

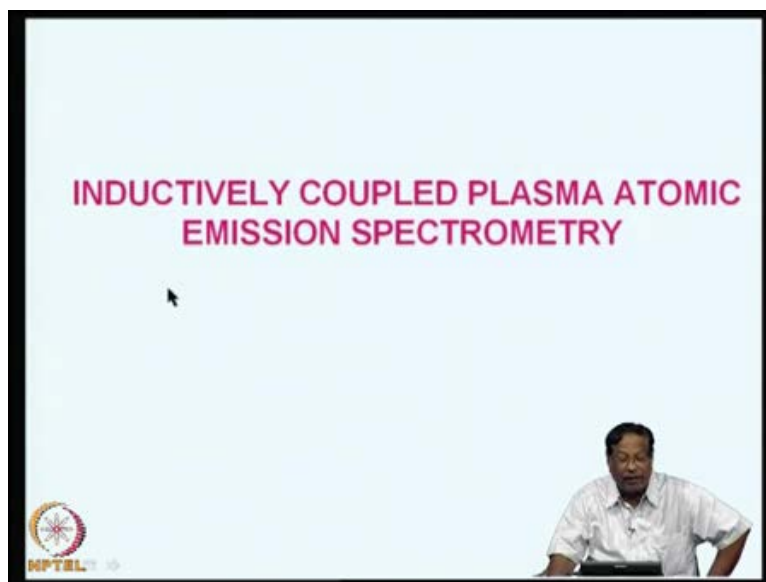
**Modern Instrumental Methods of Analysis**  
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**Department of Chemical Engineering**  
**Indian Institute of Science, Bangalore**

**Lecture No. # 28**

**Inductively Coupled Plasma Atomic Emission Spectrometry-1 Theoretical Aspects**

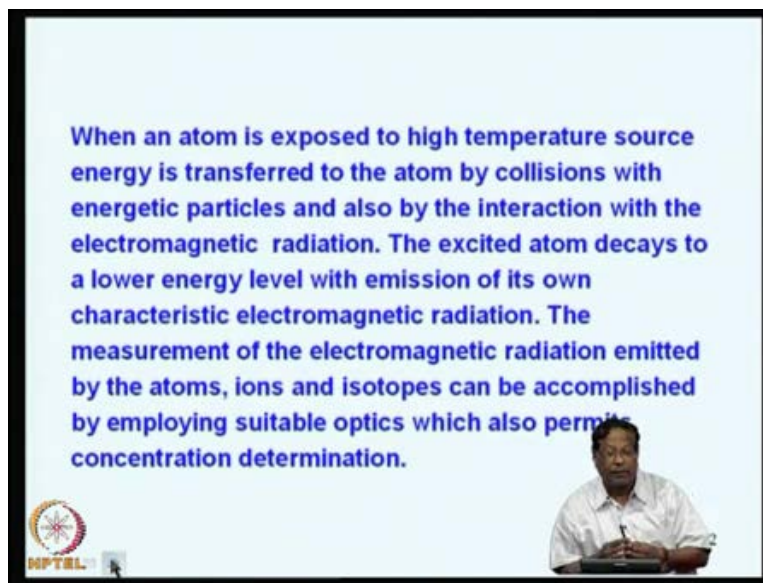
Today, we will continue our discussions on the plasma emission spectrometry - atomic emission spectrometry.

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I want to concentrate on inductively coupled plasma atomic emission spectrometry, that is, in short form, it is known as ICP AES.

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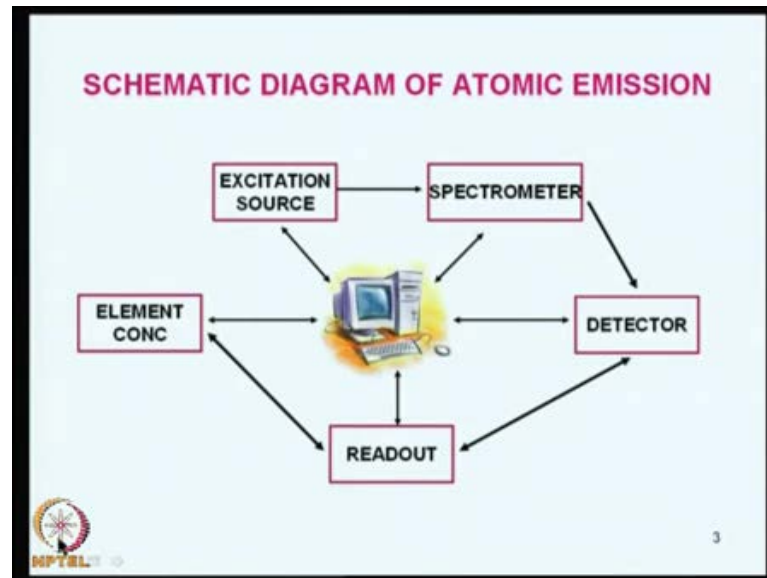


So, when an atom is exposed to high temperature, we have we know that, energy is transferred to the atom by collisions with energetic particles and also by interaction with the electromagnetic radiation. This we have been discussing as the basis of almost all spectrophotometric spectroscopic techniques. And atomic emission is no different from the previous systems, as far as excitation and other spectroscopic aspects are considered.

So, the excited atom, when it decays to a lower energy level with emission of its own characteristic radiations, especially, when you have an atom cloud exposed to high temperature, it goes to next higher energy state by collisions with energetic particles and also by the interaction with the electromagnetic radiation. The excited atom decays to a lower energy level with the emission of its own characteristic electromagnetic radiations.

This we have discussed in the first few classes, with respect to hydrogen emission lines, which are known as, Paschen series, bracket series, fund series, bummer series, etcetera. And the measurement of the electromagnetic radiation emitted by the atoms, ions and isotopes can be accomplished by using suitable optics, which also permits the concentration determination; that means, it gives us a good analytical technique, by measuring the characteristics spectra of the atoms, when they are expose to very high energy levels.

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That is what is we considered as ICP AES is one of the techniques. Now, in this, I have told you, that the technique of schematic diagram of atomic emission, I am showing you here, this is a microprocessor, the centre area represents a microprocessor, and it is controlling the excitation source, and spectrometer and this consist of the optics part, and detectors, and this also we have discussed earlier; and then the computer can give you readout and it can relate to the element concentration. So, all this functions are interactive.

So, the computer forms a short of center peace, which will conduct most of the instrument operations.

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**A. GENERATION OF EM RADIATION**

**ARC Discharge**

Sample is mixed with a conducting material such as graphite and packed into the crater of a carbon electrode. A DC arc discharge between the sample electrode and the counter electrode vapourizes the sample, decomposes molecular species produced in the plasma and atomizes the analyte. The atoms are excited to higher energy by the energetic particles in the plasma.

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Now, there are different areas in which we can consider for the generation of electromagnetic radiation. Usually, first thing will we are considering is arc discharge. Here, what happens? Sample is mixed with a conducting material such as graphite and packed into the crater of a carbon electrode. The counter electrode, a DC arc discharge takes place between the sample electrode and the counter electrode, it vapourizes the sample, it decomposes the molecular species produced in the plasma and atomizes the analyte. The atoms are as usual excited to higher energy by the energetic particles in the plasma.

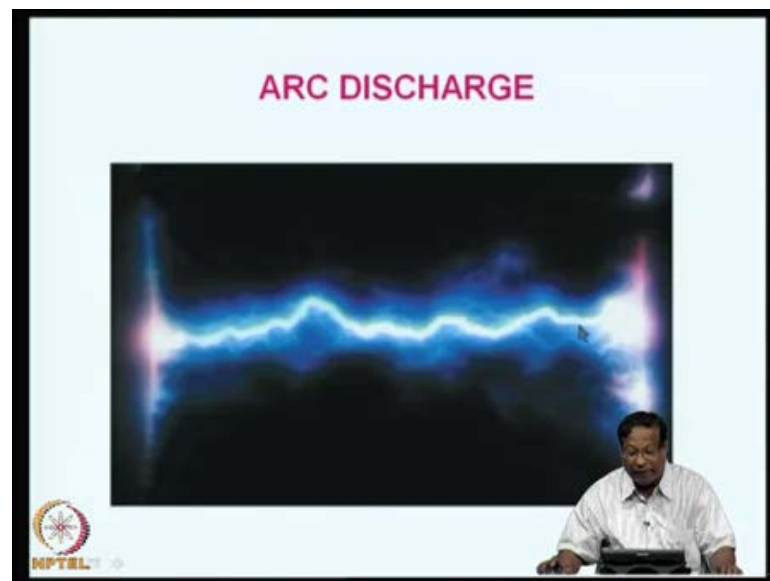
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cathode ————— anode

So, what we would like to see is, something like this. There are two electrodes, and in one, we make a cavity and fill the material we want to analyze. You bring these are electrodes; essentially, most of the atomic emission spectra are generated by using electrodes like this and bringing them together, nearer, not exactly making the contact, but somewhere near, and then you apply high energy current, so that the arc discharge takes place.

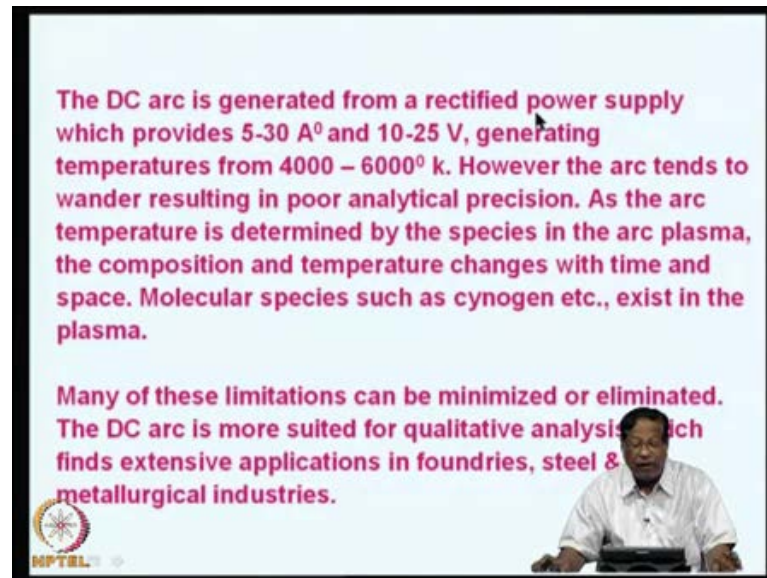
So, what we would, what I want you to see is, the DC arc discharge between the sample electrode and counter electrode vapourizes the sample, especially when a arc is struck. And this arc has got very high temperature and it vapourizes the sample and emission spectra is generated. This is one way of generating the high energy particles in the plasma.

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This is a simple example of how the electricity is gets conducted. This is an electrode, this is an electrode, you bring them apply very high current, and you will see that the plasma is generated and high temperature zone is created.

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The DC arc is generated from a rectified power supply which provides 5-30 A<sup>0</sup> and 10-25 V, generating temperatures from 4000 – 6000<sup>0</sup> k. However the arc tends to wander resulting in poor analytical precision. As the arc temperature is determined by the species in the arc plasma, the composition and temperature changes with time and space. Molecular species such as cynogen etc., exist in the plasma.

Many of these limitations can be minimized or eliminated. The DC arc is more suited for qualitative analysis, which finds extensive applications in foundries, steel & metallurgical industries.

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Now, the DC arc is generated from a rectified power supply, which provides 5 to 30 amperes and 10 to 25 volts, generating temperatures of 4000 to 6000 degree kelvin. However, the arc tends to wander resulting in poor analytical precision. For good work, what we need is very stable arc; and in this arc, whenever we are trying to take two electrodes and try to bring them together, there is reproducibility is not very good, because the arc tends to wander.

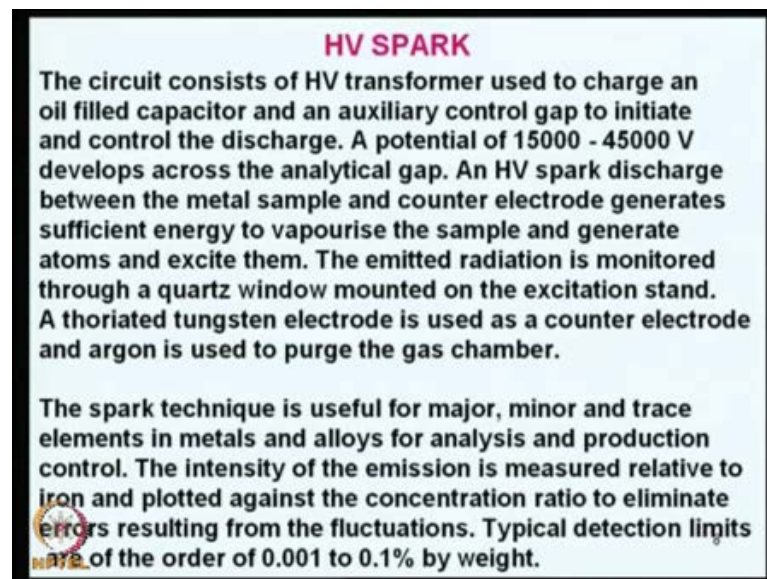
As the material gets eaten up, the distance gap between the two electrodes keeps on increasing and the arc quality changes. So, as the arc temperature is determined by the species in the arc plasma, the composition and temperature also changes with time and space. Molecular species such as, cyanogen, etcetera, they exist in the plasma. Many of these limitations can be minimized or at least eliminated. The DC arc is more suited for qualitative analysis, which finds extensive application in foundries, stainless steel industries and other metallurgical industries.

What we mean by this is that, for qualitative determination, when suppose you have a foundry, you are taking some material for production, so you want to know the quality of the melt, that means, the concentrations of the elements, whether they are, there or not; and approximate concentrations you will be able to get, by taking the melt sample and put it in an electrode, and bring the arc, generate the arc. And because it is arc is not very highly analytical and reproducible, it can be, still it can be use for qualitative analysis.

Now, we can have an AC arc, instead of DC arc, we can provide an AC arc. In AC arc, what happens is, more uniform sampling of the electrode occurs compare to the DC arc. It operates at voltages ranging from 1100 to 4400 volts. Now, your household voltage is about 230 volts, maximum is 400. In AC arcs, to generate AC arcs, what you need is, at least hundred times more than that, that is, about 4400 volts. And the polarity of the discharge is usually reversed at each half cycle, because it is AC and polarity gets reversed, and the discharge is extinguished, when the voltage drops to zero.

So, the sampling is random, it results in improved precision compare to the DC arc and the, but the sensitivity would be definitely less than that of the corresponding DC arc. Now, there is another way to generate high energy medium, that is known as high voltage spark.

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**HV SPARK**

The circuit consists of HV transformer used to charge an oil filled capacitor and an auxiliary control gap to initiate and control the discharge. A potential of 15000 - 45000 V develops across the analytical gap. An HV spark discharge between the metal sample and counter electrode generates sufficient energy to vapourise the sample and generate atoms and excite them. The emitted radiation is monitored through a quartz window mounted on the excitation stand. A thoriated tungsten electrode is used as a counter electrode and argon is used to purge the gas chamber.

The spark technique is useful for major, minor and trace elements in metals and alloys for analysis and production control. The intensity of the emission is measured relative to iron and plotted against the concentration ratio to eliminate errors resulting from the fluctuations. Typical detection limits are of the order of 0.001 to 0.1% by weight.

So, for the spark, the circuit consists of a high voltage HV transformer used to charge an oil filled capacitor and an auxiliary control gap to initiate and control the discharge. So, here what happens? A potential of about 15000 to 45000 volts develops across the analytical gap, that is, huge voltage. So, HV spark discharge between the metal sample and the counter electrode generates sufficient energy to vapourize the sample and generate atoms and excite them. The emitted radiation is monitored through a quartz window mounted on an excitation stand.

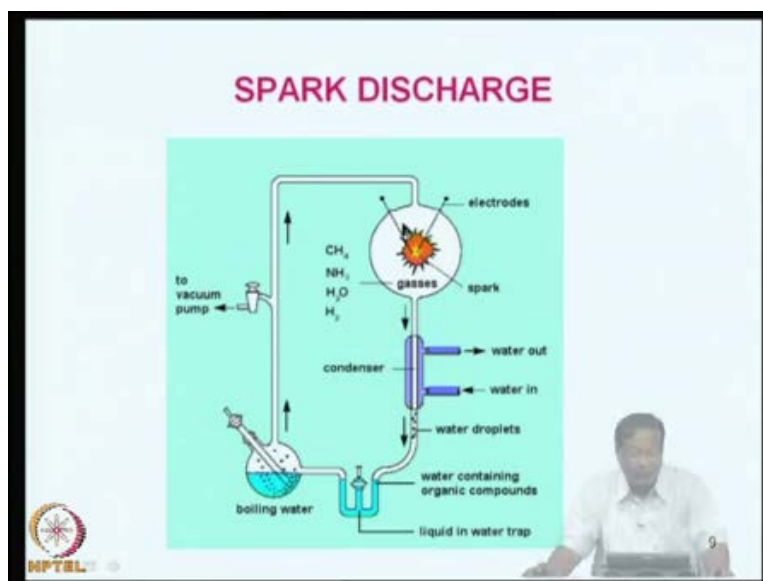
This is a very simple straight forward operation, after this spark is generated. What you do is, the emitted red in front of emitted radiation. You put a quartz window, take out the radiation, and collect it, subject it to separations of the wavelength, and monitor the reaction. So, usually what we do is, a thoriated tungsten electrode is used as a counter electrode and argon is used as a used to purge the gas chamber. So, the spark techniques is useful for major, minor and trace elements, in metals and alloys for analysis and production control also.

For example, in steel foundries, etcetera, spark technique is more referable than the arc technique. And the intensity of the emission is measured relative to one particular metal, preferably iron, and plotted against the concentration ratio to eliminate errors resulting from fluctuations; that means, typically you take the iron as the parent element and plot the concentrations of the metals with respect to their emission wavelengths, and then you take the ratio. Typical detection limits in this case also are of the order of 0.001 to 0.01 percent by weight; that means, it is not a trace technique as a priory, but it is a very fast tool for you to monitor the quality of the melt in the foundries.

Suppose you have a foundry or an electric furnace, then you would like to melt the steel and other things – metals. And then you are putting some of the alloying elements and you cannot hold the melt for longer, because it means loss of energy. So, you until the analysis is done, you want to hold it, because the composition needs to be adjusted for different values, but you cannot hold it indefinitely. So, you need a very quick method, may be within a few minutes, you should be able to get the composition analysis. So, in such cases, arc, spark, and DC arc, AC arc, etcetera, they are all useful.



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So, here I am showing you a spark discharge. So, the gases will be there; so, methane, ammonia, H<sub>2</sub>O, hydrogen, etcetera; here a spark is generated. These two represent the electrodes, and this is a vacuum pump, and this needs to be cooled using a condenser and then water droplets are collected, and all other things are essentially remaining, essentially remain the same. This is a typical generation of arc.

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### GLOW DISCHARGE

**It consists of a flat sample cathode and cylindrical anode mounted in a sealed chamber filled with argon. At 600 – 1800 V, the gas is ionized and accelerated to the cathode. Collisions with the cathode surface causes vapourization of the sample material and excitation. The emitted radiation is viewed from a quartz window.**

**The cathode block which is in direct contact with the sample is water cooled to remove excess heat. The sample is pressed against the open end of the cathode body and held in vacuum. After evacuation the chamber is filled with argon to 5-15 torr pressure. Standard calibration curves for the determination of trace elements in pure materials can be prepared over three orders of magnitude in concentration.**

So, another way of looking at it is through glow discharge. It consists of a flat sample electrode and cylindrical anode mounted in a sealed chamber filled with argon. At 600 to 1800 volts, the gas is ionized - argon gas gets ionized; and once the ions are produced, they accelerate towards the cathode. So, collisions with the cathode surface causes the metals to vaporization of the sample material and excitation. Once the excitation follows, emission has to follow.

So, the emitted radiation is again viewed through a quartz window. The cathode block which is in direct contact with the sample is water cooled to remove excess heat. The sample is pressed against the open end of the cathode body and held in the vacuum. After evacuation, the chamber is filled with argon to 5 to 15 torr pressure; it is a very low pressure. And standard calibration curves, you have to make anyway in almost all spectrophotometric or spectroscopic techniques, for the determination of trace elements in pure materials. The order of linearity is put here in the last line, the linearity is over three orders of magnitude; so, 0.1 to 1 percent and 10 percent. So, two three orders minimum, you can  $10^2$  to  $10^{-2}$ ,  $10^1$  to  $10^{-1}$ ,  $10^0$  and may be  $10^1$  sometimes, it is possible to determine the elements using glow discharge.


So, another way I would, I am describing you different types of generating the plasma, where the atoms can be excited and they analysis can be completed in real time, that is, within a few minutes. So, the next technique what I want to discuss is laser induced plasma.

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**LASER INDUCED PLASMA**

Pulsed laser beams have been used in AES of extremely small samples and occlusions on surfaces of metal alloys laser beam is focused on sample surface and the material is vapourized. The plasma plume formed above the target passed through an auxiliary electrode gap and is excited by a low voltage spark discharge.

Hollow cathode discharge :  
0.06-10 ppm for solid samples and from 0.2-1 ppm for solutions.

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So, in laser induced plasma, I want to show you in this slide, that pulsed laser beams also been used for atomic emission spectrometry of extremely small samples and occlusions on surfaces of metal alloys.

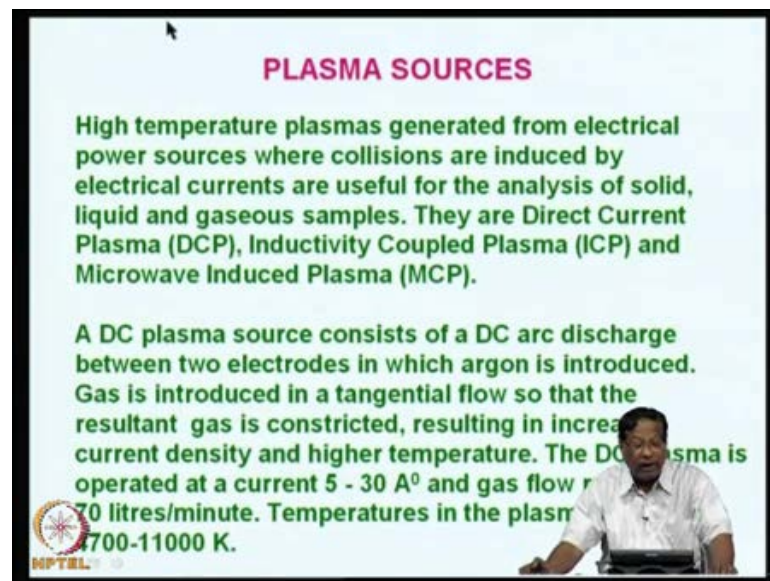
Usually laser beam is focused on the sample surface and the material is vapourized. You just take the laser beam and focus it on the sample. So, laser beam generates intense heat on interaction with the **with the** material and there is vapour is produced. The plasma plume formed above the target is passed through an auxiliary electrode gap and is excited by a low voltage spark discharge.

So, this is another way of make generating the plasma. You can also generate simple systems like hollow cathode discharge. These are this is somewhat akin to what we had discussed in atomic absorption, because where we could use 0.06 to 10 ppm for solid samples and 0.2 to 1 p p m for solutions; this is the another way of generating the discharge.

So, here in this case also, the electromagnetic radiation is resolved with a spectrograph and the spectra are recorded photographically or measured with an array detector. Now-a-days, computers have taken over this activity and they can give you digital displays straight away at the place of work; if you got the communication lines fixed near the control room, it can tell you straight away, what is the concentration if you are able to make the calibration and other things properly.

So, solid state neodymium glass, laser, a spark source, and a mirror and focusing lens, these are the components of a laser plasma. And then focusing lens, it directs the laser beam on to the surface, etcetera. And what we have is, a laser pulse with 0.1 to 1 joule, and a duration of about 2 microseconds produces a crater of 25 to 250 micrometer. The detection limit what you are observing in this case is  $10^{-9}$  to  $10^{-11}$  grams, that is almost picogram level, nanogram to picogram levels.

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**PLASMA SOURCES**

High temperature plasmas generated from electrical power sources where collisions are induced by electrical currents are useful for the analysis of solid, liquid and gaseous samples. They are Direct Current Plasma (DCP), Inductivity Coupled Plasma (ICP) and Microwave Induced Plasma (MCP).

A DC plasma source consists of a DC arc discharge between two electrodes in which argon is introduced. Gas is introduced in a tangential flow so that the resultant gas is constricted, resulting in increased current density and higher temperature. The DC plasma is operated at a current 5 - 30 A<sup>0</sup> and gas flow rate 10 litres/minute. Temperatures in the plasma are 7000-11000 K.

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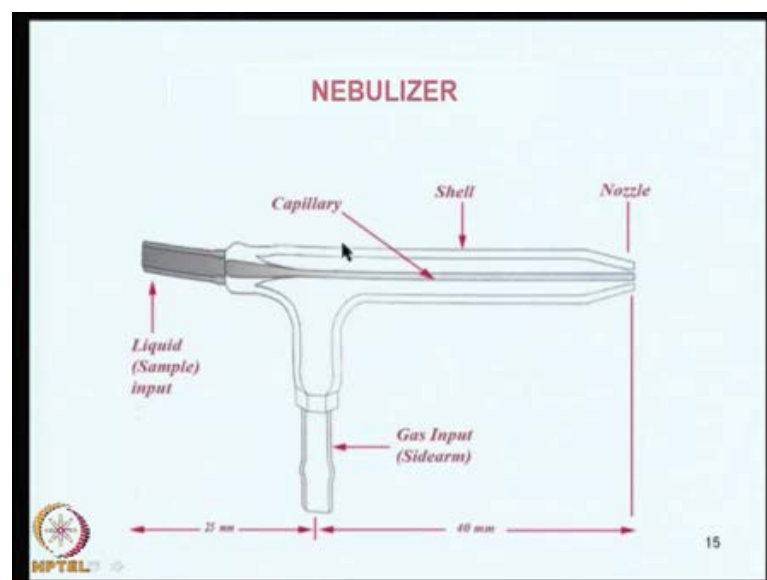
So, we can take a look at the plasma sources, how do we generate plasmas. High temperature plasmas are generated from electrical power sources, where collisions are induced by electrical currents and such high temperature plasmas are useful for the analysis of solids, liquids and gases samples as usual. There are different ways to generate the plasmas; they are direct current plasma or inductively coupled plasma, this is known as ICP, or microwave induced plasma. These are the three techniques, which can be used to generate very high temperatures in the laboratory.

So, what does a DC plasma source consist of? It consists of a DC arc discharge between the two electrodes, in which argon is introduced, that we have discussed earlier. The gas has to be introduced in the plasma in a tangential flow, so that the resultant gas is constricted; that is coming out through a very small aperture, resulting in increased current density and high temperature; the smaller the constriction, higher is the temperature.

The DC plasma is operated at 5 to 30 ampere currents and gas flow rates up to 70 liters per minute; this is fairly large, but the requirement is high. So, temperatures in the plasma range again from 4700 to 11000 kelvin. The sample is introduced as an aerosol in the plasma using a nebulizer, just like what we have discussed in atomic absorption and atomic electro thermal atomic absorption etcetera, you can take the sample through a nebulizer and introduce it into the plasma. And the plasma, inside the plasma, the nebulizer should introduce that sample. The optical measurement region, therefore, it has to be located near the base of the confluence to eliminate high background from the arc plasma; that means, the window should be adjusted exactly where you would like to see the plasma.

It is useful for solutions containing 45 percent of the dissolved solids; that means, DC arc plasma, if you are able to introduce the solids themselves as form of slurry, up-to 45 percent, solids slurry can be straight away introduced into the plasma. The advantage is that, it is a low cost DC power supply. However, continuous operation for longer periods again is not possible in this case, because the electrodes keep on eroding. So, consequently what happens is, electrode less plasma sources such as inductively couple plasma are common in atomic emissions spectrometry.

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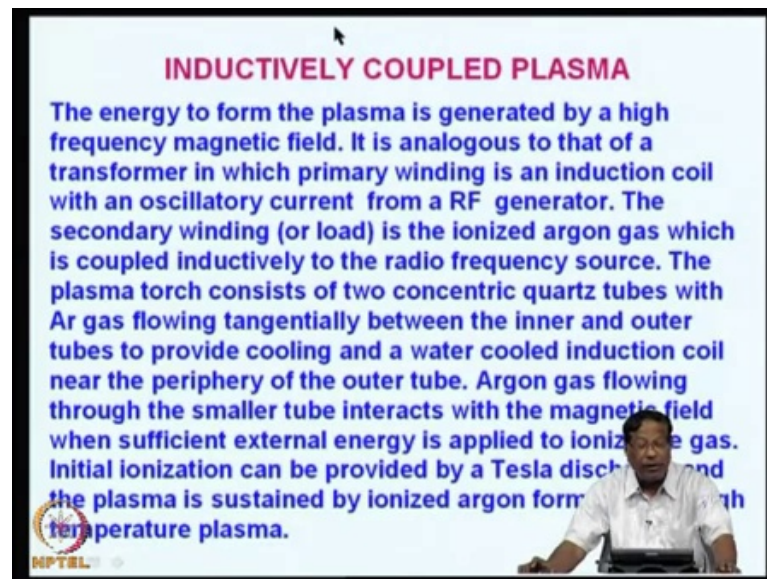


So, you can see that, this is a plasma torch; what you are seeing here, the liquid sample input is there, there is a capillary, there is a shell and the sample gas input is lay through

this and the sample comes here, and then it through a nozzle, it goes out into the plasma range.

So, you can see the typical distances in a plasma torch are about 25 mm on this side, about 40 mm on this side; this is a sidearm. So, this is how we look at the plasmas and the sample introduction takes place, using the plasma like what I have shown you here.

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So, we are going to study in more detail inductively coupled plasma atomic emission spectrometry. Currently, right now, I want to talk to you about the ICP, only plasma - inductively coupled plasma. So, the energy to form the plasma is generated by a high frequency magnetic field. It is analogous to that of a transformer, in which there is a primary winding, and there is a primary winding in is a, it is an induction coil with an oscillatory current from an RF generator - radio frequency generator.

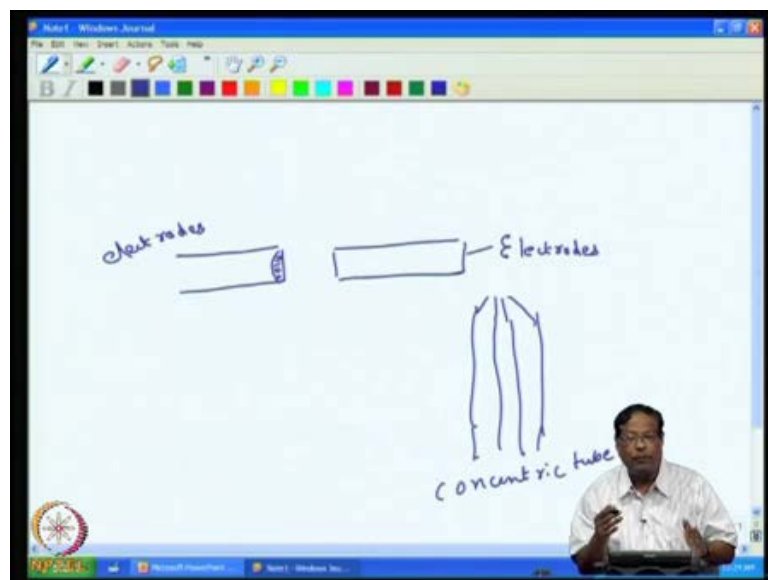
The secondary winding, you know, you remember any transformer, first there is a primary winding, inside that there is a secondary winding, and in between the electrode or the piston would be moving to and fro to generate the currents; essentially similar system exists in ICP.

Here, the primary winding is an induction coil with an oscillatory current. And it is oscillatory current is generated from an RF generator; the secondary winding or what we

call it as load. The load is the ionized, argon gas itself, gas is coming and going inside, so that itself can act as a second winding or load.

It is an ionized gas which is coupled inductively to the radio frequency source; that means, the gas flow rate is coupled to the radio frequency source to generate the desired temperatures at a fixed flow rate; so, it is prefixed in a way. The plasma torch consist of two concentric quartz tubes, that is two tubes, in which there is one more tube is inserted something like this.

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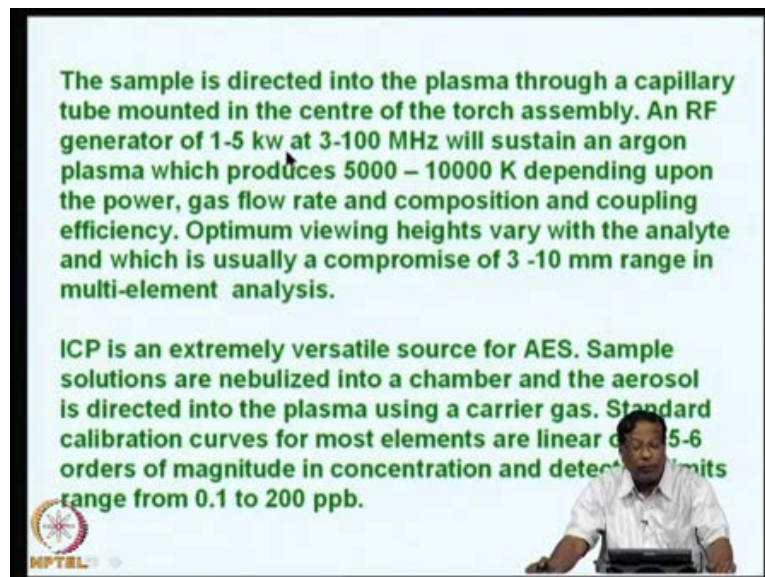
There is one more tube, and all these will end up something like this; this is a concentric tube. So, two tubes one inside the other are organized like this. And now, you can see that the argon gas, as the gas is flowing tangentially between the inner and outer tubes, inner and outer tubes to provide cooling. So, you need a water cooled induction coil **through the** near the periphery of the outer tube, because the temperature can reach very high **very high** and it may be difficult to control.

So, the it is already coupled to the radio frequency range. And argon gas flowing through the smaller tube interacts with the magnetic field, **which** when sufficient external energy is applied to ionize the argon gas. Initial ionization can be provided by a tesla discharge; first, you have to start the whole system; so, for that, you can have a tesla discharge and the plasma is sustained continuously burning by ionized argon formed in the high

temperature plasma. So, it keeps on forming; once you start plasma, it is self-sustaining, because the argon is flowing continuously through the system.

So, the sample, now you want to analyze the sample. Now, its the objective of the plasma ICP is to introduce the sample into the plasma, because plasma is a very high temperature zone. So, to introduce the sample, we have to direct the sample into the plasma; how do we do that is, through a small capillary tube mounted in between the torch assembly what I had shown you earlier, that is like this, the concentric tubes what we are having here.

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So, let us look at the system. Now, an RF generator of about 1 to 5 kilo watt at 3 to 100 mega hertz will sustain an argon plasma; that means, it will continuously generate argon plasma, which produces about 5000 to 10000 kelvin, depending upon the power, gas flow rate, and composition and coupling efficiency. So, optimum viewing heights vary with the analyte, which is usually a compromise of 3 to 10 mm range in multi element analysis, that is, optimum viewing height also in the plasma. I will show you presently a slide, which will show you the different temperature zones.

Now, what I want to tell you is, ICP is an extremely versatile source for AES - atomic emissions spectrometry; it can be used in the in the laboratory. Nowadays, instruments are available which are bench top models; that means, you can just put it on a small table and introduce the sample, and continue the analysis; bench top models are available, they

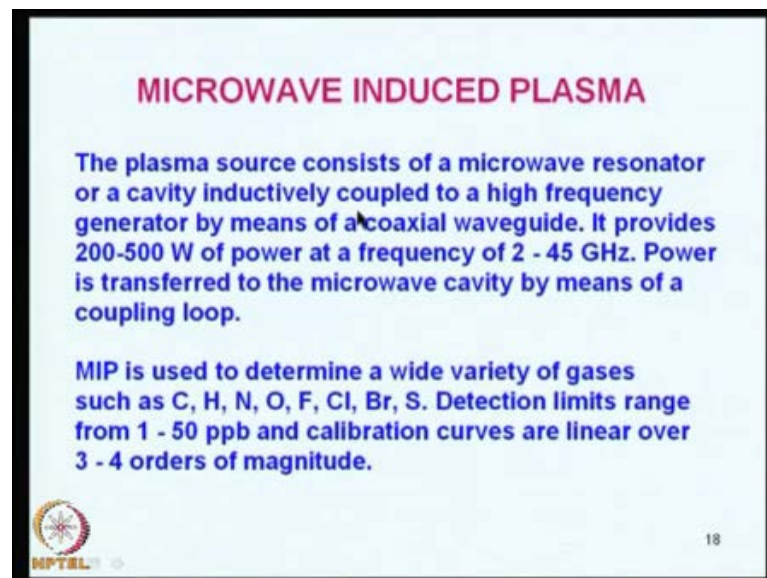


are not very big. And sample solutions are nebulized into the chamber and the aerosol is directed into the plasma using the carrier gas itself, that is argon.

So, argon serves number of functions; one is it generates the plasma, it acts as the secondary coil, and it introduces the sample, it also cools the torch ends. So, standard calibration curves for most of the elements need to be constructed as usual, but they are linear over 5 to 6 orders of magnitude in concentration, and detection limits range from 0.1 to 200 ppb - parts per billion.

So, nowadays, inductive coupled plasma atomic emission spectrometry - ICP AES - is the most preferred technique; next only in popularity to atomic absorption. And the advantages in ICP AES are that, you do not have to struggle to introduce the sample just like in a graphite tube; you have to put it through a small sample handle micro liter, ordinary 2 to 3 ml flow rate, if you maintain, that is good enough for ICP AES. And the detection limits what we are talking about is 0.1 to 200 ppb. So, microwave induced plasma, now I have discussed with you about ICP - inductive couple plasma.


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**MICROWAVE INDUCED PLASMA**

The plasma source consists of a microwave resonator or a cavity inductively coupled to a high frequency generator by means of a coaxial waveguide. It provides 200-500 W of power at a frequency of 2 - 45 GHz. Power is transferred to the microwave cavity by means of a coupling loop.

MIP is used to determine a wide variety of gases such as C, H, N, O, F, Cl, Br, S. Detection limits range from 1 - 50 ppb and calibration curves are linear over 3 - 4 orders of magnitude.

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And then, now I am coming to microwave induced plasma. This is another way of inducing the plasma, but this is not so popular, but just for the sake of brevity, I want to inform you, that the plasma source consists of a microwave resonator or a cavity which is inductively couple to a high frequency generator by means of a coaxial waveguide.

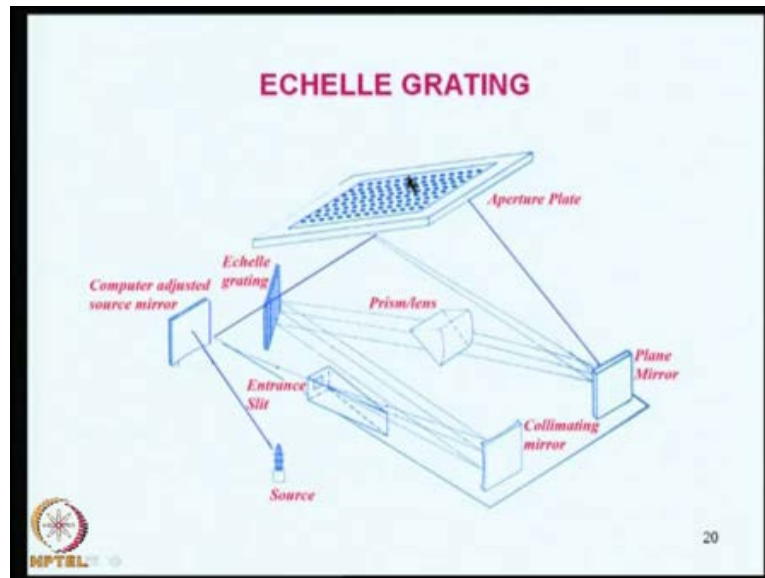
It provides 200 to 500 watt of power at a frequency of 2 to 45 gigahertz. Power is transferred to the microwave cavity by means of a coupling loop. So, MIP is used to determine a wide variety of gases rather than metals. And what are the gases? They could be carbon, species, hydrogen, nitrogen, oxygen, fluorine, chloride, bromide, sulfide, etcetera, and detection limits for these elements range from 1 to 50 ppb - parts per billion again. And calibration curves are also linear not as much as ICP, but only of the order of about 3 to 4 orders.

So, So, far we have discussed different ways of generating the plasma. Now, the whichever way you generate the plasma, the other aspects of analytical determination remain the same; that is, you have to separate the electromagnetic radiation and then use the specific wavelengths for the determination of the elements. So, electric magnetic radiation can be separated into its components by a variety of instruments and techniques; usually this we have already discussed earlier, that is, we can use prisms, we can use gratings and we can use filters, etcetera.

But in ICP AES, the gratings instruments are commonly used for high resolution spectroscopy. The incident radiation must be separated in two dimensions by an Echelle grating - two dimensions - and separating the multiple orders, we can do it with a prism. So, you can do prisms and then you can use gratings also, you can use a combination of the two, and also you can use the Fourier transform spectroscopy also to generate the information and sort out the data. This I will explain to you when we are dealing with infrared spectrometer, but essentially the principles will remain the same.

But what I want to tell you is, how to separate the electromagnetic radiation and the information we get out of the system. So, it extends the  $f t$  - Fourier transform spectroscopy - in ICP AES extends the wavelength range to ultra violet region; usually in a visible, its fine, but in ultra violet region, if you want to extend Fourier transform spectrometry is better; that is a technique, which I will be describing to you in the context of infrared radiation, when we will be discussing these things later.

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Now, this is a simple two-dimensional Echelle grating; this is a source and there is a computer adjusted source mirror, and then there is an entrance slit here in this range, and then it falls here, and then we have an Echelle grating prism lens, and there is a plane mirror and we can have an aperture plate in two dimensions.



This is very simple and effective way of separating the electromagnetic radiation. This we have discussed earlier also with respect to spectrophotometric and atomic absorption spectrometers. Now, you can use concave gratings.

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### CONCAVE GRATINGS

In Rowland mounting, the grating and the detector are attached to a rigid bar that moves relative to a fixed entrance slit. The angle of diffraction remains constant and the angle of incidence varies. The detector is always kept in a position normal to the grating. Under these conditions, the dispersion is linear over a broad wavelength range.

In Abney mounting, grating and detector are fixed and the slit moves along the axis of the Rowland circle. This is slightly cumbersome because light source and external optics also need to be repositioned when the angle of incidence is changed.

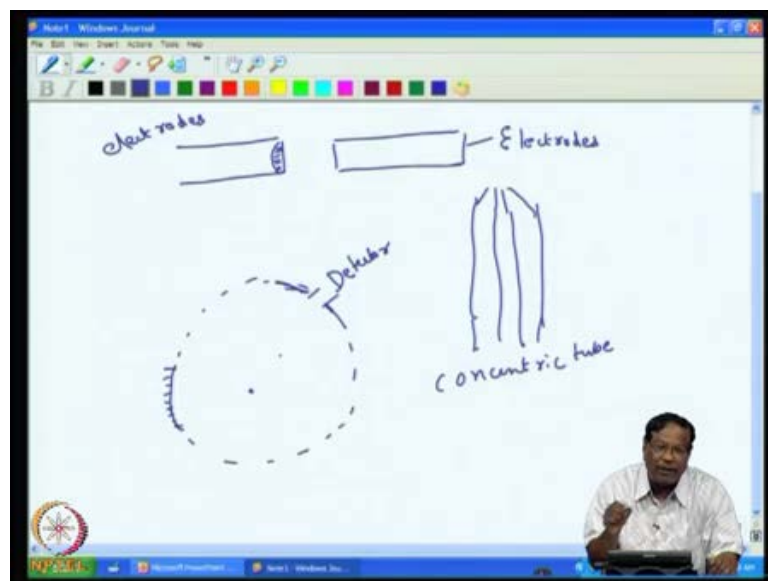


So, in concave gratings, the requirement with respect to atomic emission is that, the atomic emission, in atomic emission, **you need to** you need to determine a number of elements without a specific element source; that means, all the radiations corresponding to different excitations will be coming through plasma.

So, you do not need a separate source for like, hollow cathode lamp or electro discharge lamp, etcetera in ICP AES, because the plasma itself is going to act as a source now. And it the spectrum what you get out of plasma, after you introduce the sample contains the emission lines of almost all the elements, whether you are interested in determining all of them or not.

So, the possibility exist to determine all the elements, but you may choose to determine particular elements and not all the elements in a given sample. So, the requirement is to measure different wavelengths emanating from the plasma. So, for this, what we do is, we go for a concave grating and that grating is mounted on a circle; that means, its focal length is fixed for a any concave grating. And if you draw an imaginary circle, suppose I have a concave grating like this, its focal length is about this much, that means, I can draw a round imaginary circle like this; this is the concave grating, this is the focal point and I can draw an imaginary circle like this.

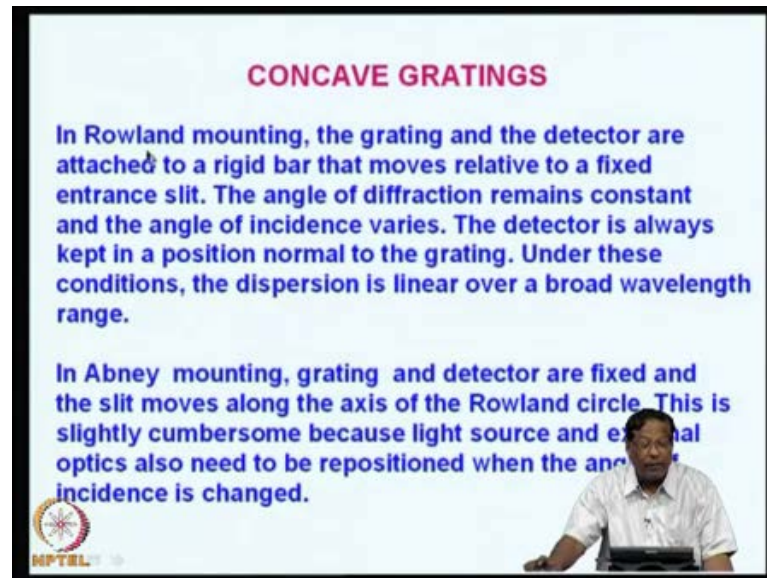
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So, I have to I need to put my mirrors and everything on this imaginary circle position them. And if I need to measure particular wavelengths, then I need to have an opening

like this, so that I can put a detector here. So, this circle tells me, that the focal length of the **concave** concave grating must be fixed and the detector should be again on the periphery of the imaginary circle; this circle is known as Rowland circle.

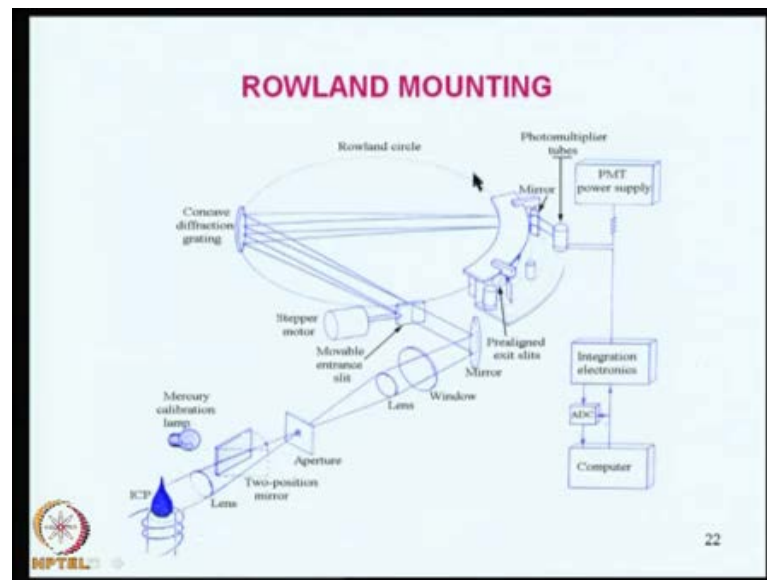
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So, in a Rowland circle, Rowland mounting, the grating and the detector are attached to a rigid bar, that moves relative to a fixed entrance slit. The angle of diffraction remains constant and the angle of incidence we can vary; that means, we have to have two slits in the Rowland circle, one for the incoming radiation, another for the separated radiation to be taken to a detector. Now, under these conditions, the dispersion is linear over a broad wavelength range.

So, we have different kinds of mounting. The another mounting is, one mounting I had told you earlier is Echelle grating and this is Rowland grating. In Abney mounting, grating and the detector are fixed, and the slit moves along the axis of the Rowland circle. This is slightly cumbersome, because the light source and external optics are also need; they need to be repositioned, when the angle of incidence is changed.

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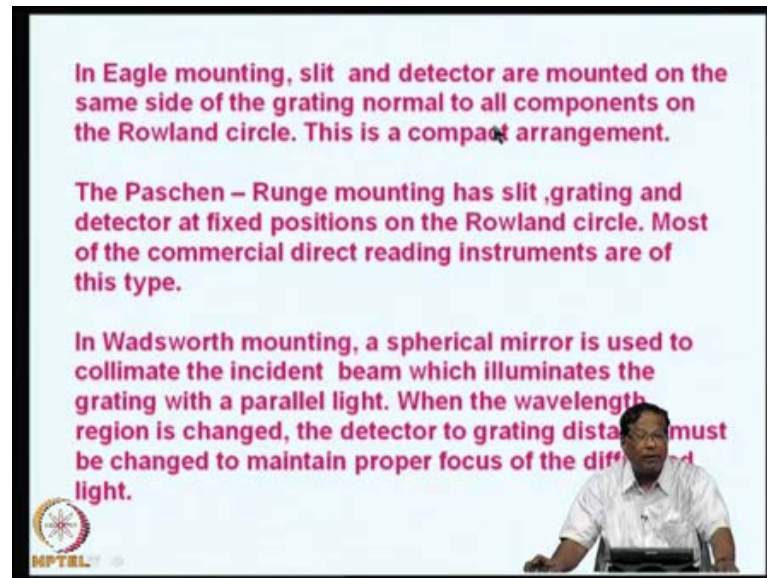


These are all details about how to separate the electromagnetic radiation coming from the ICP. Now, I am showing you a Rowland mounting; here, you can see the concave mirror is here, this is the imaginary circle and this is a movable entrance slit - this one - and stepper motor is there, and this is a mirror and then there will be another slot for photomultiplier tubes, etcetera.

And other things will remain the same, ICP, lens, this is the plasma, this is the lens and then this is a two position mirror; for this thing, there is a mercury calibration lamp to standardize the wavelength; and there is another aperture, lens, window, etcetera. Once it reaches this pre-aligned, this mirror it straight away enters through a slit on to the concave grating and then it comes out. And again, all these you can see that, everything is mounted on the Rowland circle.

So, I can there are three or four variations; **one is** one is the window and another is the mirror, another is the photomultiplier tube. So, three things are, three movable items can be fixed and their typical arrangements usually are described in my previous this thing - slide.

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In Eagle mounting, slit and detector are mounted on the same side of the grating normal to all components on the Rowland circle. This is a compact arrangement.

The Paschen – Runge mounting has slit, grating and detector at fixed positions on the Rowland circle. Most of the commercial direct reading instruments are of this type.

In Wadsworth mounting, a spherical mirror is used to collimate the incident beam which illuminates the grating with a parallel light. When the wavelength region is changed, the detector to grating distance must be changed to maintain proper focus of the diffracted light.

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That is, in Abney mounting, grating and detector are fixed, and the slit moves only; you have to refer to that figure and imagine, that the slit is moving, other things are not moving.

So, in eagle mounting, slit and detector are mounted on the same side of the grating, normal to all the components of the Rowland circle; this is a very compact arrangement. Then, we can have Paschen Runge mounting, it has a slit, grating and detector; all the three things are fixed - slit, detector and the grating. So, most of the commercial direct reading instruments, that means, in a readymade system for the determination of specific electromagnetic radiation of specific wavelength; that means, you do not have a choice of wavelengths, that means, you cannot do elements other than what the slits are fixed; that means, for particular element, particular slit and particular wavelength is coming out.

So, in readymade dedicated instruments, these things are very useful; for example, in a foundry, you do not have to do research, because it is a production unit; and this production unit can use the eagle mounting, where everything is fixed; one does not have to worry about the variations.

So, another aspect is type of mounting is known as Paschen Runge mounting **paschen runge mounting**. It has the slit, grating and detector at fixed positions on the Rowland circle. Most of the commercial direct reading instruments are of this type - direct reading

instruments. And there is another mounting known as Wordsworth mounting; this is a spherical mirror, basically it is use to collimate, spherical mirror is use to collimate the incident radiation beam, that illuminates the grating with a parallel stream of light, because you are using a collimating lens. So, what comes out of a collimating lens is, a parallel stream of light and that makes the difference in the Wordsworth mounting.

So, when the wavelength region is changed, the detector to grating distance must be changed, because there you are changing the wavelength, the detector to grating distance also must change; otherwise, there would not be any change in the frequency or wavelength. So, it is maintained in such a way that proper focus of the diffracted light must be passing through the slits. So, you can use plane gratings, that is, the two types of gratings are there which we have already discussed earlier; one is Czerny turner mounting, and I have shown you some figure also along about this systems, and another is Abert Fasty arrangement mounting.

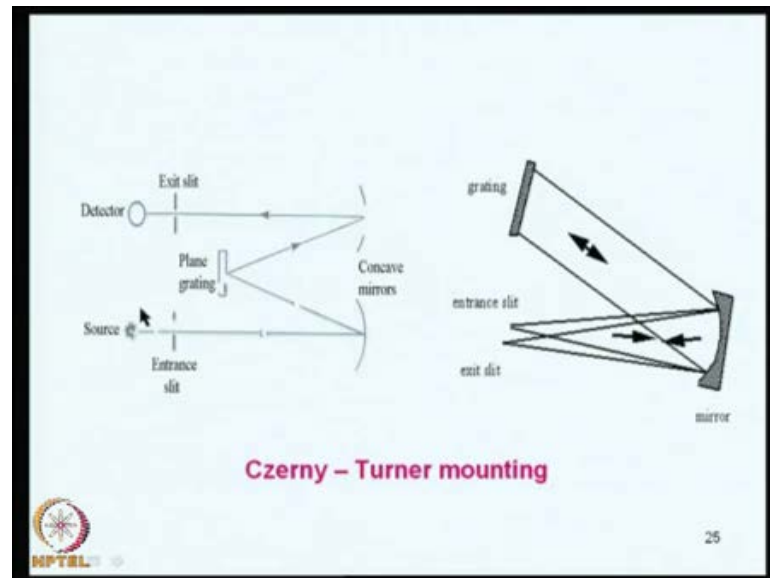
So, they utilize instead of a concave grating, they utilize a plane grating. Now, in that plane grating, he again used in combination with a spherical mirror to collimate the incident beam and to focus the diffracted light on the exit slit on the Rowland circle. So, the diffracted light passes through another grating, and then since the detector is near normal to the grating plane, the dispersion advantage, the dispersion is approximately linear; that means, you have to move the stepper motor in specific distance to get the different wavelengths; you do not have to worry about non-dispersive, non-linear dispersive scale. So, this is the advantage of Abert Fasty.

In Czerny turner mounting, it differs from the Abert Fasty; what is main focus in Abert Fasty is they use a plane grating and a spherical mirror. In Czerny turner mounting, the spectrophotometer has two spherical mirrors, and these are used in combination with array detectors, which have replaced photographic emulsions for the measurement of spectra. So, you can have a permanent record of the emission lines or you can collect the information in a computer, and then determine the chemical analysis.

So, in Czerny turner, photographic emulsion plates become redundant, because all the information is collected on the computer, in the computer, and the data can be handled using typical software.



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Now, this is a Czerny turner mounting; this a the schematic diagram, that is source, simple slit and two concave mirrors; one plane grating and one another concave mirror and then exit slit and the detector. This becomes a very compact arrangement and this is the optical diagram.

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### C. DETECTION OF ELECTROMAGNETIC RADIATION

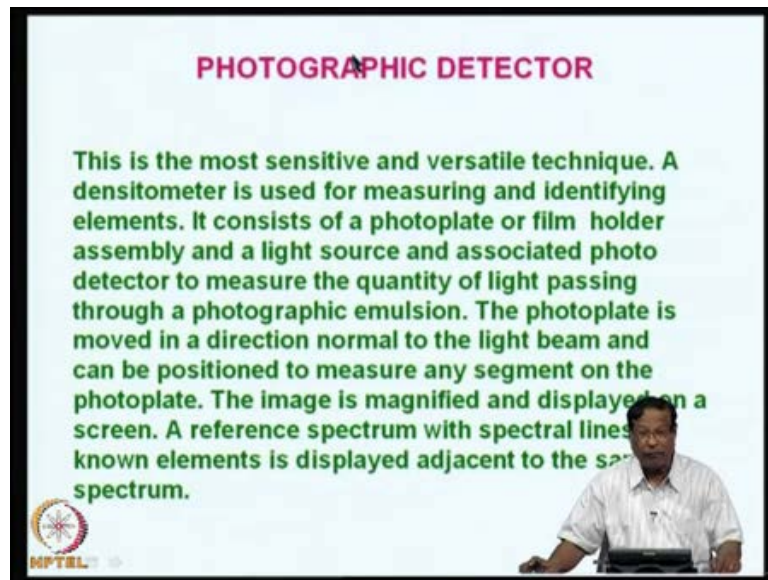
The PMT is the preferred mode of measurement. It consists of a photo cathode, a series of dynodes and an anode in an evacuated tube. The amplification is nearly 1 million. The line image is focused on the slit and directed to PMT by means of a refractor plate.

The slide features a title in red, a paragraph of text in blue, and a photograph of a man in a white shirt sitting at a desk in the bottom right corner. The NPTEL logo is in the bottom left corner.

So, now, let us come to the detection of the electromagnetic radiation. So, the best way to detect is photomultiplier tubes; and we have discussed it in number of times in almost all in instrumental techniques, photomultiplier tubes have been used and that is the

preferred mode of measurement. It consists of a photo cathode, a series of dynodes and an anode in an evacuated tube. The amplification obtained is approximately about 1 million times. The line image is focused on the slit and directed to the PMT by means of a refractor plate that, is the typical arrangement for a photomultiplier tube.

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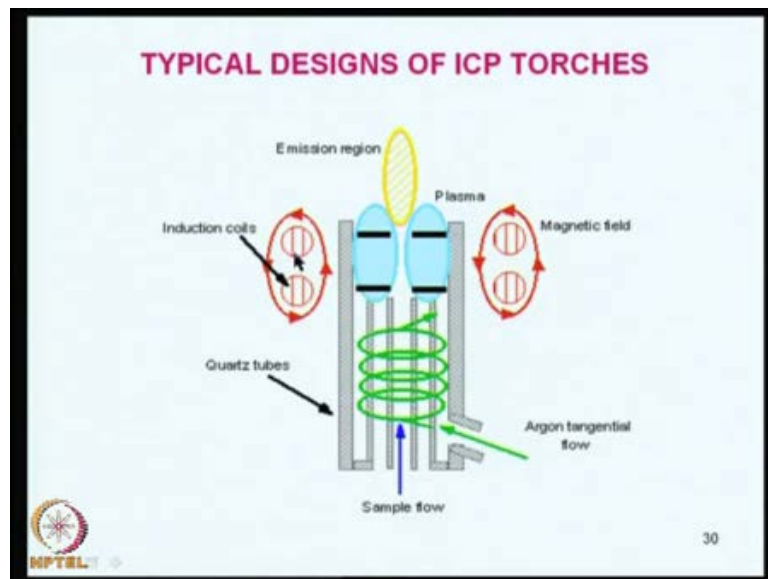
And then, for the record, we can have a photographic detector also; and this is photographic detector gives you a permanent record and this is the most sensitive and versatile technique basically. a dense for that, to use that, you need a densitometer for measuring the and identifying the elements, for that, you need to know the emission lines and you need a densitometer to measure the extent of darkening of the photographic emulsion plates. So, it consists of a photo plate or a film holder assembly and the light source and associated photo detector to measure the quantity of light passing through a photographic emulsion.

The photo plate can be moved in a direction, similar to the incident radiation direction normal to the light beam; that means, if the light beam is passing through, you can move the photo plate perpendicular to that. And the image is magnified, it can be position the photographic plates can be positioned at any specific wavelength and any segment can be measured, the images magnified and displayed on a screen straight away. So, a reference spectrum with spectral lines of known elements is displayed adjacent to the sample spectrum; that means, for easy comparison, reference sample with known concentrations.

So, that it is very easy for a, for the technician to know the different elements and their concentration. So, this is another way of detecting the emission.

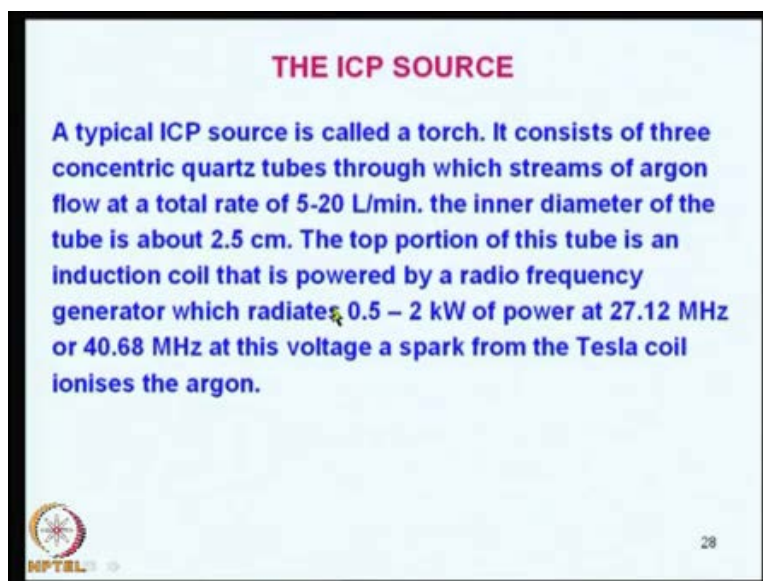
Now, we will talk about the ICP source. So, the ICP source is called as torch; it consist of three concentric rings which I had shown you earlier and I think I have put it here also; this is a figure you can see here.

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The figure this is one concentric ring and there is another concentric ring. One here, one here, middle one represents another concentric ring; this is a tube in another bigger tube and these two tubes are fitted inside another tube. So, there are, you can basically there are one this is one tube, this is second tube and this is the third tube.

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So, this is a plasma torch ICP torch and the plasma torch is used to pass the sample into the plasma. So, the flow rate, it also has to pass the argon. So, the argon is passed at a 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 an induction coil, it acts as an induction coil, that is powered by a radio frequency generator which is coupled already, that radiates 0.5 to 2 kilo watt of the power at 27.12 megahertz or 40.68 megahertz. These values have been fixed over a number of trials and found to be convenient for a laboratory instruments. And at this voltage, spark from the tesla coil you start, afterwards the plasma will take over, that is the idea.

And the resulting ions and their associated electrons basically interact with the fluctuating magnetic field produced by the induction coil. This interaction causes the ions and the electrons within the coil to flow in the closed annular paths; **the resistance of** the resistance of the ions and electrons causes ohmic heating of the plasma. So, the plasma must be heated and **how** the whole mechanism I will continue to explain to you in the next class.