Inductive Couple Plasma Atomic Emission Spectrometry (ICP-AES) for Pollution Monitoring

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Lecture – 19
Practice and Applications of ICP AES – II – Sample handling

So, we will continue our discussion on sample introduction.

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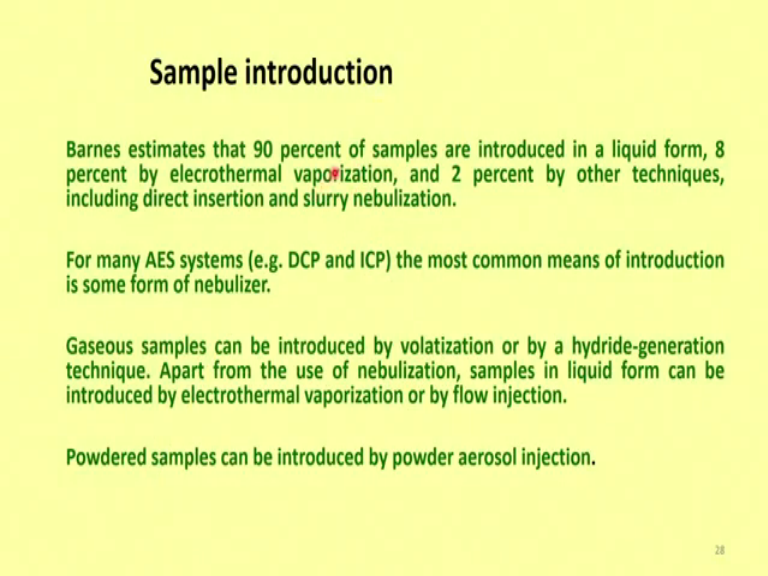

So, we have covered most of it earlier, but what I want to tell you is something slightly different that is 90 percent of the samples are introduced in the liquid form, 8 percent by electro thermal vaporization and about 2 percent by some other techniques, that is, in ICP. The, some other techniques also include direct insertion, that is, solid analysis as well as slurry nebulization; you take the slurry itself and nebulize it. So, for many AES systems the most common means of introduction is some sort of nebulizer, this we already discussed.

And, gaseous samples can be introduced by volatilization or hydride generation technique, apart from the use of nebulization. So, samples in liquid form can be introduced by electro thermal vaporization also or we can do it by flow injection technique. Flow injection technique I have covered in my earlier course on spectrophotometry, but similar systems can be employed in atomic absorption ICP and

many other systems also and the powdered samples can be introduced by powder aerosol injection, but it does not work for all the all types of powders.

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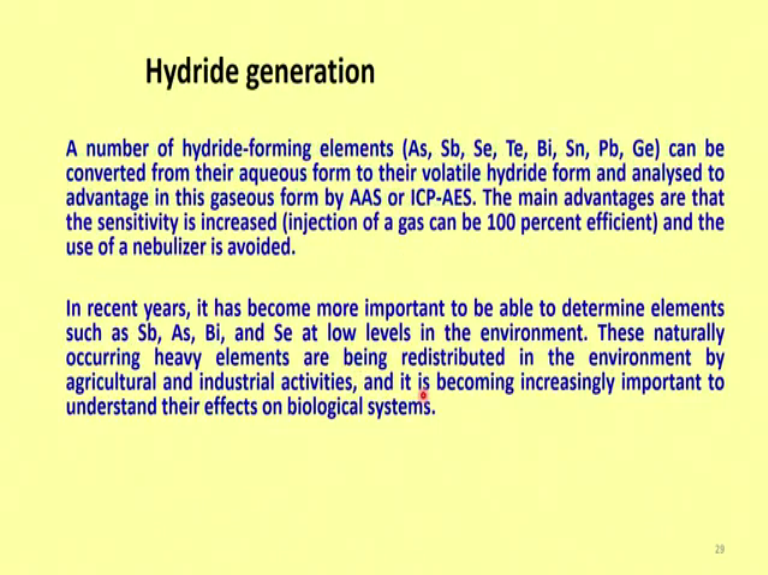

So, what is hydride generation? I want to spend some time on this hydride generation because; hydride generation analysis is usually done for elements which can form hydrides ok. So, these elements include arsenic, antimony, selenium, tellurium, bismuth, tin, lead and germanium. So, most of these elements if you want to determine in PPB a parts per billion level or something like that they need to be concentrated to certain extant and best way to concentrate is to make them form hydrides which when if we heat it to around thousand degrees all these hydrates arsenic, antimony, bismuth, selenium, tellurium, lead and germanium all these things will come out as metal hydrides ok. So, the metal hydride is in the form of gas and that gas can be directly introduced into the ICP – AES plasma.

Hydride generation has also been applied for the determination of arsenic in spectrophotometry and in atomic absorption also a separate module is available and similar modules can be employed for hydride generation in ICP – AES. Normally, people do buy a hydride generation AES module for the elements ah, only elements listed above that is arsenic, antimony, bismuth, tellurium and tin lead and germanium.

So, the main advantages are that the sensitivity is increased. See, generally what happens now the sample is in the form of a liquid, I add a little bit of a reducing agent. So,

nascent hydrogen is generated. In the nascent hydrogen all these elements will react to form hydrides and these hydrides if I pass nitrogen gas through the sample containing metal hydride the metal hydride will come out along with the carrier gas that is nitrogen, ok.

So, whatever is the concentration in the liquid I am simply separating it from all other contaminants that are present in our liquid sample. That is why most of the interferences are nonexistent in hydride generation analysis and that is the beauty. So, you can even concentrate it to about hundred times. So, the detection limit for hydride generation elements are of the order of about one 0.1 PPM and PP 0.1 PPB and nowadays, there are instruments which will measure in parts per trillion that is 10 raise to minus 12 grams quantitatively ok.

So, the in hydride generation I do not need a nebulizer ok. So, in recent years it has become very important to be able to determine elements such as antimony arsenic bismuth and selenium at low levels in the environment and aluminum also, for example, I have given you earlier the analysis of aluminum in brain is important because of Alzheimer's disease concerns and these naturally occurring heavy elements are being redistributed into the environment by agriculture and industrial activities. So, many of these elements are there in the air which we breathe. So, it is becoming increasingly important for us to understand their effects on biological systems.

For example, you may remember that arsenic is never part of any human metabolism or a physiology for that matter, but all of us have arsenic in our body. Similarly, we have lead; lead in our body whether we like it or not we do not take lead as a medicine or anything, but it comes from drinking water, pipes you know lead pipes water is carried to several towns and supplied and sometimes the lead also comes from petroleum, petrochemical industries, furnaces, coal industry, several other industries are there which keep on spewing out lead and this lead is an universal contaminant now. It is very difficult to get a sample of lead pure sample of blood or anything is impossible in any of the animal kingdom including humans.

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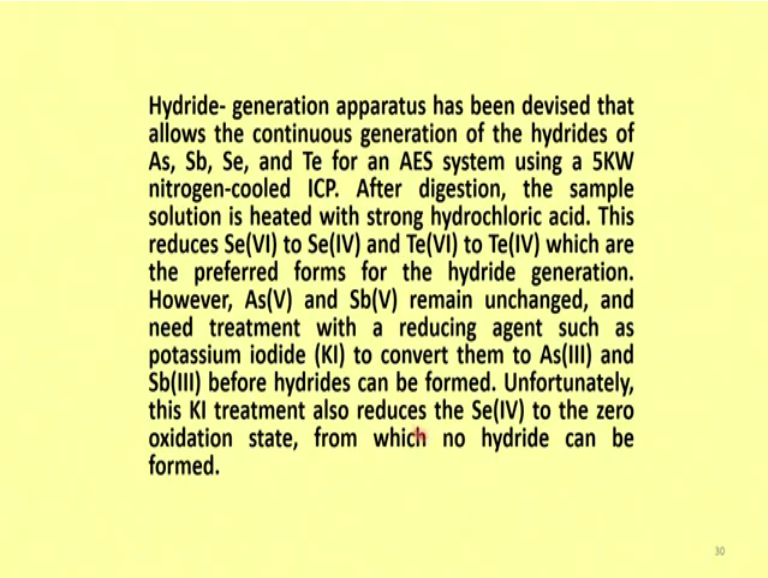

So, hydride-generation apparatus has been devised it is there since last 50 more than 100 years I think. It has been device that allows the continuous generation of the hydrides of these elements there is arsenic, antimony, bismuth, tellurium etcetera and it has been used for AES also Atomic Emission Spectrometry using a 5 kilowatt nitrogen cooled ICP that is the earlier operations. Nowadays, there are many ICP instruments which are usually which are usually taken bought rather along with ICP along with hydride generation AES not AES, ICP. AES also people do buy, but ICP also comes with hydride generation module and if you are interested in any of these elements, you should better buy a hydride generation system module along with the ICP ok.

So, arsenic you should also appreciate that the after the digestion the sample solution is heated with strong hydrochloric acid and this radius is selenium VI to selenium IV, tellurium VI to tellurium IV; these are the most preferred forms for hydride generation. However, arsenic and antimony they do not change, their oxidation state does not change. So, what we need is we need potassium iodide a little bit of chemistry here to convert them into arsenic III and antimony III, that is a valency. So, before hydrides can be found only arsenic III and antimony III will form hydrides.

So, unfortunately this potassium iodide treatment also reduces selenium IV to selenium metal. So, once it reduces the selenium metal to the metal there is no way it can be hydrated it can form hydrides, ok.

So, that is about the hydride generation AES. I have covered more of the chemistry and reactions regarding the hydride generation AES in the in my previous course that is an atomic absorption spectrometry hydride generation also recovered you may look it up in my previous course to get a more understanding of the supply, generation, delivery into atomic absorption or atomic emission spectrometry.

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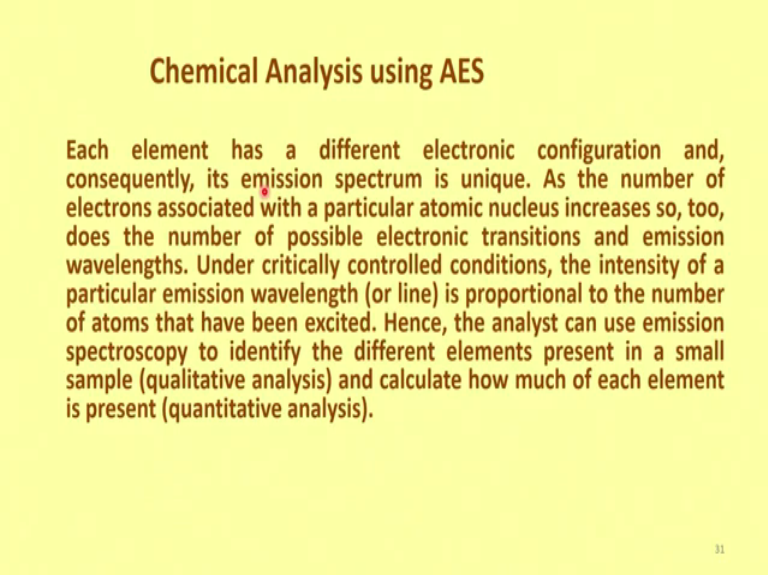

So, now I want to talk to you about chemical analysis using Atomic Emission Spectrometry. What are the things we should be looking for? So, each element has a different electronic configuration ok, this we appreciate because in the first class itself I had we have covered most of these discussions and what is important is consequently it is emission spectrum is also unique, this also we know. So, as the number of electrons associated with particular atomic nucleus or an element increases the number of possible electronic transitions and emission wavelengths also increase, that means, a sample containing different elements will have atomic emissions coming from all the elements generated in the ICP ok.

So, the it is important for us to find out the actual emission wavelength for a particular element and that should be proportional to the number of atoms that are present in the actual sample which we dissolve. So, the analyst can use emission spectroscopy to identify different elements present in a small sample, that is qualitative analysis. So the quality in qualitative analysis what we want to do is just pass fail test. I want to

emphasize again that a pass fail test is possible in ICP – AES. You just look for a particular element and particular wavelength and if it is there it is there otherwise it is not there. So, the that is qualitative.

Second is, to calculate how much of each element is present in quantitative analysis that is also important. So, quite often we are not satisfied with whether a particular element is there or not, but we also want to know how much of the analyte sample is present. So, for that what you should do you have to prepare a calibration curve, because in the beginning of this course also I had told you that ICP – AES is a reference technique, that means, if you have a good sample you have to do a calibration curve and then refer your unknown to the calibration curve. So, calibration curve is made of the concentration versus response curve, ok.

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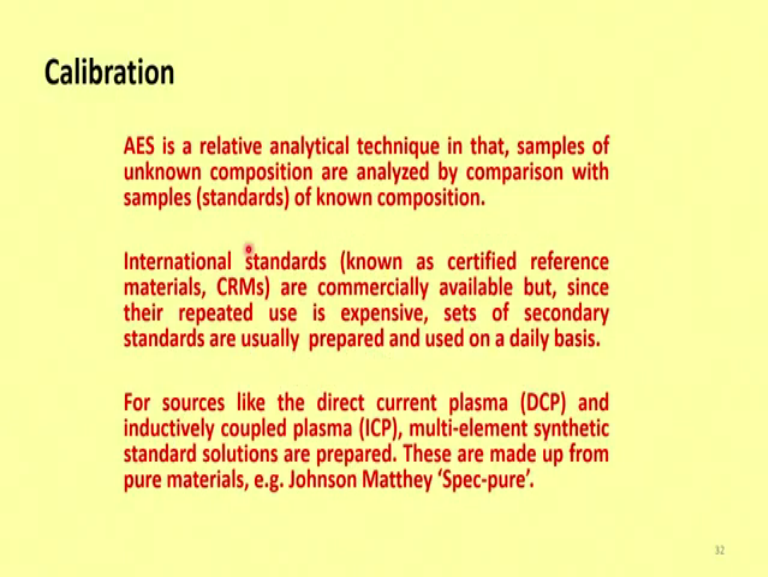

So, the atomic in atomic emission samples of unknown composition are analyzed by comparison with samples of known concentration that is the basis of all spectrophotometric procedures. So, there are international standards are marketed they are available for a price these are known as certified reference materials CRM and then sometimes we also call them SRM, standard reference materials, they are also commercially available, but since they are repeated use these things are very costly you know.

Ah, suppose, you want to determine particular element gold in seawater you cannot take say you can there are standards available in which metals have been put in seawater and then packed and sold. So, the concentration of the element in the seawater standard reference material is known that has that is that it itself is a great exercise because such standard reference materials are prepared using the number of laboratories, number of workers and number of analysis methods different analytical methods and then take the average stay treat them statistically and then the certificate carries a certificate that the concentration of such an element cadmium is 0.02 PPM or not or 0.02 plus or minus 0.005 PPM, like that they it comes with a certificate and that itself is a great scientific exercise, but such materials are very costly, so, expensive.

So, a set of secondary standards we can go for. These are usually prepared on a daily basis; that means, we can take suppose you want to determine cadmium what I do is I take a pure cadmium salt 99.99 percent or pure salt dissolve it take it to take it to the ICP for analysis and I know that the initial concentration of the cadmium and then unknown sample I compare if 5 PPM gives you hundred workouts and another sample that is standard another sample gives you a 80 PPA, 80 counts then you can say that it contains about 4 PPM, that is as simple as that. So, we have to construct a calibration curve in ICP as well as spectrophotometry, as well as the atomic absorption or any other technique whichever is not an absolute technique ok. So, the secondary standards are normally prepared on a daily basis.

So, for sources like DCP direct current plasma and ICP we can also go for multi element synthetic standard solutions. This is a very important concept that many people do because whenever you want to the sample can contain only 1 element or 10 elements also the standard. So, why not use this prepare a standard itself containing 10 elements, such things are very important. Especially, when you want to do ball bearings and other special alloys you want to analyze and also you should have the matrix that is the other components of the sample if your ball bearing is in a solution or oil and the we can determined ball bearings dissolve the ball bearings are simple in the oil itself and then extract and then determine the metal content.

So, for DCP and ICP we can use multi element synthetic standard solutions and these are made up from pure materials of course, that is understood normally Johnson Matthey Spec-pure compounds are available and these are available at a cost and you should be

able to buy them in your laboratory for routine purposes, but remember they are all secondary standards, not the primary standards.

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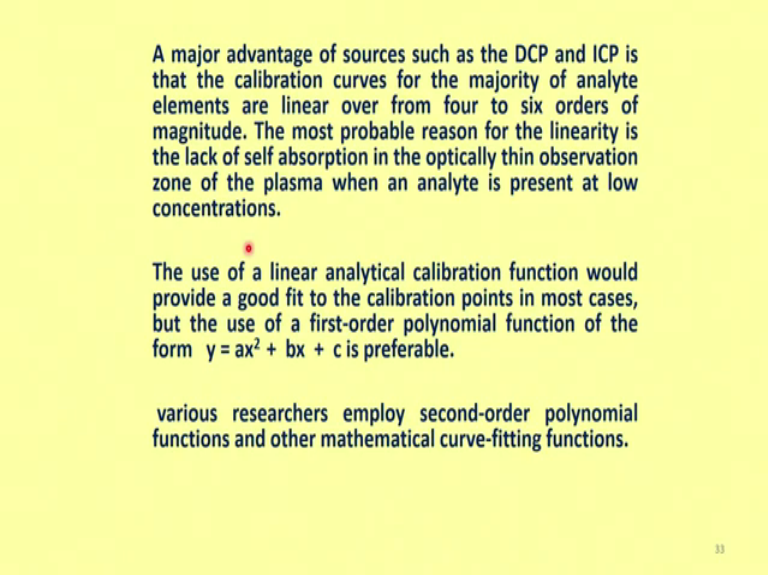

So, a major advantage of the sources such as DCP and ICP is that the calibration curves for the majority of the analyte elements are linear from four to six orders of magnitude. This you should remember, I have again and again emphasized that in spectrophotometry calibration curve would be 2, 4, 5, 6, 10 or 10, 20, 30 or 100, 200, 300 all in the same order depending upon the sample. But, in ICP it is same thing is true with the AES also atomic absorption 1, 2, 3, 4, 5, PPM or maybe up to 10 PPM like that for different elements. But, in ICP the sample should be 1, 10, 50 and 100, 1000 also you can go.

So, the most probable reason for the linearity is the lack of self absorption. See, generally we have discussed that self absorption effects are minimum that means, what is self absorption a sample is there it emits radiation, but the emitted radiation is also absorbed again that is self reversal. So, in ICP the elements come out and then go out of the system causing there is a very short residence time. So, self there is no there are not enough elements which are in the way in the 0 excited state which can absorb that emitted radiation. So, self absorption is almost nonexistent in inductive couple plasma atomic emission spectroscopy.

So, the calibration can vary up to several orders of magnitude that is the trick and it helps also. So, use of a linear analytical curve we are all very familiar if a calibration curve is

linear. It is very simple for us to determine the response and then analyze it corresponding to the linear curve. But, in 90 percent of the cases in ICP it is not linear or very low concentrations. So, the to make it linear or to fit the data it fits betters with quadratic equation first order second order that is y is equal to ax square plus bx plus c. So, that kind of response is possible you when you have the first order polynomial function of the form a y is equal to m x plus c no we do not want that we want ax square plus bx plus c. So, this fits the calibration curves much better than the single straightforward linear analysis. So, many researchers also have employed second order polynomial functions and other mathematical curve fitting techniques also. So, these are slightly in the higher reams of uses of spectrophotometer, but the we can use a higher polynomial no problem.

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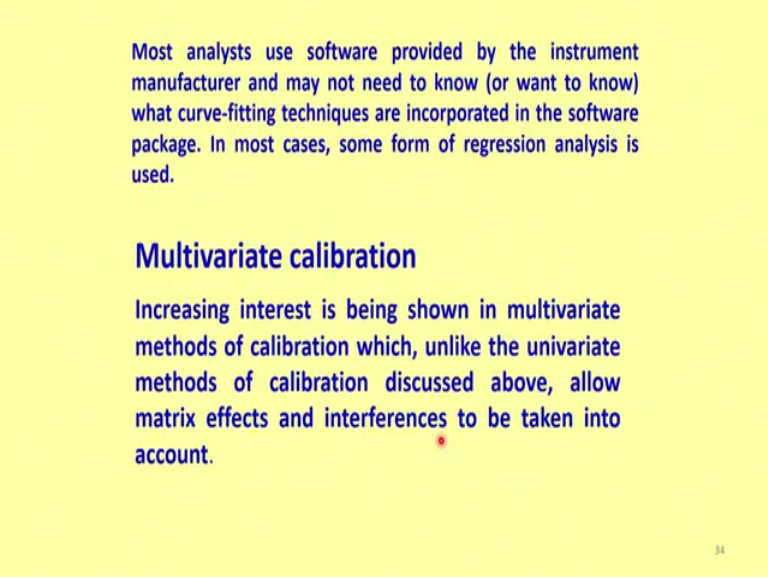

So, most of the analysts use the software provided by the instrument itself. Normally, whenever you do the chemical analysis and the data is generated the computer software ask you do you want to fit the data into linear curve or quadratic curve or polynomial? So, you can choose, look at the apply all the three and see which one looks better the calibration curve which one looks more linear. So, that is possible and it is also important that some sort of regression analysis is used.

So, in multivariate calibration that is several factors are varying increasing interest is being shown in multivariate calibration which unlike univariate, one sample one analyte

at a time that is univariate multivariate one sample many elements. So, these things multivariate analysis allow matrix effects and interferences which takes care of several types of interferences in ICP also, ok.

So many times we always say that ICP is remarkably free from interferences it is remarkably free of self reversal and all that, but still in practice you will find that the signal gets enhanced or reduced in ICP analysis. So, the multivariate analysis takes care of some of the variables with respect to composition, with respect to other elements, with respect to viscosity such standards you can use all the time ok.

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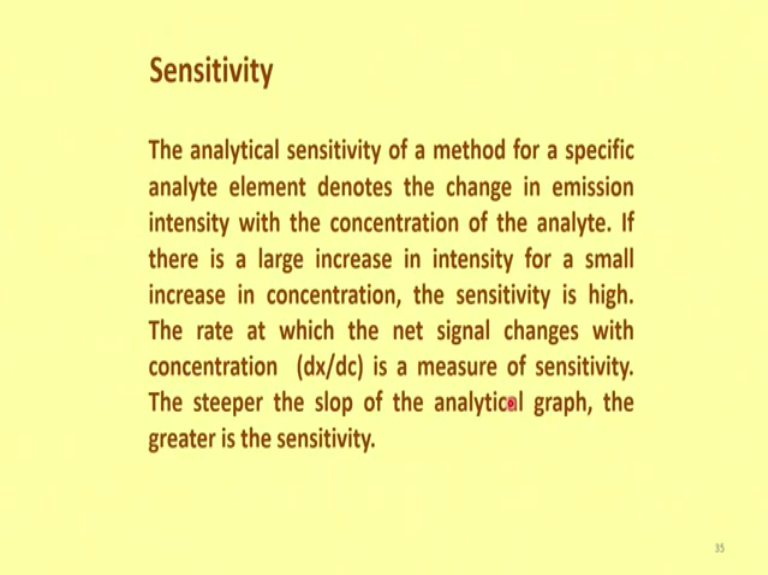

So, now I want to talk to you about some of the chemical terms and a analytical terms you may be familiar, but it is important for us to know what are we talking about. For example, sensitivity I have used the term sensitivity a number of times in this class and what is the sensitivity? The analytical sensitivity of a method tells us up to what level minimum level I can determine an element with confidence, ok. So, for a specific analyte element, sensitivity denotes the change in emission intensity with respect to concentration of the analyte.

In general, the there is a large increase in the intensity for small increase in concentration. So, the curve can be curved polynomial. So, if there is a large increase in the signal for a small increase in the sample concentration then we say the sensitivity is very high. So, what does it mean? So, we say the rate at which the net signal changes

with respect to concentration that is dx by dc you plot the concentration and signal and you take the ratio and that is the slope of the linear line that is a measure of the sensitivity; the steeper the slope, the greater is the sensitivity.

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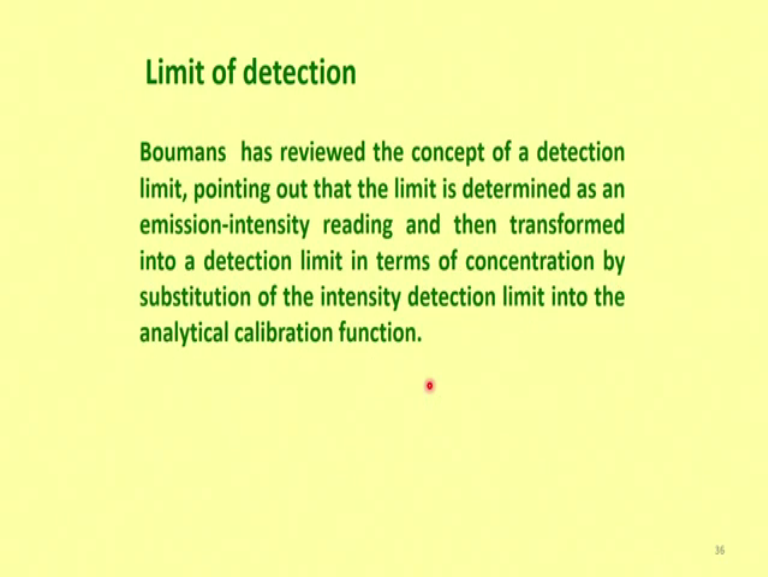

Now, I want you to understand that another concept that is limit of detection. So, what is the limit of detection? So, far we are discus sensitivity. Sensitivity refers to the method ok, sensitivity refers to the method where the signal is measured with respect to concentration. Now, what is limit of detection then? That is, the sample which we can say with confidence that yes there is a sample the sample analyte is there in a given sample.

So, the how do we say that? Normally, when you are not passing the sample you are passing only the water, let us say it gives you some sort of a signal and when you put the sample it gives you higher signal ok. So, the emission intensity reading, what you get minus what is from the blank, that is, without the analyte that tells us how much minimum of the sample can be detected. So, the in terms of in emission intensity reading what we look for is the intensity detection limit of the calibration function.

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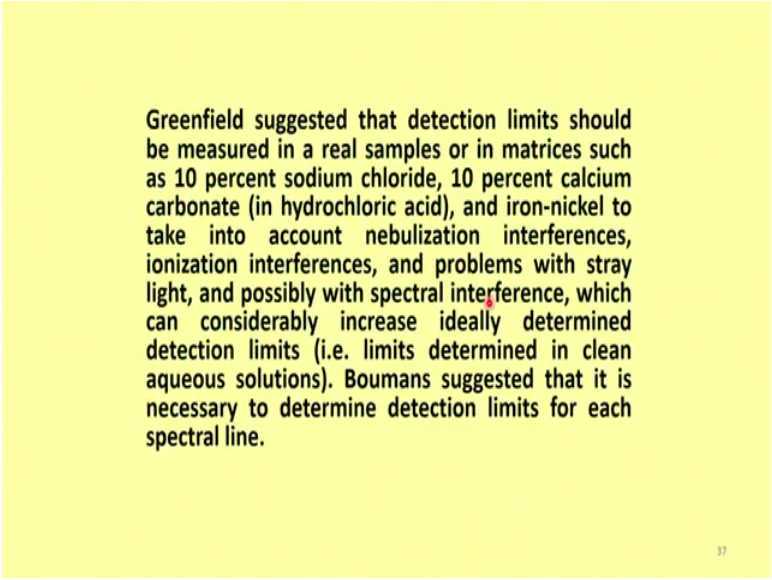

Normally, we take that the detection limit is may should be measured not in pure sample, but in a real sample. So, what is a real sample? A real sample is one where the sample is in the same form as what you get it is not subjected to dissolution or anything like that ok. So, you want to determine lead in blood you take blood it is a blood containing without the lead as a reference sample. So, that also will give some amount of signal.

So, Greenfield suggested that all the detection limit is a method dependent system and it should be measured in real samples not in calibration standards or in secondary standards, but it should be measured in real samples or in matrices with 10 percent sodium chloride or 10 percent calcium carbonate in hydrochloric acid anyway in general. In general, the sample should match the matrix of these a material which in which you want to analyze. So, this reduces the nebulization interferences, ionization interferences and problems which stray light possibly with spectral interference which can be considerably increasing ideally determined detection limit. So, what we are saying is it is necessary to determine detection limits for each spectral line, ok.

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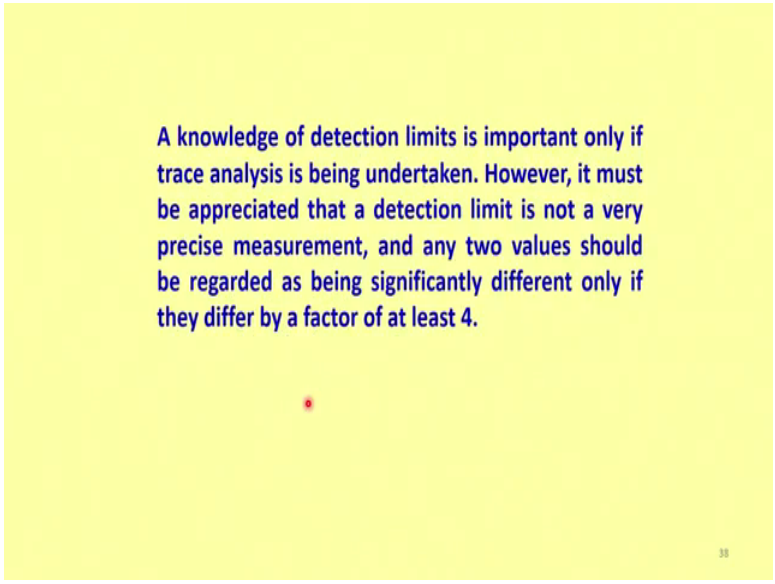

So, I want you to understand that the detection limit is important only if trace analysis is being undertaken it does not work for all kinds of analysis, but trace ultra trace yes it is required. However, it must be appreciated that a detection limit is not a precise measurement, it is a calculated an analysis ok, it is a calculated data. So, any two value should be regarded as being significantly different only if they differ by a factor of about three or four.

Normally, standard deviation of the blank and standard deviation of the sample, if there is three times difference of the blank sample and the standard sample we take it as the detection limit ok, but the detection limit should be applicable for each only analytical line, for some other analytical line sensitivity will be different. So, we should choose a line in which the sensitivity is very high. Such data is available in databases and manufacturers manuals and several other Google you can find out most of such data.

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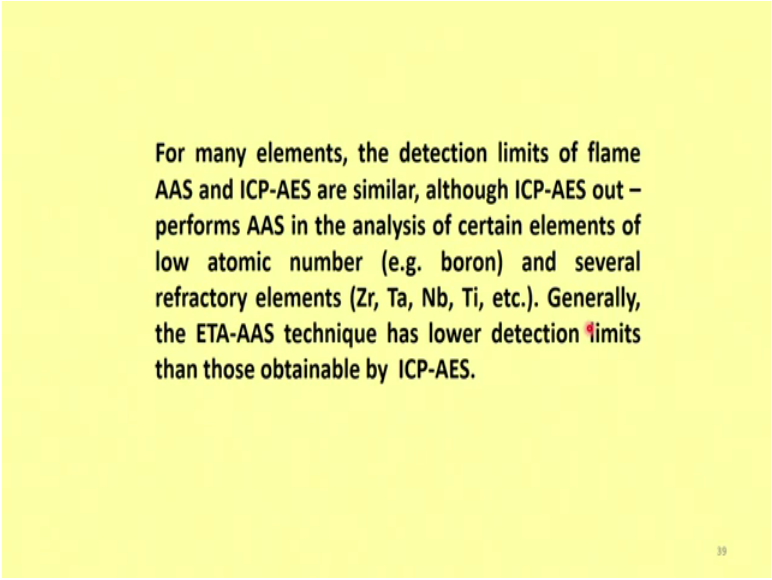

So, for many elements detection limits of ICP and flame AAS and ICP – AES they are all almost similar ah. Although ICP – AES outperforms which is much better than AAS, in the analysis of certain elements of low atomic number and several refractory elements, why? Because in elements of low atomic number there is no way you can determine the concentration because the sample required would be very very small and your even to prepare standards it becomes very difficult ok, but, for example, boron hydrogen, helium, lithium, beryllium, boron only four elements. So, atomic weight would be about eight or ten; ten, I think hydrogen, helium, lithium, beryllium, boron five, approximately ten.

So, several refractory elements are there, in atomic absorption techniques for this will fail. Because, most of these elements do not melt in atomic absorption temperatures of about 2200 or 2300 maybe even up to 3000, many elements do not melt at all. Once, if they do not melt they will not produce the atoms they do not vaporize. So, it is important for us to achieve higher temperatures where we ensure that the sample is evaporated. So, refractory elements like this zirconium, tantalum, niobium, titanium, vanadium, molybdenum all these things they do not melt easily. So, if I introduce it in ICP – AES, the temperature of about 6000 is required, it is available. So, it is easy to determine such elements preferably with ICP – AES then with atomic absorption.

So, the ETA – AAS electro thermal atomic in AAS technique has lower detection limit than those obtainable with ICP – AES also, there is a some improvement in atomic emission spectrometry ok.

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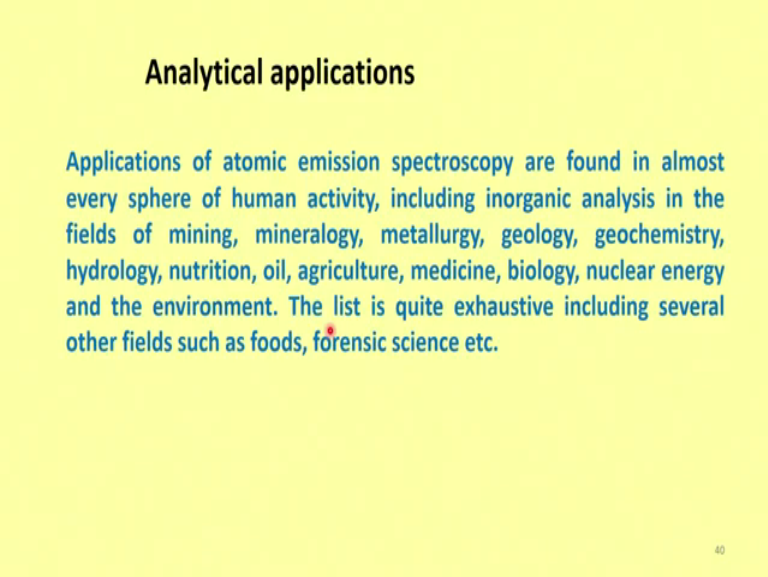

So, analytical applications ah, I want to continue in the next class that is in atomic emission spectroscopy are found in almost every sphere of human activity, including inorganic analysis in the field of mining, mineralogy, metallurgy, food, this that geology, geochemistry, agriculture, medicine, biology, nuclear energy, in environment and so many other fields. We keep on doing the atomic emission spectroscopy and the list is quite exhaustive including several other fields such as foods, forensic science all those things are important for the determination of metals and I will in the next class that is my last class I will try to cover most of the applications what all samples you can handle using ICP. So, thank you very much. We will meet in the next class that will be my last class.

Thank you very much.