# Modern Instrumental Methods of Analysis

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## Lecture No. # 24

## Atomic Absorption Spectrometry-8

## Hydride Generation AAS

Let us continue our discussion on the hydrogen generation technique.

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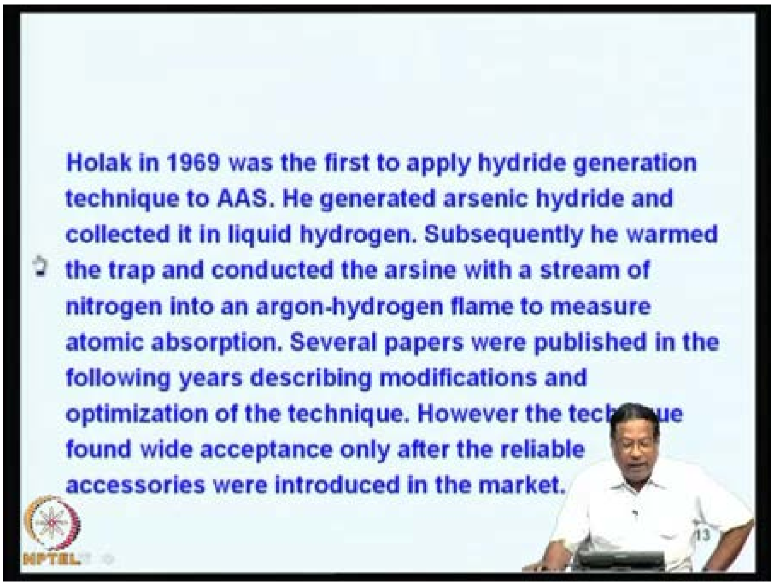

Holak in 1969 was the first to apply hydride generation technique to AAS. He generated arsenic hydride and collected it in liquid hydrogen. Subsequently he warmed the trap and conducted the arsine with a stream of nitrogen into an argon-hydrogen flame to measure atomic absorption. Several papers were published in the following years describing modifications and optimization of the technique. However the technique found wide acceptance only after the reliable accessories were introduced in the market.

Now, this slide I was showing you, that Holak was the first person to apply hydride generation technique to atomic absorption spectrometry; what he did was, he generated arsenic hydride and collected it in liquid hydrogen; subsequently, he warmed the trap and conducted the arsine with a stream of nitrogen into an argon-hydrogen flame to measure atomic absorption. Several papers were published in the following years describing modifications and optimization of this technique. However, the technique found wide acceptance only after the reliable accessories were introduced into the market for atomic absorption.

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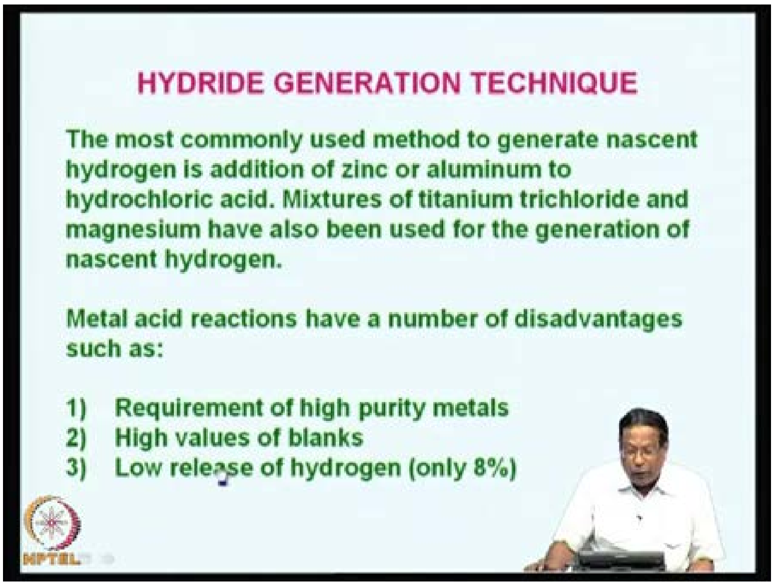

HYDRIDE GENERATION TECHNIQUE

The most commonly used method to generate nascent hydrogen is addition of zinc or aluminum to hydrochloric acid. Mixtures of titanium trichloride and magnesium have also been used for the generation of nascent hydrogen.

Metal acid reactions have a number of disadvantages such as:

1) Requirement of high purity metals
2) High values of blanks
3) Low release of hydrogen (only 8%)

So, the hydride generation technique is used most commonly by generating hydride in a given system. Suppose, you have a metal salt and then you add acid, it generates hydrogen. So, the most commonly used method was to take zinc or aluminum and add hydrochloric acid to that. Mixtures of titanium trichloride and magnesium, also, have been used for the generation of nascent hydrogen. Metal acid reactions, in general, have a number of disadvantages because, the requirement of high purity metals is one such, and the metal high values of blanks are obtained and low release of hydrogen; because it releases only about 8 percent of hydrogen.

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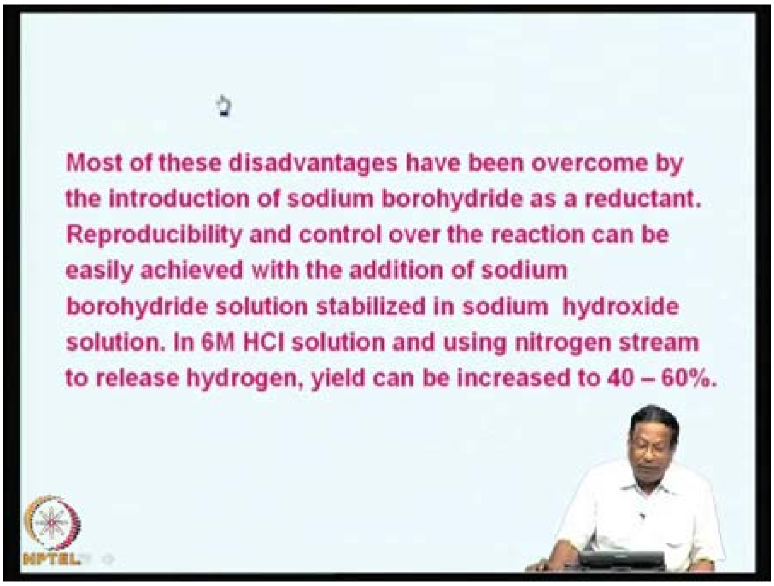

Most of these disadvantages have been overcome by the introduction of sodium borohydride as a reductant. Reproducibility and control over the reaction can be easily achieved with the addition of sodium borohydride solution stabilized in sodium hydroxide solution. In 6M HCl solution and using nitrogen stream to release hydrogen, yield can be increased to 40 – 60%.

So, the alternate methods where people were looking for, and most of the disadvantages what I had shown in the previous slide have been overcome by the introduction of sodium borohydride as a reluctant. This is a very, very significant advance in the generation of hydride, because this reaction afforded the reproducibility and control over the reaction, and sodium borohydride solution could be stabilized in sodium hydroxide solutions also. So, in 6 molar HCl solution and using you just pass nitrogen stream to release; hydrogen yield can be increased to 40 to 60 percent, compared to only 8 percent with metal acid reactions.

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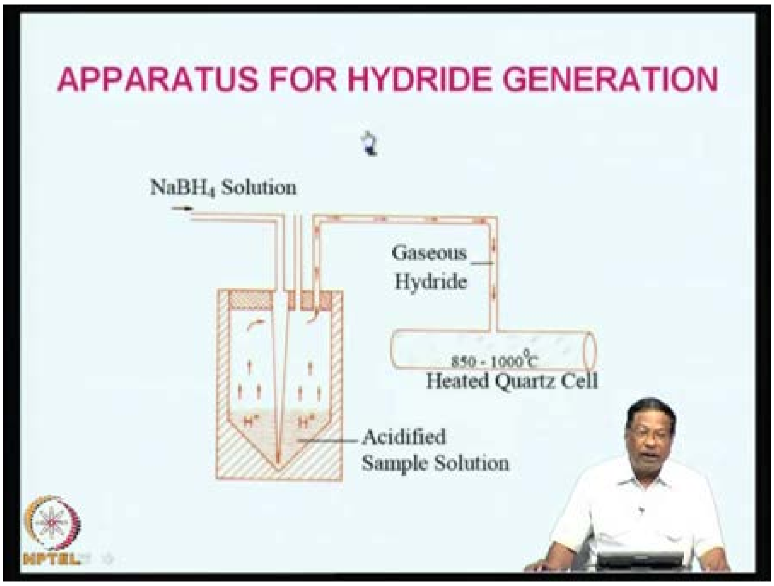

APPARATUS FOR HYDRIDE GENERATION

So, this is a very simple arrangement used for the generation of metal hydrides. Here, we have a sodium borohydride solution coming in a flask, and this is your sample solution; usually, it should be acidified; and the hydride metal hydride metal hydrogen gas will be generated, and metal hydride also would be mixed along with this; it will be held in this space and it will be taken to the heated quartz cell of the atomic absorption. You remember that we used a flame in a flame atomic absorption. What you do now is, you take a T-tube like this, and then connect the gas into this and introduce this T-tube, just into the flame, and you will get, at that flame temperature, quartz also will get heated to about 850 to 1000 degree centigrade, which is enough to destroy metal hydrides and release the metal atoms; and metal atoms, as usual, get excited and then ground state atoms would be produced.

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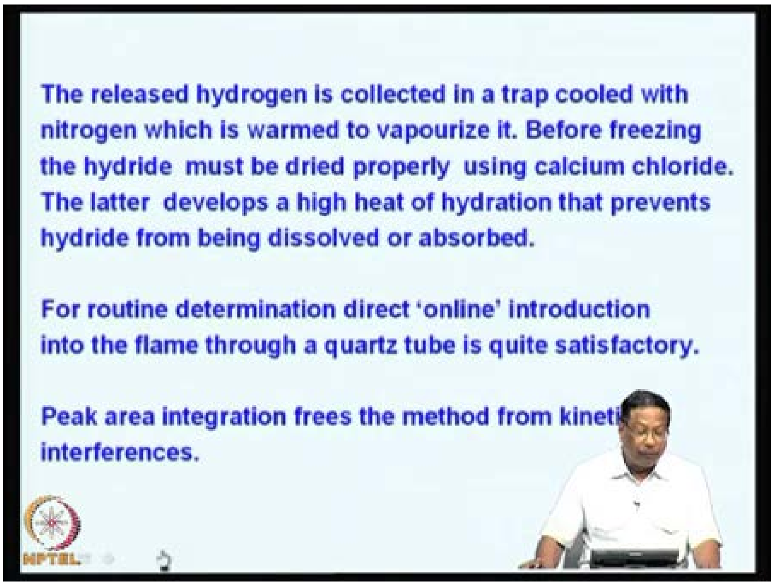

The released hydrogen is collected in a trap cooled with nitrogen which is warmed to vapourize it. Before freezing the hydride must be dried properly using calcium chloride. The latter develops a high heat of hydration that prevents hydride from being dissolved or absorbed.

For routine determination direct 'online' introduction into the flame through a quartz tube is quite satisfactory.

Peak area integration frees the method from kineti interferences.

So, the released hydrogen is collected in a trap cooled with nitrogen, which is warmed again to vaporize it. Before freezing, hydride must be dried properly; this is a precaution you should take. So, you must pass it through calcium chloride; so, what happens is, the calcium chloride develops a high heat of hydration by utilizing the moisture associated with the solution that prevents hydride from being dissolved or absorbed. So, for routine determination, direct online introduction into the flame through a quartz tube is quite satisfactory - routine determination; but, if you want to do special determination, wait for some time, may be collect a few samples and then analyze number of samples like that, then it is slightly difficult; but for routine determination, you need not even pass it through calcium chloride solution.

So, the peak area integration, as usual you will get a dynamic signal, and peak area integration usually frees the method from kinetic interferences. We call these things as kinetic interferences because, only 8 percent of hydride is hydrogen is released in one case; and in a sodium borohydride case, about 40 to 60 percent remaining is hydrogen, and all this, the reaction kinetics are different. So, the rate of release of hydride also would be different in each case. So, it is better to go for peak area integration, rather than peak height measurement in hydride generation technique.

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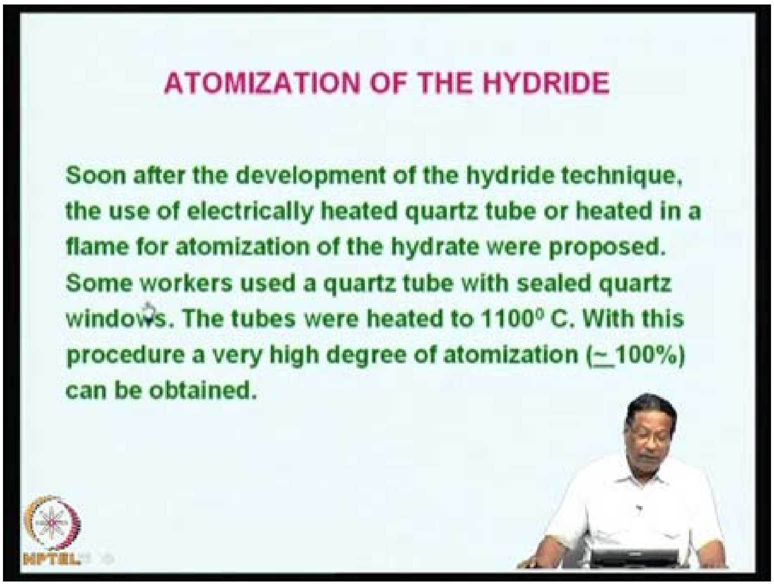

ATOMIZATION OF THE HYDRIDE

Soon after the development of the hydride technique, the use of electrically heated quartz tube or heated in a flame for atomization of the hydrate were proposed. Some workers used a quartz tube with sealed quartz windows. The tubes were heated to $1100^0$ C. With this procedure a very high degree of atomization ($\underset{\sim}{\phantom{x}}$100%) can be obtained.

So, how do we automate the hydride technique? So, it is a very simple system; soon after the development of the hydride technique, the use of electrically heated quartz tube was proposed. So, you just keep the hydride connected to, connected to, an electrically wired system which can be heated; and, the hydride, the moment it comes in contact with the tube into the flame, some it gets decomposed.

Some workers used a quartz tube with sealed quartz windows because this is important. Because, quartz windows are required to let the radiation from the hollow cathode lamp to pass through that; otherwise, if you use glass window, it could be a problem; because, some of the radiations in the U-V would be blocked, and you will not be able do the analysis for arsenic, selenium, tellurium etcetera; and, the tubes must be heated to about 1100 degree centigrade. With this procedure, a very high degree of atomization could be obtained; almost nearly 100 percent atomization.

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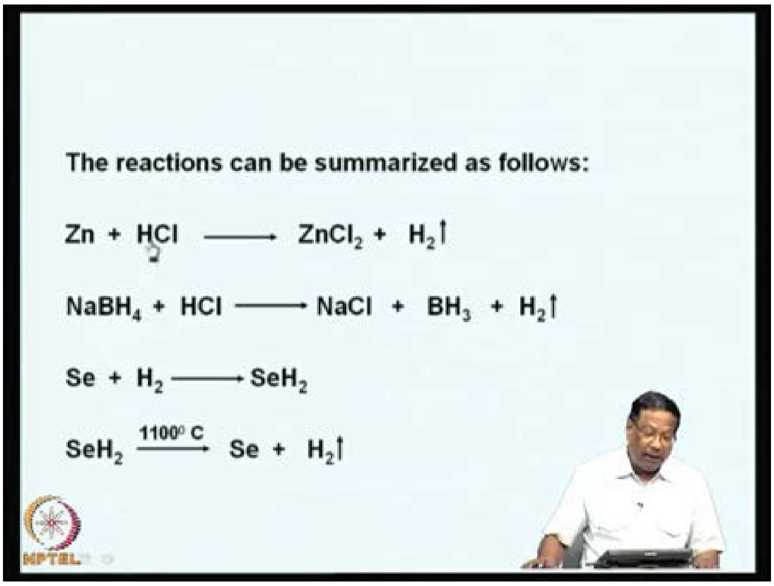

The reactions can be summarized as follows:

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

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

$Se + H_2 \longrightarrow SeH_2$

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

So, the hydride generation technique has become a very strong technique with respect to the analysis of arsenic, selenium, beryllium; no, sorry, arsenic, selenium, tellurium, germanium, antimony, lead, mercury etcetera. So, the reactions are very simple to understand. You have zinc; to this, you add hydrochloric acid, it produces zinc chloride, and hydrogen gas is released. So, similarly, if you take sodium borohydride, that is, NaBH 4, react it with HCl, you will get sodium chloride and boron hydride and hydrogen, all; and you should remember that both these hydrogens are nascent hydrogens and very reactive, highly reactive. So, this hydrogen would react with selenium to form selenium hydride SeH 2, and this would again decompose in the quartz tube at 1100 degree centigrade to give you selenium atoms and hydrogen gas. So, these are the basic reactions, you can write similar reactions for tellurium arsenic etcetera.

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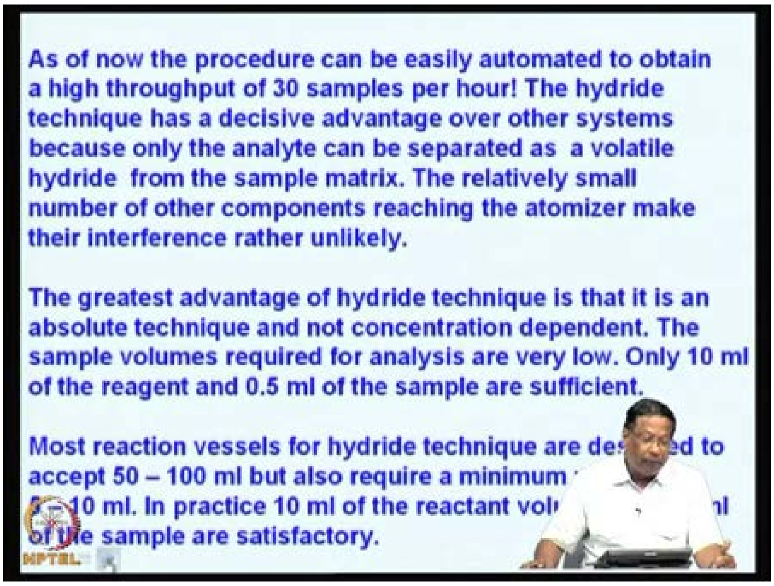

As of now the procedure can be easily automated to obtain a high throughput of 30 samples per hour! The hydride technique has a decisive advantage over other systems because only the analyte can be separated as a volatile hydride from the sample matrix. The relatively small number of other components 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 de[illegible]ed to accept 50 – 100 ml but also require a minimum [illegible] 5 – 10 ml. In practice 10 ml of the reactant vol[illegible] [illegible]ml of the sample are satisfactory.

So, you can, as of now, the procedure can be very easily automated to obtain high throughput of 30 samples per hour; that means, every 2 minutes, you can do one hydride generation. If you have enough number of samples, the hydride technique has a decisive advantage over other systems, because, only the analyte, only these element - hydride, etcetera. They get separated as volatile hydrides, all other metal ions present in the system would remain in solution, they will not react with the acid to form the hydride.

So, the relatively small number of other components reaching the atomizer will make the interference rather unlikely; that means you almost have a specific reaction for selenium, arsenic etcetera; most of the hydride forming elements. So, the greatest advantage of hydride technique is that, it is an absolute technique and not a concentration dependent technique. For example, you can have the sample in a 10 ml solution or you can have a sample in 25 ml or you can have 50 ml solution. So, the concentration of the element in the solution does not matter, because, when you add HCl and sodium borohydride, all the hydride forming element, whatever is the concentration, it will react with the hydrogen to produce hydride; so, it is not concentration dependent.

The sample volumes, therefore, required for analysis, are also very low, you can manage with only 10 ml of the reagent and 0.5 ml of the sample are more than enough to conduct a chemical analysis, and to get parts per billion, 10 raise to minus 12 grams parts per billion ppb, 10 raise to minus 9 and parts per trillion also it is possible to do the analysis, because you are simply separating all the hydride forming elements into gas, whatever is the volume of the your sample.

So, most of the reaction vessels for hydride technique are designed to accept about 50 to 100 ml of the sample solution, but they also require a minimum volume of about 5 to 10 ml; it is a practical difficulty. So, with 5 to 10 ml, you can should be able to analyze hydride. In practice, what we do is, 10 ml of the reactant volume and 0.5 ml of the sample are quite satisfactory. So, with such small samples, it is possible to determine selenium, arsenic etcetera. So, what happens to the atomization mechanism? It is very simple; atomization is brought about by free radicals produced in the primary reaction zone of the deficient flame; you remember, even in the case of atomic absorption, still you have a flame, but you are going to introduce a quartz tube, which is connected to hydride generator into the flame.

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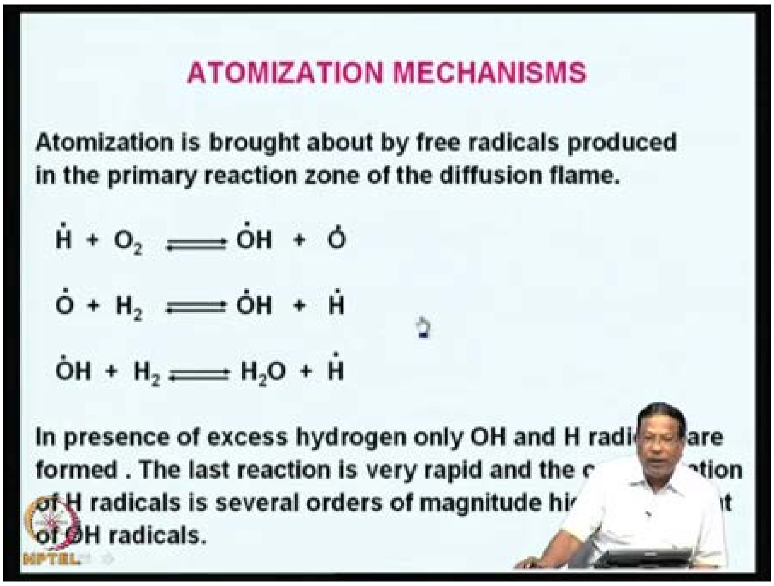

ATOMIZATION MECHANISMS

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 radi are formed . The last reaction is very rapid and the c ation of H radicals is several orders of magnitude hi t of OH radicals.

So, the reaction, reactions can be summarized like this. During atomization, we have hydride free radicals; they will react with oxygen to give you OH radicals and oxygen radicals. The oxygen radicals can combine with molecular hydrogen to give you OH radicals again and hydrogen radicals. So, OH radicals can combine with OH hydrogen molecule to form water and H plus. So, in general, most of the produced free radicals are OH oxygen and hydrogen. So, in presence of excess hydrogen, because, the basic reaction of, basic reaction of this hydride generation is hydrogen generation. So, only

OH and H radicals are formed; because hydrogen, the reaction equilibrium will be shifted to the right. So, you would have only H and O H radicals.

So, the last reaction, this one, OH plus H 2 going to H 2 O, and H plus is are is, it is very rapid reaction, and the concentration of H plus hydrogen radicals is several orders of magnitude higher than that of OH radicals; that means, the radical concentrations of H plus is about 10 raised to 4 times than that of OH radicals.

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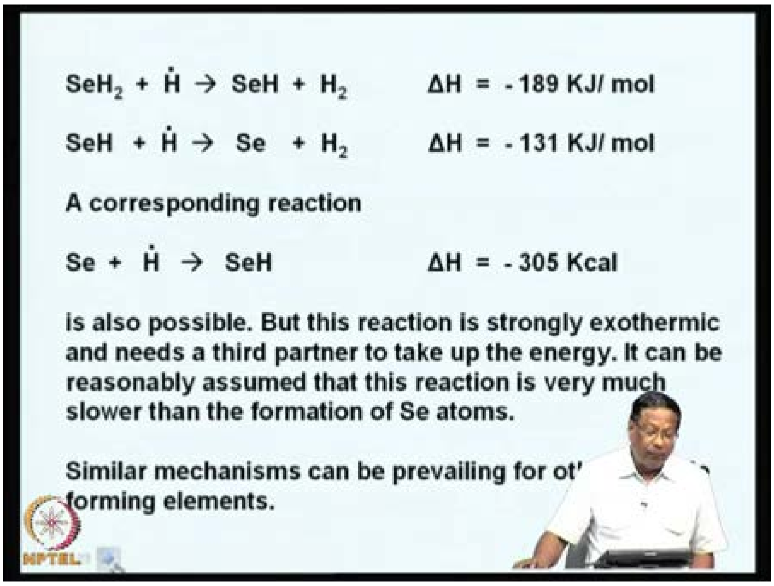

$SeH_2 + \dot{H} \rightarrow SeH + H_2$ $\Delta H = -189$ KJ/ mol

$SeH + \dot{H} \rightarrow Se + H_2$ $\Delta H = -131$ 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 ot' [illegible] forming elements.

So, now what happens? If H plus radicals are more in number, we should consider the reaction of selenium hydride with hydride radical. So, SeH 2 plus H hydrogen radical H dot, will give you SeH plus H 2, again hydrogen molecule is produced during the decomposition, and the enthalpy of this reaction is minus 180 kilo joules per mol; that means, it is a highly exothermic reaction. Similarly, this SeH, selenium hydride, can react with one more molecule, one more free radical of hydrogen, giving you selenium and hydrogen. So, for this reaction, delta H is minus 131 kilo joules per mol.

So, a corresponding reaction, that is, Se plus H dot, this also is possible; this selenium can react with one more H plus and producing SeH, selenium hydride again; for this reaction, delta H is minus 305 kilo calories; this is also possible, but this reaction is so strongly exothermic, it needs a third partner to take up the energy, Therefore, the probability of occurring this reaction is quite low, it can, it is slower also, because three molecules have to form, react in kinetics; they should, the atom, the molecules should come and hit each other to for this reaction to go; but the decomposition of SeH is much more simpler, because it is a two molecule reaction.

So, similar mechanisms can be prevailing for other hydrides also. We can write similar reactions, I want to give you the reactions of other hydride as an homework; other hydride elements, what type of reaction can occur? You can look up some of the text books, they are described there in.

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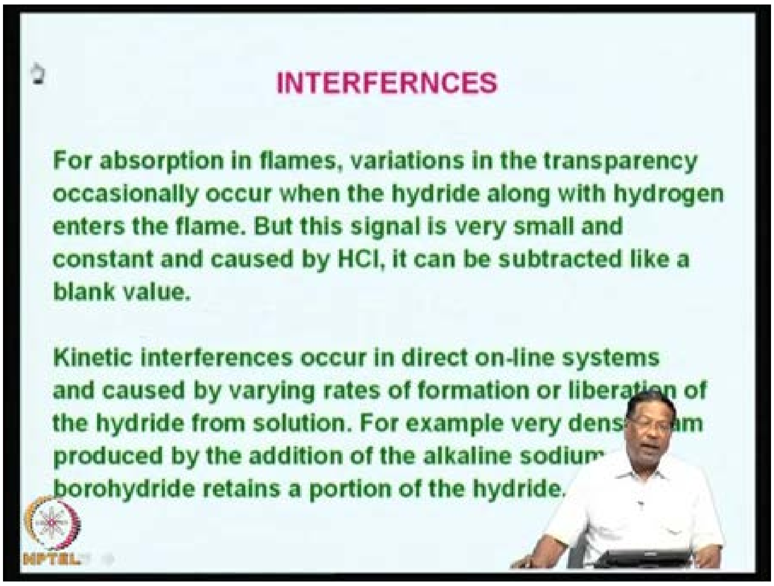

INTERFERNCES

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 dens am produced by the addition of the alkaline sodium borohydride retains a portion of the hydride.

Now, let us discuss about the interferences. So, when we say you can separate hydride from the most of the metrics elements, the variations in the interference of the other elements, it does not mean that the system is absolutely interference-free, because, there are possibilities that different various kinds of transport interferences can occur. For example, for absorption in the flames, variations in the transparency occasionally occur when hydride along with hydrogen enters the flame, but this signal is so small, and it is constant; it is caused by HCl, and it can be subtracted like a blank value. So, if you are able to, if you have a background character, this problem does not arise.

Sometimes, kinetic interferences occur in direct online systems, caused by varying rates of formation of the hydrides or liberation of the hydride from the solution, or from the decomposition of the metal hydrides, For example, very dense foam produced by the addition of alkaline sodium borohydride, that itself will retain lot of metal hydride. So, whenever you are carrying out a reaction, you have to take sodium borohydride, you have to add HCl, and there will be high speed reaction, producing lot of hydrogen, coming all the time; and then, there will be foam, and this foam itself will retain part of the metal hydride instead of letting it out of the system into the flame.

So, such a possibility exists, whenever you are using sodium borohydride; so, very dense foam is not very, is not desirable in the atomic absorption system, where you have to do online analysis. So, for elements of fifth a group, for example, the sensitivity difference in peak heights between plus 3 and plus 5, because, these elements can be present in different balance states also.

So, plus 3 and plus 5 oxidation, it is less than by a factor of 2; this difference can be primarily partly eliminated by peak area integration. Suppose, you have got only plus 3, then the signal will be slightly different; plus 5 signal will be slightly different; they do not occur at the same time. So, the peak will be broader and of irregular shape if you have the sample in both plus 3 and plus 5 states.

So, for arsenic, for example, plus 5 states, gives you 80 percent of the signal as compared to arsenic 3, third valence 3. So, similarly, for antimony, 550 percent reduction in the signal occurs as compared to antimony 3. So, this kind of valence change in the valance state in the sample, can cause you a little bit of trouble, if you want to make peak height as the measurement system. So, for group 6 elements, common oxidation states are plus 4 and plus 6, so, plus 4 gives a measurable signal, but plus 6 does not. Therefore, if you got any of the sample, containing plus 6 state, it is better to reduce them to plus 4, and then go for hydride generation.

So, this procedure of a reduction, gives you another tool in quantifying different valance states, thereby permitting you to give to do the speciation - how much of the sample is in the plus four state, how much of the sample is in the plus 6 state? Suppose, you do the reduction reaction in plus 6 state, the plus 4 state you will get two signals. Suppose, you reduce it to plus 4, the difference between the first signal and the second signal would give you... What is in the plus 6 state? It is a very simple logic, and this type of analysis can be done using hydride generation analysis. In practice, what we do is, we go for pre-reduction of selenium and tellurium, and we have to… It is always required in it, is pre-reduction must be done in hot 4 molar or 6 molar HCl medium.

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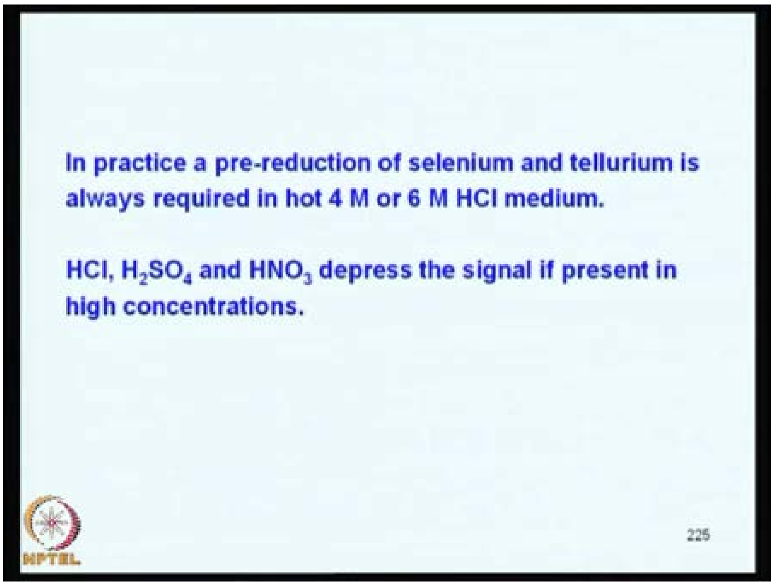

In practice a pre-reduction of selenium and tellurium is always required in hot 4 M or 6 M HCl medium.

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

Now, I would like you to understand that the HCL, H 2 SO 4 and nitric acid; all these things, if they are present in large quantities, they depress the signal; if present in high concentrations also, large quantities as well as concentration.

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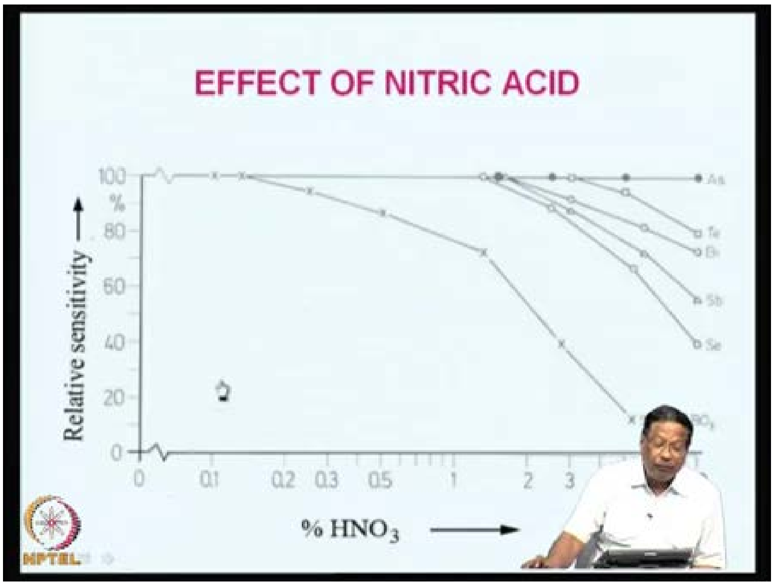
## EFFECT OF NITRIC ACID



For example, you can take a look at this figure. Now, this is the determination of tin in with NaBH 4. H 3 BO 3 is one of the products; here, you can see, I have plotted the percent of HNO 3 on the x-axis, and relative intensity on the y-axis. As the acid concentration increases from 0.1 up to 0.2, the signal is almost 100 percent, but suppose, you re-increase it to 0.3 percent HNO 3, there is a reduction in the signal. Similarly, around 0.5, there is about 80 percent reduction in the signal. If you increase it to still further acidities 1, 2, 3 percent, then the signal for tin almost comes down to 10 percent here.

So, you should always be very careful to check the acidity in your sample, before you proceed with hydride generation. Similarly, you can, this is for selenium; for selenium is more tolerant to nitric acid, because, almost up to 1 percent of nitric acid, there is no change in the signal, and after that, the reduction is rather rapid. Similarly, this one is for antimony, again up to 1 or 2 percent, there is no problem; and bismuth, almost up to 1.5 percent; and tellurium, you can do up to 3 percent of HNO 3. There is no problem; there would not be any attenuation of the signal, because of the acid concentration. So, arsenic, there is no difference even up to 10 percent HNO 3; you can always determine arsenic in presence of 10 percent HNO 3.

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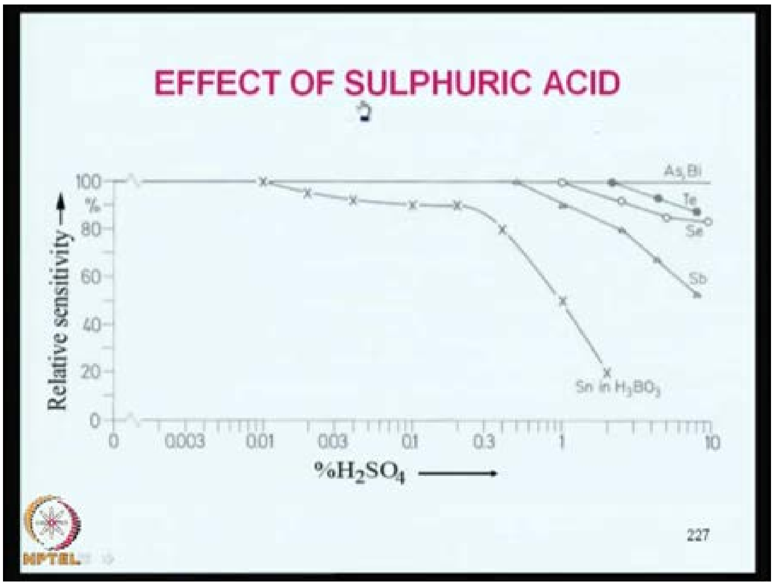

EFFECT OF SULPHURIC ACID

Now, take a look at this figure. This is the effect of sulphuric acid; again, I have done the same analysis. What I have done is, I have determined the signal in almost 003 percent H 2 SO 4, and I keep on increasing. You can see how the graph behaves; tin and then, this is antimony, this is selenium and tellurium, arsenic, bismuth etcetera. So, what you can draw? A lesson from this is, up to .01 percent nitric acid, tin is... But, all other things you can manage up to 0.3 percent higher. Acidity will always give you some amount of reduction in the signal; you can conclude this as interference also. So, this type of interference can be minimized by adjusting the acidity in such a way, that it is always less than 1 percent

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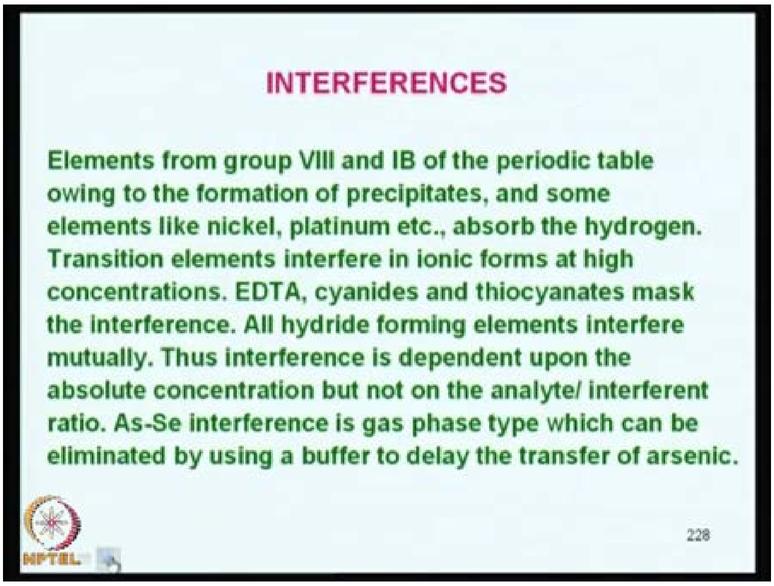

## INTERFERENCES

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.

Now, the interferences; we can continue the discussion, because, elements from group 3 and 1B of the periodic table, owing to the formation, they form precipitates; group 1B mercury, selenium, this silver etcetera, they form precipitates; and some elements like nickel, platinum etcetera, they can absorb hydrogen. So, the transport, there will be some amount of transport interference from such elements; transition elements interfere in ionic forms at high concentrations, then there could be some amount of EDTA cyanides and thiocyanates etcetera, which can mask the interference.

So, if some of these elements are there, like nickel, you can add EDTA cyanides or thiocyanates, cyanide-mask the reaction, and go ahead as usual with the determination of hydride. So, all hydride forming elements, what about their interference? So, it is expected that all hydride forming elements interfere mutually; thus, the interference is dependent upon the absolute concentration, but not on the analyte interferent ratio.

For example, in the determination of selenium, tellurium also would give you some amount of interference, but the measurement of selenium is always at a different wavelength, characteristic wavelength, and it can be converted into the interference, can be negligible, because the wavelength is different; but there is a certain amount of interference, for example, this arsenic, selenium interference is a gas phase type, which can be eliminated by using; you can add just a little bit of a buffer to delay the transfer of arsenic, and selenium can be determined as usual, first; and then, once the delay selenium is completed, other systems would be forming. You can have arsenic analysis; so, this can be done using a buffer. So, little chemical tricks, we always employ whenever we see some kind of interference.

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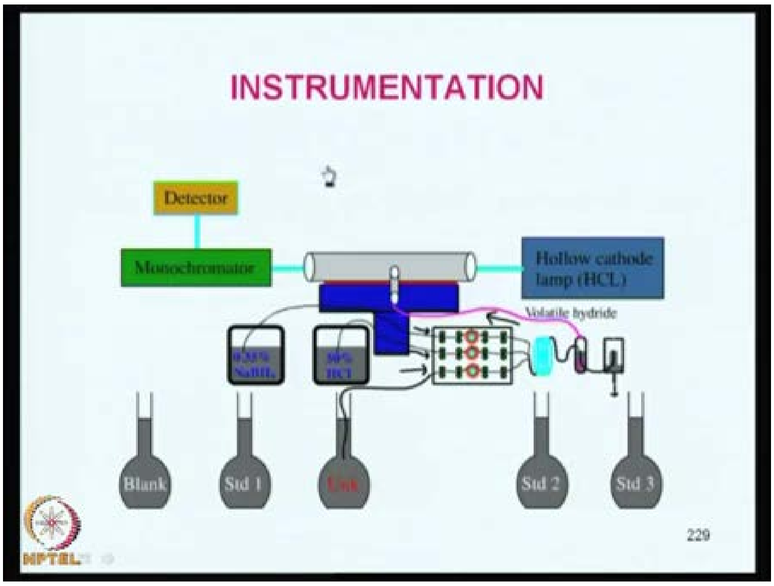
INSTRUMENTATION

Now, I want to show you the instrumentation part of this. You can see here, I have a standard, I have a blank, I have an unknown; there is a standard, standard 1, standard 2, standard 3 etcetera. I have two pumps here, and then, the sample will be transferred here; I have a sample manifold in this region, and from the sample manifold, I have the gas and I need a dryer, and from the dryer I have to take the volatile hydride and take it to this tube; I am showing it to this pink line, is how the sample enters the hydride; and this is a T tube of cords, and this tube will be introduced on the flame.

This blue support is basically a flame, that is where the flame of atomic absorption is coming, and you just introduce it there, and the optical other optics parts will remain the same, and this is the radiation coming from hollow cathode lamp, and I put a monochromator here; all other things will remains the same. You do not have to do anything, except that, you add, take this sample, add NaBH 4, add acid, collect it and bring it here, and then, dry it; and from there, you just have to connect it, and sometimes, both these windows are open, so that, hydride can escape from this side, from the sides also.

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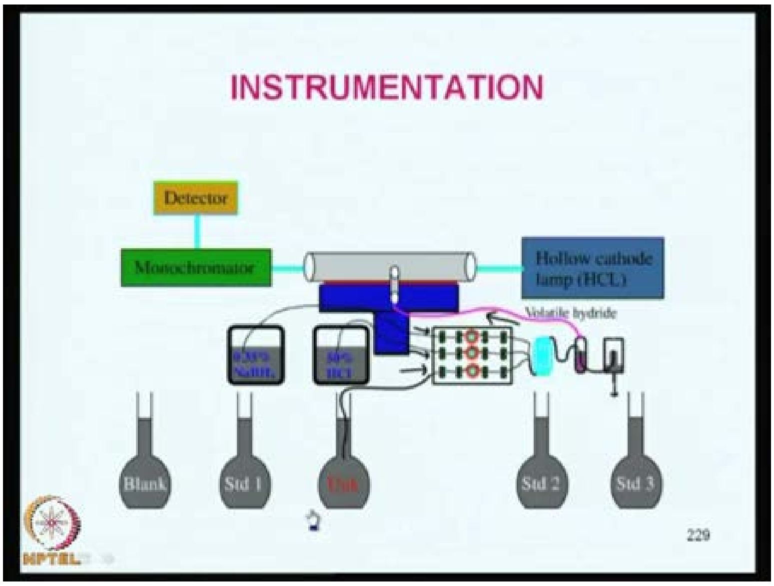

## INSTRUMENTATION

So, this is a very simple arrangement which is employed in most of the analytical instruments, in some with modifications, but the basic structure remains the same. You take the standard; you take standard 1, standard 2, find out the peak area, and then determine the unknown in the same way, and analysis can be completed.

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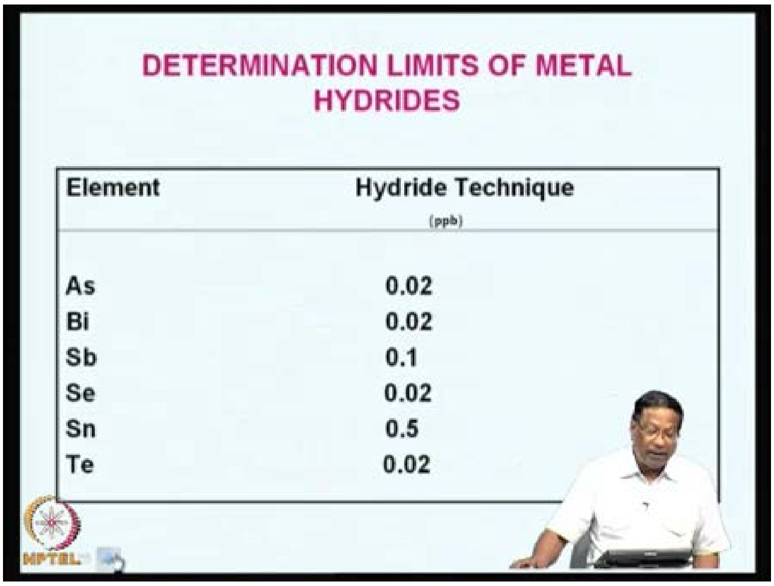

## DETERMINATION LIMITS OF METAL HYDRIDES

| Element | Hydride Technique (ppb) |
|---|---|
| As | 0.02 |
| Bi | 0.02 |
| Sb | 0.1 |
| Se | 0.02 |
| Sn | 0.5 |
| Te | 0.02 |

Now, the determination limits. I want to give you, you will be impressed with the determination limits of metal hydrides; for example, this element, arsenic, it can determine up to 0.02 ppb, bismuth 0.02, antimony 0.1, selenium 0.02 ppb, tin 0.5 and tellurium is 0.02; this is a hydride generation and because, most of these elements are pollutants, environmental pollutants, we have a wonderful technique for the determination, monitoring of these elements in the environment, in the effluents as well.

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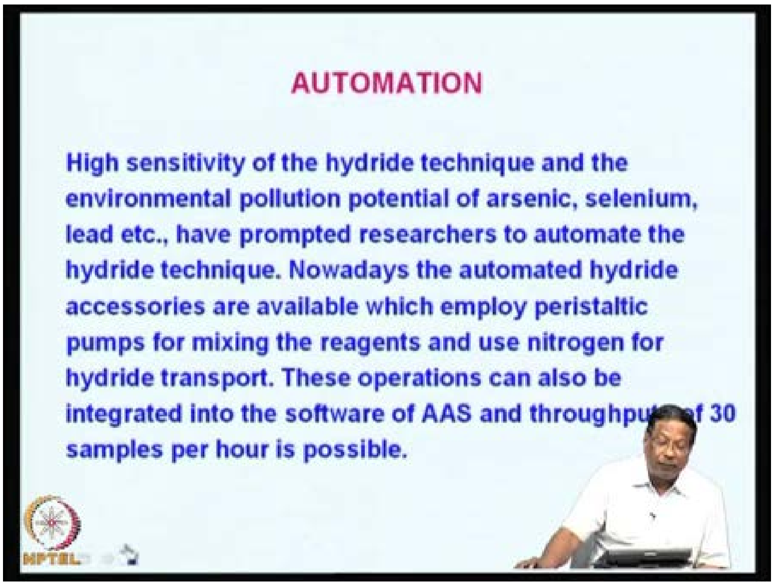

## AUTOMATION

**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 throughput of 30 samples per hour is possible.**

So, high sensitivity of the hydride technique and environmental potential of arsenic, selenium, lead etcetera, have prompted researchers to automate the whole hydride technique; that means, you do not have to do any work, you just, take the, take a carousel and pass the acid. So, the acid addition can be automated, sample collection can be automated, drying will be automated; the sample introduction can be monitored by, can be controlled by solenoid wall, and you can time it at different rates, so that, standard 1, standard 2, standard 3 are analyzed. And then, the sample is analyzed, and then you can take the readings, and then feed it to the computer to determine the rates, to determine the concentration.

So, almost, all the operations of peak height or peak area can be integrated into the software of the atomic absorption, and that is what is available in the market also, and throughputs of about 30 samples per hour is quite possible.

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MERCURY COLD VAPOUR TECHNIQUE

So, now, I want to stop here regarding hydride generation because, there is another technique which I want to discuss with you; that is, mercury cold vapor technique. This is, I had referred to this in my introductory remarks on atomic absorptions, that mercury was the first element to be determined as early as 1913 using cold, this cold vapor technique.

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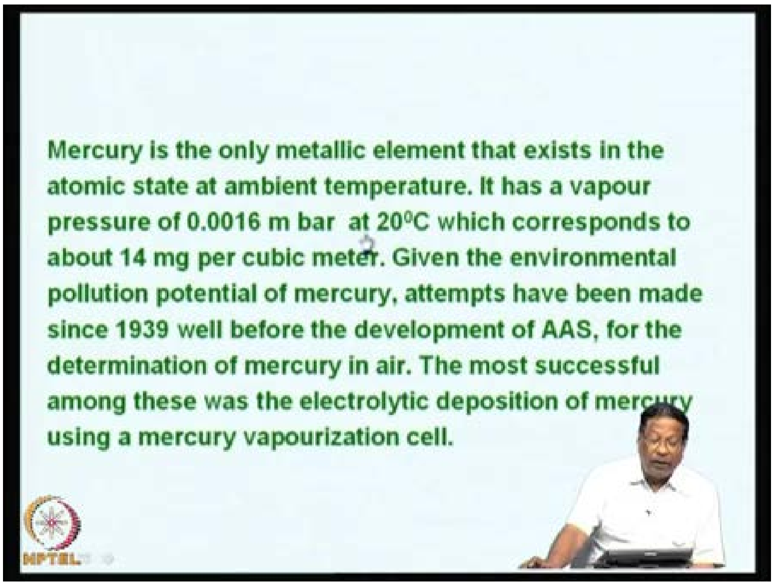

Mercury is the only metallic element that exists in the atomic state at ambient temperature. It has a vapour pressure of 0.0016 m bar at $20^{0}$C which corresponds to about 14 mg per cubic meter. Given the environmental pollution potential of mercury, attempts have been made since 1939 well before the 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 is the beauty of mercury? It is only metallic element; it is a only metallic element that exists in the atomic state at ambient temperature. You fill a mercury in your lab, there will be mercury vapor in the laboratory; it has a high vapor pressure of about 0.0016 millibars at 20 degree centigrade, that is, room temperature which corresponds to about 14 milligrams per cubic meter, given the environmental pollution potential of mercury. Nowadays, everybody is scared about mercury in the environment. Attempts have been made since 1939, well before the development of AAS itself, for the determination of mercury in air. The most successful among these was the electrolytic deposition of mercury using a mercury vaporization cell.

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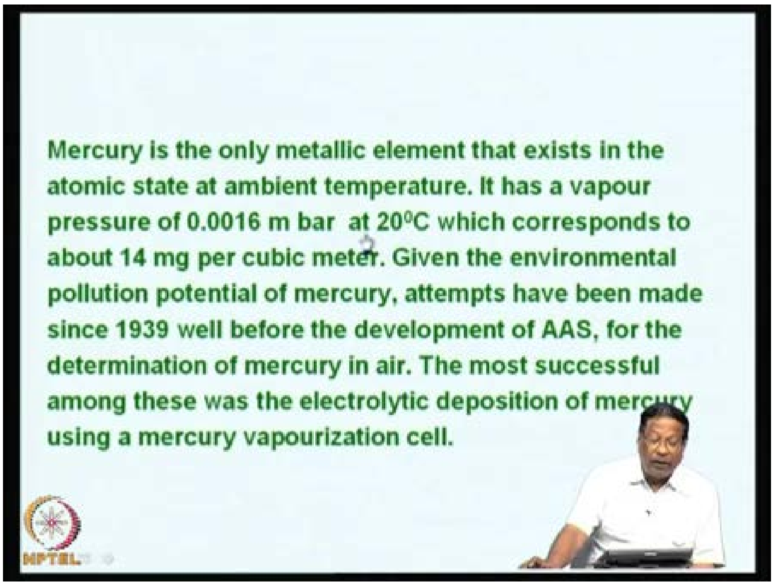

Mercury is the only metallic element that exists in the atomic state at ambient temperature. It has a vapour pressure of 0.0016 m bar at 20$^{0}$C which corresponds to about 14 mg per cubic meter. Given the environmental pollution potential of mercury, attempts have been made since 1939 well before the 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, we will continue the discussion regarding atomic absorptions. Now, Polluktov and Vitkun were the first to use stannous chloride to reduce mercury in sample solutions, which resulted in an unusually large absorbance signal for mercury in atomic absorption. What they did was, basically, you take mercury and determine as usual in atomic absorption; by mobilizing a sample, and they get some amount of signal; the difference is, they added a little bit of stannous chloride. We all know that stannous chloride is a reducing agent, so, stannous chloride reduces mercury at room temperature without any heat into mercury element.

And, if the mercury element is there in the sample, all you got to do is, pass a little bit of nitrogen or hydrogen to see, that all the vapor mercury vapors is transported into the analytic AAS signal. You do not need a flame or because you just have a job of transferring the vapor into the optical path of the atomic absorption signal, then it is possible. So, what they did was, subsequently, they eliminated the flame itself and nebulizer also, and passed only air to conduct the mercury vapor through a 30 centimeter quartz cell, mounted in the optical path of the radiation.

All you got to do is, just put some amounts of tin, just pass air and put a tube in the AAS furnace; do not light the flame, but simply measure the absorbance; this is, with this technique, they were able to obtain detection limit of 0.5 nanogram of mercury in using this cold vapor technique. This cold vapor technique is also available as a routine accessory in most of the atomic absorption systems.

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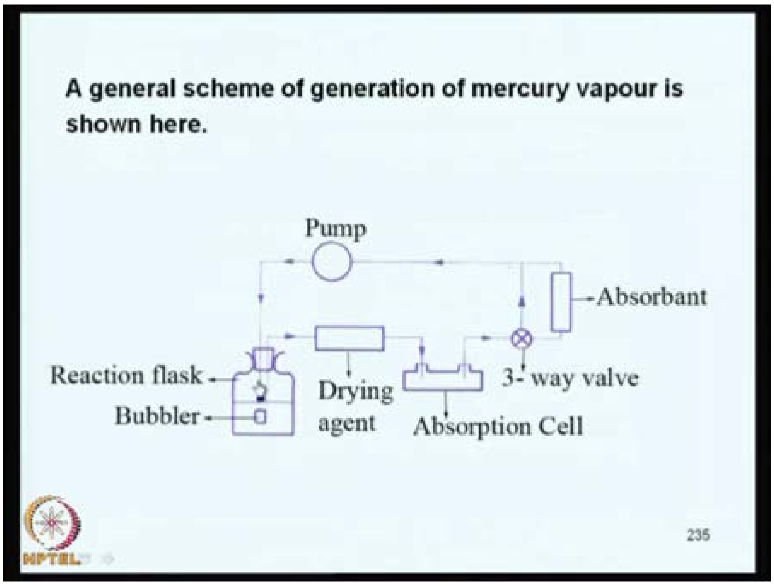

A general scheme of generation of mercury vapour is shown here.

So, the general scheme of generation of mercury vapor is,  I am showing you here, it is a very simple system; you just have a flask of your sample, and you connect a bubbler and pass the compressed air into this; you add sodium chloride in this through a tube, and keep on passing air, compressed air through this. And then, pass it through a drying agent to remove moisture and the dry air is passed into an absorption cell, and this absorption cell is put into the optical path of the flame, and then we have a three way valve absorption cell etcetera. But all other details are mundane, except that the sample is converted into vapor and put into the optical path.

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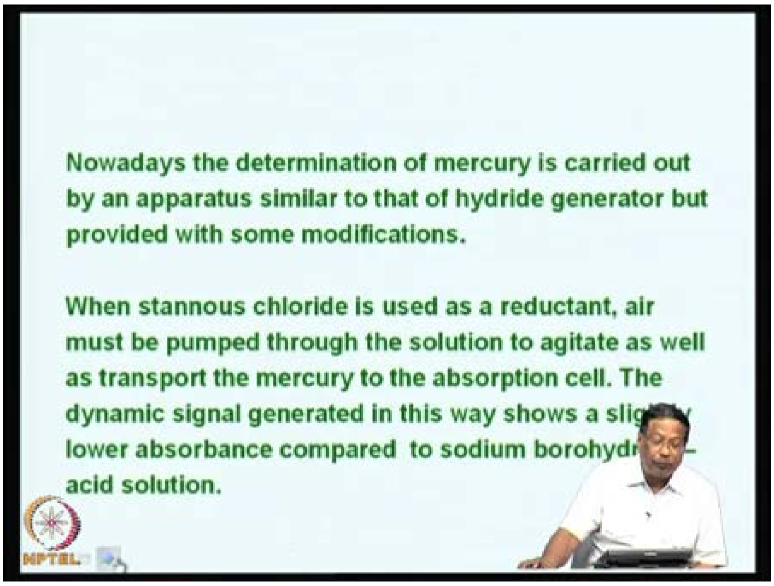

Nowadays the determination of mercury is carried out by an apparatus similar to that of hydride generator but provided with some modifications.

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 slig y lower absorbance compared to sodium borohydr – acid solution.

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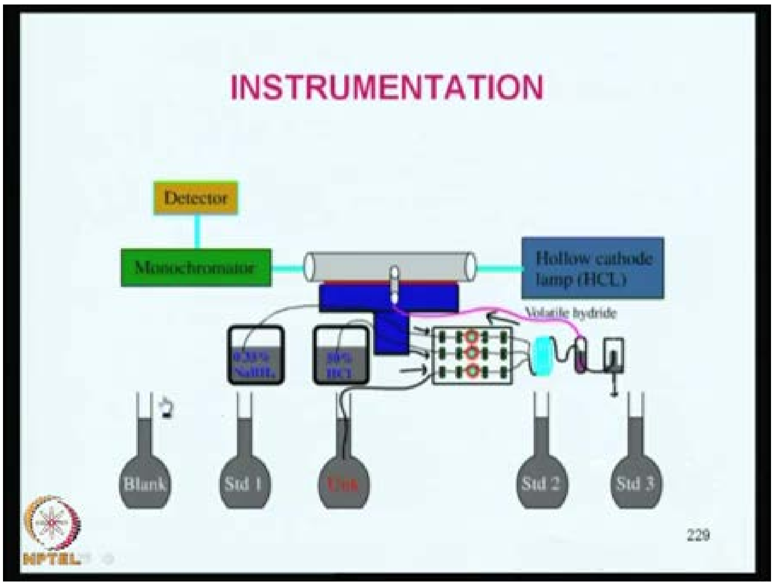

## INSTRUMENTATION

So, nowadays, the determination of mercury is carried out by an apparatus, carried out by an apparatus similar to the hydride generation system. What I had shown earlier, you remember, I had shown this system; that a similar system can be used instead of standard 1, standard 2 etcetera; you just have to, each of these, you have to add tin chloride, and the remaining system remains the same. So, the hydride generation, as well as cold vapor, mercury accessory are almost one and the same. All you got to do is, change the standards or flasks.

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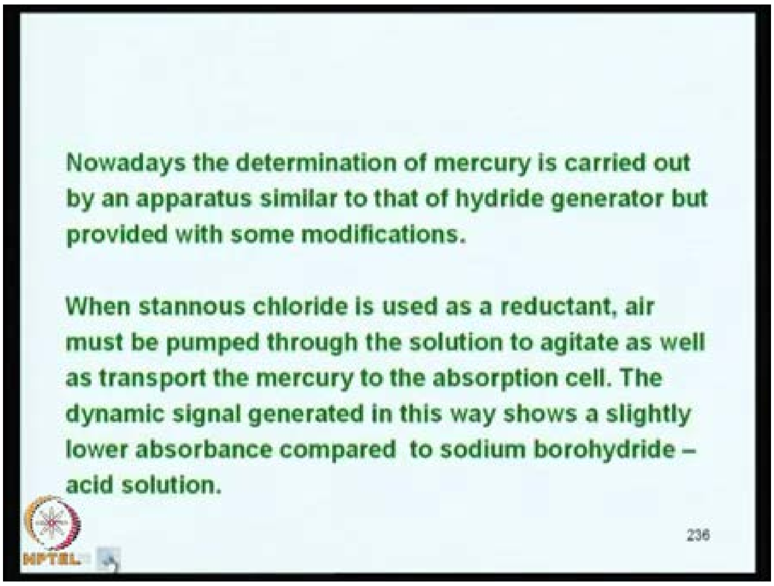

Nowadays the determination of mercury is carried out by an apparatus similar to that of hydride generator but provided with some modifications.

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, with stannous chloride as a reluctant, air must be pumped through the solution to agitate as well as transport the mercury. So, this is a slight deviation from the system what I had described earlier. Earlier, in hydride generation, we had to add HCl, and then sodium borohydride, and then nascent hydrogen will be coming out continuously and it will be transferred. But, when stannous chloride is used as reluctant, mercury remains in the solution.

So, air must be pumped throughout through the solution to agitate as well as transport the mercury. The reaction must go to completion as well as transport; it must be, the mercury should be transported to the absorption cell also; the dynamic signal generated in this way, shows a slightly lower absorbents compared to sodium borohydrite, as sodium borohydrite and acid solutions. So, you can even reduce it using sodium borohydrite also, because, you will get a slightly better signal.

With sodium borohydrite, a great quantity of hydrogen is liberated; anyway, when acid is added, this hydrogen helps in transporting the majority of the metallic mercury to the absorption cells; further, the reaction with sodium borohydrite is much faster than the stannous chloride, so that, peak height itself, we can use it for monitoring the mercury analysis. With the open system, it is almost equal to that of stannous chloride. But, in a closed system, there is absolutely no problem; you can go ahead in the... we can go ahead and determine the mercury in this way.

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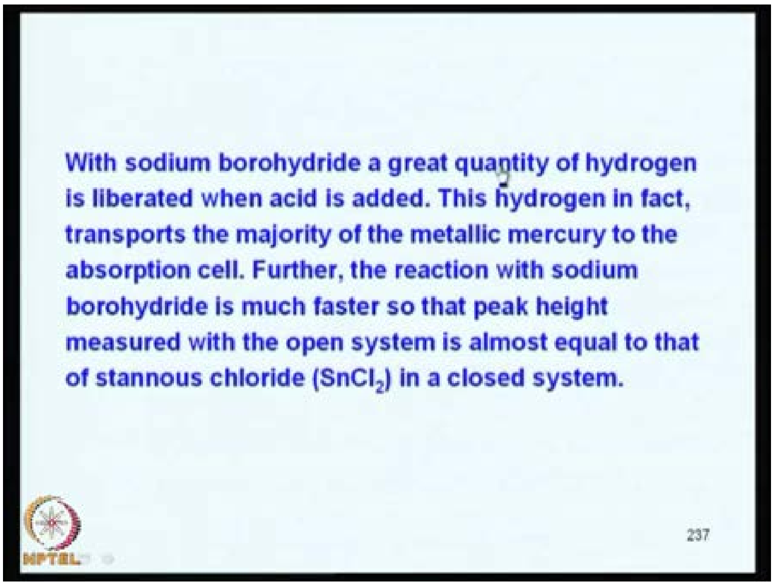

With sodium borohydride a great quantity of hydrogen is liberated when acid is added. This hydrogen in fact, transports the majority of the metallic mercury to the absorption cell. Further, the reaction with sodium borohydride is much faster so that peak height measured with the open system is almost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

Actually, this slide, in this slide, I have put, that, I the, my thoughts into simple sentences for the sake of brevity; but actually, the requirement of learning about mercury hydride is so simple, that it can be converted; it can be used as a routine technique. There are several laboratories which do the determination of mercury, day in and day out continuously.

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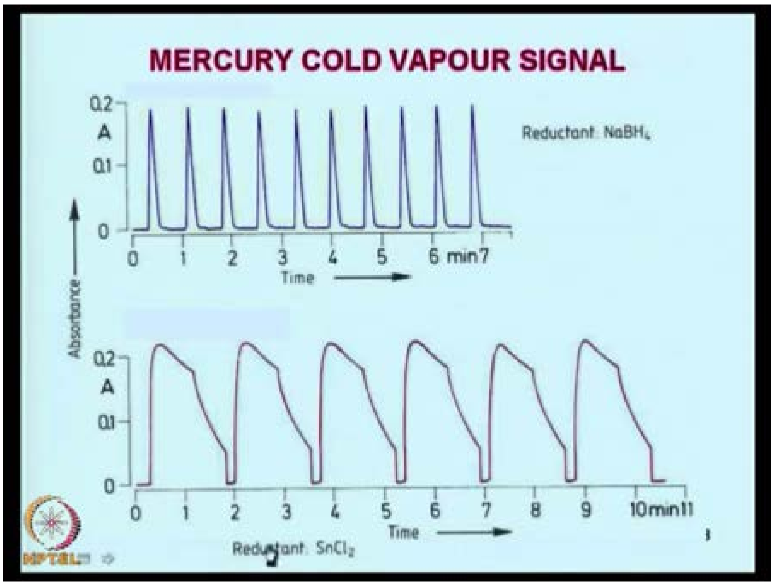

MERCURY COLD VAPOUR SIGNAL

So, in this figure, you can see that the reduction with NaB, sodium borohydrite; the advantage, you can see here; each analysis each peak corresponds to is so sharp, and then it comes back and falls to background; and then again, it, with every sample, you can determine it like this; but, if you do the same reaction with stannous chloride, you can see the signal is like this; it does not immediately, it is not as sharp as the one at the top, when the reaction is conducted with sodium borohydride.

With stannous chloride, this reaction is fairly big one, big broad signal; and there is a requirement of peak area, but you can, usually, you can use the peak height also; because, the peak height can be used if you follow the reaction in a very systematic manner. Earlier, people used to do reaction with peak height only, but peak heights are much more reproducible in the case of sodium borohydride compared to this; because of the presence of arsenic 3 and arsenic 5, there will be a delay in the separation. But, even for mercury, what we are discussing right now is, mercury, mercury can also exist as mercury 1 and mercury 2, plus 1 and plus 2 valence states.

So, you will see a signal like this because of the transport reactions; but if it is single cell with single valency, we can see that even if it is mercury 1 and mercury 2, you will see that the signals are much sharper, so that, the presence of both valence states do not matter if you carry out the reaction with sodium borohydrite; if you carry out the reaction with stannous chloride then it could make some difference.

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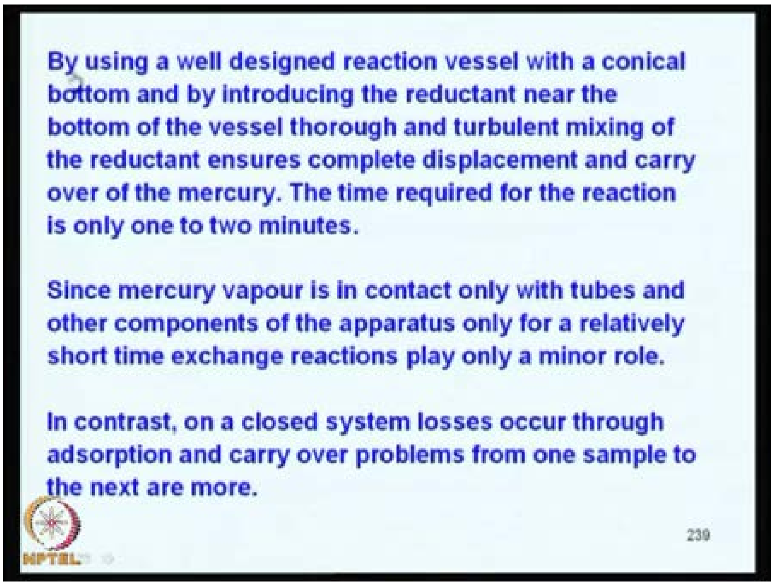

By using a well designed reaction vessel with a conical bottom and by introducing the reductant near the bottom of the vessel thorough and turbulent mixing of the reductant ensures complete displacement and carry over of the mercury. The time required for the reaction is only one to two minutes.

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, always, sodium borohydrite reduction is preferable. So, what we do is, 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 takes place, and the mercury can be displaced very easily. The time required for this reaction is only 2 minutes; not more. So, since mercury vapor is in contact only with the tubes, and other components of the apparatus only for a very short time, the exchange reactions also play a minor role; that means the reaction can be almost specific for mercury.

Again, the advantage of independence of sample concentration is there, because the sample could be in 10 ml or 15 ml or 50 ml or 100 ml; it does not matter. So, in contrast, on a closed system, losses do occur through adsorption, and carry over problems carry over problems also occur. So, giving you enhanced signals, sometimes, because, you are analyzing before the previous signal is completely dissipated, because part of it would be would have been absorbed. So, from the one sample to the next one, whenever you are analyzing, you have to make sure that memory effect does not cause interference.

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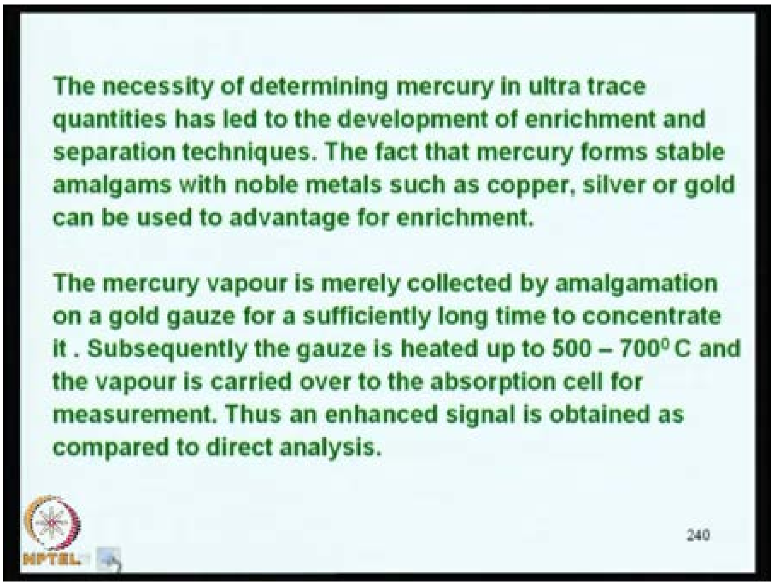

The necessity of determining mercury in ultra trace quantities has led to the development of enrichment and separation techniques. The fact that mercury forms stable amalgams with noble metals such as copper, silver or gold can be used to advantage for enrichment.

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, the necessity of determining mercury in ultra trace quantities has lead to the development of enrichment and separation technique. We just do not want the mercury to be analyzed in a given system, because the mercury system, mercury can be analyzed in a given sample if the concentration is fairly high. But, we have another typical property of cold wave mercury, that is, amalgamation; I can take a small 10 ml sample, add the reagent, take the mercury and put a gold gauge on the way in the tube; so, what happens? Mercury gets carried and reacts with the gold to form mercury amalgam; this is a unique property of mercury, because it can form amalgam with any element.

So, I can put, I can take another sample again, transport it to the same mercury, same gold gauge, and then concentrate mercury in that. So, even if the sample has very low volume, low concentration of mercury, still I will be able to do number of reactions and then concentrate it on the gold gauge. Subsequently, heat the gold gauge and collect the mercury on to the absorption tube. So, the fact that mercury forms stable amalgams with noble metals such as copper, silver, gold etcetera, they can be used to advantage for enrichment; the mercury vapor is merely collected by amalgamation on a gold gauge for a sufficiently long time; and to concentrate it, subsequently the gauge can be heated.

So, this is an advantage of over-hydride generation, AAS in hydride generation. We have 1 sample, 1 1 sample, 1 signal, whereas in mercury, I have 10 samples, and 1 signal is also possible. So, what I do is, first I run the reaction; with the first sample removed, the sample removes the mercury, and takes another sample, remove the mercury and connect it to the same one, like that if you do, you can see in this next slide, that, what I am showing here, you can determine 20 nanograms of mercury with amalgamation technique.

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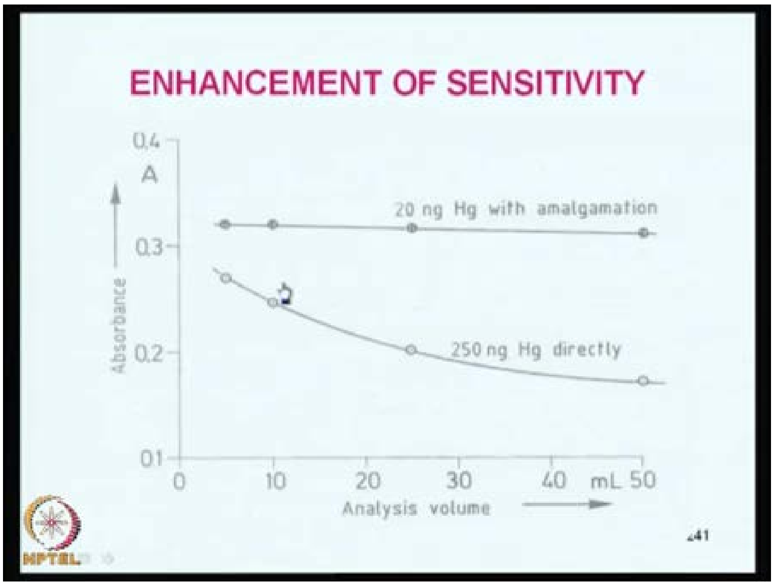

ENHANCEMENT OF SENSITIVITY

20 nanograms in quantitative level; you can see that absorbencies of the order of about 0.3, 0.3 absorbance. So, 0.3 absorbance is quite large with respect to atomic absorption

signals, because the minimum that can be determined is 0.004. Now, 0.3 is quite significant and 20 nanograms; so, about even 1 nanogram can be determined quantitatively with amalgamation. Whereas, if you determine mercury directly without amalgamation, you can see that the signal decreases up to you can get a signal almost up to about 0.2527 with 250 nanograms, directly 250 where is 250 nanograms; and where is 20 nanograms? That is almost ten times lower than without amalgamation, that is a beautiful advantage special of mercury.

Even if you and you are analysis volume is large, you can see that, if the analysis volume is about 5 ml, you have a signal which is about 0.32 and 0.32 here; but with 50 ml, with amalgamation, you would hardly get for the same 20 nanograms, the signal is constant up to 50 ml. Whereas, direct determination will not give you the same signal like this; with 5 ml signal is more, and 50 ml signal is approximately 0.08 directly; so, most of the atomic absorption instruments offer you a choice of a amalgamation technology; that means, all they go, all they do is, they take a tube, put a gold gauge in that, and then, you, there is a provision to heat you the gold gauge to 250, 100, 250 degree centigrade, and it will release the mercury and take it to the analysis absorption cell. So, the amalgam technique pre-concentrates the mercury; the method becomes independent of the volume of the sample, and absolute determination of mercury is possible. In this way, the detection limit is also improved to a vast extent.

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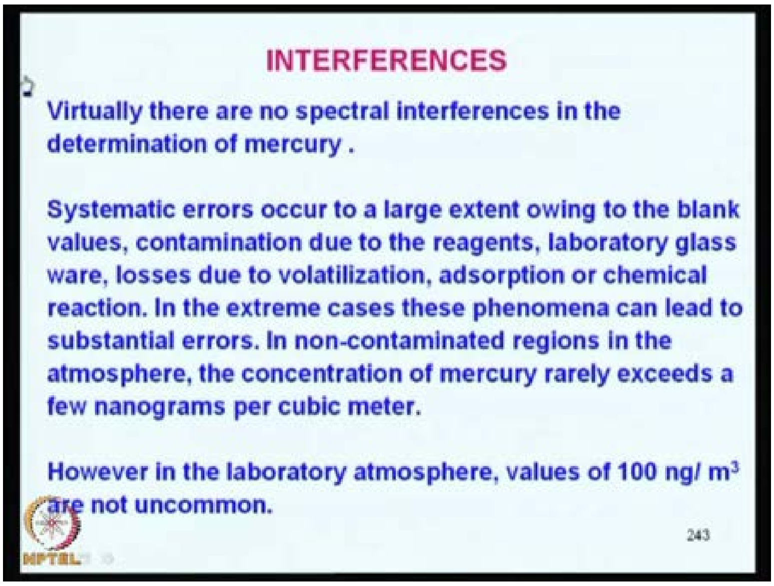

## INTERFERENCES

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.

Now, again, the question of interference is, we keep on recurring to this theme of interferences, because, no analytical science is a complete method, is complete without knowledge of the interferences. One has to be always vary of the interferences, and as good analytical scientist, we also should be aware of what are the pitfalls of mercury analysis. But, technically speaking, virtually there are no spectral interferences in the determination of mercury, because none of these spectral lines match with that of mercury.

Systematic occurring errors, they do occur to a large extent, owing to the blank values contamination due to the reagent, laboratory glassware; laboratory glassware, they can get contaminated and give you a signal, even if the mercury is not there. Because, if they are contaminated, you can do nothing, and losses due to volatilization can occur, adsorption or chemical reaction can occur. Suppose, you are passing it through a rubber tube, mercury can get adsorbed around rubber tube, and you will not see any signal. So, these types of interferences related to adsorption of mercury on glass or rubber tube or PVC tube, they are quite common.

So, many times, they lead to wrong error results, wrong conclusions, because, when the sample is not there, you may get signal; and when the sample is there, it may get adsorbed; if you are not very careful about the tubings and other things, which you are not familiar. So, in the non-contaminated regions in the atmosphere, the concentration of mercury rarely exceeds a few nanograms per cubic meter; this is a very interesting thought, because, in the environment the concentration of mercury, is only in few nanograms.

Suppose, you want to measure mercury in the atmosphere, about 5 kilometer height or the equator, then the concentration of mercury is directly measurable. If you are able to reach that height and sample a small quantity of the air, you do not have to do any additional work to bring it to the lab etcetera, and then treat it. All you got to do is, be at that height, collect an air sample and simply pass it through cold vapor, mercury cold vapor cell; that is it.

So, in the laboratory atmosphere, there could be a problem; because, values of 100 nanogram per meter cube, are the blank values. So, if you are determining 20 nanograms in the samples, if your blank value itself is 100 nanograms, then you have a problem. So, in the determination of mercury, one has to be always very, very, very careful, especially if you want to determine ultra trace quantities of mercury that is required.

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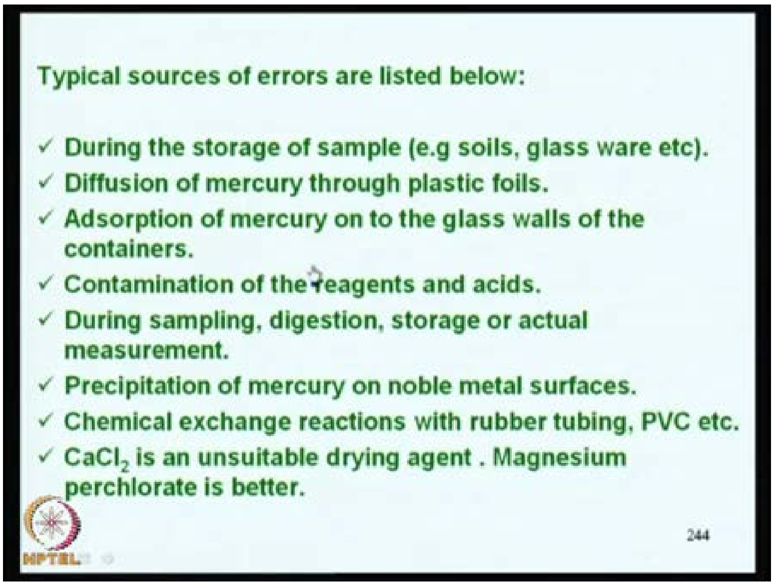

**Typical sources of errors are listed below:**

- ✓ 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, the typical sources of error, I have listed here. During the storage of the sample, for example, if you want to determine the mercury in the soils, you will have problem of adsorption, glassware adsorption, diffusion of mercury through plastic foils; it is possible. Then, adsorption of mercury on to the glass walls; it is a well known fact, since, last 6, 50, 60 years, that in stress quantities, mercury adsorbs on to the glass. So, you should use polythene glass, conical flask polythene beakers etcetera. So, contamination of the reagent and acids, a very, very serious problem, so, during sampling digestions storage, actual measurement etcetera, one has to be extremely careful regarding the contamination.

Precipitation of mercury on noble metal surface, that also happens; and copper, for example, if you have copper tubing, you should not be using copper tubing, because mercury will form an amalgam straightaway; so, you will never get a signal if you use a copper tubing. Stainless steel, it is possible; but again, even in stainless steel, some of the components may form an amalgam. So, you should use rubber plastic tubing only; chemical exchange reactions with rubber tubing PVC etcetera, it is quite possible; and calcium chloride is an unsuitable drawing agent, it is not suitable. So, you should use magnesium perchlorate; that is better.

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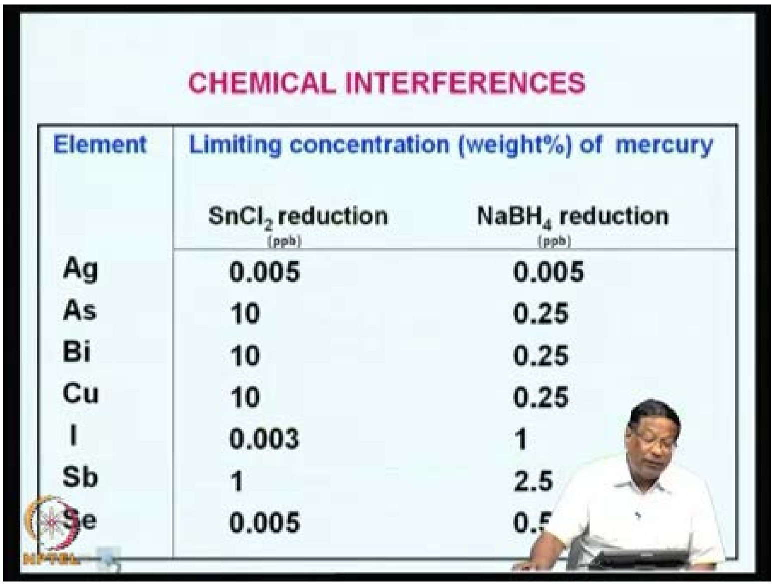

## CHEMICAL INTERFERENCES

| Element | Limiting concentration (weight%) of mercury | |
|---|---|---|
| | $SnCl_2$ reduction (ppb) | $NaBH_4$ reduction (ppb) |
| 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, some of the sources of errors are like this; for example, if you want to determine mercury, the interferences with this, for example, with silver 0.005 ppm, it interferes in the stannous chloride reduction, and NaBH 4 also it is there. So, you have to make sure that silver is not present around in the path of mercury carry over; and arsenic, it gives us about 10 ppm here, and about 0.25 in the case of sodium borohydride. That is why we prefer sodium borohydride reduction of mercury rather than stannous chloride reduction nowadays. So, we can see that arsenic is 10 and 0.26 here, bismuth is 10 and 0.25 copper is 10 and 0.25 iodine is 0.003 and 1. So, whenever there is iodine, you want to determine mercury, and see water etcetera; you should be slightly careful; antimony also is there, is interference, but things happening like this are rare similarly selenium.

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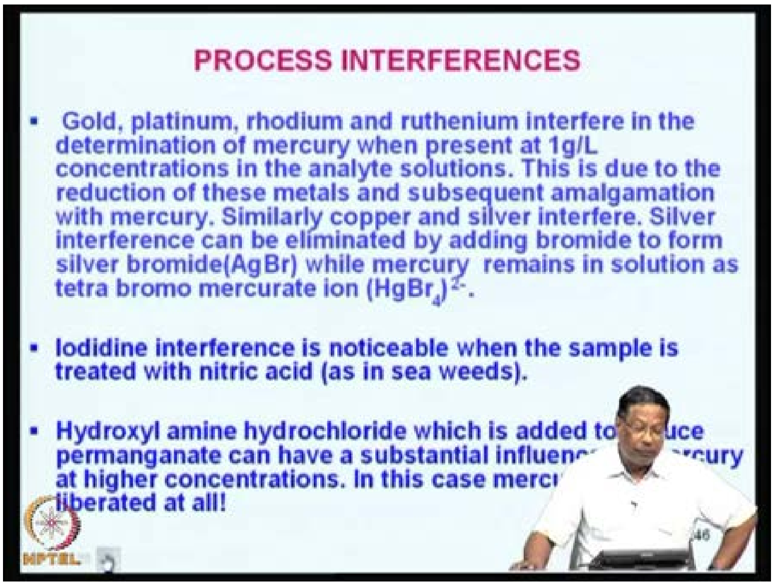

## PROCESS INTERFERENCES

- 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 uce permanganate can have a substantial influen rcury at higher concentrations. In this case merc liberated at all!

So, we will continue our discussion on the process interferences in the next class. Afterwards, we will move onto Flame at Emission Spectrometric.