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

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Lecture – 15

Instrumentation for ICP AES-VII Plasma Characteristics

Hello everyone we are back to continue our discussion on the ICP. I had in the last class I had shown you different types of sample introduction systems and I had also talked about the peristaltic pump for sample introduction. So, I am going to show you the same slides a little bit more quickly and we will proceed ahead with our programme.

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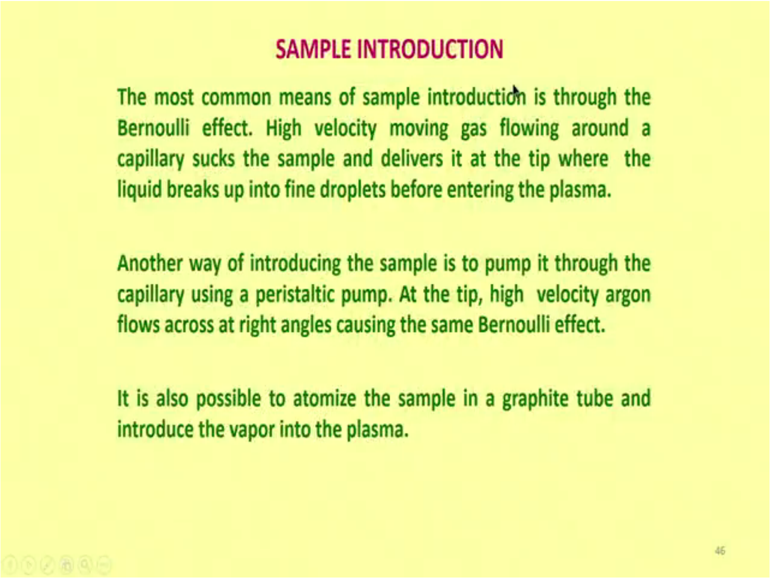

SAMPLE INTRODUCTION

The most common means of sample introduction is through the Bernoulli effect. High velocity moving gas flowing around a capillary sucks the sample and delivers it at the tip where the liquid breaks up into fine droplets before entering the plasma.

Another way of introducing the sample is to pump it through the capillary using a peristaltic pump. At the tip, high velocity argon flows across at right angles causing the same Bernoulli effect.

It is also possible to atomize the sample in a graphite tube and introduce the vapor into the plasma.

So, the sample introduction means these most common means of sample introduction is through the Bernoulli effect; that is high velocity moving gas flowing around a capillary sucks the sample and delivers it at the tip. Here the liquid breaks down into fine droplet us before entering plasma.

Another way of introducing the sample is to pump it through a capillary using a peristaltic pump at the tip the high velocity argon flows across at right angles causing the same Bernoulli effect. So, it is also possible to atomise the sample in a graphite tube and introduce the vapour into the plasma.

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So, I had shown you the bottom figure in the here, this is how we introduce the sample through a peristaltic pump.

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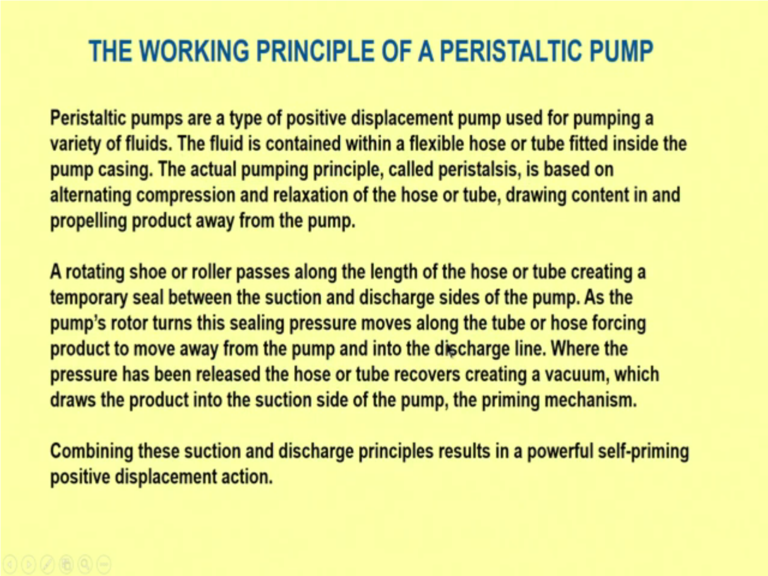

THE WORKING PRINCIPLE OF A PERISTALTIC PUMP

Peristaltic pumps are a type of positive displacement pump used for pumping a variety of fluids. The fluid is contained within a flexible hose or tube fitted inside the pump casing. The actual pumping principle, called peristalsis, is based on alternating compression and relaxation of the hose or tube, drawing content in and propelling product away from the pump.

A rotating shoe or roller passes along the length of the hose or tube creating a temporary seal between the suction and discharge sides of the pump. As the pump's rotor turns this sealing pressure moves along the tube or hose forcing product to move away from the pump and into the discharge line. Where the pressure has been released the hose or tube recovers creating a vacuum, which draws the product into the suction side of the pump, the priming mechanism.

Combining these suction and discharge principles results in a powerful self-priming positive displacement action.

So, Peristaltic pumps I had shown you this figure I had shown you I had told you that there will be bearings, around which a tube is going round and round one below one above one above one below the bearings, and the tube carries the sample through a conical flask and the here you can see the principal of the sample introduction using a peristaltic pump, here the these are all ball bearings you can see this black systems on the top. Here you can see near the top there is a ball bearing there is one more ball bearing here there may be more also. So, these are these are the 3 different systems where the 3 different stages where the liquid is sucked in and delivered.

For example in the first figure on the top you can see that the sample is moving here it gets squeezed inside the ball bearing and the tubing outer tubing and then the liquid gets sucked, as this ball bearing moves in the liquid will be sucked inside and then it will be flowing through this is the second stage where the ball bearing has moved slightly to the left and liquid will move to the right, and same thing. So now the liquid has been sucked up to this point, and then in the third stage when the ball bearing moves like this completely the liquid will be sucked like this and then it will be going through the peristaltic pump.

The advantages of such a peristaltic pump, is that the sample does not come into contact with the metal parts of the peristaltic pump. I do not know how many of you are aware generally pumps are used for the delivery of liquid, it can be anything it can be a subversive pump bore well what you might have heard or it is meant for transferring liquid alkalis acids etcetera, which for which the samples are hazardous in nature. So, the use of pumps in all spheres is very well known.

So, these pumps have a characteristic that some of them are positive displacement pumps some of them are negative displacement pumps. So, most of these pumps have operate in contact with the liquid for example, if you want to suck a sample from the from a bore well. You need a submersible pump in which the pump will be pushing it up and down up and down so, that the liquid will be coming out. So, there the submersible parts pump parts are in contact with the liquid that is bore well water. So, if it is acid then you can use special materials because rubber and other tubes will not work because the acid will attack the rubber. So, sometimes we use PVC pipes, and sometimes we use Teflon pipes, sometimes we use stainless steel like that, different components are introduced in the pumps.

But in peristaltic pumps the liquid does not come in contact with any of the material a metal parts; that means, the contamination is minimal here, that is required because we are going to determine many elements at parts for million parts for billion level parts for trillion also. So, any small contamination and can disrupt the result. So, the one has to be very weary of contamination and for this purpose a peristaltic pump is used and this peristaltic pump is also used in our day today life where the people with diabetes undergo dialysis.

For example, blood has to be taken out from a body and then re put inside the body again, then we need a peristaltic pump because we do not want the blood to come in contact with any of the external agencies like air water metal parts and many other things. So, this is how the peristaltic pump works.

The principle is very same very (Refer Time: 07:06). So, this, the working principle of a peristaltic pump. They are positive displacement pumps used for pumping a variety of fluids. The fluid is contained within a flexible hose or tube which I have shown you in the previous slide inside the pump casing. So, actual pumping principle called as is called as peristalsis; that is based on alternating compression and relaxation of the tube drawing content in and propelling the product away from the pump without coming in directly in contact with the sample.

So, a rotating shoe or roller passes along the length of the hose or tube creating a temporary seal between the suction and discharge sides of the pump. You can see here in my previous slide here there will be expansion there will be compression there will be expansion there will be compression. Like that there will be a succession of compression and expansion. And so, as the pump’s rotor turns this, sealings moves sealing pressure moves along the tube.

So, the sample, get sucked in and then moves without coming in contact with the pump. So, the tube or the hose force it forces the product to move away from the pump and into the discharge tube discharge line. So, such peristaltic pumps are available in the market and they have been adopted in analytical science because an automatic sample delivery system ensures a trouble free chemical analysis.

So, very small size pumps are available in the market. So, the pressure in the hose gets released and the tube recovers creating a vacuum, normally what happens is when the bearings compressed liquid will get sucked in so after sometime bearings will move away and then liquid will be pushed out pushed out like that and there by how does it get pushed out because of the vacuum it generates a small quantity of vacuum through which the liquid will rush in through the tube until the delivery point.

So, this draws the product into the suction side of the pump and that is the priming mechanism. So, once the pump is primed the out you will not even feel that the sample is being sucked and then expanded vacuum created and all these things. So, combining these suction and discharge principles results in a powerful self-priming, positive displacement action that is peristaltic pump for you.

So, you have to be very careful when you want to buy a ICP aes, because the

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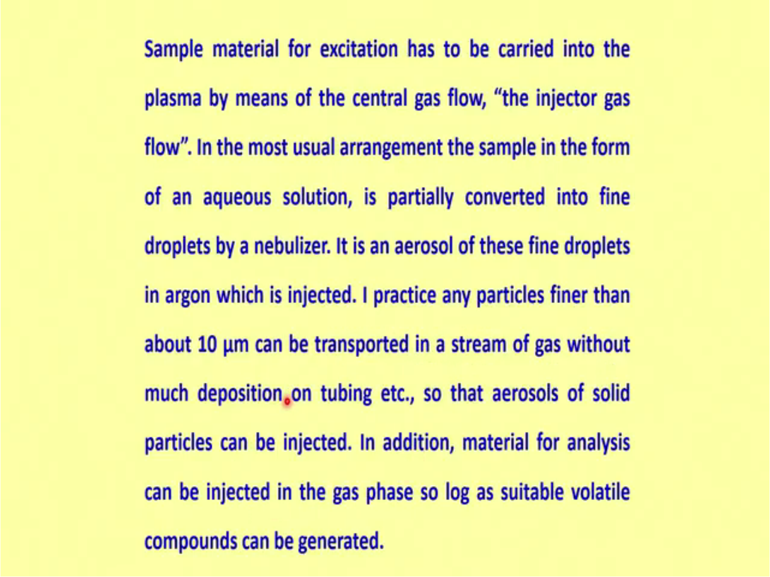

Sample material for excitation has to be carried into the plasma by means of the central gas flow, "the injector gas flow". In the most usual arrangement the sample in the form of an aqueous solution, is partially converted into fine droplets by a nebulizer. It is an aerosol of these fine droplets in argon which is injected. I practice any particles finer than about 10 µm can be transported in a stream of gas without much deposition on tubing etc., so that aerosols of solid particles can be injected. In addition, material for analysis can be injected in the gas phase so log as suitable volatile compounds can be generated.

Sample should not come in contact with the metal parts of the pump. So, the sample material foe excitation has to be carried out into the plasma by means of the central gas flow. The injector that is called as injector gas flow all these I have covered earlier except for the, your working principle of the peristaltic pump I had covered most of these. So, in the most usual arrangements the sample is in the form of an aqueous solution and that is partially converted into fine droplet us by the Nebulizer.

So, it is an aerosol of these fine droplet us in argon that is injected; that means, the argon is used as a media to create aerosol because why I am telling you this is the plasma will not tolerate liquid inside the toroidal space of plasma. So, if you (Refer Time: 11:16) liquid plasma will put off. So, the fine droplet us are generated by the argon gas it is an aerosol of these fine products in argon which is injected.

In practice any particles finer than about 10 millimetre can be transported in a stream of gas without much deposition in the tubing. So, that, aerosols of solid particles can also be injected in addition material for analysis can be injected, in the gas phase. So, long as suitable volatile compounds can be generated.

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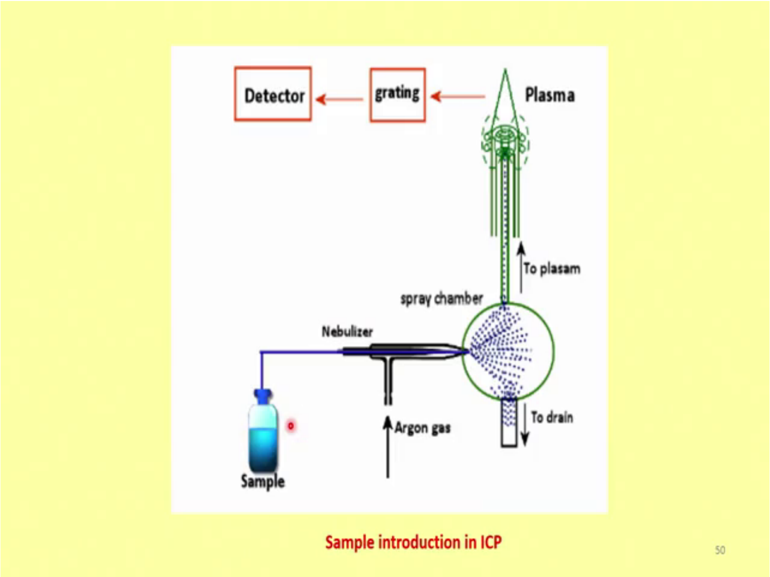

Sample introduction in ICP

So, this figure also I had shown you in the last as a last slide in my last interaction with you, the sample is here it enters the Nebulizer and then the there is argon gas coming through argon gas is coming excelling alone in one of the along with the concentric tubes and then it enters this aerosol enters this liquid enters here inner the plasma and in the plasma toroidal space the sample enters gets excited to higher energy levels and then emission takes place and the emitted radiation is separated by the grating and which is collected by the detector. So, when I do not have the sample I do not have any grating at all. The sample if I have a blank sample then there is no grating, but if there is a sample contains the analyte and then I have some photons coming out of the emission lines.

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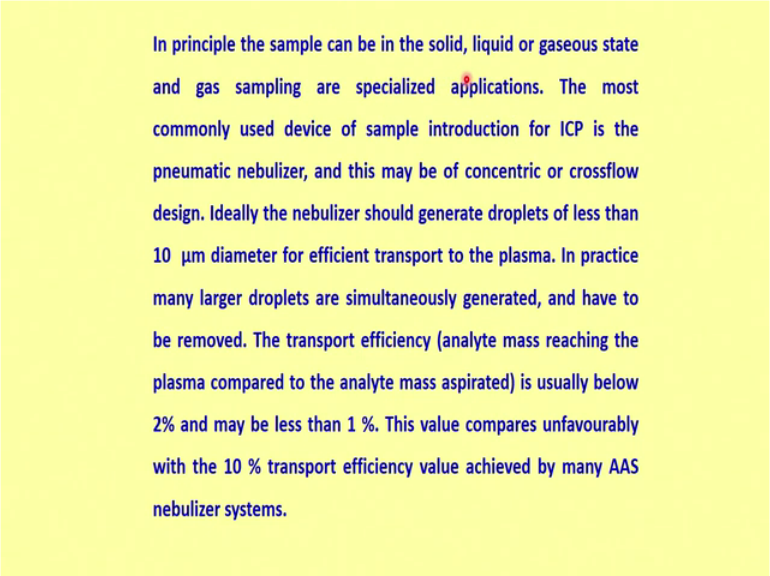

In principle the sample can be in the solid, liquid or gaseous state and gas sampling are specialized applications. The most commonly used device of sample introduction for ICP is the pneumatic nebulizer, and this may be of concentric or crossflow design. Ideally the nebulizer should generate droplets of less than 10 µm diameter for efficient transport to the plasma. In practice many larger droplets are simultaneously generated, and have to be removed. The transport efficiency (analyte mass reaching the plasma compared to the analyte mass aspirated) is usually below 2% and may be less than 1 %. This value compares unfavourably with the 10 % transport efficiency value achieved by many AAS nebulizer systems.

So, in principle sample can be in solid, liquid or gaseous state. And the gas sampling is a very specialised application by itself. Normally what I expect is the introduction of a sample as a liquid is simpler than introduction of sample as an aerosol, because in analytical sciences most of the time we have been talking about parts per million parts per million analysis only.

So, the sample introduction for ICP is basically pneumatic Nebulizer only. And this may be of concentric or crossflow both designs are possible. So, ideally the Nebulizer should generate droplet us of about 10 micro metre in diameter for efficient transport into the plasma suppose the particles are bigger then what happens? If the particles are bigger they will not form the aerosol, but they will fall down and the water droplet us it will drain out that is waste of the sample. So, the more sample is introduced as an aerosol we have a better sensitivity.

So, the droplet us fine droplet us need to be collected as aerosol bigger droplet us need to be removed as a waste. So, the transport efficiency what we call the conversion efficiency of the sample into aerosol, that is analyte mass that reaches the plasma. Compared to the analyte mass aspirated suppose I inject 5 ml and all the 5 ml does not form aerosol, it will form only about may be 1 ml or about 13 to 20 percent is the efficiency whatever is the liquid you take you want to make an aerosol about 13 percent gets into air and remaining becomes bigger droplet us and needs to be drained out.

So, that is usually below 2 percent, and sometimes it goes even less than 1 percent of the total liquid introduced; that means, if you introduce about 100 micro litre, only about one micro litre gets converted into aerosol may be 2 percent may be 2 ml out of 100 ml. So, this value compares unfavourably with about 10 percent transport efficiency that is achieved by atomic absorption spectrometer why? See the point is in atomic absorption spectroscopy we have the gas flow about 6 litres to 10 litres per minute.

Here in ICP it is one litre per minute. So, the difference is in the efficiency of the sample to be converted into an aerosol. So, the efficiency of a Nebulizer if you have taken the course you can compare the Nebulizer design in AAS as well as this scoog and other books which I have recommended for reference, also show this figures you can compare how the design of a Nebulizer works and there you can see lot of fundamental difference between the AAS and ICP values, but in general it is not favourable with respect to AAS compare to AAS.

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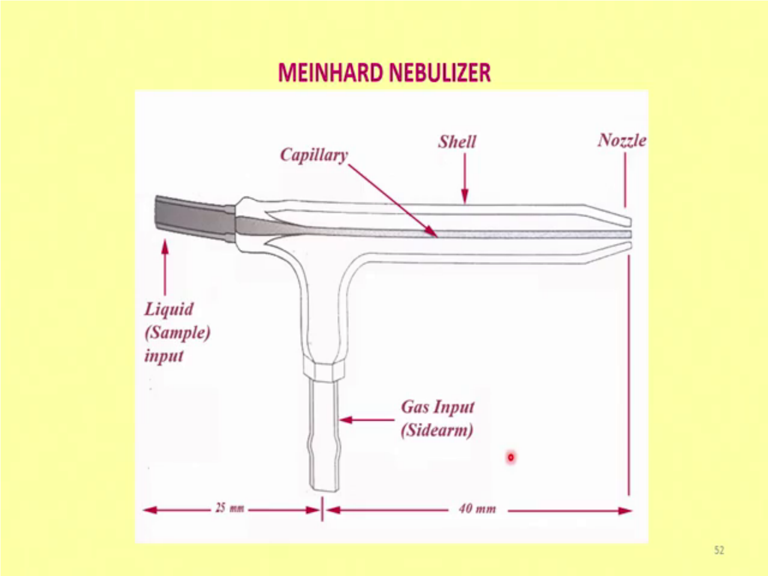

MEINHARD NEBULIZER

So, this is the Meinhard Nebulizer here I have the liquid sample coming through and then; obviously, we assume that the peristaltic pump somewhere here. And then liquid sample input is there it enters the capillary comes out and there is a shell here that creates one more tubing and argon gas input is from the bottom and it goes like this.

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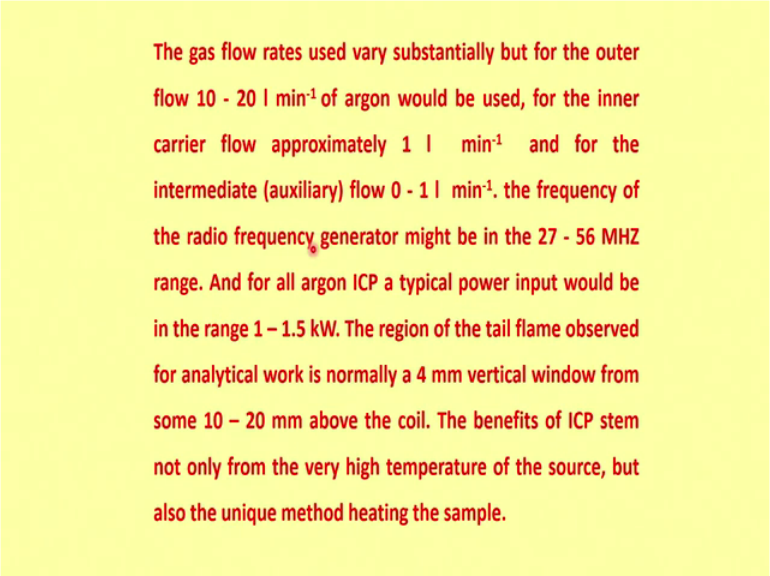

The gas flow rates used vary substantially but for the outer flow 10 - 20 l min^{-1} of argon would be used, for the inner carrier flow approximately 1 l min^{-1} and for the intermediate (auxiliary) flow 0 - 1 l min^{-1}. the frequency of the radio frequency generator might be in the 27 - 56 MHZ range. And for all argon ICP a typical power input would be in the range 1 – 1.5 kW. The region of the tail flame observed for analytical work is normally a 4 mm vertical window from some 10 – 20 mm above the coil. The benefits of ICP stem not only from the very high temperature of the source, but also the unique method heating the sample.

So, the gas flow rates used vary substantially, but for other outer flow 10 to 20 litres per minute of argon would be used. For example, the inner carrier flow should be approximately about 1 litre per minute which I had already mentioned and for the intermediate or auxiliary flow 0 to 1 litre per minute also is fine. So, the frequency of the radio frequency of the generator might be in the 27 to 56 mega-hertz range.

These are all technical details you will find most of these details in your in the instrument manual in general they will recommend what should be the flow rate, what should be the what is the mega-hertz range radio of frequency generator an all that will be mentioned in the literature or the menu card of the instrument manuals operating, and per all argon ICP a typical power input would be in the range of one to one point 5 kilo watt per kilo watt; that means, the power required to put the sample into the toroid space of the plasma is about 1 to 1.5 kilo watt.

So, the region of the tail flame observed for analytical work is usually a 4, 4 mm vertical window from some 10 to 20 mm millimetre above the coil. Usually if remember this; that means, the plasma will extend approximately 20 millimetre, but the sample measurement needs to be within 4 mm vertical window. So, the benefits of ICP is stem not only from the very high temperature of the source, but also the unique method of heating the sample that is ICP for you.

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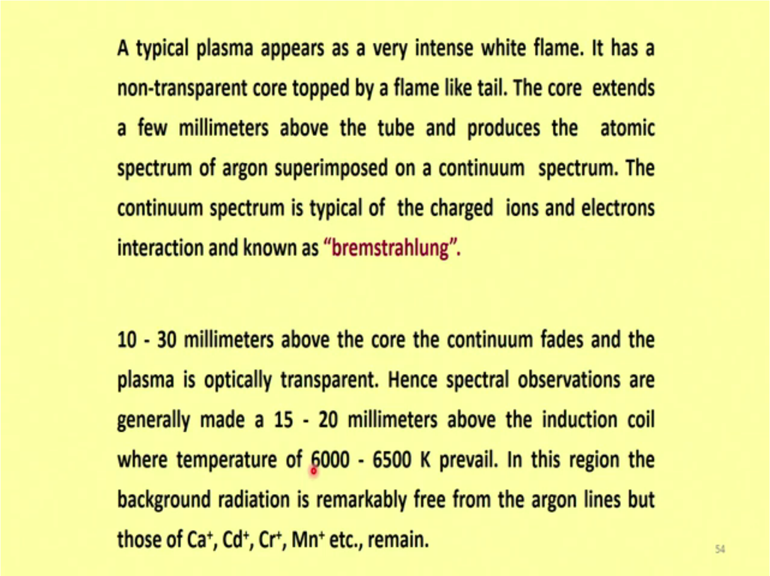

A typical plasma appears as a very intense white flame. It has a non-transparent core topped by a flame like tail. The core extends a few millimeters above the tube and produces the atomic spectrum of argon superimposed on a continuum spectrum. The continuum spectrum is typical of the charged ions and electrons interaction and known as "bremstrahlung".

10 - 30 millimeters above the core the continuum fades and the plasma is optically transparent. Hence spectral observations are generally made a 15 - 20 millimeters above the induction coil where temperature of 6000 - 6500 K prevail. In this region the background radiation is remarkably free from the argon lines but those of Ca^+, Cd^+, Cr^+, Mn^+ etc., remain.

So, a typical plasma appears as a very intense white flame, it has a non-transparent core topped by a flame like tail the core extends a few millimetre above the tube and produces the atomic spectrum of the of argon, superimposed on a continuum spectrum this sentence I want you to understand carefully what I am saying is the non-transparent core is like flame like tail of the plasma.

So, the core extends a few millimetre above the tube and produces atomic spectrum of argon also as well as the super imposed in that argon the emission line there will be if our sample is introduced as an aerosol, the argon also gives out emission lines and the sample also gives out emission lines, water vapour is there so hydrogen and oxygen and several other things they also decompose around 10,000 degree centigrade or Kelvin. So, they also emit radiations so you have to choose which is the correct analytical line emission line for each element you want to determine, otherwise the whole spectrum if you see in an ICP what you will see is the combined spectrum of oxygen hydrogen water and then the sample and argon. And argon line would be very intense because our argon fluoride would be approximately about 20 to 30 litres per minute.

For sample introduction one litre per minute, but the remaining argo argon also gives out a fantastic spectrum that is a continuum spectrum from that continuum spectrum there will be super imposed lines for different elements. So, we have to pick up only that line;

that means, whatever line wavelength you choose for the estimation there will be certain amount of argon emission associated with that is background.

So, the background is of that of argon and the spectrum is that of continuum spectrum. So, this continuum spectrum is typical of the charged ions and electrons an interaction and that is known as bremsstrahlung. This bremstrahlung is nothing but a sort of additional lighting, additional spectral feature coming from argon it is a German word bremstrahlung strahlung means radiation in German brem means external additional.

So, this is known as bremstrahlung. So, there is no typical English equivalent for this because the sometimes most of the ICP work was done in Germany the development work for analytical applications. So, that name has stuck as bremstrahlung.

So, about 10 to 30 millimetre above the core of the continuum 10 to 20 millimetre above the core, the continuum argon radiation fades away; that means, it becomes very less and the plasma is optically transparent; that means, you will have very less bremstrahlung for the system. So, the spectral observations have to be made about 10 to 20 millimetres above the induction coil. So, that the temperature of about 6 to 8000 kelvin should be available there in this region the background radiation is remarkably free from argon lines that is good for us, but those of calcium cambium chromium manganese nickel iron whatever element you want to determine they remain available to us to choose for the emission monitoring.

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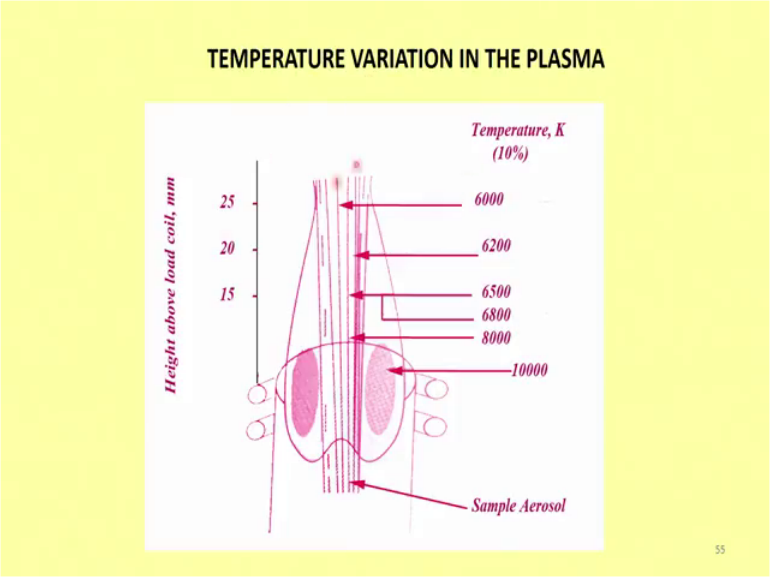
TEMPERATURE VARIATION IN THE PLASMA

So, the, this is how the temperature varies in the plasma. So, what do we see here? We have the concentric tubes here this is the plasma height above the load coil that is these are the load coils here you can see 2 round circles, where my pointer is here and another here. So, it is a circular feature that is for rf and sample introduction comes through the tubing, and the plasma general shape of the plasma is like this and the argon gas will be flowing through all these concentric circles, and the plasma will be available slightly above this.

So, approximately near the plasma near the tip of the, this thing we have temperature of about 10 thousand degrees. At this temperature bremstrahlung would be very high, and then you go slightly up temperature is around 8000 and then 6800, 6500 around 15 millimetre the temperature of the plasma will come down from 10000 to 6500 go for by another 20 millimetre go by another 5 millimetre up to 20 the temperature prevailing will be approximately 6200 kelvin, and still above around 25 the temperature will be around 6000 kelvin, and this temperature will constitute approximately 10 percent of the total radiation; that is coming out and this is how you may say why not measure here itself in 10000 or 8000, but in general it does not make much difference because only around 6000 degree kelvin range will make the measurement because bremstrahlung will be less.

Moreover, many of the analytical samples do get vaporised and start emitting radiation around 6000. Suppose some elements do not then you go down measure it around 15 millimitre that will be around 6500 or you can go still nearer up to 8000 you can measure, but the background radiation will be much more.

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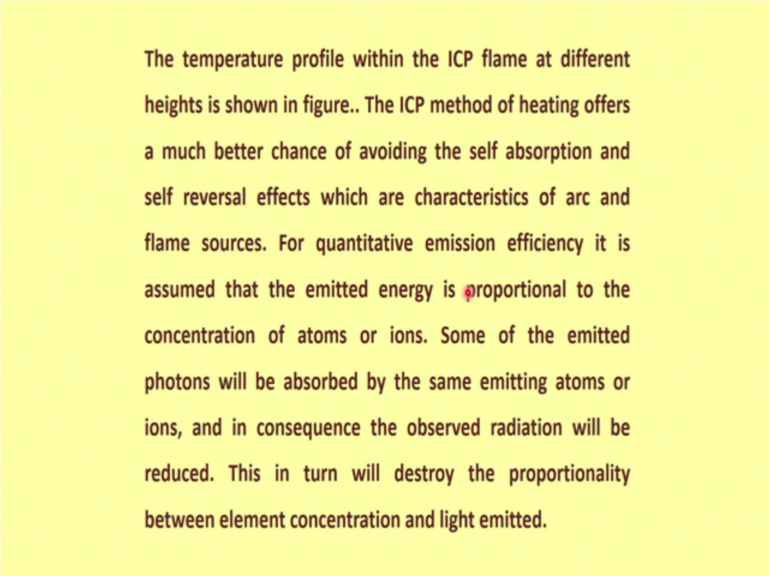

The temperature profile within the ICP flame at different heights is shown in figure.. The ICP method of heating offers a much better chance of avoiding the self absorption and self reversal effects which are characteristics of arc and flame sources. For quantitative emission efficiency it is assumed that the emitted energy is proportional to the concentration of atoms or ions. Some of the emitted photons will be absorbed by the same emitting atoms or ions, and in consequence the observed radiation will be reduced. This in turn will destroy the proportionality between element concentration and light emitted.

So, the temperature profile within the ICP flame which I showed you just now at different heights I have shown in the figure the ICP method of heating offers a much better chance of avoiding the self-absorption and self-reversal are also effects are also very minimum unlike atomic absorption spectrometer. So, the main problem with ICP with AAS is that the signal gets reduced because of self-reversal; that means, the ions generated atoms generated also absorb the same radiation that is coming out.

So, this self-reversal that is absorption of the same radiation what is coming out is a little bit of a problem, that reduces the calibration in quality and it also introduces some sort of a curvature in the when you do the calibration curve.

So, we want minimum self-reversal fortunately it works. So, in ICP inductive couple plasma atomic emission spectrometer so, the for quantitative emission efficiency it is assumed that the emitted energy is proportional to the concentration of the atoms are ions why self-reversal is minimum that is why we should assume that the proportion of the emitted radiation is one to one correspondence with respect to that of atoms or ions.

Some of the emitted atoms will be absorbed by the same emitting by the same emitting atoms or ions and in consequence the observed radiation will be reduced. This in turn will destroy the proportionality between the element concentration and the light emitted. I urge you to go through this slide more carefully try to understand the ideas if you have any doubt you can write to me and I will be able to help you out with understanding of the subject much better.

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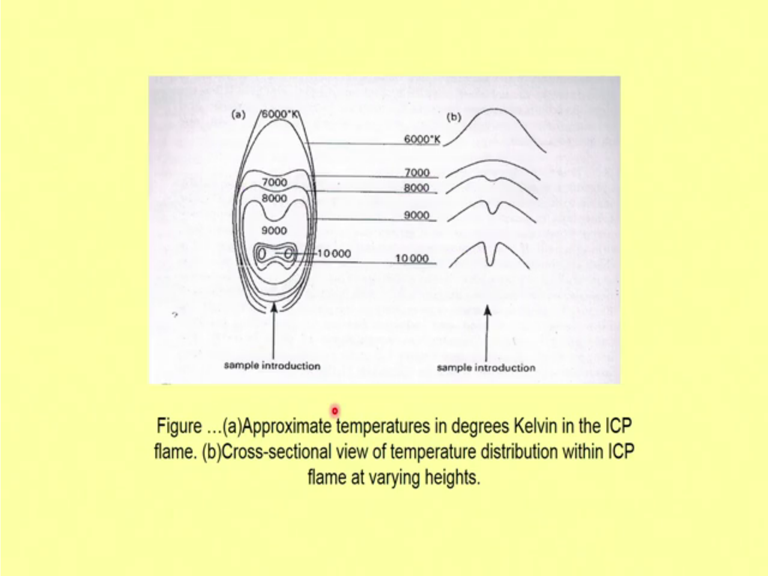

Figure ...(a)Approximate temperatures in degrees Kelvin in the ICP flame. (b)Cross-sectional view of temperature distribution within ICP flame at varying heights.

So, this is another profile of the plasma here what I am showing you is approximately 10000 it also extends not only vertically, but also horizontally above the tip. So, this is how the where the movement here it is 10000 here it is 9, 7, 8, 6000 etcetera. That is near the edge about 25 millimetres above the plasma. So, the profile how the temperature varies across not vertical not vertical, but across are the profiles shown here and when the sample is introduced there will be a dip in the temperature.

That is how the sample introduction sample should be as less as possible, but the temperature comes down drastically the movement where the sample is being introduced you can see the big dip here and above this the dip is very less here it is still less here it is almost non-existent. So, approximately temperatures in degrees kelvin in the ICP flame and cross-sectional view also I am showing you I may ask you about these in the examination if you are taking a test.

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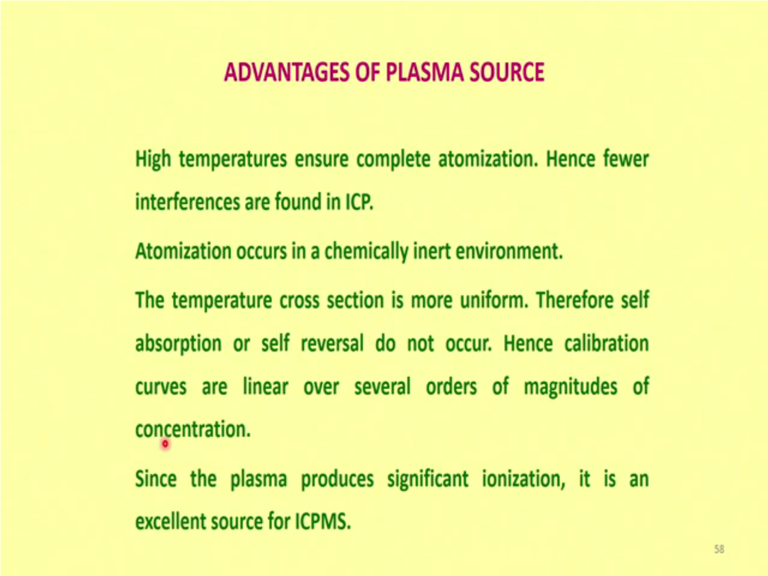

ADVANTAGES OF PLASMA SOURCE

High temperatures ensure complete atomization. Hence fewer interferences are found in ICP.

Atomization occurs in a chemically inert environment.

The temperature cross section is more uniform. Therefore self absorption or self reversal do not occur. Hence calibration curves are linear over several orders of magnitudes of concentration.

Since the plasma produces significant ionization, it is an excellent source for ICPMS.

So now I would like to tell you about the advantages of plasma source. So, coming back to our discussion about why ICP AAS compared to atomic absorption that is an eternal debate I think. So, the main advantage is high temperatures ensure complete atomisation. So, fewer interferences are found in ICP, why because high temperatures ensure complete atomisation. So, atomisation occurs in a chemically inert environment this is another advantage. So, temperature cross section is more uniform above a 15 mm and therefore, self-absorption or self-reversal do not occur this point I have conveyed to you so many times now.

Hence calibration curves are linear over several orders of magnitude of concentration. I had had earlier mention to you that whenever you want to make a calibration curve we work with 10 ppm, 50 ppm, 100 ppm 1000 ppm like that. It is not in arithmetic progression 1, 2, 3, 4, 5 or 10, 20, 30 40 no not like that. So, 20, 40, 60 no what is required is 10, 50, 100, 1000 like that you can make the calibration curve, but the problem is the curvature the calibration curve may be a little bit curved, since the plasma produces significant ionisation it is an excellent source for ICPMS also.

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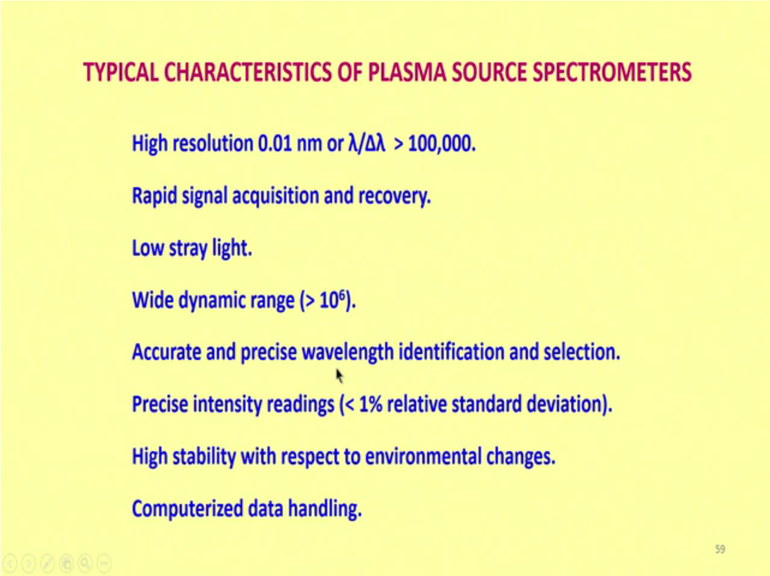

TYPICAL CHARACTERISTICS OF PLASMA SOURCE SPECTROMETERS

High resolution 0.01 nm or $\lambda/\Delta\lambda > 100{,}000$.

Rapid signal acquisition and recovery.

Low stray light.

Wide dynamic range ($> 10^6$).

Accurate and precise wavelength identification and selection.

Precise intensity readings (< 1% relative standard deviation).

High stability with respect to environmental changes.

Computerized data handling.

So, a typical characteristic of plasma source spectrometers is that, the resolution for the wavelength is 0.1 nanometre or the delta lambda to delta lambda ratio should be more than 100000. And computer is there then things are automatic. So, the rapid signal acquisition and recovery is another advantage stray light almost nill because the plasma is transparent, why dynamic range this I have already explained to you, accurate and precised wavelength identification and selection.

That is possible with the help of computer and stepper motors. So, precise intensity readings can be obtained with less than 1 percent relative standard deviation. So, high stability with respect to environmental charges changes are possible and computerized data handling makes the ICP operation very simple and straight forward. We will continue our discussion in our next session.

Thank you.