot{O}H + \dot{H}$$

$$\dot{O}H + H_2 \rightleftharpoons H_2O + \dot{H}$$

In presence of excess hydrogen only OH and H radicals are formed . The last reaction is very rapid and the concentration of H radicals is several orders of magnitude higher than that of OH radicals.

We had discussed that it is the generation of hydride radial and this recombination reaction of selenium.

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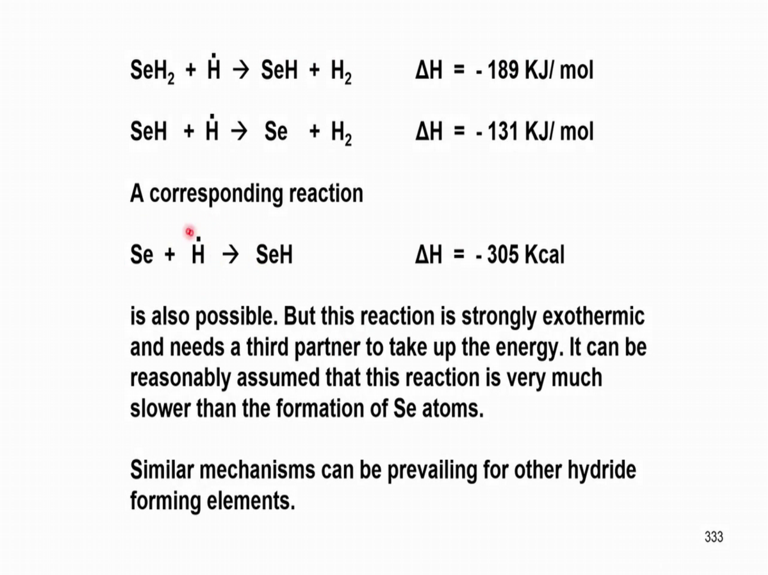

$SeH_2 + \dot{H} \rightarrow SeH + H_2$ $\Delta H = -189$ KJ/ mol

$SeH + \dot{H} \rightarrow Se + H_2$ $\Delta H = -131$ KJ/ mol

A corresponding reaction

$Se + \dot{H} \rightarrow SeH$ $\Delta H = -305$ Kcal

is also possible. But this reaction is strongly exothermic and needs a third partner to take up the energy. It can be reasonably assumed that this reaction is very much slower than the formation of Se atoms.

Similar mechanisms can be prevailing for other hydride forming elements.

Hydride even though it is minus 3.5 kilo calories, thermodynamically it does not go through because it requires a third party according to thermal kinetic principles, ok.

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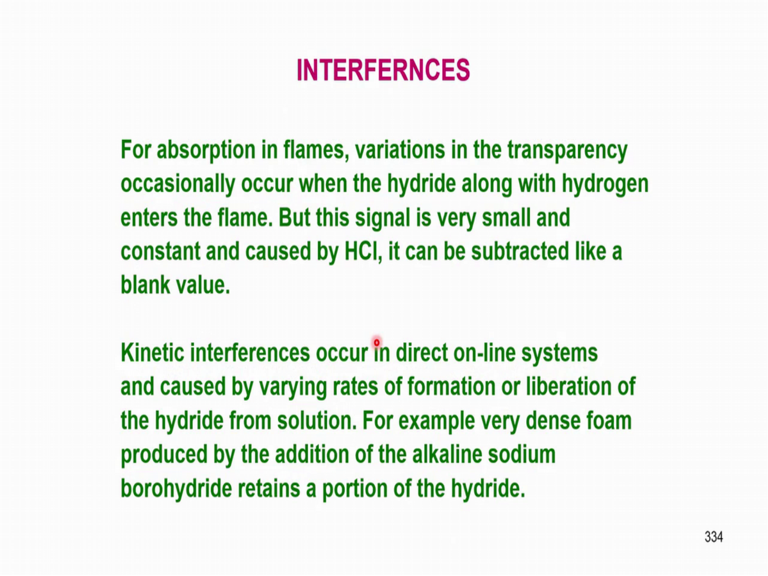

INTERFERNCES

For absorption in flames, variations in the transparency occasionally occur when the hydride along with hydrogen enters the flame. But this signal is very small and constant and caused by HCl, it can be subtracted like a blank value.

Kinetic interferences occur in direct on-line systems and caused by varying rates of formation or liberation of the hydride from solution. For example very dense foam produced by the addition of the alkaline sodium borohydride retains a portion of the hydride.

We had discussed interferences. The interferences mostly arise from kinetic problems that is carrying out the reaction and taking it into the flame, ok.

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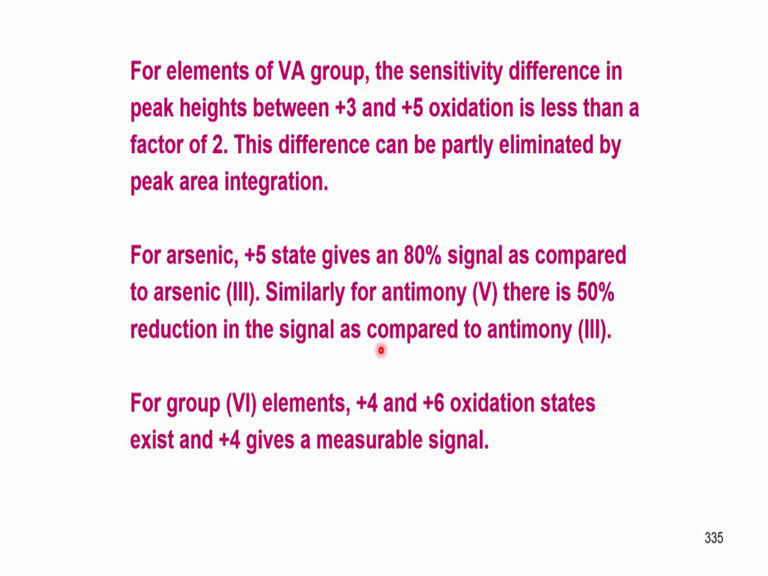

For elements of VA group, the sensitivity difference in peak heights between +3 and +5 oxidation is less than a factor of 2. This difference can be partly eliminated by peak area integration.

For arsenic, +5 state gives an 80% signal as compared to arsenic (III). Similarly for antimony (V) there is 50% reduction in the signal as compared to antimony (III).

For group (VI) elements, +4 and +6 oxidation states exist and +4 gives a measurable signal.

So, it is possible for us to estimate whether an element is in plus 5 state or plus 3 state because plus 5 state suppose I have taken one sample, oxydized everything to plus 5 state. I have all the reaction and then, reduce it and then, have plus three state. What is the difference between that two? That gives me spaciation where arsenic is plus 5 and arsenic is plus 3. So, plus 5 is more dangerous than plus 3. Like that chemical speciation is something very important that has been achieved using this arsenic hydride generation, but for group six elements, it is not plus 5 and plus 3, but it is plus 4 and plus 6.

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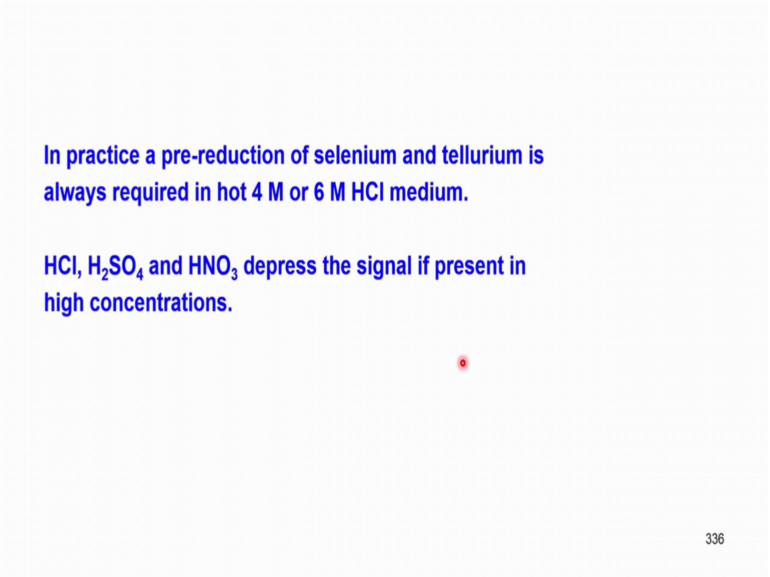

In practice a pre-reduction of selenium and tellurium is always required in hot 4 M or 6 M HCl medium.

HCl, H_2SO_4 and HNO_3 depress the signal if present in high concentrations.

So, that gives a measureable signal. We had discussed up to this level. This is only for your benefit again reproduction and then, in practice a pre reduction of selenium tellurium is always required in hot 4 molar or 6 molar Hcl. These kind of details nobody will teach you in the class or anywhere else. This you have to learn it from experience, but from my experience I am trying to give you a typical method how you should intuitively should go for the chemical analysis because especially selenium and tellurium are the most toxic elements we have ever known.

Many health episodes and many other things and toxic spills and other things have happened because of this selenium and selenium is one of the known contaminant along with lead. Also, normally if I have lot of acid HCl H2SO4 HNO3 etcetera, they depress the signal in high concentration. So, we have to be very careful that the concentration of the acid should be as low as possible whenever we want to do this atomic generation using hydride generation.

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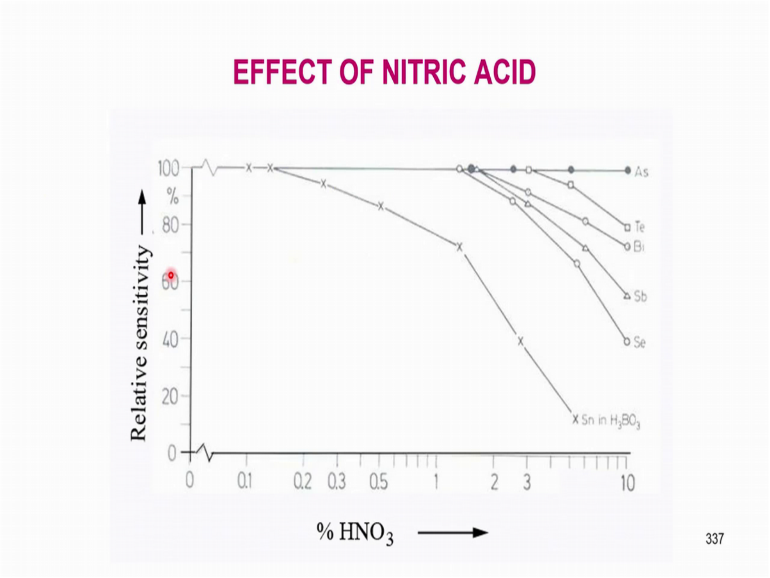

EFFECT OF NITRIC ACID

So, what is the effect of nitric acid? You can see here I have plotted relative sensitivity. Now, that is approximately 1 PPB, one part per billion chemical analysis of arsenic selenium etcetera. What we have done is, we have increased the acidity from 0.1.2.3.5123 and 10. It is normal 10 percent and not normal percent. So, if I have 0.1 percent of the nitric acid, the nitric acid signal is somewhere here almost 100 percent. That means, acid does not have much effect on the signal.

Now, suppose I increase it to 0.3, where do I end up? I end up about 92 to 93 percent. Increase the acids till further 0.5 percent. I have about 80 percent. Increase it till around 1. We have about 70 percent and increase it further for 10 to about 4 5. Normal we can see that signal is hardly less than 10 percent. So, this shows you the effect of acid in the sample. So, whenever you collect a sample for arsenic analysis, what you should be doing is, you must find out what is the acidity in that you may perform a small titration and find out what is that and then, you try to decrease the acidity to fit back into 0.1 normal or 0.2 normal, where the signal will not be affected.

Same thing is true with selenium because selenium is slightly more acid tolerant because upto 1-1.5 percent, you can see that I have drawn a logs scale here in percentage NHO3, where this is relative sensitivity. It is in transmittance with selenium upto almost upto 1 percent. I do not have a problem, but the moment the acid percentage increases in the sample, it is decreasing to about 80 percent, no around 90 percent. 2.5 in the acid increase the acid.

Again there will be problem. So, this is all part of my own research which I had conducted earlier on atomic absorption. So, this data is fresh from my stock rather than from a textbook. Same thing is true. Similarly, we had done all this antimony and you know about 0.2 percent in general you can say that above 2 percent, there should not be more acid, but suppose more acid is there, then what happens is the hydride generation will be more.

So, the formation of this hydride, this metal hydride is more, but the signal will decrease say it is a compromise. You have to organize between these elements for arsenic tellurium say arsenic, you can see here its absolutely no problem up to 10 percent acid also. That is one. Why would do this acid this effect of acid because we take a sample, dissolve it in acid. 99 percent of the chemical analysis we do dissolve it in acid. That is why we should be worried about the acid content in that hydride generation as similarly. Quite often we use sulphuric acid also for dissolution. This is the effect in sulphuric acid.

For example, look at tin where it comes by about 1 percent tin is gone sample analysis signal. This is approximately only 20 percent antimony is slightly more tolerant like that; you can study all this reaction, arsenic etcetera.

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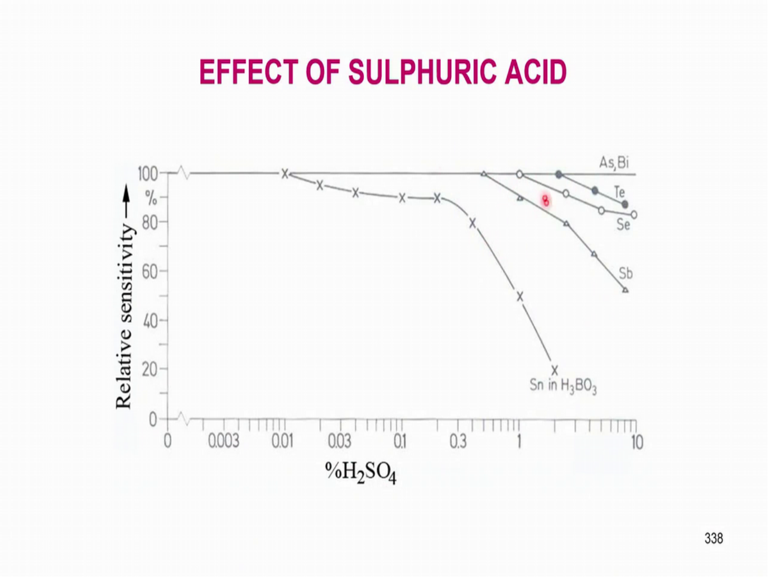

EFFECT OF SULPHURIC ACID

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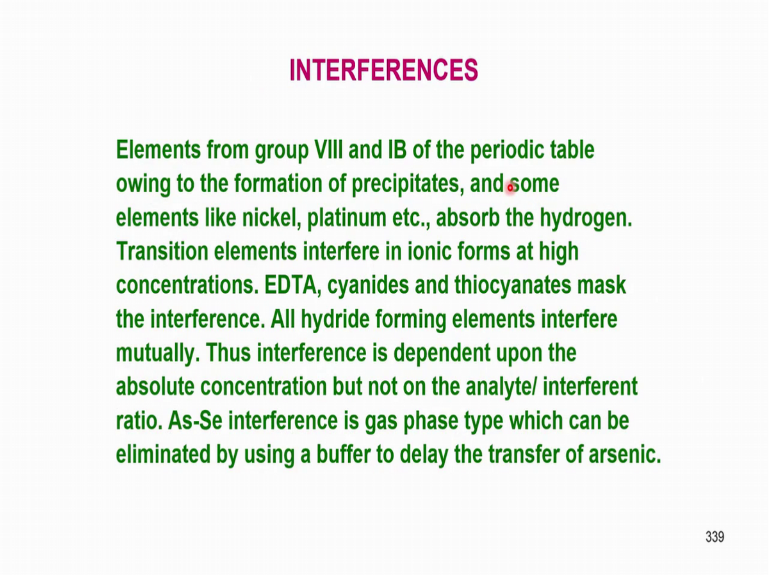

INTERFERENCES

Elements from group VIII and IB of the periodic table owing to the formation of precipitates, and some elements like nickel, platinum etc., absorb the hydrogen. Transition elements interfere in ionic forms at high concentrations. EDTA, cyanides and thiocyanates mask the interference. All hydride forming elements interfere mutually. Thus interference is dependent upon the absolute concentration but not on the analyte/ interferent ratio. As-Se interference is gas phase type which can be eliminated by using a buffer to delay the transfer of arsenic.

Then, we have other interferences in hydride generation you see I have already told you so many times that atomic absorption is basically an interference free analysisSo, long as only the metal atoms are there, it is interference free, but interference can come from flame, it can come from precipitate, it can come from so many other spectral interferences are there, copper phased interferences are there, transport interferences. All these things do contribute some of amount of interference in the determination of almost all elements.

So, what happens is I try to gather some amount of information regarding the hydride generation interferences. So, sometimes precipitates form, for example nickel, platinum etcetera, they absorb hydrogen. They are all very well know hydrogen absorbents even in petrochemical reactants and we cannot use platinum as example, the moment we have platinum, you do not have hydride generation at all because it absorbs all the hydrogen and you will be wondering what happened to the hydrogen generation reaction. Sometimes transition elements interfere in the ionic forms.

So, EDTA, cyanide and thiocyanides, these things mask the interference. So, these are the techniques people use whenever there is certain amount of interference in the sample. So, all hydride forming elements basically they interfere naturally mutually also. So, if you are determining arsenic, then some amount of selenium, again there may be some amount of interference, but not much because it is element specific.

Whatever is the frequency coming from, only hollow cathode lamp if it matches the other elements, then there will be interference, otherwise not much. That is what makes the hydride generation atomic absorption a very beautiful technique capable of determination of parts per billion, parts per trillion. Quantitatively it is not. It is like finding a needle in a haystack, but not just one or two, but the total needles in the haystack. So, interference is dependent upon the absolute concentration, but not on the analyte or interference. So, arsenic selenium interference is a gas phase that we cannot do much. We just have to use a technique that is using a buffer.

What do we do is, we use a buffer to delay the arsenic relation and then, you do the selenium.

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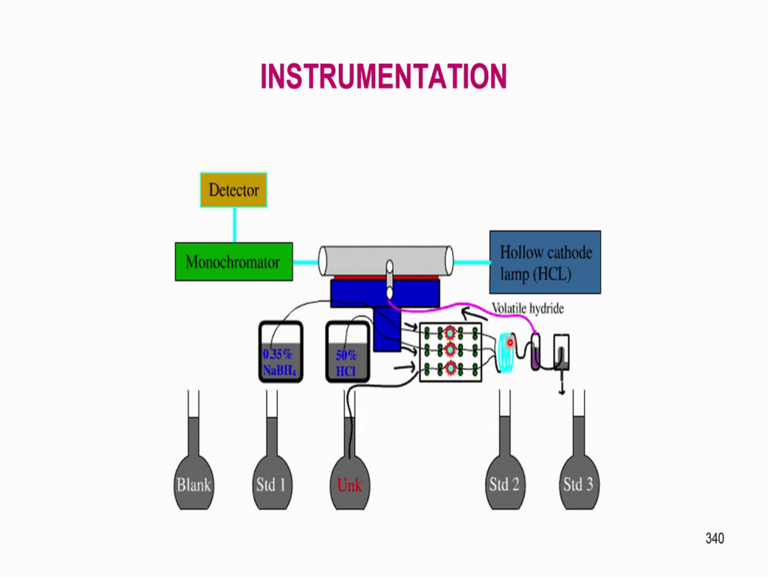

INSTRUMENTATION

Then, you do the arsenic and then, we can determine both of them in same sample and then, I want to show you what is the basic technique here. I have the monochromator. This green colour and radiation comes through this and here I have put a detector on the back side actually and then, this is my T tube through which the sample will come and this is the volatile hydride generator. Volatile hydride generator is here. I have a standard, blank standard 1 and then standard 2, standard 3 unknown. It is basically manifold. I can choose any of sample. I can introduce in the flame and this T tube.

So, the basic procedure basically remains the same. You introduce the blank generate hydride, take it through this manifold into this blank will b 0, then you introduce your standard one, then again take it through the same thing, manifold standard 2, standard 3, measure your unknown. It is as simple as that. Basically it is a relative technique. Any atomic absorption there is a technique where you can do absolute analysis, but that will come in a graphite formation that I will teach bit you later, ok.

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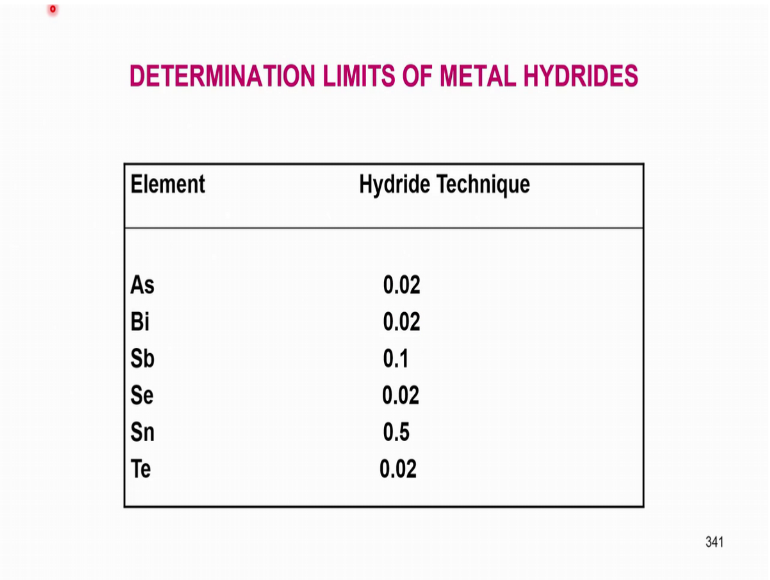

DETERMINATION LIMITS OF METAL HYDRIDES

Element	Hydride Technique
As	0.02
Bi	0.02
Sb	0.1
Se	0.02
Sn	0.5
Te	0.02

Now, here is the proof that how much sample can be determined using hydride technique. Arsenic is there 0.02 ppb parts per billion and bismuth 0.02, antimony is 0.1, selenium is 0.02 and tin is 0.5, tellurium is 0.03. I can increase the sample volume, increase the detection limit also because it becomes an absolute technique because it is taken out of the system. Whatever is the concentration in the sample, it does not make a difference because only the arsenic hydride will come out.

So, interference from other system will also be very less, but you have to remember that we can determine only hydride forming elements because most of the components which form hydrides decompose into metal and hydrogen. They do not decompose into ions, ok.

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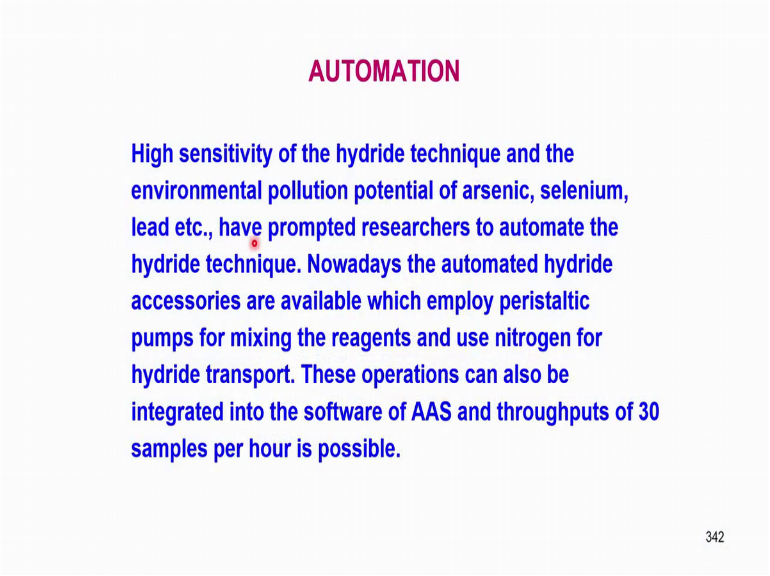

AUTOMATION

High sensitivity of the hydride technique and the environmental pollution potential of arsenic, selenium, lead etc., have prompted researchers to automate the hydride technique. Nowadays the automated hydride accessories are available which employ peristaltic pumps for mixing the reagents and use nitrogen for hydride transport. These operations can also be integrated into the software of AAS and throughputs of 30 samples per hour is possible.

So, this gives rise to a beautiful automation technique whereas, the high sensitivity and the environmental pollution, potential of arsenic, selenium, lead etcetera, people have been working on this automation. There is a river, all the time river is flowing and somebody is polluting all the time. You need to determine the pollutant all the time maybe 10 samples, 20 samples, 100 samples. Today Ganga is polluted and tomorrow also it is polluted. So, you want to know how much of arsenic is there, how much of selenium is there. Everybody somewhere something will be coming from. So, automation becomes a very important technique whenever you have to do repetitive analysis.

So, this kind of work requires peristaltic pumps. So, you just put the sample and it will keep on generating adding and then, taking it into the sample detector and sample holder. Automatically results will come that can be analyzed, evaluated, even statistically also. So, we need pumps for mixing the reagents and then, we need nitrogen for hydride transports. Sometimes what happens is the moment we add mixing reagents, we take it into the flames. So, I had to pass hydrogen nitrogen because nitrogen will fill the liquid and push out the hydride gas mechanically. It is is a mechanical process. So, there is a time lag between the addition of the sample and by the time it is taken to the sample. So, this time lag can be automated let say I add the sample. Now, after one minute let this pump, the nitrogen gas will switch on and push all the sample. So, it gives me all the way of control of all reactions for a number of sample analysis. That is the beauty. So, this operation can be integrated into the software of atomic absorption and through put of 30 ml is possible and there we end our discussion with respect to hydride generation atomic absorption.

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MERCURY COLD VAPOUR TECHNIQUE

If you need more information, I would refer you to some of the books which I had already given in the beginning of the course. For more information, of course there are many journals dedicated to atomic absorption spectrometry which can be consulted for more recent applications. Most of the applications of atomic absorption nowadays, they refer to sample treatment and increase in the sample specific. That means, whatever is the interference that has to be minimized make the analysis very specific.

So, another technique which I want to introduce to you is mercury cold vapour technique. This beautiful technique you must understand because it is not necessarily a part of atomic absorption which I am teaching you as a course, but it can be a part of atomic absorption as a modular attachment, ust like this hydride generation phase is here.

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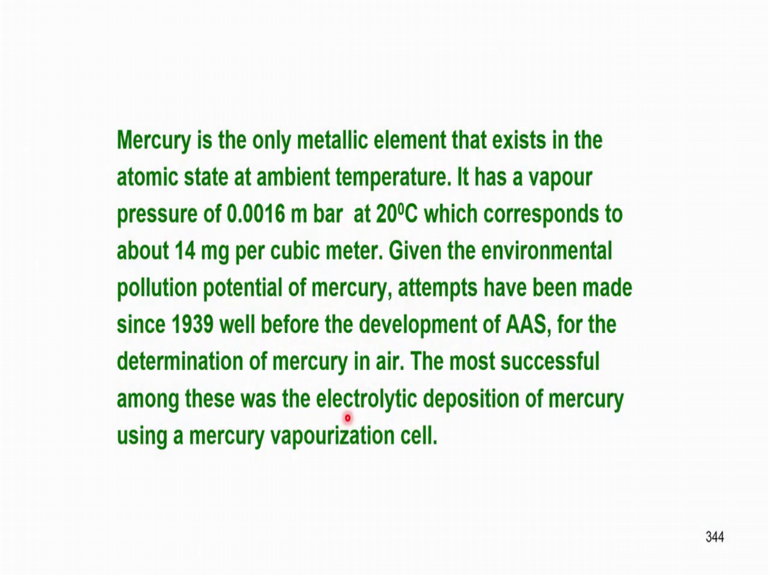

Mercury is the only metallic element that exists in the atomic state at ambient temperature. It has a vapour pressure of 0.0016 m bar at 20^0C which corresponds to about 14 mg per cubic meter. Given the environmental pollution potential of mercury, attempts have been made since 1939 well before the development of AAS, for the determination of mercury in air. The most successful among these was the electrolytic deposition of mercury using a mercury vapourization cell.

So, what happens here is mercury is the only metallic element that exists in the atomic state at ambient temperature. Still certain amount of mercury here, it will be there in the air and mercury is very toxic. It is very well known because mercury since 1955, ever since that Minimata disease in Japan where mercury containing affluence used to enter the sea, fish used to absorb them through their gills and then, people used to eat the fish because I think Japanese must be very happy to eat fish. They all like it just like our Bengali brothers and the problem was mercury created lot of health problems there.

So, the factory making benzaldehyde used to let out mercury because they used mercury as a catalyst, but this disease was identified as Minamata bay because it occurred in Minamata. Still earlier during medieval times, people used to wear big hats in Europe. The hats used to contain feathers and these feathers people, the hat makers used to fix it with mercury paste. They used to get affected and mercury has got a neurological effect on the brain. So, they used to call it Mad Hatters disease. Over a period of time some of the hat makers used to go mad.

So, it used to be called Mad Hatters disease, but the world concentration on mercury toxicity happened because of Minamata bay disease because earlier at that time during medieval times, then people might not have bothered about the toxicity where it came from etcetera because many of the alchemist used to work in very high polluted atmospheres. Even Marie Curie used to work in radioactive laboratories where pitch blends etcetera, where she died of cancer. So, that time awareness was not much.

So, coming back to this atomic absorption mercury, it has a vapour pressure of about 0.0016 milli bar at 20 degrees which corresponds to 14 milligram per cubic meter. So, that means, nowadays the standard is about 0.001 milligram per cubic meter. That is the standard we are suppose to breathe, but normal spilling in the laboratory gives you 14 milligrams. So, given the environmental pollution potential, attempts have been made since 1939, well before the development of AAS for the determination of the mercury.

In fact, the determination of the mercury was achieved upto 0.13 ppm in 1913 itself by the same vapour technique. So, the most successful among these was electrolytic deposition of mercury using a mercury vaporization cell. What do we do is take out mercury from a given sample, put it on a metal. We know that mercury forms number of amalgams with any metal. What they did, what they take out from a given sample to release mercury as an element and then, the mercury vapour will be carried out into a tube on which it will be connected on which it will be contacting at metal place. So, mercury amalgam will form. So, the beauty of mercury amalgam is to decompose mercury. Any amalgam you heat, it will release mercury.

So, technique of analysis what happens is, you take the mercury, put it on a metal, heat it, release the mercury, take it to atomic absorption because we already have the mercury in the gaseous phase. Mercury atoms are already there. So, the determination of mercury was one of the most successful in quite early days of atomic absorption.

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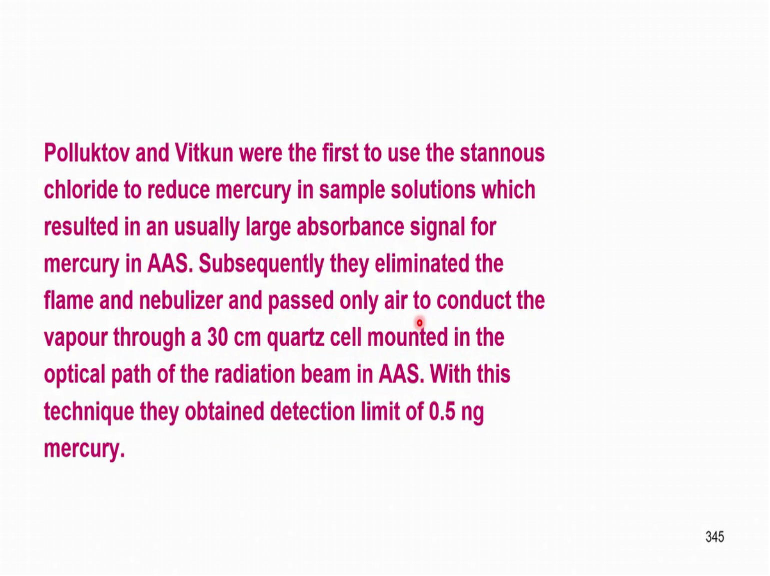

Polluktov and Vitkun were the first to use the stannous chloride to reduce mercury in sample solutions which resulted in an usually large absorbance signal for mercury in AAS. Subsequently they eliminated the flame and nebulizer and passed only air to conduct the vapour through a 30 cm quartz cell mounted in the optical path of the radiation beam in AAS. With this technique they obtained detection limit of 0.5 ng mercury.

So, Polluktov and Vitkun were the first to use the stannous chloride to reduce mercury in sample solutions which resulted in unusually large absorbance signal for mercury in AAS.

Subsequently, they eliminated the flame and nebulizer, both of them. They eliminated and passed only air to conduct the vapour through a 30 centimetre quartz cell mounted in the optical path of the radiation beam. That means, instead of the flame, they put a 30 centimetre quartz cell in which the mercury was carried out carried in. So, with this technique they obtained a detection limit of 0.5 nanogram per mercury.

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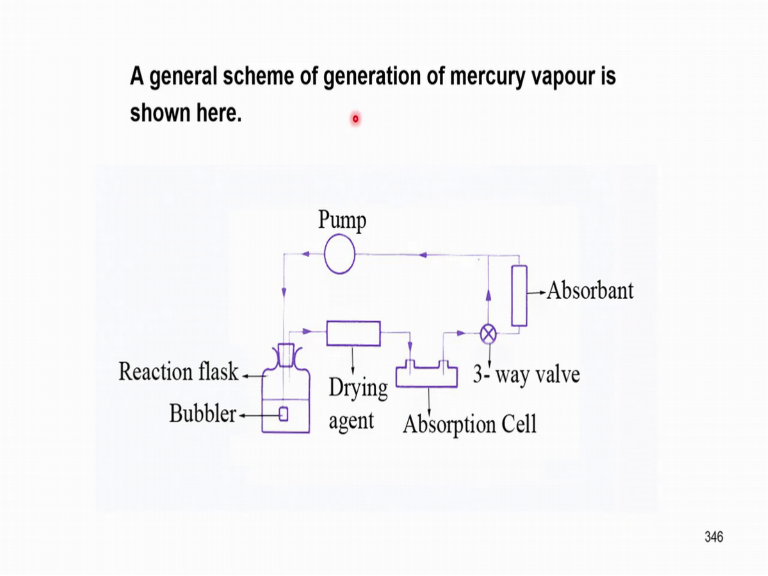

A general scheme of generation of mercury vapour is shown here.

So, a general scheme of generation of mercury vapour is shown here. What do we have here? We have a sample flask containing, the sample I have a bubbler here and then, I have a pump, then this is the three way valve, then absorbent and then, sample comes here. I just bubble the sample and then, take out the mercury vapour through the drying tube into the atomic absorption cell and measure the absorbance like this and this goes out, mercury goes out and then, the requirement is sometimes we need the drying agent. It is a very important aspect of determining mercury.

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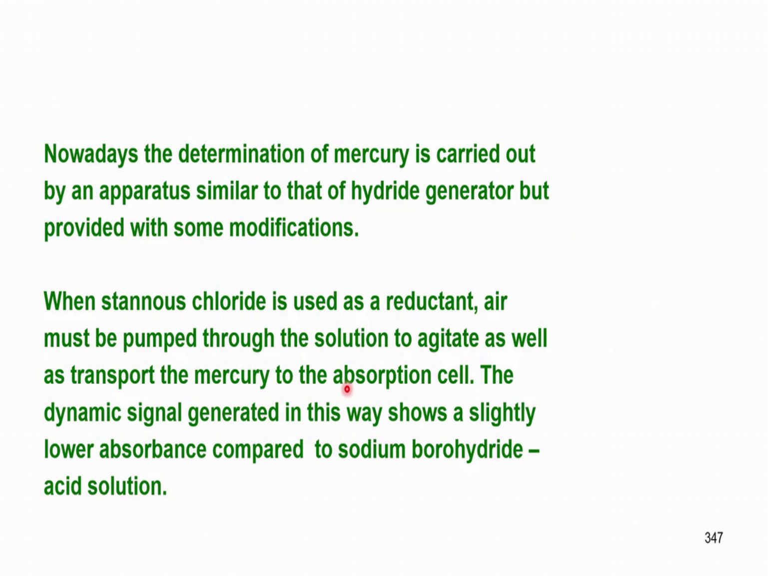

Nowadays the determination of mercury is carried out by an apparatus similar to that of hydride generator but provided with some modifications.

When stannous chloride is used as a reductant, air must be pumped through the solution to agitate as well as transport the mercury to the absorption cell. The dynamic signal generated in this way shows a slightly lower absorbance compared to sodium borohydride – acid solution.

So, nowadays the determination of mercury is carried out by an apparatus similar to that of hydride generator, but provided with some modifications because stannous chloride is used as a reductant. So, air must be pumped through the solution to agitate as well as transport the mercury to the absorption cell. The dynamic signal generated in this way shows a slightly lower absorbance compared to sodium borohydride acid solution. So, you can use sodium borohydride acid or stannous chloride and HCl both. We have got the capability to reduce mercury ions into atoms.

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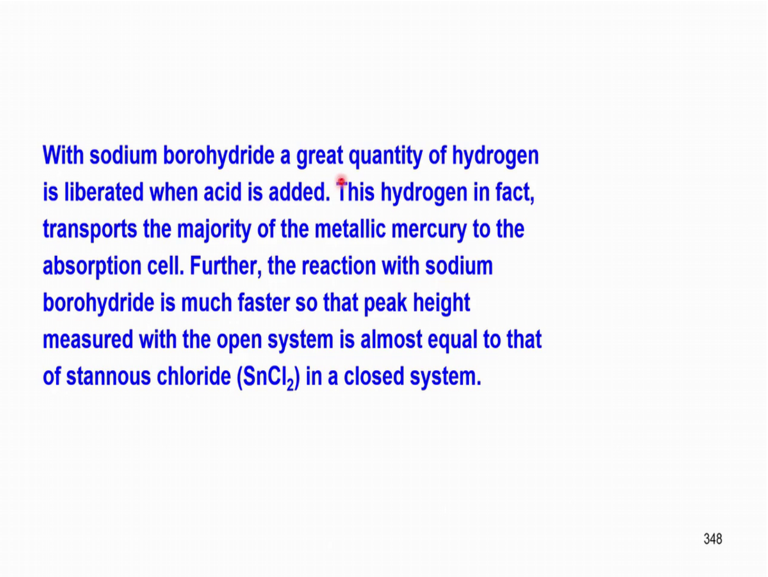

With sodium borohydride a great quantity of hydrogen is liberated when acid is added. This hydrogen in fact, transports the majority of the metallic mercury to the absorption cell. Further, the reaction with sodium borohydride is much faster so that peak height measured with the open system is almost equal to that of stannous chloride ($SnCl_2$) in a closed system.

So, sodium borohydride, a great quantity of hydrogen is liberated when acid is added to this hydrogen. In fact, it transports the majority of the metallic mercury into the absorption cell. So, it is helpful. Further the reaction with sodium borohydride is much faster, so that the peak height is measured with the open system and it is almost equal to that of stannous chloride in a closed system. That means, you can use peak height for measurement. Whether you use sodium borohydride or stannous chloride, only difference is with sodium borohydride, it is a much faster reaction than the stannous chloride.

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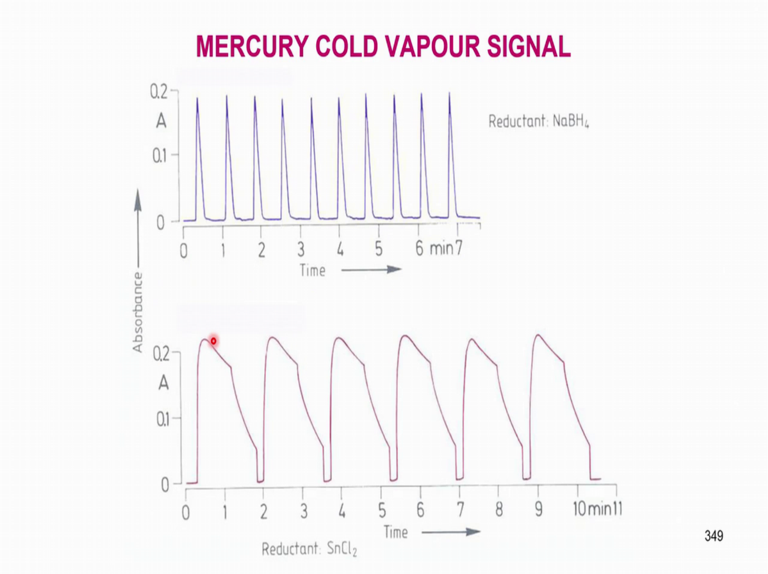

MERCURY COLD VAPOUR SIGNAL

Now, mercury cold vapour signal is like this sometimes you have to make automated signal with sodium borohydride. You can see that sample analysis here the reaction is so fast and everytime you have a sample, the signal is the same sample I am injecting.

So, the peak is very uniformed. So, the peak area also seems to be uniformed, first peak, second peak, third peak, fourth peak etcetera and all of them seem to be uniformed. That means, consistency of mercury determination is very good in sodium borohydride whereas, with stannous chloride, you can see the peak is like this I give a gap, take one more signal comes out like this. So, in this case peak area measurement of peak area makes more sense than peak height like this. So, quite often the reproducibility is very important with respect to peak height.

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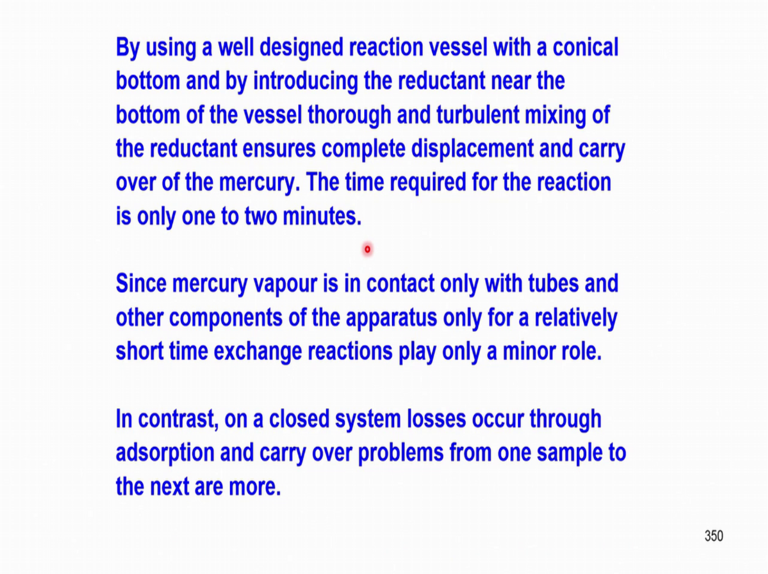

By using a well designed reaction vessel with a conical bottom and by introducing the reductant near the bottom of the vessel thorough and turbulent mixing of the reductant ensures complete displacement and carry over of the mercury. The time required for the reaction is only one to two minutes.

Since mercury vapour is in contact only with tubes and other components of the apparatus only for a relatively short time exchange reactions play only a minor role.

In contrast, on a closed system losses occur through adsorption and carry over problems from one sample to the next are more.

So, by using a well designed reaction vessel which I had shown you earlier with a conical bottom and introducing the reductant near the bottom of the vessel and thorough and turbulent mixing of the reductant, all these things ensure complete displacement and carry over of the mercury. The time required for further reaction is only 1 or 2 minutes. This is also very important in atomic absorption measurement or method. The time saving is most important. The whole measurement should be over within a few minutes, maximum 1 or 2 minutes or maybe a few seconds, maybe 30 seconds 40 seconds. That means, whenever you are doing integration, you have to do it for longer time because the signal will not come to baseline.

So, the mercury with sodium borohydride, the reduction has assumed more importance with respect to this stannous chloride reduction. Since mercury vapour is in contact with only the tubes and other components of apparatus only for a very short time, the exchange reaction play a major, a minor role. That means, the exchange of the metals absorption of on the pipes tubes etcetera, it is not much because it is in contact with the tubes and other things for a very short time.

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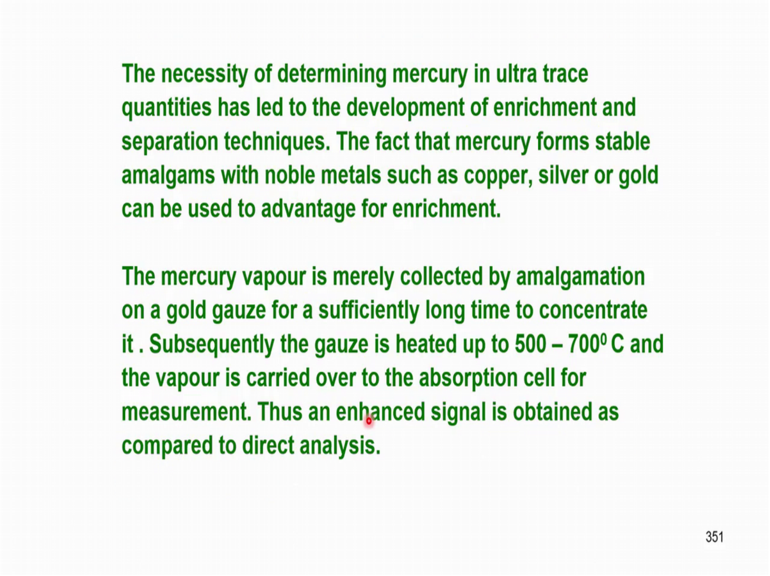

The necessity of determining mercury in ultra trace quantities has led to the development of enrichment and separation techniques. The fact that mercury forms stable amalgams with noble metals such as copper, silver or gold can be used to advantage for enrichment.

The mercury vapour is merely collected by amalgamation on a gold gauze for a sufficiently long time to concentrate it . Subsequently the gauze is heated up to 500 – 700^0 C and the vapour is carried over to the absorption cell for measurement. Thus an enhanced signal is obtained as compared to direct analysis.

So, in contrast on a closed system losses occur through absorption and carry over problems also from one sample to the next are more. What do you mean by carry over problems? The carry over problems means the signal is not totally free from the blank or from the previous sample.

See basically whenever we do a chemical analysis, first we introduce the blank and then, we introduce one first standard, then second standard, third standard etcetera and then, put the sample, take the absorbence and refer it. So, whenever we are doing a integration, what do we want to do is during integration, we give a time gap that is at our disposal. Suppose I give one minute. The sample has not yet come out totally. Some small portion is remaining that will get carried over to next sample. That means, the absorbance reading what you get would be different than what it should be.

So, first one will be less second, 1 will be more. Third one will be much more like that. Whole calibration will become biased. This should not happen. So, an enhanced signal is normally obtained and that is carried over the necessity of determining mercury in ultra trace quantities has led to the development of enrichment and separation techniques. The fact that mercury forms stable amalgam with noble metals, such as copper, silver, gold can be used to advantage for enrichment.

What I can do is suppose mercury is in parts per trillion level, ok. So, the first I take a small sample, add the sodium borohydride, take the mercury, put it take it to an electrical, take it to gold foil and absorb the amalgam and that is then I can take another sample, carry it to the same metal and then, mercury gets absorbed on that because mercury amalgam does not have a specific composition. So, it can keep on concentrating. So, I take 5 milliliter concentration to put it on the gold plates, small 1 centimeter or 0.5 square centimetre gold foil will do. On that I can take 100 samples. That means, then I can divide the total result by about 100. If I can divide it by 50, I can divide it by 50. That means, for each determination the actual concentration can be increased. There is no limit theoretically, but I can do it 3 times 4 times etcetera. That should not be a problem at all.

So, the mercury vapour is merely collected by amalgation on a gold gauze that is for a sufficiently long time to concentrate it. Subsequently the gauze is heated to 500 to 700 degrees and the vapour is carried over to the absorption cell for measurement. Once you heat the mercury electrical piece that is gold piece, all the mercury will get released and gold will become fresh, ready for another analysis and mercury is transported to the atomic absorption system. The beauty is you do not need a flame in atomic absorption. The mercury vapour, the gold vapour generates the mercury in the vapour flame, mercury atoms in the ground state and that is the bottom line.

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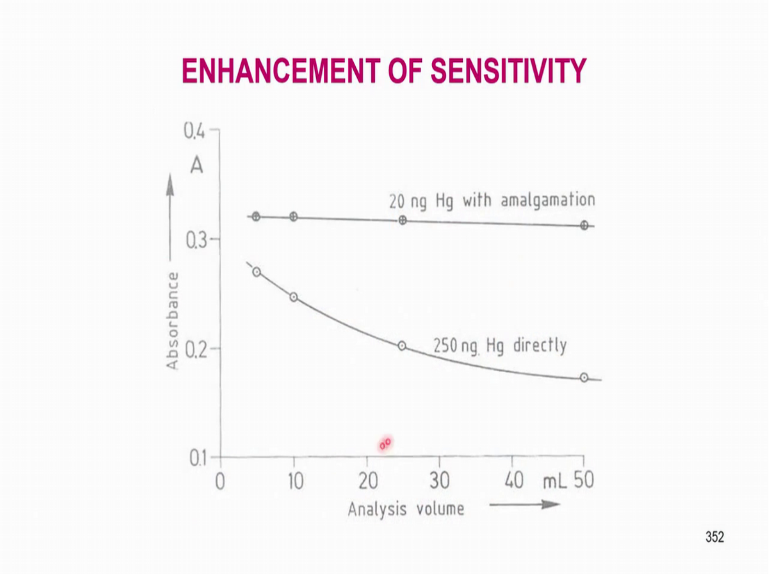

ENHANCEMENT OF SENSITIVITY

So, an enhanced signal can be obtained for multiple analysis for direct measurement. So, this is what happens with amalgamation. What am I doing here is, I am with 250 nanogram mercury. If I do analysis directly that is with tin etcetera, we can see here the signal will keep on going down. This is the analysis volume, this is effect of volume. If the sample is about 10ml, I have absorbance of about 2.5 and the same sample if I increase the volume to 25ml, then it is approximately 0.2.

Like that there will be a problem with this, but with amalgamation you see my signal whatever is the analysis volume, it does not matter 10 20 30 40, but my absorbance is 0.32432, 0.32 for 25ml and same 0.32 even for 50ml. So, that is the beauty of amalgamation, ok.

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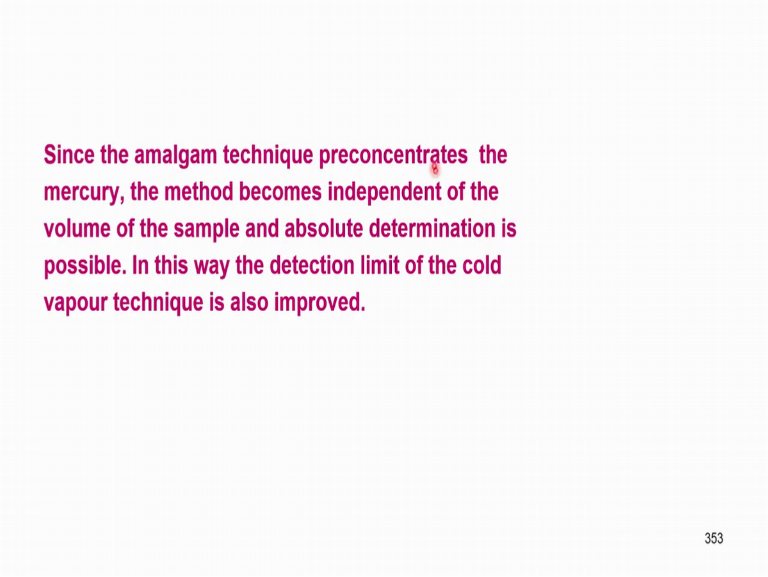

Since the amalgam technique preconcentrates the mercury, the method becomes independent of the volume of the sample and absolute determination is possible. In this way the detection limit of the cold vapour technique is also improved.

Since the amalgam technique pre-concentrates the mercury, the method becomes independent of the volume of the sample and absolute determination is possible. In this way the detection limit of the cold vapour mercury is also improved.

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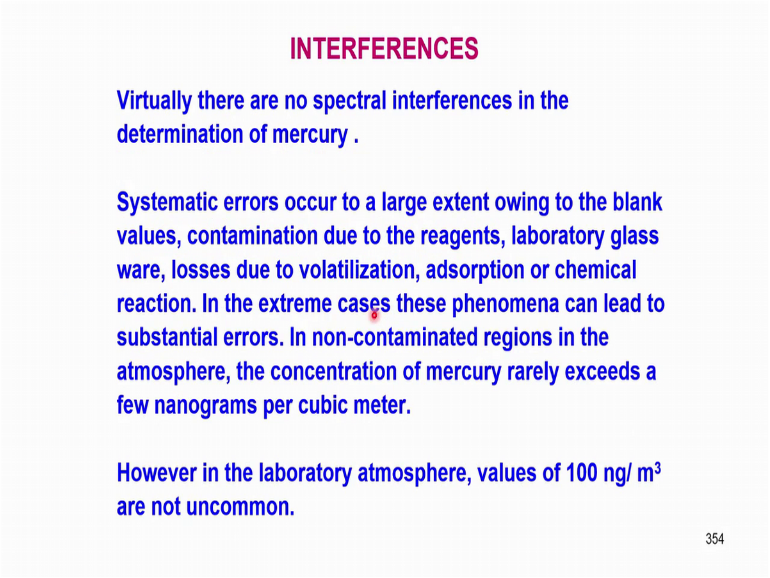

INTERFERENCES

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, we will continue our discussion on the interferences slightly in the next class. And then we will move on to flame emissions spectrometry.

Thank you very much.