

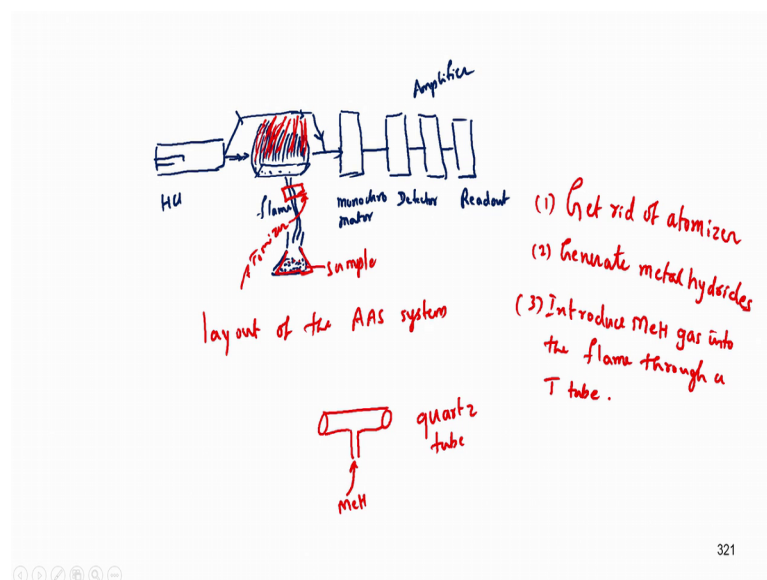
**Trace and ultra trace analysis of metals Using atomic absorption spectrometry**  
**Dr. J R Mudakavi**  
**Department of Chemical Engineering**  
**Indian Institute of Science, Bangalore**

**Lecture – 27**  
**Hydride Generation AAS and Cold Vapour Hg AAS**

Today we will discuss about the Hydride Generation Atomic Absorption Spectroscopy. Actually, hydride generation atomic absorption is only a small part of the atomic absorption technology, but it serves a very important purpose of detecting some of the elements especially those forming hydrides: that is the arsenic, antimony, bismuth, tellurium, germanium, lead etcetera. And this hydrogen generation atomic absorption technique is basically very well known method for the determination of arsenic. This technology was available as an additive or as an special a modular attachment for spectrophotometry also.

So, basically what we do is, we use a generate hydride and then insert into the flame of the atomic absorption spectrometric, that is the basic technology. So, if you remember, right.

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This is the method we had proposed that this is the symmetric representation of atomic absorption system. So, here we have a hollow cathode lamp on the left side, and then we have the flame, and then at the background is the other one, and then we have a

monochromater, we have a detector, and we have a amplifier, and then we have a radar. And the sample comes from below here.

So, what we are going to do is we are going to get rid of atomization that is sample introduction area, and we are going to get rid of it. Instead, we are going to generate metal hydrides. And third is we introduce metal hydride gas into the flame through a T tube ok. Now, this T tube is essentially a tube like this, quartz tube in which metal hydride is introduced into the flame. That is all the mod technology that is involved in hydride generation atomic absorption.

So, basically what we want to do is tech method to generate hydride in a solution and then we want to take out the hydride from the solution by passing nitrogen or any other gas. So, metal hydride as a gas is taken out in to the tube, that is a quartz tube and that quartz tube is going to be introduced into the flame; that is manually or you can have an attachment into the atomic absorption whenever you want to use this the system is available also.

So, those who do not have such a readymade modular attachment you can make your own arrangement for introducing this T tube into the flame. And we will study about this mechanism today, ok.

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**Arsenic, antimony, bismuth, selenium, tellurium, lead, mercury and a number of other elements of the periodic table belonging to group IV, V and VI are known to form volatile covalent hydrides with nascent hydrogen. Marsh's test and Gutzeit's test have been employed for the detection of arsenic since more than 100 years.**

**The property of volatilization as a gaseous hydride can be utilized to advantage for the separation and enrichment of the analyte element which also accomplishes the reduction and even complete elimination of interferences.**

So, what are the elements that form the hydrides? These are arsenic, antimony, bismuth, and then selenium, tellurium, lead, mercury, and a number of other elements of the periodic table belonging to group IV, V and VI. These are known to form volatile covalent hydrides with nascent hydrogen. That means we have to generate nascent hydrogen in the solution along with these metals.

So, if you have a sample containing antimony or selenium bismuth etcetera any of the elements you want to determine them, it is easier to introduce nascent hydrogen: from a hydride take it into the flame and decompose it into the flame into metal and hydrogen. That is all the technology is there.

The technique for generation of hydride is known as Marsh's test. This technique was known almost since about 70-80 years and that is the generation of hydride. And Gutzelt's test also have been employed for the detection of arsenic almost since more than 100 years. We are using the same technology to introduce to form the hydride and introduce into the flame.

So, this property of volatilization as a gaseous hydride can be utilized to advantage for the separation and enrichment of the analyte element which also accomplishes the reduction and even complete elimination of interferences. You will be surprised to know that most of the elements what are written here that is arsenic, antimony, bismuth, selenium, tellurium, lead, and mercury are one of the most toxic elements in the environment. We want to determine arsenic in the environment, arsenic in the food, arsenic in the soil, arsenic in the metal, arsenic in the metals, arsenic in water so many other places. Same thing is true with respect to selenium, it is also one of the most carcinogenic element we know; and tellurium and lead and mercury, I do not have to teach you about the toxicity of these metals in the environment, ok.

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In the early 1950s a number of analytical methods based on colorimetry were introduced for the determination of arsenic and other hydride forming elements.

The hydride was formed in acid solution using zinc powder and the gaseous reaction products were conducted into solutions containing ammonium molybdate or hydrazine sulphate which formed characteristic colored complexes with the hydride. Some of these techniques are still in use even today.

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So, we want to say that in the early 50s a number of analytical methods had been developed based on colorimetry. They were introduced for the determination of the arsenic and other hydride forming elements also. So, how do we produce a hydride? The hydride was formed in acid solution using zinc powder and gaseous reaction products were conducted into solution.

So, you take any metal, for example zinc you add a little bit of hydrochloric acid into that. So, zinc will react with hydrochloric acid generating zinc chloride and hydrogen gas. This hydrogen gas is called nascent hydrogen, because it evolves like a bubble continuously until the zinc is converted into zinc chloride. So, this hydrogen is freshly produced, it is known as nascent hydrogen this nascent hydrogen reacts with the selenium to form the selenium hydride, and this selenium hydride is conducted through a tube into the flame that is the technology.

So, this hydride was formed in acid solution using zinc powder. If you use powder the reaction is much better than if you use the metal block or metal pieces. So, the gaseous reaction products are conducted into solutions containing ammonium molybdate and hydrazine sulphate. This is the spectrophotometric procedure I am describing which formed colour complexes with hydride. That means, arsenic would react with hydrogen to produce arsenic hydride, arsenic hydride would be reduced to arsenic using hydrogen sulphate and ammonium molybdate which formed a characteristic colour and spectra

photometric it is always well known that any colour substance can be utilized for spectra photometric determination. That is the basis.

Some of these techniques are still even used even today where people do not have atomic absorption. So, that is known as Marsh's test and Gutzelt's test. Technically there is not much difference except in the method of generation of the hydride and taking out the hydride from the solution as a gas. Now whenever I take something from the solution as a gas the remaining compounds which do not have form hydrides they remain in the solution, you understand, so only the hydride forming element will be coming out in the flame.

Now, it means that all the other elements that are present in the sample which do not form hydrides will remain in the solution. That means, it is free from interferences of all the other elements. So, it is a way of separation of the element from the given matrix also and then determination as usual, but the beauty of this reaction is you can take 10 ml of the sample, you can take 100 ml of the sample, you can take 500 ml sample, even if the substance is in one parts per billion- one ppb the formation of hydride takes place metal hydride. And it gives you the detection limits of parts per billion using a spectral photometric procedure earlier. Now the same thing we are transferring into atomic absorption as a separate module.

So, a little bit of history now. Holak in 1969, he was the first to apply hydride generation technique to atomic absorption spectrometry.

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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.

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He generated arsenic hydride and collected it in liquid hydrogen. Subsequently, what he did he warmed the trap and conducted the arsine that is known as AsH<sub>3</sub>- arsine gas with a stream of nitrogen into an argon hydrogen flame to measure the atomic absorption, very simple. Several papers were published later in the following years describing the modifications and optimizing the technique.

However, the technique found wide acceptance only after the reliable accessories were introduced into the market, because generation of arsenic is little bit of problem if you do not have good equipment. So, you need to have air tight conical flask and then you need a system for generating gas through that and then conduct it into the flames; all those things. Once the modules were developed to connect it to the T tube which would be introduced into the flame this technique was somewhat of research curiosity rather than a regular analytical tool, ok.

So, once the atomic absorption manufacturer instrument manufacturer realized the potential of this method then attempts were made to produce as a separate module to be introduced into the flame. That is how hydride generation atomic absorption came into the market. Sometimes what happens is people specifically want to determine arsenic, selenium, etcetera routinely in their day to day activities. For them dedicated atomic absorption instruments can be employed which is nothing but the attachment of this module into the flame.

So, what is hydride generation technique?

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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%)

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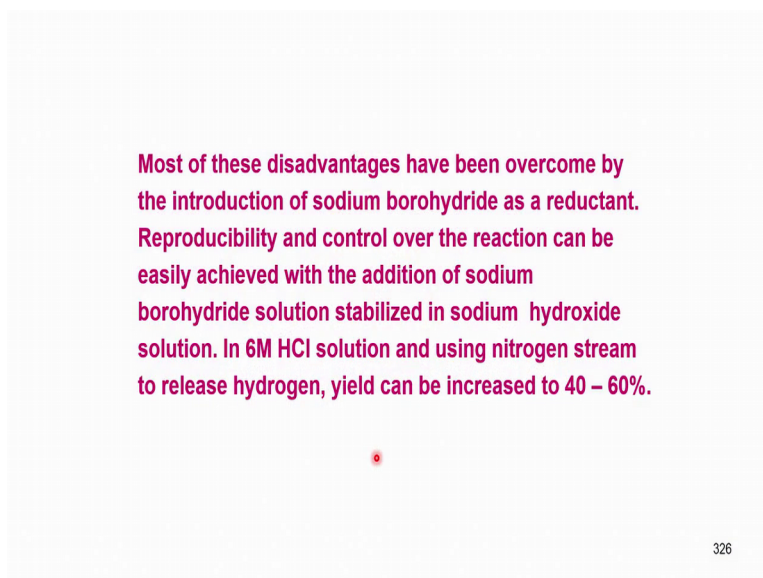
So, the most commonly used method to generate nascent hydrogen is addition of zinc or aluminum to the hydrochloric acid. So very simple reaction- mixtures of titanium, trichloride, and magnesium also people have tried we can take magnesium powder add a little bit of HCL that also gives you nascent hydrogen, you can take titanium trichloride that to that you can add a acid that also gives a metal hydrides.

So, metal acid reactions have a number of disadvantages. Usually, most of the metal hydride acid reactions require high purity metals. So, one of the requirement is you must have high purity zinc or high purity magnesium high purity titanium to conduct the reaction: that is number 1. Number 2: it used to give very high value of blanks. We do not want to correct in atomic absorption very high value of blanks, because earlier we have studied that more than 0.5 absorbents or more than 2 absorbents is difficult to correct in atomic absorption- background sample should be background should be as low as possible. So, upto 0.5 upto 1 absorbents is fine that can be corrected, but above 2, 1.5 etcetera it is little difficult to correct the blanks.

This was one of the problem the hydride generation as give high values of problems Sometimes the hydrogen released was not satisfactory: that means, the rate of the reaction was not fast enough to generate hydrogen. And that is known as low release, sometimes maximum it can reach is up to 8 percent. So, this was one of the problem.

So, we had to get very high purity zinc powder or magnesium powder to react with hydrochloride acid to generate faster metal hydrides- metal hydrides at a faster rate. So, most of this advantages have been overcome by the addition of sodium borohydride as a reductant.

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So, with the addition of sodium borohydride it overcame most of the difficulties and today it is the most accepted technique for the determination of metals- hydride generating metals as a reductant. Because sodium borohydride is available as a high purity material also as a tablet, we can just add a tab small tabs a small tablet of sodium borohydrides, it works.

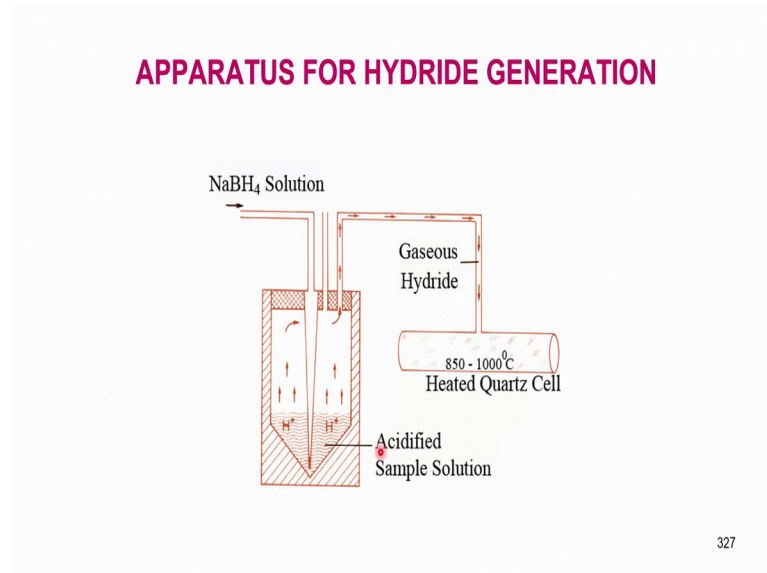
So, reproducibility and control over the reaction can be easily achieved with the addition of sodium borohydride solution; that we have to dissolve it in sodium hydroxide basically. So, in 6 molar HCL solutions we need to use and we need to use nitrogen streaming to release hydrogen. So, because most of the hydride or hydrogen generated in a reactant will remain in the solution. So, that has to be released.

How do you release a gas held up in a liquid. So, if you want to release the gas held up in a liquid you have to pass another gas which has very low solubility. And nitrogen is the cheapest gas that is available and it is non soluble, so it will just push out mechanically the hydrogen. So, the hydrogen will react with the metal in the solution.



So, with this technique we can be increased to 40 to 60 percent of the metal hydride not the metal. So, this is apparatus for hydride generation.

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So, what do we have here? We have a sample of sodium borohydride comes through this and I have the sample here acidified sample- this acidification is a run upto 6 molar HCL. We will study more about the acidity effect on hydride generation. And then we have seal here and then all I have to do is take the sample in the dissolved form in this flask.

So, in this it is already acidified, so sodium borohydride will react with the hydrochloric acid in the solution and it will generate hydrogen which I had shown it by arrows here. And this is the way through which nitrogen enters middle one. And then this nitrogen will be pushing out the hydrogen or hydride from the liquid which will be carried over into a T tube. This is the T tube and the gaseous hydrogen is transported mechanically into the T tube. This T tube is introduced into the path of the optical path of the hollow cathode lamp in the flame, inside the flame. That means, you need the flame also.

So, what happens? In the flame the quartz cell gets heated upto 850 to 1000 degree centigrade. So, this is the technique. Very simple technique, but it has to be a air sealed and all those attendant problems need to be taken care of, ok.

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The released hydrogen is collected in a trap cooled with nitrogen which is warmed to vaporize 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 kinetic interferences.

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So, the released hydrogen is collected in a trap cooled with nitrogen which is warmed to vaporize it. You can have a trap also. Before freezing the hydride it must be dried properly. That means, you cannot have a lot of moisture along with that, because again the hydride would be decomposing. So, we need a calcium chloride, we need to pass it through calcium chloride to remove the moisture. And because of the moisture it develops a high heat of hydration that prevents hydride from being dissolved or absorbed. Basically, what you have to understand is the hydride generated must pass through calcium chloride. That is the bottom line.

So, for the routine determination direct online introduction into the flame through a quartz tube is satisfactory. That means, if you are going to introduce it immediately, analyze it immediately you just have to connect the tube and introduce it there measure the record absorbents take out the tube again. Once the absorbents recording is over all you have to do is take it out and again connect it back to the hydride generation unit. So, the T tube must have an arrangement to remove and put, remove and put for routine determination.

So, the idea is peak area integration we can do. Because of the problem with hydride generation I had told you the rate of reaction is very slow, it may not be only 8 percent or something and then it has to be mechanically transported. Sometimes if the gas flow is more it will pass out quickly. And then there would not be enough time for the sample to

remain in the flame so that atomic absorbents signal is recorded properly. So, you may not get very uniform peaks, but with the introduction of sodium borohydride that has been taken care of.

So, normally what we do is whenever we determine hydrogen this hydride forming elements we go for peak area integration instead of peak height. So, this frees the kinetic interference; that means mechanical interference where hydride is to be conducted over times space or over through the tube, ok.

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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° C. With this procedure a very high degree of atomization (~100%) can be obtained.

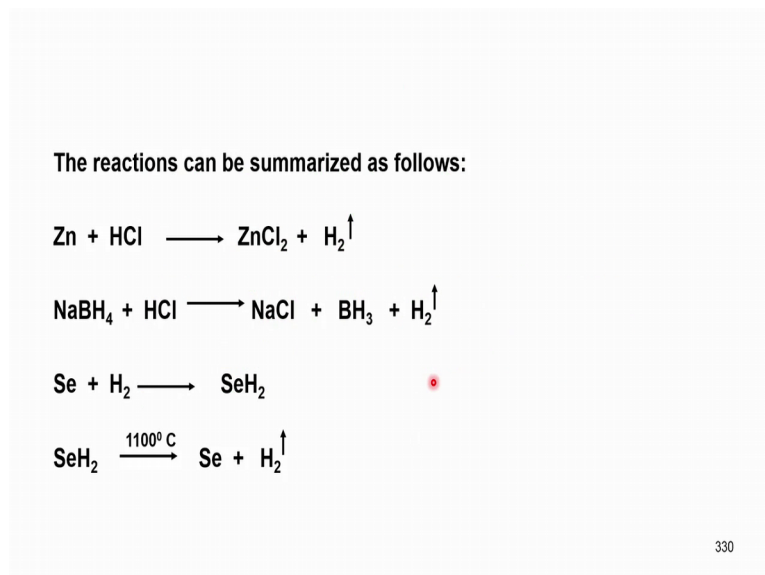
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So, soon after the development of hydride technique use of electrically heated quartz tube or heated in a flame for atomization of the hydrate were proposed. Some people said why now why put it in the flame you can as well heat it electrically. So, some workers used quartz tube with sealed quartz windows. They said T tube where to be fitted with quartz windows only and in between it can be ordinary tube or quartz tubes also. So, the tubes we are able to control the heating to 1100 degree centigrade that also makes lot of difference, because reproducibility is always there whenever I am heating the tube to 1100 degree centigrade that can be programmed.

So, with this procedure a very high degree of atomization can be obtained. That means, the metal hydride needs to be decomposed into metal and hydride. So, the metal atoms are produced in the T tube, in the flame and they get excited to higher energy level and absorb the radiation coming from the hollow cathode lamp. So, a the degree of

atomization if I maintain it around 1100 degree then the it is almost 100 percent decomposition, that can be assured.

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So, the reactions we can summarize it like this: first we have zinc, and then we had HCL, zinc chloride will form and hydrogen will form, and then we have sodium borohydride, then I had HCL, sodium borohydride tablet we are adding or a solution that will react with HCL producing sodium chloride and then borohydride plus hydrogen.

So, this borohydride is of no use to us, but this hydrogen will react with selenium to produce selenium hydride. So, the selenium hydride will react in the flame, it will just decompose producing the selenium atoms and hydrogen gas which will be going out through the U tube, because we have already detached it before we introduce and then that can be taken care of, ok.

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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.

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So, 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; this point I had told you but again once again I am repeating because only the analyte element which form hydride will be taken over there into flame. And AAS being a element specific even if any other hydrides forming element are there the analyst will take place only of that element for which hollow cathode lamp is being put, ok.

So, only the analyte element can be separated as a volatile hydride from the sample matrix. So, a relatively small number of other components reaching the atomizer makes the interference rather unlikely. So, if I used hydride generation in atomic absorption I almost have a specific reaction, 99 percent of the analysis. Nowadays in hydride generation take place only through hydride generation analysis.

So, the greatest advantage of the hydride technique is that: it is an absolute technique, it is not a concentration dependent technique. That is why the sensitivity gets increases because; suppose 1 ppm is there 1 microgram is there in 100 ml suppose I do dilute it in to 1000 degrees. So, 1 microgram will become 1000 microgram. So, the same 1000 microgram corresponding to one later all of it will be coming onto flame; that means, the detection limit will be lowered by 1000 times. So, you can understand the difference between the specificity of this reaction and the beauty of the analysis.

So, it is not concentration dependent. And the sample volume required for analyst are also very low. I can have only 0.5 ml of the sample here instead of 1 ml, 10 ml, 1 liter etcetera. I can reduce this add sodium borohydride more all of it will be converted into hydride. So, as small as 0.5 ml of the sample is more than sufficient to determine the hydride forming metals.

So, most reaction vessels for hydride technique are designed except 50 to 100 ml of the total volume, but they also require a minimum volume of 0.5 to 10 ml. We can dilute the sample and introduce 5 to 10 ml. In practice we prefer approximately 10 ml of reactant volume and 0.5 ml of the sample are more satisfactory.

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**ATOMIZATION MECHANISMS**

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

$$\dot{\text{H}} + \text{O}_2 \rightleftharpoons \dot{\text{O}}\text{H} + \dot{\text{O}}$$

$$\dot{\text{O}} + \text{H}_2 \rightleftharpoons \dot{\text{O}}\text{H} + \dot{\text{H}}$$

$$\dot{\text{O}}\text{H} + \text{H}_2 \rightleftharpoons \text{H}_2\text{O} + \dot{\text{H}}$$

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.

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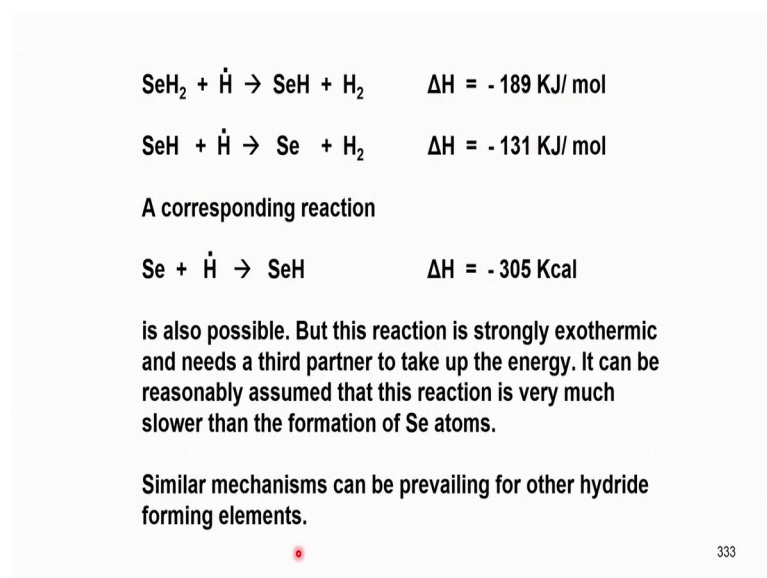
So, how does the atomization takes place? Atomization is brought about by the free radicals produced in the primary reaction of the diffusion flame, ok.

So, what happens here? In the flame we have hydrogen atoms, we have oxygen and hydrogen radical also is there free radical. So, it will react to give you an OH radical, and oxygen radical. So, oxygen radical can react with hydrogen to produce an OH radical and hydrogen radical, both ways. A hydrogen radical can react with oxygen molecule or an oxygen radical can react with hydrogen molecule both of them will produce OH radicals and oxygen and hydrogen radicals.

Another reaction is it is possible that OH radical may also combine with hydrogen coming from the reactor to produce water and hydrogen radical. So, in presence of excess hydrogen only OH and H hydrogen radicals are formed, because normally we have excess of hydrogen coming from sodium borohydride.

So, the last reaction is very rapid this reaction. And the concentration of H radicals is several orders of magnitude higher than that of OH radicals. This means that the reactivity of hydrogen radical would be much faster than OH radicals. That is what we want, we want hydrogen concentration or hydride radical concentration to be much more than the OH radicals or water; OH radicals or water does not make any difference to the determination or the formation of hydride, because for the formation of hydride what we need is hydride radical. So, this hydride radical is generated in the flame and that will react with this thing.

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So, now what happens? We have a SeH<sub>2</sub> radical; that is selenium hydride. So, this selenium hydride will react with hydrogen radical to form selenium mono hydride and hydrogen molecule. The heat of reaction is about minus 189 kilojoules per mol.

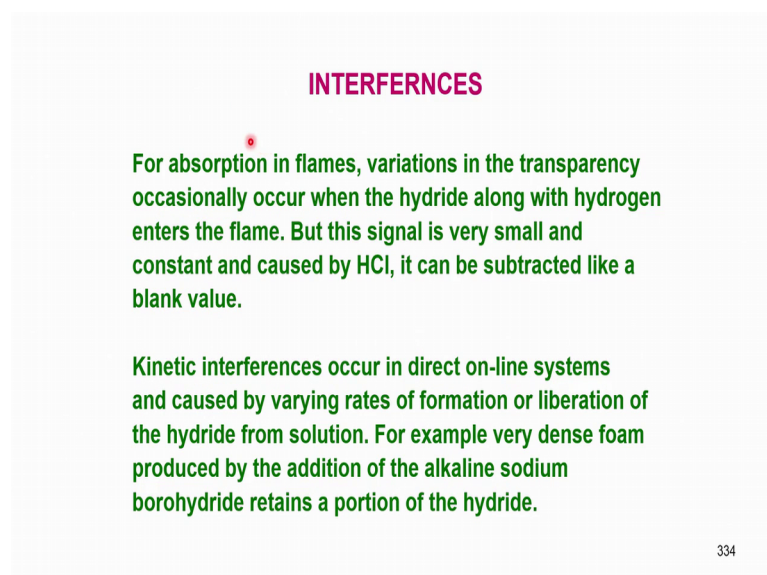
And this SeH selenium monohydride can react with another hydrogen radical to form metal and hydrogen. So, this is also extremely exothermic reaction and all in all the decomposition of the metal hydride, decomposition of selenium hydride will increase temperature of the flames and which helps in the formation of selenium metal.

So, corresponding reaction is a; this is also possible selenium can react with hydride hydrogen radical to form  $\text{SeH}$ . And this is what minus 3.5, this is also possible. But this reaction is strongly exothermic and needs a third partner to take up the energy. Those who studied the chemical kinetics will know that most of the chemical reactions are facilitated by third atom which is not a part of the reactant. So, this is known as the third partner reaction. So, you need a third partner to which the radical will get attached and that radical will react with selenium to produce a selenium from hydride.

So, this reaction selenium plus H dot radical, even though it is thermodynamically it is more favorable, but because of the absence of the third element this reaction will not go through. That means, only these two reactions will proceed giving you the selenium metal. So, it can be reasonably assumed that this reaction is very much slower than which reaction that is last reaction; selenium and hydride is much slower than the formation of selenium atoms.

So, similar mechanisms can be prevailing for other hydride forming elements also. I do not have to write tellurium hydride  $\text{TeH}_2$  plus H radical going to  $\text{TeH}$  etcetera, almost all of them will have similar reaction you can practice it yourself, ok

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**INTERFERENCES**

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.

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Now, let us talk about the interferences in hydride generation. See, most of the time we always feel that atomic absorption is as specific for the element which analyze, but we had also seen in the flame atomic absorption there could be no of interferences. That



could come from metal, spectral interference, non-spectral interference all that we discussed earlier. Now what we are going to do is discuss about interferences in the flame with the hydride generation system.

So, for absorption in flames variations in the transparency occasionally occur, because basically we are measuring only the transmittance or absorbents. So, when hydride along with hydrogen enters the flame sometimes variations occur. This signal is very small, which one the hydrogen flame when hydrogen enters the flame there will be some transparency; that means it will burn without red flame. So, this signal is very small and constant and it is caused by HCL, it can be subtracted like a blank value.

So, there is no worry when we want to determine hydride, whenever we are using HCL we do not have to worry about the hydrogen radical or gas. But, kinetic interferences do occur in direct online systems and caused by varying rates of formation or liberation of hydride from the solution.

For example, very dense foam produced by the addition of sodium borohydride alkaline, no that is retains a portion of the hydride sometimes this is a problem; it is a basically kinetic problem and it happens.

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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, for elements of VA group the sensitivity difference in the peak height between plus 3 and plus 5 oxidation state; that is arsenic we are talking about arsenic. Arsenic can exist

in plus 3 and plus 5, there will be some difference in peak height and it is less than a factor of 2. So, this difference can be partially eliminated by peak area integration. So, peak area integration whenever you want to do any atomic absorption go for the peak area instead of peak height; that is the bottom line.

So, for arsenic plus 5 state gives 80 percent signal compared to arsenic III. Similarly, for antimony V; that is antimony with pentavalent antimony there is 50 percent reduction in the signal compare to antimony III. So, for group IV elements plus 4 and plus oxidation states exist not plus 3 and plus 4: but for group VI elements sorry, for group VI elements plus 4 and plus 6 oxidation states exist and plus 4 gives a measurable signal, not the plus 6.

So, whenever we want to determine the group VI elements I can have a speciation, that meets the element whether it is in plus 6 oxidation state or plus 4 oxidation states.

So, we will continue our discussion in the next class.