Modern Instrumental Method of Technique
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Lecture No. # 29

Inductive Coupled Plasma Atomic Emission Spectrometry-2 Instrumentation

We were discussing the ICP source in the last class; we will continue from there. And what I was I had told you was that, a typical ICP source is called a plasma torch; it consists of three concentric tubes, through which streams of argon flow at a total flow rate of 5 to 20 liters per minute. The inner diameter of the tube is about 2.5 centimeter;; the top portion of the tube is a induction coil powered by radio frequency generator, which radiates 0.5 to 2 kilowatt of power at 27.12 megahertz or 40.68 megahertz at the at this voltage and you need a spark from the tesla coil to start ionizing the argon.

And the resulting ions and their associated electrons usually interact with the fluctuating magnetic field produced by the induction coil. The interaction causes the ions and electrons within the coil, to flow in the closed annular paths. The resistance of the ions and electrons in general causes the ohmic heating of the plasma.

So, the temperature of the plasma that usually reaches in inductively couple plasma, is approximately 4000 to 6000 kelvin. This requires thermal isolation of the outer quartz cylinder, because the quartz will melt at this temperature; this is achieved by argon flowing around it tangentially around the walls of the tube and entering the plasma radially. In most of that, this arrangement helps cool the plasma near the edge of the quartz tube, retaining its mechanical measurements.

In most of the instruments, torch is positioned at 90 degrees and aligned actually with a spectrometer system. The radiation emitted from the plasma is used for the analysis, because that is why most of the ions will form the atoms and the excitation to higher energy states takes place, and the emission spectrum emerges in the plasma. So, the plasma, the radiations coming from the plasma need to be treated in a spectrometer, to separate the specific wavelengths.

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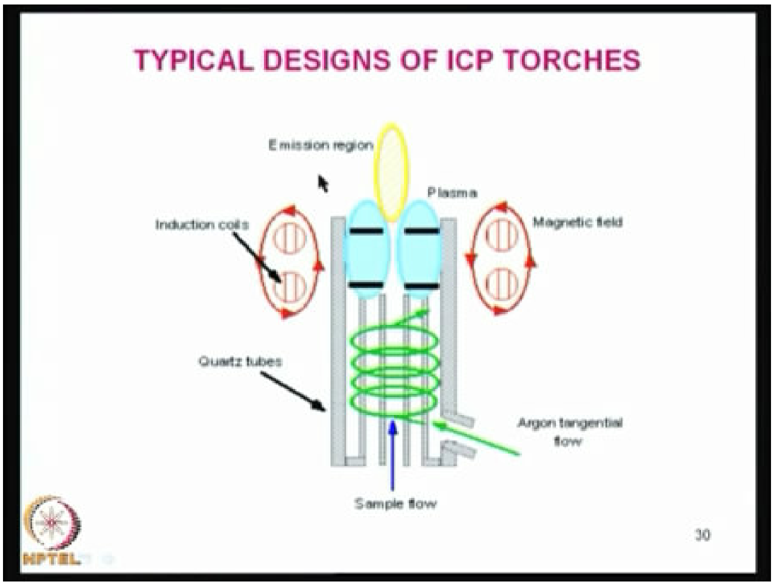

TYPICAL DESIGNS OF ICP TORCHES

So, this slide shows you the typical design of an ICP torch. This I had shown you in my last class also, the outer one is first coil and concentric coil; and this and this, the next outer as the second coil, and third one is the inner one is the place where the sample will flow from the bottom. And argon gas coming tangential flow will flow like this in concentric circles around the tube, and then the plasma is generated here. The emission region is above this; the yellow portion that is shown here and these are typical induction coils and the magnetic field is generated here; and the quartz tubes and argon tangential flows, sample flow, all these things I have shown in this slide.

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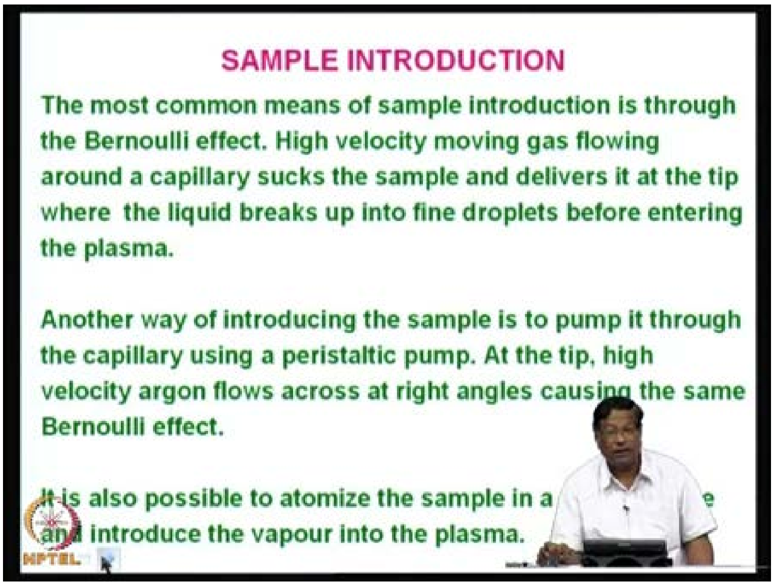

SAMPLE INTRODUCTION

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 e
and introduce the vapour into the plasma.

So, the sample introduction forms a most important part of the ICP analysis, because the sample must be introduced in a continuous manner, so that there is no breakage of the plasma, and the sample must be introduced into the plasma in a reproducible manner. So, the most common means of sample introduction is through the Bernoulli effect, that is, suction. High velocity moving gas flowing around the capillary sucks the sample and delivers it at the tip, where the liquid breaks up into very fine droplets just like in atomic absorption, and the droplets will enter the plasma again.

Another way of introducing the sample is, to pump it through the capillary using a peristaltic pump; and what is a peristaltic pump? A peristaltic is a pump, where the liquid does not come into contact with any of the pump machine parts; for example, a peristaltic pump, suppose you have a tube mounted on a ball bearing like this, the tube will pass like this, so the tube will go like this; and as the sample comes here the tube will move like this, the tube will have a system like this; this is where the ball bearings are situated, this is a an expanded view.

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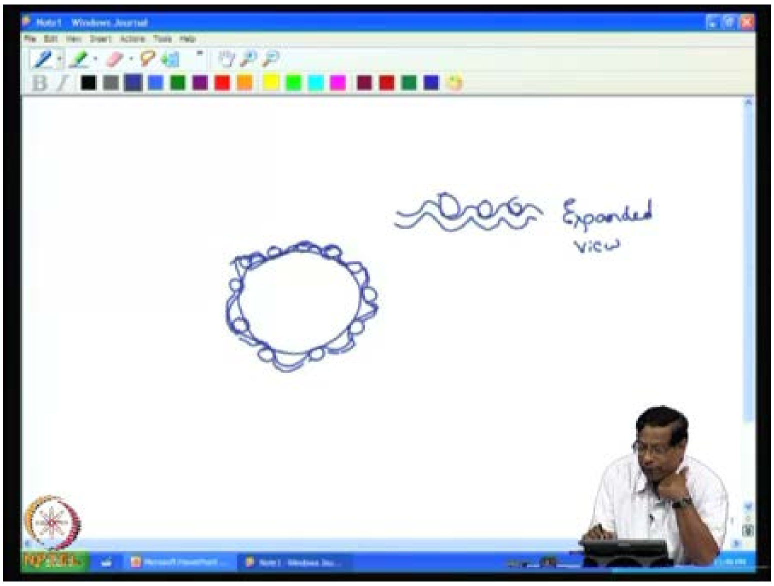

So, the sample will move like this, and without touching any of the parts, it will be coming; and the tube finally enters the concentric tube in the plasma; that what we had shown here earlier. So, this is a peristaltic pump; a similar peristaltic pump is used in the blood transfusion for kidney patients. There the blood has to be taken out from the patient and needs to be purified, and then go it pumps back into the body. So, dialysis and many other operations are done routinely, where the chemical or the fluid does not come into contact with any of the machine parts; a similar machine is used in the spectro in ICP spectrophotometer.

And then, the sample must be introduced through the pump using a peristaltic pump. At the tip, high velocity argon is flowing 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, but most of the routine chemical analysis are always conducted using a liquid sample.

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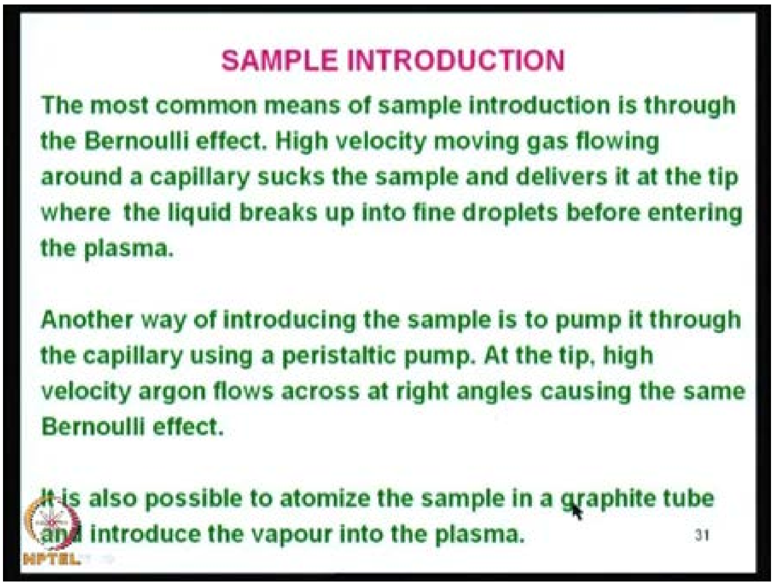

SAMPLE INTRODUCTION

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

So, this slide is, this slide shows you the typical arrangement of the sample introduction.

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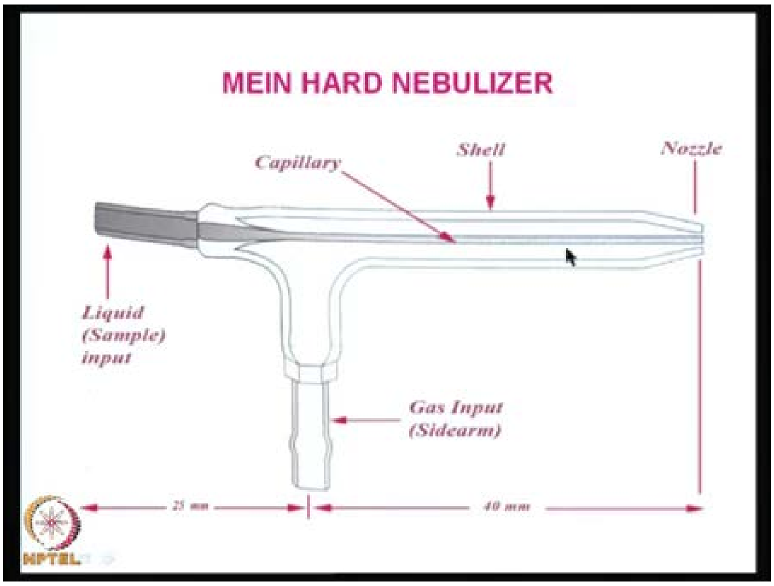
MEIN HARD NEBULIZER



Now, this slide also I have shown you earlier, this is known as Mein hard nebulizer. And the liquid sample is coming here, there is a capillary, there were here near the nozzle there was a Bernoulli effect, because the gas is flowing all around it at a very high velocity; and the gas input is like this and this is the outer shell, this is the capillary through which the sample is flowing and the nozzle is here at this edge.

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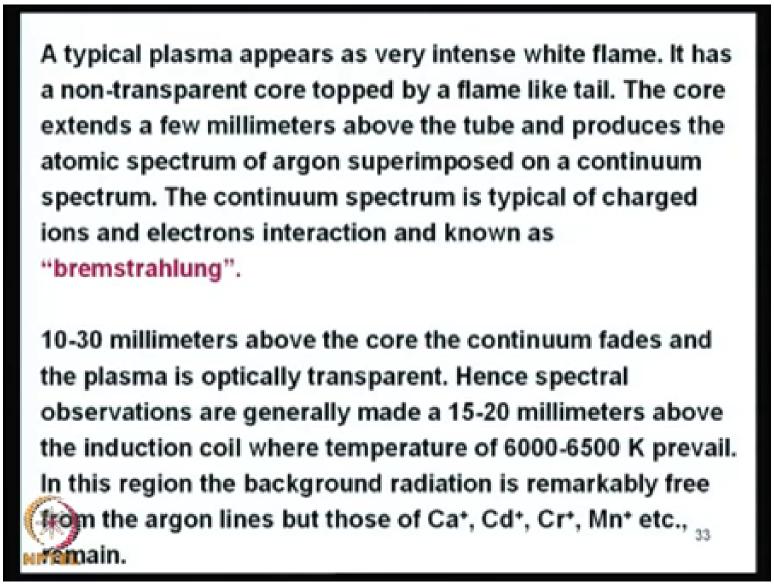

A typical plasma appears as very intense white flame. It has a non-transparent core topped by a flame like tail. The core extends a few millimeters above the tube and produces the atomic spectrum of argon superimposed on a continuum spectrum. The continuum spectrum is typical of charged ions and electrons 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 very intense white flame. In most of the ICP instruments, you will not be able to see the plasma as such, but you will see a something like a white flame - a small white flame - and this I had shown you here in this region.

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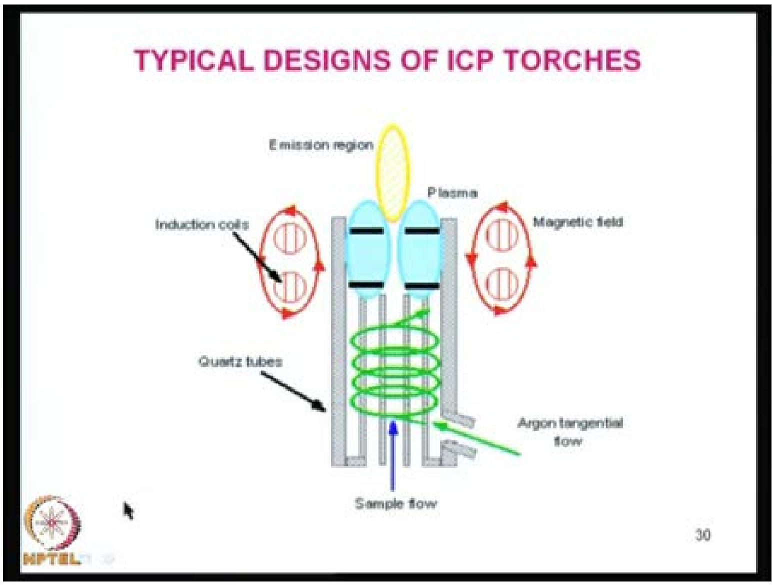
TYPICAL DESIGNS OF ICP TORCHES



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This appears as a very very intense white flame, and you may not quite often you may not even see the flame, if the plasma is very is having very high temperature. So, it has a non transparent core topped by a flame like tail, and the core extents a few millimeters above the tube and produces the atomic spectrum of argon super imposed on a continuum spectrum, because continuum spectrum comes from the argon itself; sometimes line spectrum of argon, continuum spectrum of argon and then any of the sample that is present in your analytic analyte.

So, the analyte spectrum also is there in the plasma is generated, argons line spectrum is generated and argon continuum spectrum is generated. So, the continuum spectrum is typical of the charged ions and electrons interaction, and it is known as Brehmstrahlung; it is basically a German word, it means radiation. So, approximately 10 to 30 millimeters above the core, the continuum fades of. You should try to remember this figure here, this figure 20 to 30 mm, the argon continuum fades away and the plasma is optically transparent; therefore, spectral observations are generally made at a this height about 15 to 20 millimeters about the induction coil, where the temperatures of about 6000 to six 6500 degree kelvin prevail. In this region, the background radiation is remarkably free from argon lines also; apart from the continuous radiation has already faded, argon line spectrum also fades in this region, and the except those of calcium, cadmium, chromium, manganese, etcetera, these are the elements which you want to analyze in the spectrum. So, one you will be getting almost pure spectrum of the all the elements that are present, except the gaseous, ions and the spectrum.

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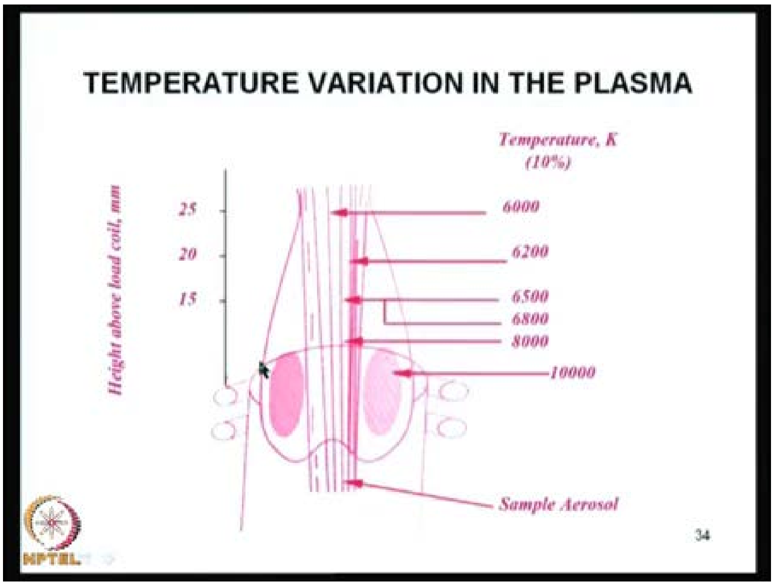

TEMPERATURE VARIATION IN THE PLASMA

So, you can see here this slide, I have drawn the plasma and this is the height - height above the coil, this is the plasma like this, and the sample is coming inside and the temperature, this is the sample aerosol coming here, and here the temperature near the bottom of the plasma is around 10000 kelvin, slightly above that, it is about 8000. And then, somewhere in this region, you will see the temperature profile to be around 6500 to 6800 and is this is approximately 15 millimeter. Now, between 15 milliliter and 15 mm sorry, 50, between 15 mm and 20 mm, the temperature again drops down to 6000 to 100, and above this region is the absolutely transparent region.

So, our spectrometer should optics should be put somewhere in this region, not here, not here, not here, but only in this region, so that we can take out the emission lines using a standard spectrometer.

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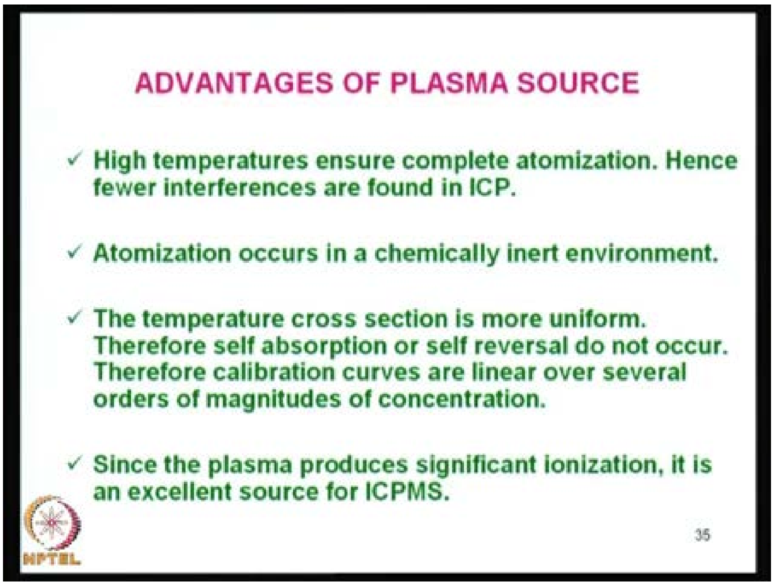

ADVANTAGES OF PLASMA SOURCE

- ✓ 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. Therefore calibration curves are linear over several orders of magnitudes of concentration.
- ✓ Since the plasma produces significant ionization, it is an excellent source for ICPMS.

Now, what are the advantages of the plasma source? I would like you to remember that, high temperature always ensures complete atomization; hence, fewer interferences are always there in ICP, because atomization is almost complete, and the interferences of cyanogen gas and other gases, nitrogen, etcetera, they are not there.

So, atomization essentially occurs in an argon flame. So, the argon flame is inert and therefore there are not many interactions that the atoms will undergo like hydrolization, thermal dissociation, and many other things are not happening in the ICP. The temperature cross section is more uniform in the plasma, that is another advantage, because if you remember the previous slide what I had shown you, in this region, the temperature differences hardly 200 degree kelvin in the in this region, whereas here the temperatures are very high with respect to increasing the height.

So, in this region temperature, variations are minimal; that means, the emission characteristics will remain constant with respect to the temperature, because higher the temperature, you would still be able to get the different spectrum; atomization, efficiency will be more, but for normal routine analysis, what we need is a constant output; and this constant output is ensured by the constant temperature, plus or minus two hundred kelvin does not matter very much in the plasma. So, the temperature cross section is more uniform; therefore, the concentration of the atoms will remain the will remain uniform. And if the concentration is more, then in we have discussed in atomic absorption, especially Smith Hieftje effect, that sometimes self absorptions do occur, when we give very high current; and that is because the high current means more temperature, more reversal, more atom production and these atoms will absorb the radiation, also that is being emitted by other atoms and you will not see any of the emissions.

Now, in because the temperature is constant here, self absorption or self reversal is eliminated automatically. This is another great advantage in ICP; therefore, the calibrations - calibration curves - are essentially linear, you will get linear calibration curves over several orders of magnitude from ppm to even, sometimes even up to percentage level; that is, ten raise to minus six, ten raise to minus five, ten raise to minus four, ten raise to minus one also sometimes, that means, the range is variable in ICP AES.

So, if you want to determine in ppm level, you can make your standard concentrations only in ppm. But if the range is varying from p p b to milligram level, you can make differents standards starting from micrograms to sub micrograms, and milligram, nanogram, etcetera. So, it is in a way it is comparable to florescent spectrometry, because there also you do not concentration is linear over several orders of magnitude; and this is another advantage in ICP. And another advantage is since the plasma itself produces significant ionization, it is an excellent source for ICP m s also; that means, you can couple mass spectrometer, which measures the ion concentrations - molecular ions and other concentrations, if they are there in ICP m s.

Nowadays, there are several instruments called as hyphenated instruments; and ICP m s is one such instrument, that is available in the market. Similarly, there are other equipments like g c m s, g c h p l c m s and then the graphite furnace again can be coupled to other equipments, and such hyphenated instrumental techniques can be adopted for ICP. So, this is another advantage.

Now, let us talk about plasma source spectrometers. What are the requirements? The requirements are basically you need a high resolution of the order of about 0.01 nanometer; that means, m delta lambda, lambda or delta lambda should be more than hundred thousand; that means, in 0.1 nanometer range. So, another requirement is, you should be able to acquire the information electronically at a very rapid rate and then you should be able to recover the data also. And then, low stray light, because most of the time we do use photomultiplier tubes, etcetera, and any stray light also should be as minimum as possible. And why dynamic range I have already explained to you, that is, ten raise, from ten raise to minus six to minus ten raise to minus four ranges, you can always organize when you are doing the ICP analysis.

Now, the plasma source spectrometers also give precise intensity readings with less than one percent relative standard deviation. And this is important, especially when you are doing repetitive analysis, there should not be much variation in the response; that is counts, that are actually measured in ICP. And for the same concentration, the count should be reproducible. And high stability with respect to environmental changes is another aspect, and computerized data handling, of course, as I have explained to you in the in my first lecture, how the ICP is architectured around a computer; such instruments so we can generate or make for the analysis of multiple elements.

Now, how do you go about making a multiple element analysis from a given spectrometer? Essentially, there are two types of instruments in inductive couple plasma AES - atomic emissions spectrometer. One is sequential; that means, you want to determine one element and then complete the analysis, choose another wavelength and then complete the analysis, choose another wavelength, like that you can do the different chemical analysis for different elements one after the other; one after another, you should be able to determine such instruments are called as sequential ICP instruments.

So, the scanning how do you do is, you choose a particular hollow graphic grating monochromator of about 2400 to 3600 grooves per mm; and scanning is accomplished by rotating the grating that we have seen in the in my last lecture, that we use hollow graphic gratings and prism and slit arrangement on the rowland circle; and you can keep on changing the wavelength, depending upon the element what you want to analyze. So, you can move the grating with a digitally controlled stepper motor, so that precise wavelengths are focused on to the exit slit of the spectrum monochromator.

In some designs, the grating is fixed, and the slit and photomultiplier tubes are moved; grating the grating is fixed, but you can move the slit and one slit, and the corresponding grating along the Rowland circle. So, for ultraviolet and visible range, separate sets of slits and p m t's are used; you can use number of slits, you can move the slit along the Rowland wavelength. And then, photomultiplier tube also is coupled, so that as the slit moves, photomultiplier tube also will move along the Rowland circle to collect the desired wavelengths.

The switch between the two is affected by the movement of a plain mirror located between two transducers. These are all slightly technical arrangements, but I am telling you all these things for the sake of brevity; how these things can be coordinated using a computer and very simple arrangements?

So, this is sequential, the scanning of the spectra itself can be controlled by the computer in a series of small steps of 0.01 to 0.001 nanometer. So, usually whenever there is no emission, the spectra is scanned quickly; you can scan the spectra and get pass or fail test. Suppose there are number of elements, you want to know whether they are there or not; then, you can scan the spectrometer quickly, and you will see for each element, that means, for each wavelength, whether you get a response or not. And the spectrum, whenever there is no emission, that means, there is no that corresponding element is not present; the spectra is scanned quickly and it slows down near a peak.

You can make the computer to move quickly, until there is no wavelength, the moment until there is no emission. The moment and emission peak starts, the computer can be slowed down to smaller digital components, so that you scan the emission peaks, they which permits you to determine peak areas also in ICP AES, that is important. Such an arrangement is known as slew scan spectrometer - slew s l e w - slew scan spectrometer.

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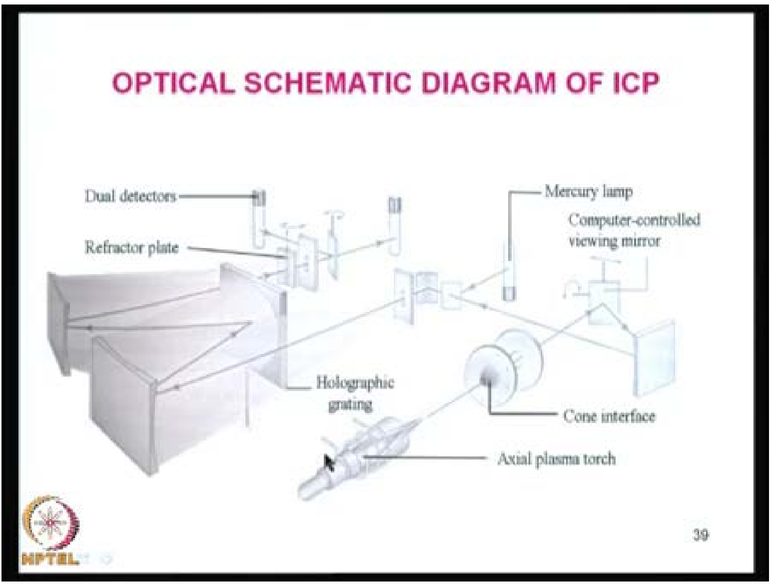

OPTICAL SCHEMATIC DIAGRAM OF ICP

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And this is the optical diagram of the ICP. So, here you can see that, this is the plasma torch - axial plasma torch and then there is a cone interface and then there is a mirror - computer controlled viewing mirror. And then from the mirror, it reflects to a grating and then comes here, and then it is taken onto the holographic grating that is here and then mirrors are there concave mirrors.

So, you can trace the light path from the plasma and guide it here, and then there is one more grating, it separates and then a number of refractor plates are there. And then the detectors, you can these are the dual detectors, they can be used straight away; and this mercury lamp helps to helps to standardize the wavelength spectrum, because mercury we know that it gives number of lines at emission lines at precise wavelengths; that is why most of the spectrometers - ICP spectrometers - we do use a small mercury lamp to every time to calibrate the wavelengths.

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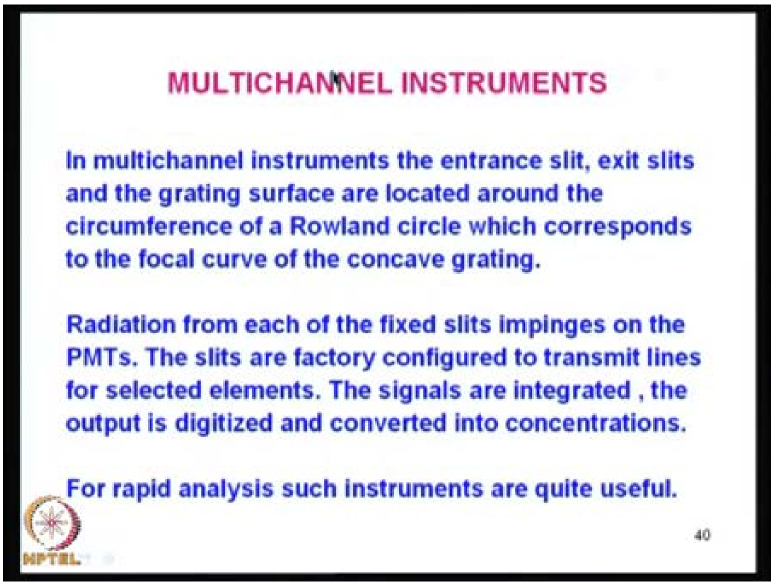

MULTICHANNEL INSTRUMENTS

In multichannel instruments the entrance slit, exit slits and the grating surface are located around the circumference of a Rowland circle which corresponds to the focal curve of the concave grating.

Radiation from each of the fixed slits impinges on the PMTs. The slits are factory configured to transmit lines for selected elements. The signals are integrated , the output is digitized and converted into concentrations.

For rapid analysis such instruments are quite useful.

Now, we move onto multichannel instruments. In multichannel instruments, the entrance slit, exit slit and the grating, they are all located around the circumference of the Rowland circle; that we have to always assume that, we always work in the Rowland circle with in ICP all the time. Now, entrance slit, exit slit and the grating surface, they are all located around the circumference of the Rowland circle, which corresponds to the focal curve of the concave grating. Now, radiation from each of the fixed slit impinges on the p m t’s, the slits are factory configured to transmit lines for selected elements.

Suppose you want to do about five elements, like cadmium, copper, nickel, etcetera, the wavelength are chosen, and there is a corresponding slit and a photomultiplier tube at that fixed at the measuring wavelength. Similarly, we can organize number of slits on the Rowland circle corresponding to different wavelengths; that means, simultaneously you are able to collect all the signals corresponding to a number of elements; the signals are subsequently integrated, and the output is digitized and converted into concentrations directly. So, for rapid analysis of number of elements, such instruments are quite useful.

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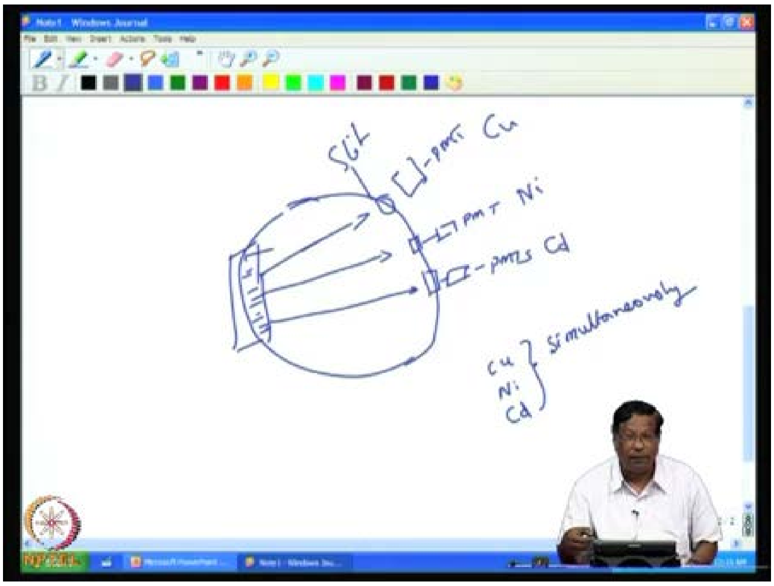

For example, this will show you, suppose this is the Rowland circle and here is your mirror and it concave grating, it will be emitting different wavelengths. Now, what I do is, I will make one slit here and a photomultiplier tube here. So, similarly, I will make one more slit here, this could be for another photomultiplier tube, this is p m t; this is slit and this is another p m t, like that I can make number of slits and number of I had to use number of p m t's - dedicated p m t's - and the radiation will be coming through all these slits, corresponding to different elements and the data can be integrated.

So, if this is for copper, this could be for nickel, this could be for cadmium. I can use a multiple element analysis with the same sample, which will give me the concentrations of copper, nickel and cadmium simultaneously. Now, you can buy an instrument, multiple spectrum ICP from a company, and when you buy the multichannel instruments, the company will ask what type of elements you want to determine, so that they can fix the wavelengths and slits depending upon your requirement. So, for routine analysis in a process industry, where the elements to be analyzed are fixed, then you can go for multichannel instrument. Suppose you want to you are in a research laboratory working on a particular element, and you may be working on a copper now, after somebody else may be working on nickel, somebody else may be working on cadmium, aluminum and such instruments, where the same instrument is to be used for different elements at different times, then the multichannel instrument does not give you that freedom to work on unspecified elements.

But if you choose a sequential instrument, you can choose the slit, you can choose the wavelength; that means, you have the capability to do any element, that is easily determined by ICP. But in multichannel instrument, your freedom is restricted to the pre-determined elements. So, one has to be slightly careful, when you want to choose a multichannel instrument and when you want to choose a sequential instruments. In general, research organizations prefer sequential instruments, because many of the research projects would be based on the analysis of different kinds of elements, but industry, process industries, etcetera, you do not have to worry about, because they are all something like a dedicated instrument. So, for rapid analysis multichannel instruments are very useful.

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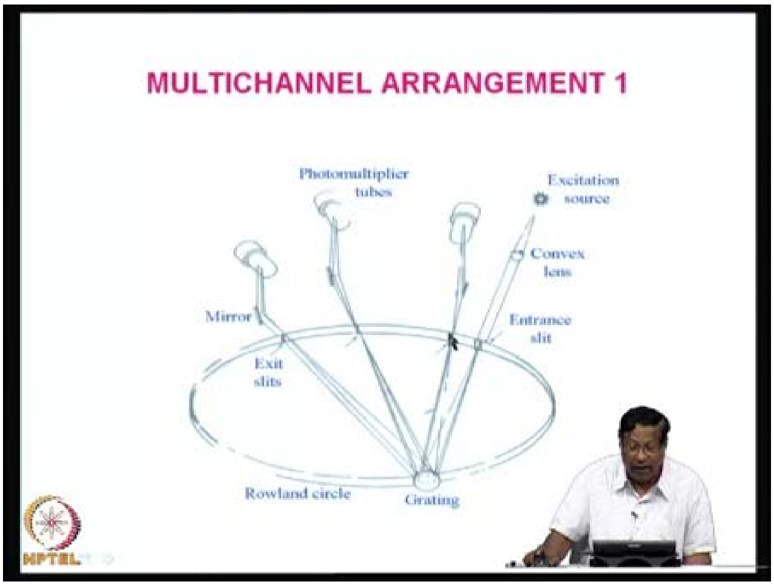

MULTICHANNEL ARRANGEMENT 1

Now, this is the arrangement I had shown you earlier window journal. Now, I am showing you the multichannel arrangement, this is the grating, here there is a slit and there is a this is a excitation source, and here there is a slit and a p m t, one more slit another p m t, one more slit another p m t, like this you can use different slits, and these slits are made in the spectrometer at the predetermined factory sites.

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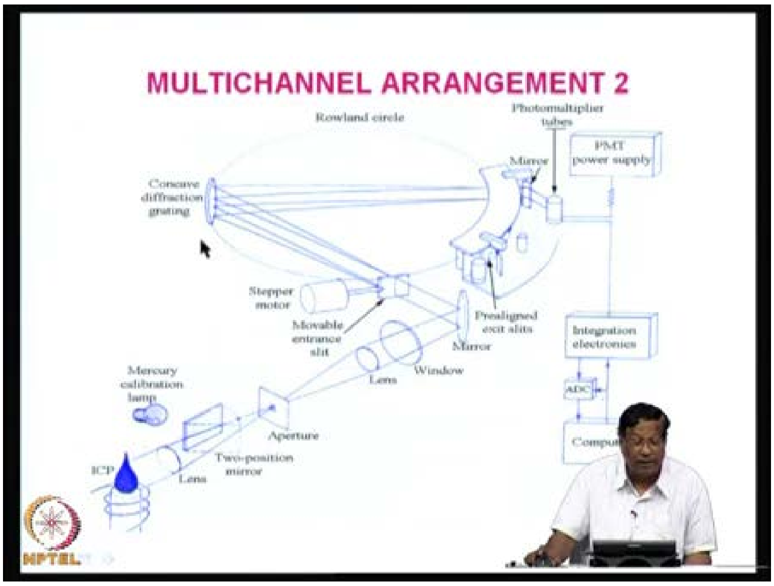

MULTICHANNEL ARRANGEMENT 2

So, this is another way of multi channel arrangement. Here is essentially ICP is there, mercury calibration lamp, and then lens to position, mirror, aperture and then to make it collimated and then get parallel lines. And then the radiation will be going through to the, and here I have a stepper motor and the radiation will be going to the concave grating, diffraction grating; and then mirror and p m t’s are arranged here, you can see in this range, one p m t, second p m t, third p m t, etcetera. And the arrangements for p m t power supply, you can choose a single power supply; and then computer control for integration, electronics, and a d c and the computer itself. So, this is a typical arrangement for multichannel instrument.

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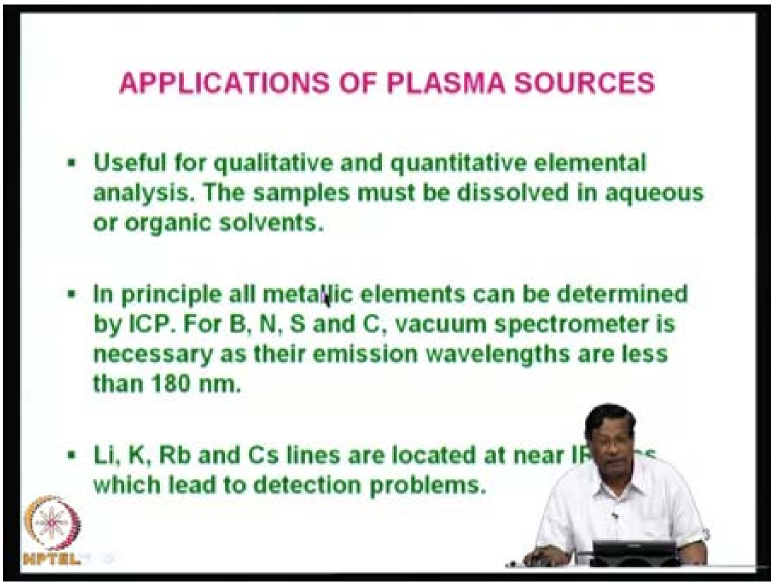

APPLICATIONS OF PLASMA SOURCES

- Useful for qualitative and quantitative elemental analysis. The samples must be dissolved in aqueous or organic solvents.
- In principle all metallic elements can be determined by ICP. For B, N, S and C, vacuum spectrometer is necessary as their emission wavelengths are less than 180 nm.
- Li, K, Rb and Cs lines are located at near IR which lead to detection problems.

So, the applications of plasma sources are also varied, depending upon the requirements of your analysis; for example, the as I was explaining to you, the qualitative and quantitative elemental analysis, ICP is very useful - pass or fail test. Suppose you are processing an ore, for gold or platinum, is simply push the sample into an ICP; and then, if the you get a gold line, the gold is present; if you do not get any peak, gold is absent. Same thing is true, if you are processing platinum, nickel, silver and whatever elements - metal elements - are there. Similarly, if you are handling effluents, all you got to know is, whether a particular element is present in the affluent or not.

So, again you just push the sample into the ICP and see whether you get a peak or not; if you do not get a peak, you have the affluent free from that element. Now, in principle, all metallic elements can be determined by ICP; most of the metallic elements can be determined. For boron, nitrogen, sulphur and carbon, a vacuum spectrophotometer spectrometer is necessary, because their wave emission wavelengths are less than 180 nanometers. If you remember our first previous discussion on the electromagnetic radiation and in ultraviolet spectrophotometry, we had stated that the quartz is required; for ultraviolet, glass is required for a visible, but in ultraviolet range, there is far ultraviolet and near ultraviolet; and the vacuum region up to 165 nanometers, it is vacuum ultraviolet.

So, a vacuum spectrometer is necessary as their emission wavelengths are less than 180 nanometers. Now, the there is another problem, that is, suppose you want to determine lithium, potassium, rubidium, cesium, etcetera, such elements alkaline earth elements, their emission lines are located near the infrared range; that means, in ICP spectrometers depending upon the element, what you want to use the whole electromagnetic range from vacuum ultraviolet to near infrared, that whole region needs to be monitored, depending upon the element you want to determine. So, I want to show you a typical detection limits and ICP also.

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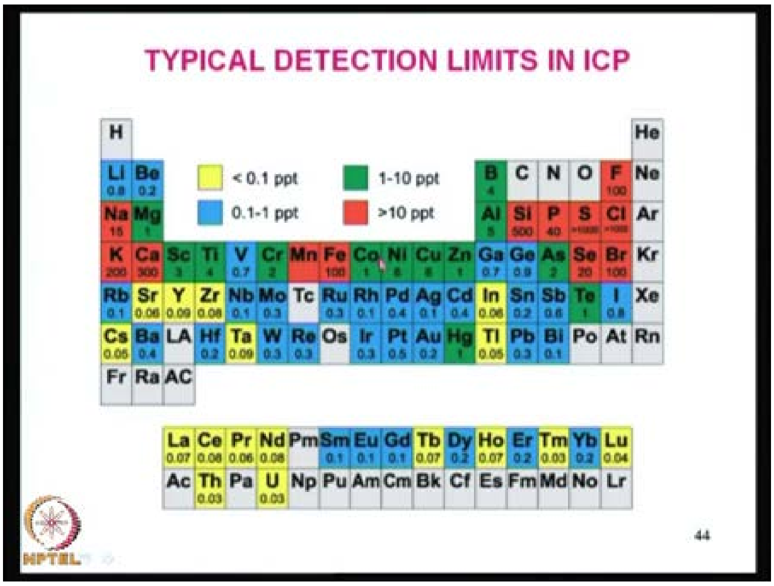

TYPICAL DETECTION LIMITS IN ICP

🟨 < 0.1 ppt
🟦 0.1-1 ppt
🟩 1-10 ppt
🟥 >10 ppt

H																	He
Li 0.8	Be 0.2											B 4	C	N	O	F 100	Ne
Na 15	Mg 1											Al 5	Si 500	P 40	S >1000	Cl >100	Ar
K 200	Ca 300	Sc 3	Ti 4	V 0.7	Cr 2	Mn	Fe 100	Co 1	Ni 6	Cu 6	Zn 1	Ga 0.7	Ge 0.9	As 2	Se 20	Br 100	Kr
Rb 0.1	Sr 0.06	Y 0.09	Zr 0.08	Nb 0.1	Mo 0.3	Tc	Ru 0.3	Rh 0.1	Pd 0.4	Ag 0.1	Cd 0.4	In 0.06	Sn 0.2	Sb 0.6	Te 1	I 0.8	Xe
Cs 0.05	Ba 0.4	LA	Hf 0.2	Ta 0.09	W 0.3	Re 0.3	Os	Ir 0.3	Pt 0.5	Au 0.2	Hg 1	Tl 0.05	Pb 0.3	Bi 0.1	Po	At	Rn
Fr	Ra	AC															

La 0.07	Ce 0.08	Pr 0.06	Nd 0.08	Pm	Sm 0.1	Eu 0.1	Gd 0.1	Tb 0.07	Dy 0.2	Ho 0.07	Er 0.2	Tm 0.03	Yb 0.2	Lu 0.04
Ac	Th 0.03	Pa	U 0.03	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

This is the periodic table. And here, there are red marked, manganese, iron, silicon, phosphorous, sulphur, chlorine, selenium, bromine, fluoride; and this side on the left side, we have here on the left side, we have sodium, potassium and calcium. You can see that most of the elements marked red are, it is possible to determine these elements at ten parts per trillion - ten p p t – range; and the green ones, that is, magnesium, scandium, titanium, etcetera; chromium one is here, another four are here; boron, aluminum, arsenic, tellurium and mercury, these are all marked green, and they can be determined in the range of one to ten parts per trillion. You can imagine the requirement of analyzing a given sample at ten parts per trillion, that is ten raise to minus twelve pico gram levels; they can be determined.

Now, there are blue elements, vanadium, niobium, molybdenum, etcetera, some rhodium, ruthenium, rhodium, palladium, silver, ir, pt, au, platinum, gold, gallium, germanium. So, the blue elements can be determined in point one to one parts per trillion; and the yellow ones like, strontium, atrium, zirconium, cesium, tantalum, some of these radioactive the lanthanides and actinides elements are also; it is possible to determine them at less than point one parts per trillion.

So, you can appreciate the beauty of the ICP with just one picture like this; it will it will act as a simple guide for you to determine these elements.

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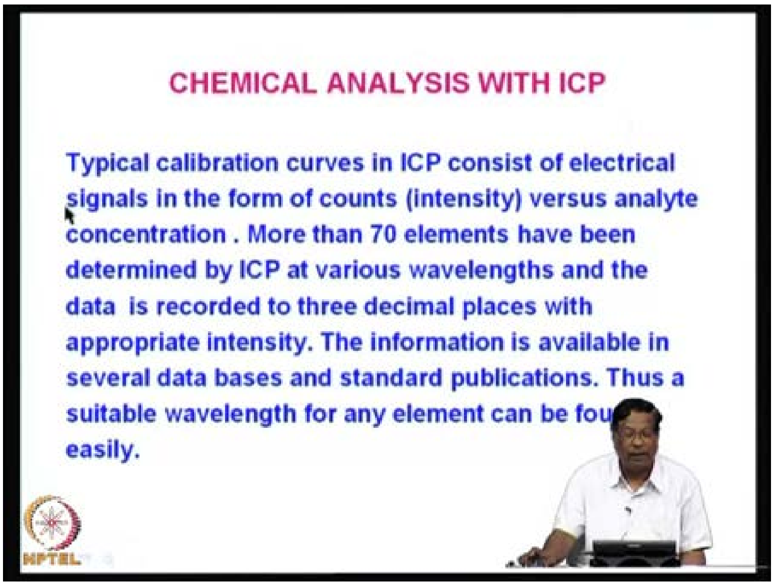

CHEMICAL ANALYSIS WITH ICP

Typical calibration curves in ICP consist of electrical signals in the form of counts (intensity) versus analyte concentration . More than 70 elements have been determined by ICP at various wavelengths and the data is recorded to three decimal places with appropriate intensity. The information is available in several data bases and standard publications. Thus a suitable wavelength for any element can be fou easily.

Such maps are available with the manufactures; they will the manufacturers. When you are buying an instrument, they will be able to tell you, what kind of elements, what are the levels, etcetera, they can be determined using ICP.

So, chemical analysis using ICP can be done using calibration curves as usual. Now, you have to prepare the standards and fire the standards one by one through a peristaltic pump into the plasma and note down their responses for the particular elements. So, it consists of calibration curves; they are consists of actually electrical signals in the form of counts. So, it is not elements specific in the sense, that only the electrical counts available at a particular wavelength what you have chosen, and slit and other conditions at that time, at the time of making the calibration, we are using only the counts, that is, the number of hits - the photon hits - are recorded.

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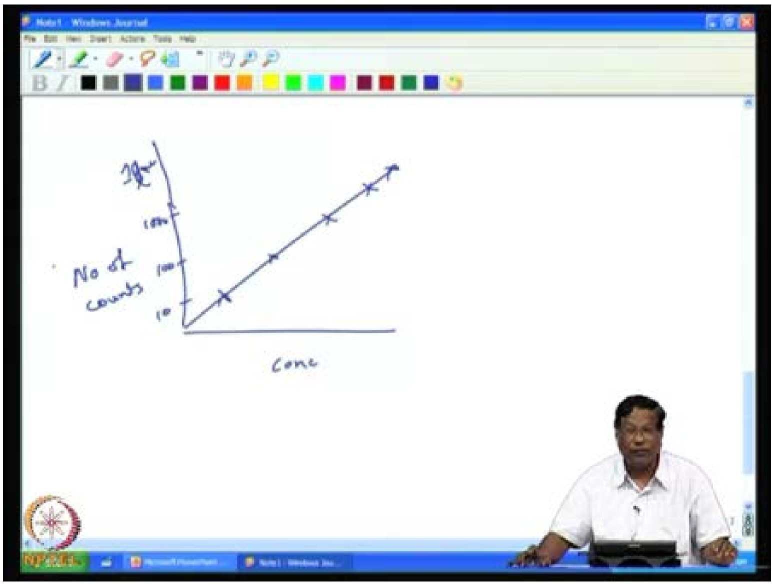

So, in the calibration, what you are recording is the, what you would be using is number of counts verses concentration. So, these counts can be the same, counts are same whatever element you want to determine. So, it could be 10, it could be 100, it could be in 1000, it could be in one lakh in lakhs, hundred thousand or one lakh. So, the calibration curve we would be drawing like this; what you are plotting is only the counts.

So, the these counts need to be treated statistically to determine the concentrations, of course, computer does this job, but the what has to appreciate, that it is just the number of counts you are counting and plotting. It has nothing to do with the element; the calibration is always relative with respect to the counts only. So, whether you use the, whether you want to determine cadmium or copper, it is always the counts. So, the counts have nothing to do with the element. So, that makes more, one has to be very careful, especially with respect to interferences that occur in spectrophotometer in ICP AES.

So, any interference will always reflect as change in the number of counts. So, you will have to try to correlate the number of counts, with the calibration, with the concentration, etcetera. So, more than seventy elements have been determined by ICP at various wavelengths, and the data is recorded to three decimal places with appropriate intensity; that is how a calibration curve looks.

The information is available in several data bases; so, the standard publications are there. And the data bases will tell you, what is the wavelength to choose, what are the concentrations to be prepared and what are the exact conditions of the plasma, gas flow rate and then optical wavelength, and then slit arrangement, all these things are put in a data base, so that you do not have to worry about trying to remember the various experimental factors given required for each analysis, that is the beauty of using a computer in ICP AES.

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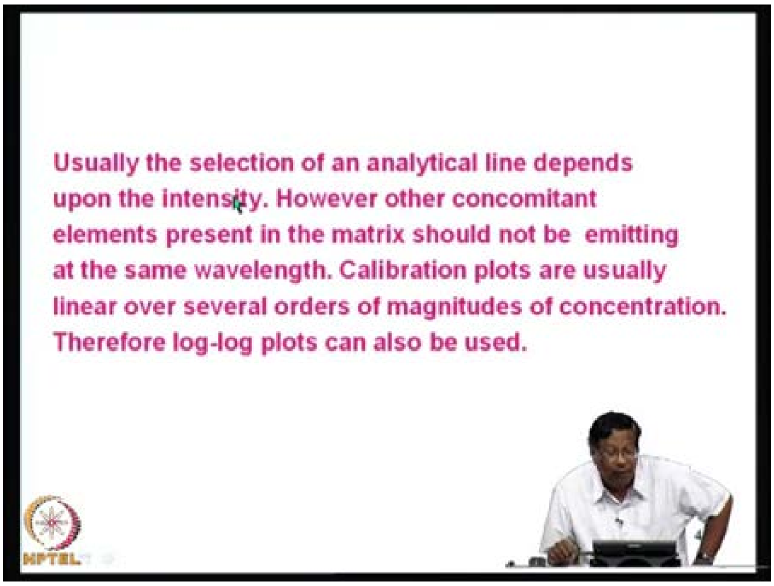

Usually the selection of an analytical line depends upon the intensity. However other concomitant elements present in the matrix should not be emitting at the same wavelength. Calibration plots are usually linear over several orders of magnitudes of concentration. Therefore log-log plots can also be used.

Now, look at this slide. What I have written here is usually the selection of an analytical line depends upon the intensity. However, other concomitant elements present in the matrix should not be emitting at the same wavelength. See the whole idea is the any of the concomitants emitting at the same wavelength will increase the number of counts. You may not be able to identify which element is interfering, that is the problem in ICP; unless you know about the matrix, what are the different kinds of elements, you will not be able to know what which element or what species is causing interference, because what you are seeing is only the total number of counts. So, the calibration plots as usual are linear over several orders of magnitudes and this presents a problem, because if the order is very high, then you will have to use not just a simple graph, but you may have to use log-log plots - log of concentration verses log of counts - because you are varying from a few counts to several lakhs of counts in the same calibration curve. So, it is not possible to use a ordinary graphs linear graphs, but log plots semi log plots you can use, and log-log plots are also required, when you are doing the chemical analysis spread over several orders of magnitude.

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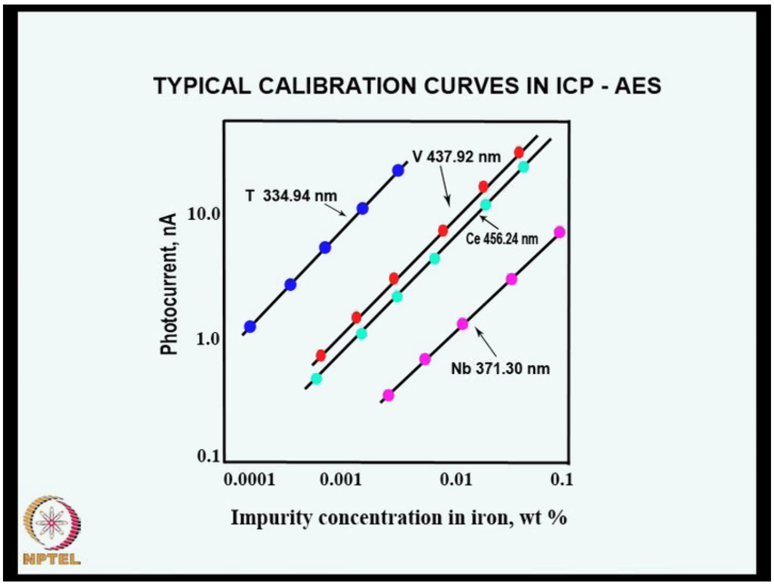

TYPICAL CALIBRATION CURVES IN ICP - AES

Now, here I am showing you typical calibration curves. Here photocurrent is plotted verses concentration; you can see that the concentring, this is the impurity concentration in ion; and the first one is for thallium and first one is for vanadium, and this is for second one is for vanadium, first one is for thallium, this third line from the top is for cerium and fourth one is for niobium. And you can see that, the concentrations are always plotted from 0.0001 to 0.1 percent - weight percent - impurity concentration is also is also in the same range.

You can see that, the order is approximately ten raise to four in this case. So, this is ten times, hundred times, thousand times, ten raise to four times; and the photocurrent queries one to ten etcetera, and this would be somewhere about fifteen or a this would be hundred. So, this will be approximately about 20, 30, 160 up to 16 nano angstroms; nano amperes is the scale on the vertical side, and on the horizontal side, it is four orders of magnitude. These are the typical curves - calibration curves - in ICP AES.

So, you can see that both are on the log-log scale, you can see the bunching here occurring here, bunching occurring here, bunching happens here. So, it is not uncommon for you to come across log-log plots in ICP AES measurements. Departures from linearity, that is, another big problem, because if the number of several any other element adds to the number of counts, so the counts when plotted when against the concentration always give you departure from the linearity, if there is interference. So, they often occur, especially when large concentrations are used, definitely you will see the departure from linearity. Self-absorption also becomes evident only at high analyte concentrations. So, you should not be doing very high concentrations, especially in milligram level, it is not possible; one should not be doing it. So, because the self-absorption is always a sort of a relative phenomenon, depending upon the concentration, self absorption also will vary; we have to make sure that self absorption does not occur; if we it will be it is possible, if you work at low concentrations, then self absorption will be minimum.

When self absorption is occurring, what happens to the calibration curve? The calibration curve bends towards the concentration axis, instead of a sort of a linear curve, and it bends towards the horizontal axis. Non-linearity also arises from erroneous background correction, from ionization, and from non-linear detector response also. These are all slightly more involved, especially when you are working in parts per trillion level, ten raise to minus nine, ten raise to minus ten level, all these things will become slightly important.

So, I am not going into the details of such, how to go about correcting such interferences, but what people generally do is, use a ICP; in the ICP, they use a internal standard. So, that is, you can take any other element and then determine the vertical axis in the calibration curve. You plot it as a ratio or the log ratio of the detector signal for the analyte and that of the internal standard. You measure the internal standard response and measure the total response, and take the ratio and then plot it as the ratio versus concentration. So, this is typically internal standard method.

Here the intensity improves to a considerable extent, that is the beauty of using internal standard. The intensity when it improves, the concentrations will be more reliable; I am showing you a figure.

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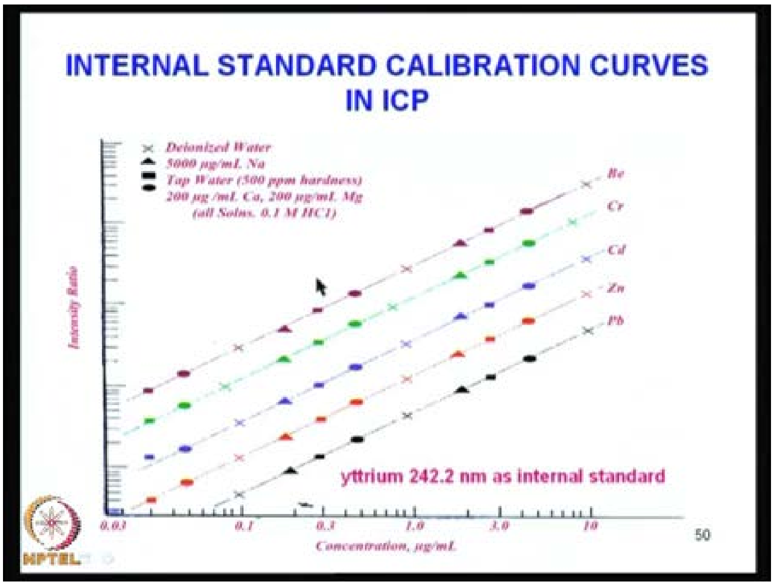

INTERNAL STANDARD CALIBRATION CURVES IN ICP

yttrium 242.2 nm as internal standard

here and the same thing what I have explained to you. Here in the form of a curve, this is internal standard calibration curves in ICP; this is for top one is for beryllium, this is for chromium, cadmium, zinc and lead. Here, what I have shown you, yttrium, 242.2 nanometer measure at this wavelength is used as an internal standard.

So, here, the you can see that, it is not the counts, that are there on the vertical axis, but it is the intensity ratio. And we have analyzed deionized water and sodium, and then tap water of 500 ppm hardness and containing 200 microgram per milliliter of calcium, 200 ppm of magnesium, etcetera, and all these solutions are in 0.1 molar hcl. The details are not important, but what is important is, you will be able to see a beautiful calibration curve for each of these elements, when plotted as the intensity ratio versus concentration; this example illustrates you to you the beauty of internal standard analysis.

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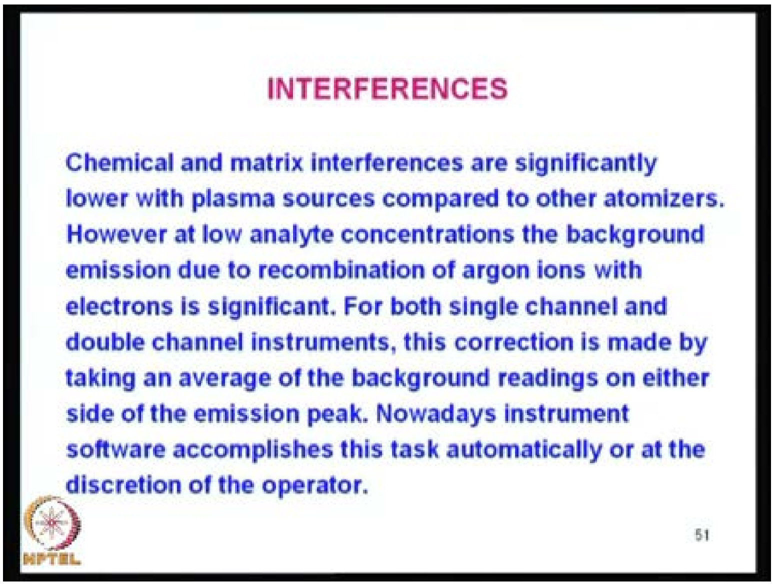

INTERFERENCES

Chemical and matrix interferences are significantly lower with plasma sources compared to other atomizers. However at low analyte concentrations the background emission due to recombination of argon ions with electrons is significant. For both single channel and double channel instruments, this correction is made by taking an average of the background readings on either side of the emission peak. Nowadays instrument software accomplishes this task automatically or at the discretion of the operator.

So, that is one way of looking at the calibration over a broad range. Now, I want to talk to you about the interferences, because as I was telling you, no amount of interference is appears as a interference from a particular element, because the response is always in the counts. So, chemical and matrix interferences are significantly lower with plasma sources compare to other atomizer; this you have to understand, because the temperatures are so high, that hardly any chemical compound formation and matrix elements, interferences do occur.

However, at low concentrations, background emission due to recombination of the argon atoms, ions with electrons is significant; for both single channel and double channel instruments, this correction is made by taking an average of the background readings. You can take the average of the background readings and keep on subtracting that, on either side of the emission peak; that means, you should draw some short of a tangential curve to the emission peak.

I will explain this in the next class again, because nowadays instruments software itself accomplishes this task automatically or at the discretion of the operator; that means, you can also have some say at, at what level the background correction should be employed, at the left side of the peak and on the right side of the peak. We will continue our discussion on the interferences in the next class.

Thank you.