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

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Lecture – 11
Instrumentation for ICP AES –II

Greetings to you. In my last class, we had started our discussion on the instrumentation for atomic emission spectroscopy. Earlier we had looked at the atomic structure and then nature of electromagnetic radiation and then you had also looked at the interaction of electromagnetic radiation with matter. Now we are coming to the specific instrumentation for inductive couple plasma atomic emission spectroscopy. I had shown you about 6 or 7 slides in this module just for the sake of continuity.

I will just show you those slides once again, but very quickly.

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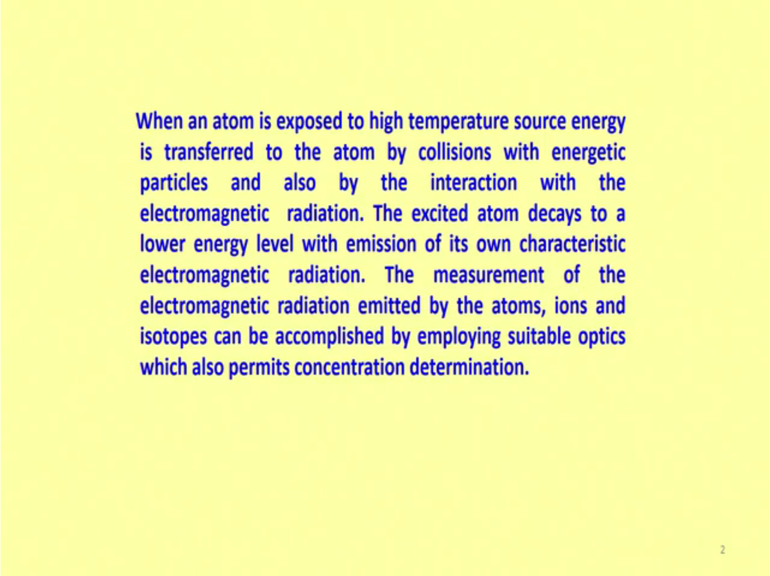

When an atom is exposed to high temperature source energy is transferred to the atom by collisions with energetic particles and also by the interaction with the electromagnetic radiation. The excited atom decays to a lower energy level with emission of its own characteristic electromagnetic radiation. The measurement of the electromagnetic radiation emitted by the atoms, ions and isotopes can be accomplished by employing suitable optics which also permits concentration determination.

So, we had discussed that when an atomic exposed to high temperature, source energy is transferred to the atom by collisions with energetic particles and also by interaction with the electromagnetic radiation. The excited atom decays to a lower energy level with the emission of it is own characteristic electromagnetic radiation. So, the measurement of the electromagnetic radiation emitted by the atoms, ions and isotopes can be accomplished by employing suitable optics and measuring the incident and emitted radiation. You have to measure both and the difference can be attributed to the concentration. That is the theory of spectroscopy, emission spectroscopy also.

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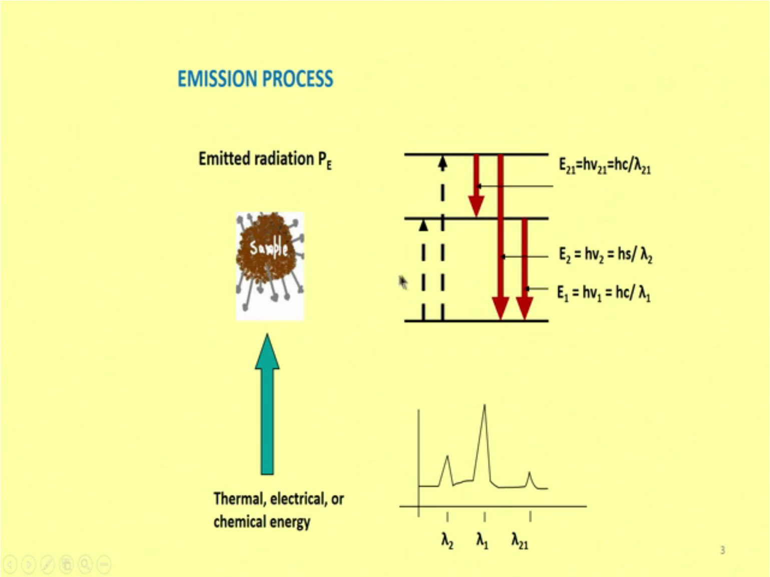

EMISSION PROCESS

So, this is the pictorial representation of the emission process. What we have is a sample here subjected to electromagnetic radiation. The electron goes to the next higher energy level and then in after sometime due to several reasons in terms molecular collision etcetera, the emitted excited electron comes back to the ground state with the emission of corresponding wavelength. So, the excitation can be thermal, electrical or chemical energy. If you plot the energy in the y axis, I am looking here energy in the y axis and plot with different wavelengths; these emission wavelengths are the characteristics of the elements that are present in the sample.

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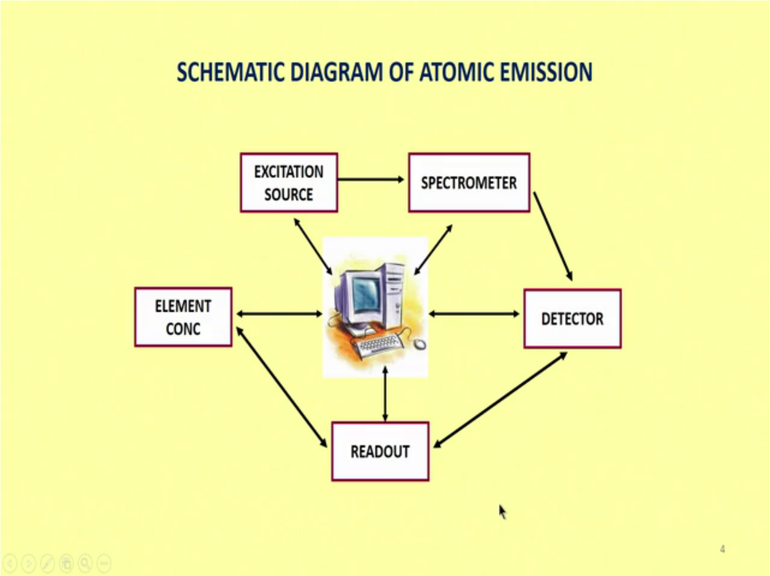

SCHEMATIC DIAGRAM OF ATOMIC EMISSION

So, the basic schematic diagram is something like this.

There is one excitation source and that is connected to the spectrometer and to measure the emitted radiation we have to convert the radiation into some sort of an electrical signal. That is done by the detector and then the detector needs to have a read out some number and this number is recorded in the computer and then the computer will do the calculation for the element concentration. So, all these things are interactive with the central computer. Here this is the result of current electronics state of the analytical science. It has nothing to do specifically, but the emission the computer is only a recent addition to make things simpler.

Otherwise also things could have been measured using different techniques, but we have not going to discuss them. Because, photographic plate and other things etcetera. If we use as detector will have to have different kinds of interpretation. Now things have become very simpler and everything can be read out as a concentration or some number which is directly correlated to the concentration.

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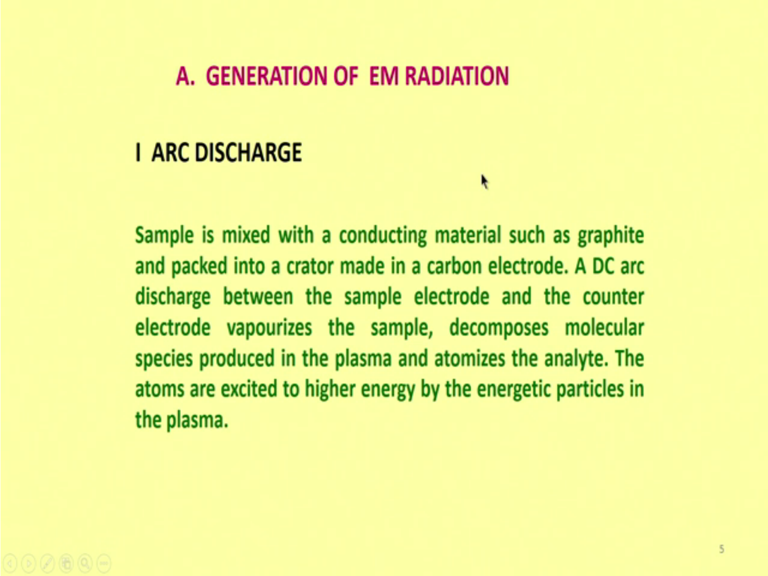

A. GENERATION OF EM RADIATION

I ARC DISCHARGE

Sample is mixed with a conducting material such as graphite and packed into a crator made in 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.

So, now first of all we have been discussing about the generation of electromagnetic radiation. There are different types. One is the arc discharge. Here we had suggested that you take 2 metal rods. Then try to bring them nearer and nearer. Pass the electric current. In one electric rod you make a small hole. Put your sample in that.

And strike an arc between the 2. So, this arc generates very high temperature of about 6 to 8000 degree centigrade and then the difference can be used for generation excitation of the sample.

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ARC DISCHARGE

So, this is the very typical example of an arc. You must have seen in lightening etcetera and this is how the arc is generated.

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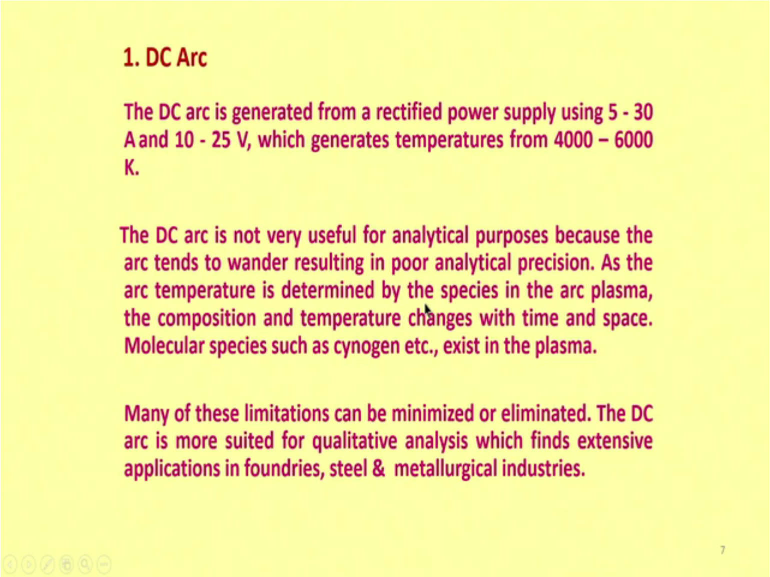

1. DC Arc

The DC arc is generated from a rectified power supply using 5 - 30 A and 10 - 25 V, which generates temperatures from 4000 – 6000 K.

The DC arc is not very useful for analytical purposes because 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.

And then we have been discussing the DC arc. That is the DC arc is generated from a rectified power supply using 5 to 30 angstroms and 10 to 25 volts. Which generates temperature of 4 to 6000 Kelvin.

The DC arc is not very useful for analytical purposes. Because, the arc tends to wonder resulting in poor analytical sensitivity. As the arc temperature is determined by this species. In the arc plasma the composition and temperature changes with time and space. So, molecular species such as cyanogens etcetera exists in the plasma. So, many of these limitations can be minimized or eliminated. The DC arc is more suitable for qualitative analysis. Which finds extensive use in the foundries.

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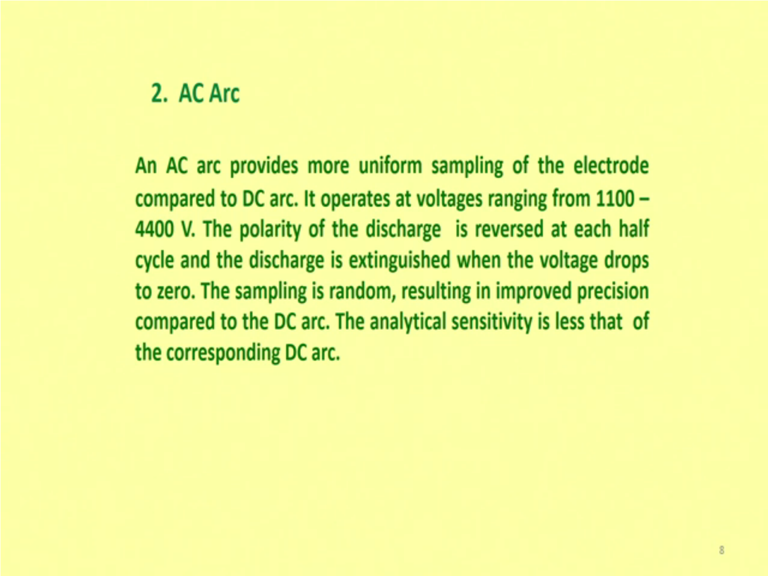

2. AC Arc

An AC arc provides more uniform sampling of the electrode compared to DC arc. It operates at voltages ranging from 1100 – 4400 V. The polarity of the discharge is reversed at each half cycle and the discharge is extinguished when the voltage drops to zero. The sampling is random, resulting in improved precision compared to the DC arc. The analytical sensitivity is less that of the corresponding DC arc.

Next we had discussed about the AC arc. This is where I had stopped in my last class. So, an AC arc provides more uniform sampling of the electrode compared to the DC arc. Why? Because it operates at voltages ranging from 1100 to 4400 volts and the polarity of the discharge is reversed at.

Each half cycle and the discharge is extinguished when the voltage drops to 0. So, the sampling is random. That resizes results in improved precision compared to the DC arc. The analytical sensitivity of course, would be less than that of the corresponding DC arc. Because, the half of the cycle of the electrical signal goes to 0, maximum, 0, maximum like that. So, the sensitivity would be lower than DC arc, because it is not a continues system.

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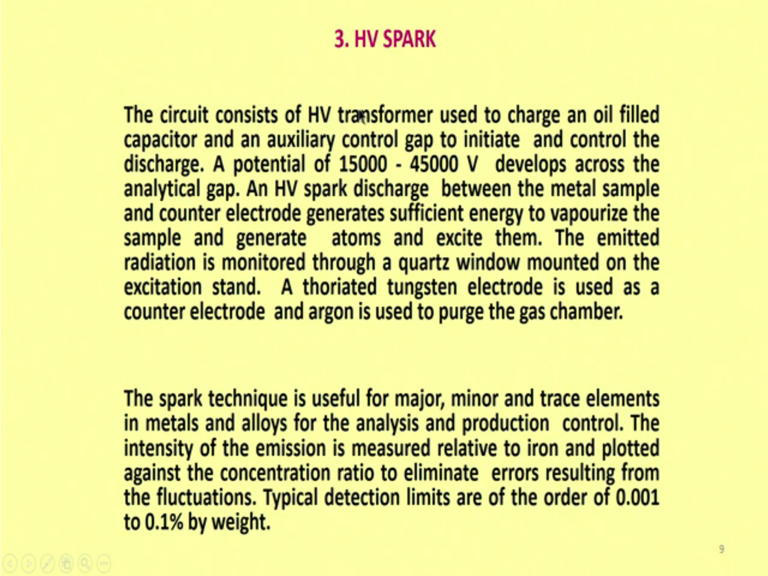

3. HV SPARK

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 vapourize 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 the 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, then there is another way of generating a spark that is HV spark, high voltage spark. So, here the circuit consists of HV transformer, high voltage transformer used to discharge an oil field capacitor and an auxiliary.

Control gap to initiate and control the discharge. So, the voltage difference, potential difference of 15000 to 45000 volts develops across the analytical gap. A HV is high voltage spark discharge between the metal sample and the counter electrode generates sufficient energy to vaporize the sample and generate the atoms and excite them. The emitted radiation is monitored through a quartz window mounted on the excitation stand. So, what do we do? We use a tungsten electrode. Which is coated with thorium. That is what it means a thoriated tungsten electrode is used as a counter electrode and argon.

Is used to purge the gas chamber. So, what you need is a gas chamber. In which 2 electrodes are being used and you use for 15 high voltage transformer filled with oil. Strike the spark and it generate for 15000 to 45000 volts across the analytical gap and the temperature would be extremely high. So, at that temperature atoms get excited as usual, go to the next higher energy layer level and when they come down to the ground state, they emit the radiation. That is as simple as that. This spark technique is basically useful for major minor and trace elements. That is in metals.

And that is also used for the analysis of the alloys and for production control. See the point is whenever you are producing a metal or an alloy, generally the procedure is you take the 2 metals and then melt them and then mix them together and then allow it to collision. Then the moment it is quenched and becomes an alloy. You just take a small sample and you need to analyze it immediately to adjust the composition. Otherwise the melt will be held in the molten form. We have to take a small sample of the metal. Put it in a (Refer Time 10:42). Analyze it for such analysis. Where immediate analysis of the components major, minor and trace elements are required. It is very important for us to take the sample analyze quickly. So, what is the best way? Best ways is to heat it quickly to.

Very high temperature that is done by HV spark. So, for production purposes whenever there is a requirement of the quick analysis high voltage spark is the method of choice. It is not necessarily meant only for analysis, but also for the quick quality control. So, the spark technique is useful for major, minor and this thing, but normally what we do is we measure the intensity of the radiation with respect to a reference sample. Otherwise Spectroscopic technique is always a technique where it is only relative. You have to have something on which you depend.

And that dependent is iron. So, we just put a small sample of iron which is pre measured and then compare the signal. See that the iron sample matches with what you have put in. Which means that all other elements also would be relatively free from interferences or if the results would be more accurate. As far as long as iron analysis is accurate we assume that other samples also are results are accurate. So, this is known as an internal standard analysis. We use iron, a small quantity of iron are and measure the signal relative to that and that is plotted against the concentration ratio to eliminate the errors resulting from the fluctuations.

So, normally what happens is even the iron signal fluctuates depending upon the voltage. The signal also will keep on increasing up and down, up and down like that. So, whenever you want to measure a signal with respect to any alloy, what you should do is you put a small amount of iron and then analyze iron. See that the iron is already analyzed. If your iron analysis is correct, assume that all other analysis is also correct. That is how we use an internal standard and it is a very important concept as far as the chemical analysis is concerned using spectroscopy because.

Spectroscopy is always a relative technique. It is not an absolute analysis technique, never. So, the concentration ratio we have to plot rather than the actual signal. Concentration ratio is measured with respect to iron and this job is best done using a computer. Because computer can store the data and measure the signal and compare it, ratio it. All those mechanical calculations can be best done by the computer rather. Now a days that is one advantage of the computer entering into analytical sciences. So, the typical detection limits are of the order of 0.001 percent to 0.1 percent by weight; that means, it is not a technique for trace elements. Because, normally whenever we want to analyze for trace elements.

We want them in micrograms, nanograms and pictograms. Pictogram is 10 raise to minus 12 grams. So, it is not meant for ultra trace, but trace is fine 0.001 percent. Whenever you want to make an alloy for example, this is chromium the tip. This tip was chromium. We want to know how much of chromium is there along with manganese, along with nickel, along with iron etcetera. That will be 0.1 percent plus or minus. So, during the production of the metal you want to measure it is all melted and you have put the sample. There is a liquid mild. You take out a small sample solidify it. Put it in the spark and then emission bomb and then it goes to next higher energy level. When it comes down, you get the analysis before you make the metal in guts.

So, when they have operator is operating to make the alloy in the liquid form, there is a laboratory man standing using high voltage spark to quality control. That is the beauty. Quick analysis at trace levels.

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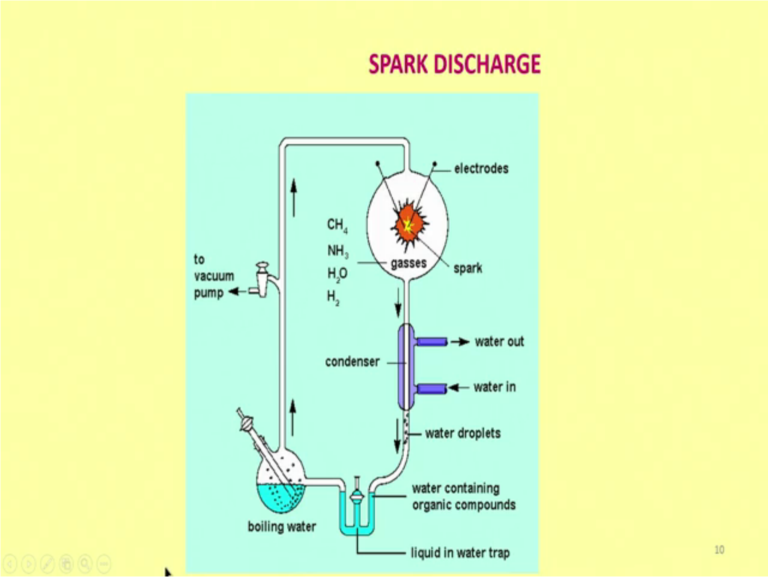

SPARK DISCHARGE

This is how a spark discharge normally happens. What do we do? We have boiling water is here. There is a vapor is here and everything is taken off to vacuum and then we have water containing organic compounds. All these things are dissolved and then normally whenever you heat something, you get water vapors first. So, all those water vapor etcetera should be removed by the vacuum pump. That is why this is a slightly elaborate arrangement for the removal of the water vapor.

And then what I have here the gases coming out of the system. See here I am showing electrodes on the top. This is one electrode, this is another electrode. These 2 electrodes are brought like this nearer and nearer and then strike a spark and then warm. So, that is what happens. When the arc is strike high voltage spark is struck. First thing is all organic compounds will evaporate. What would be the products? All carbons will react with hydrogen to form methane or other organic homolog's methane, ethane, butane, propane anything it can form, but at that high temperature organic compounds also will be great to the simplest chemicals. So, that is how you we get only methane.

Suppose there is butane. Then what happens? Butanes also is not stable at that temperature. Maximum concentration will be methane. So, similarly what is the next highest molecular weight you can get? Ammonia. This ammonia will be there and then water vapor that also will be there. Hydrogen will be there. So, all these things when the spark strikes these are generated in the reactor. This is the white one is the reactor. These are all condensed. There is water in, there is water out. Water droplets are taken off and remaining organic compounds are here and then there is a liquid water trap. All these things are pass through electromagnetic radiation will pass through the bulb. You see that white bulb there, they will pass.

Through the bulb. These things will absorb the radiation and then abet the radiation after excitation and I have a resembled detector and other things just like what I had showed you in the arrangement of ICP. So, this is I had shown you know. This is how excitation source I have here and then spectrometer. That is electromagnetic radiation detector is there, read out is there, element concentration all these things will be done automatically.

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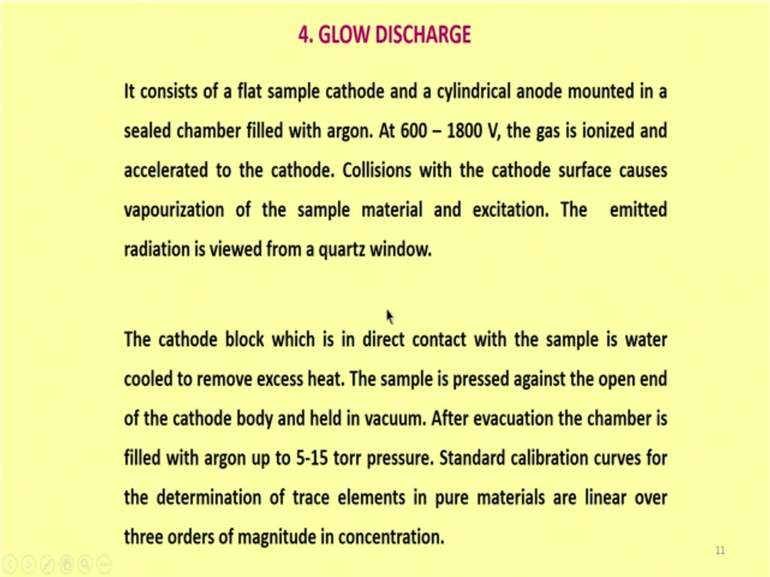

4. GLOW DISCHARGE

It consists of a flat sample cathode and a 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 up to 5-15 torr pressure. Standard calibration curves for the determination of trace elements in pure materials are linear over three orders of magnitude in concentration.

So, another way of generating high temperature. How do you do that? That is glow discharge I had thought you earlier when I was teaching atomic absorption. That it is in hollow cathode lamp. What we use is a low pressure neon gas or organ gas which is excited very easily and once the.

Ions are generated. They hit the metal cathode and then they will start sputtering and then they will emit radiation. So, that is how you see most of the in if you see go to MG road or somewhere you see neon lights now a day’s. LED lights most of them are generated from low concentration of argon gas or neon gas. Neon lights you must have heard. Most of the neon lights are operated like that. So, basically it is a glow discharge. It is not something which is highly technology. Nothing is high technology in this and at 600 to

1800 voltage the gas is ionized. What do we do? You make a tube and what we can write coca cola and then make a tube of coca cola. Fill you neon gas or argon gas.

Put a vacuum of order of above 10 raise to minus 4 atmosphere. One atmosphere is what you get on the sea beach. So, reduce the pressure. You will get 10 raise to minus 1, 0.1, 0.01, 0.001, 0.0001 is the pressure inside the coca cola tube. Then you strike the arc and then ionize. They will get ionized and then off to ionize how much you have to apply voltage? 600 to 1800 volts. So, the gas is ionized at that level and accelerated. Ions, what is he do ions? If I have a positive electrode, if I have a negative electrode, positive ions will get attracted to negative electrode and negative ions will get attracted to positive electrode. So, they will start moving and then they collide each other. Once the collision.

Ah takes place the cathode surface causes vaporization of the sample and then excitation next higher energy level. Then it comes down to the lower energy level, emission takes place. Again put a prism this side, put a prism that side, pass electromagnetic radio, measure the excitation. That is how the chemical analysis is completed, but the problem is all of it will not be in the visible region. So, sometimes you will see if you go to any commercial center, you will see yellow light, blue light, red light, white light. All those things, but generally what happens is 99 percent of the elements will emit radiation in ultraviolet range. So, if it is ultraviolet range our eyes are not sensitive to.

See the reddish. Even the glass if I put a glass prism, they will absorb all the radiation you would not say anything. You have to put quartz. Quartz is transparent to ultra violet. So, most of the components in a spectrophotometer or spectrometer should use components made of quartz. What is quartz? Quartz is nothing but silica. Pure silica. That is quartz. Glass is what? That is also silica, but it is sodium silicate. Quartz is only silica.SIO2, SIO2, SIO2 you can look up the structure in your text book. Co-silica structure. The cathode block which is in direct contact with the sample in a spectrophotometer or a spectrometer ICP.

It has to come in contact with your sample to vaporize it. So, the sample must be cooled to remove excess heat. Otherwise it takes no signs. Because, the excess heat will normally decomposed many other components also. It is no more a characteristic emission of the sample elements you want to analyze. So, what happens is the sample is pressed against open end of the cathode body inside press it and seal it and then bring cathode and anode together and then strike an arc. if neon gas is maintained at low level ions will be generated and after sometime the instead of the neon gas the sample ionization will be more. They will overtake the neon gas energy. That is how you will get different colors.

So, the sample must be pressed against the open end put it there and then strike the glow and then hold it in vacuum that is important. After evacuation the chamber is filled up again with gas with 5 to 15 torr pressure. What is torr? Torr is 1 atmosphere. So, 5 to 15 torr pressure is 15 atmospheres. Then you should make a calibration curve as usual for the determination of trace elements in pure elements just like what you do in spectrophotometry etcetera. Plot the emission versus concentration and make the interviewing. Unknown also should be referred to that. The beauty is in spectrophotometry.

Or in atomic absorption. The calibration is normally 1 ppm, 2 ppm, 3 ppm, 5 ppm maximum 10 ppm may be 100 ppm. If this method is very less sensitive. Here the linearity what you get a straight line extends from 1 ppm to 100. 1, 100, 1000, 10000 and 1 lakh ppm also. That means the range which you can measure in emission is not 1 order, but it is about 5 orders. So, the concentration if you want to plot, you cannot plot it on a arithmetic scale. You should plot it in log scale. Why log 1 is 0, log 10 is 1, log 100 is 2, log of 1000 is 3. So, 1, 2, 3.

Log x scale, y scale would be simple emission. So, log scale versus a normal scale. That is how the calibration curves are made in ICP as well as in any emission spectrum that is why the concentration range to be measured in atomic emission is always of the about 3 to 4 orders. So, you can make an alloy, you can make the determination in very simple systems, from ppm to ppb same system. Otherwise if you want to determine in normal chemical analysis, if it is major element you take a very small sample and do the analysis and complete. If it is 0.1 percent, you some other technique gravimetric volumetric. If it is ppm, go to spectrophotometry, but in atomic emission 1 single unit will do from.

0.1 ppm to 100, 1000 ppm. That is how the range will extend. So, the calibration curves are linear over minimum 3 orders of magnitude 1, 10, 1000. So, in ICP your calibration concentration should be 1 ppm, 10 ppm, 100 ppm, 1000 ppm that is it. So, that is the beauty compared to spectrophotometer or atomic absorption.

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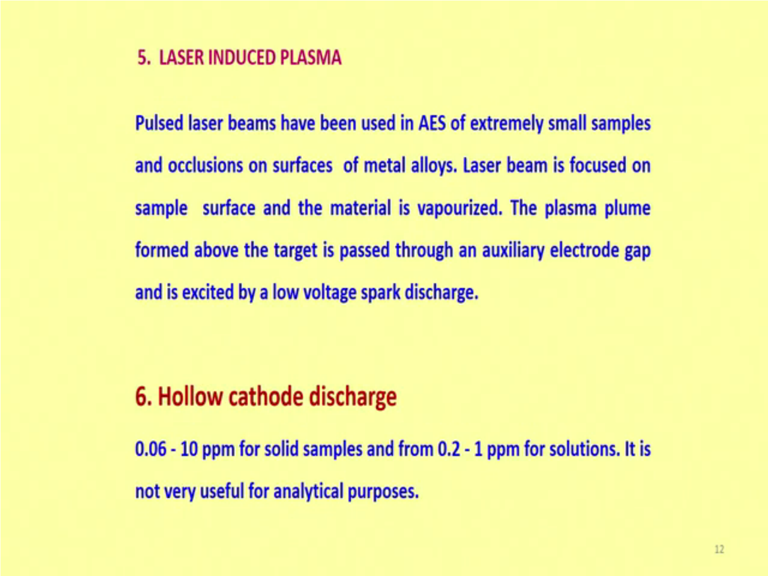

5. LASER INDUCED PLASMA

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 is passed through an auxiliary electrode gap and is excited by a low voltage spark discharge.

6. Hollow cathode discharge

0.06 - 10 ppm for solid samples and from 0.2 - 1 ppm for solutions. It is not very useful for analytical purposes.

So, another way of doing this emission atomic emission is used lasers. You must have seen many laser play and other things if you go to any tourist spot normally you will see a long distance laser images being measured.

You know they show pictures how they do that? Pulsed laser beam they use. So, in the pulse laser beam what we do is in atomic emission spectrometry of very small samples and occlusions on surface of the metal ions, you take metal surface. Hit it with laser, it goes out. The laser beam is. Sharp that it will interact only with a very small portion of the sample and then it will go off. So, the changes in the concentration of the electro intensity of the laser is what determines the small concentration. Only in that space where laser is contacting that maybe 1 or 2 square millimeter at the highest end. Otherwise it may be of the order of about few microns. You have a metal surface. A laser beam will come and go of.

Then what happens? That will be 0.1 square millimeter. So, that is the beauty. The plasma plume formed above the target. That is passed through a spectrometer. The electrode gap is already there. That is excited using a low voltage spark discharge. This is another way. One more way of doing the emission bringing about excitation of the atoms in the given sample is by hollow cathode discharge. This I have thought you. When I was started teaching in the previous course on atomic absorption, there we use hollow cathode lamps as a source for atomic absorption radiation. Because if I make a tungsten lamp you know you must have seen.

Tungsten lamp you know earlier tungsten bulbs used to come in all houses. So, 60 watts, 100 watts like that. Instead of tungsten, if you use iron, then you will get iron radiation. If you use chromium, you will get chromium copper. All you have to do is change the filament and I have taught you how to make hollow cathode lamps using neon discharge. Same way what we had discussed earlier in this class. I will not go into details about how to go about hollow cathode, doing hollow cathode discharge, but what is important is it has not taken off in the commercial market for hallow cathode discharge because ICP is another way simpler way of doing it and, but for the sake of record I want to tell you that.

0.06 to 10 ppm of the solid sample you know solid sample and from 0.2 to 1 ppm for solutions. These things can be analyzed using hollow cathode discharge. Basically what it means now I am going to strike a discharge using hollow cathode lamp. So, the idea is since it has not taken of the commercial way. Many commercial instruments are also not available and the other instrumental analysis techniques like inductive couple, plasma, atomic emission, spectroscopy which you are going to study in detail are can be done. The beauty is you take the solid sample and simply put it there and you get the analysis done. You do not have to dissolve it. Put acid, dissolve it, take it to fume hood you dissolve it.

And then let the flume go it is none of those dirty businesses. Take the solid sample. Put it in this spectrometer and you get the result. That is the beauty of hollow cathode discharge lamps.

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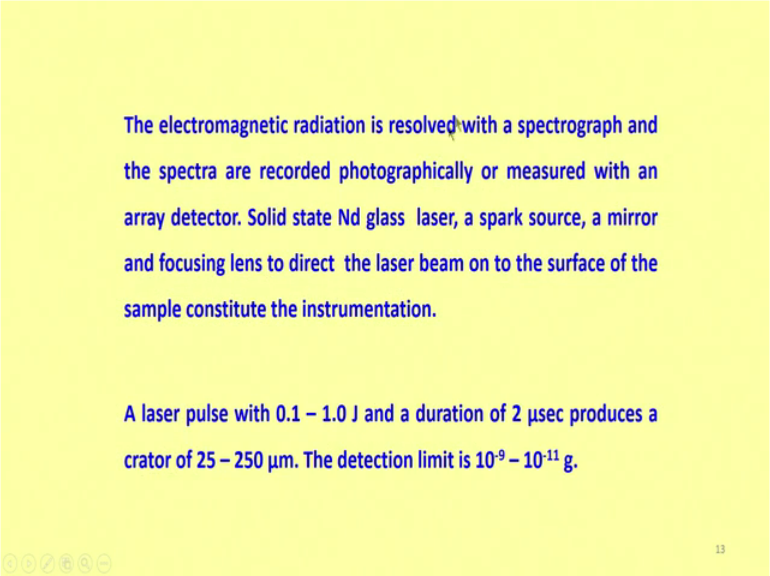

The electromagnetic radiation is resolved with a spectrograph and the spectra are recorded photographically or measured with an array detector. Solid state Nd glass laser, a spark source, a mirror and focusing lens to direct the laser beam on to the surface of the sample constitute the instrumentation.

A laser pulse with 0.1 – 1.0 J and a duration of 2 μsec produces a crator of 25 – 250 μm. The detection limit is $10^{-9} - 10^{-11}$ g.

Now, how do we do that? We have to resolve the electromagnetic radiation using a spectrograph. That is using a prism. What prism? Quartz prism. So, the spectra are recorded photographically. You just put your sample. Put a photographic plate. If the sample is there, intensity of the radiation coming out will be less. If it is emission, more light will come. So, it will become the photographic. C1 line signal becomes less dark. If it is absorbs, it becomes very dark.

If there is emission, it will become less dark. So, the intensity of the photographic plate it is more dark into 0.1 percent.

It is less dark. So, it has to be 0.01 percent. So, something like that can be analyzed very easily using photographic plate, but for that you must have lot of experience. You just see 100's of photographic plates to differentiate the moment you take and look at it, you should say this is slightly more than this, less than this. Like that we should be able to pin point the known concentrations. That takes a little experience and it is not. So, easy now a days computers do that job. You do not have to really worry about whether you are accurate or not. Because, computer will tell you an exact difference in the density it can measure. So, this normally what happens in solid state niobium glass laser.

That is a spark source and mirror and focusing lenses. That is all is require which laser? Niobium laser and then you need a spark source. It can be low discharge. It can be AC discharge. It can be high voltage discharge or it can be hollow cathode or it can be a laser. So, any of those and then it must be fade on to the surface of the sample to constitute the instrumentation. That is how you have to put it in the electrode. Once you have it in the electrode, strike the arc. That is the beauty. So, a laser pulse with 0.1 to 1.0 joules and a duration of 2 microseconds produces a crater. If you take a laser, heat it on the metal. It create, it burns and then evaporates the sample. So, when something goes off, a crater has to form.

So, that craters what is the size? The size is 25 to 250 micrometers. It is not millimeters. 1000 times smaller than a millimeter that small piece. So, if I want to determine the concentration of a metal in a painting monalisa, you know a big painting. I cannot destroy the whole lot to find out what paint that Davinci had used. What I do is I take a laser, make a 250 micrometer laser cavity and then analyze. An onlooker will not know that painting has been subjected to examination also because our eye is not sensitive enough to sense 250 micrometer crater in a paper also. That is the beauty.

Of the chemical analysis using lasers and what are the detection limits 10 raise to minus 9 to 10 raise to minus 11 gram. That is pictogram level. That is quantitative. It is not qualitative. So, if I say you got about 2 into 10 raise to minus 11 gram of chromium in that paint on monalisa, it is 2 into 10 raise to minus 11 grams only. Many grams per square meter or something like that we will have to manage. What we will do is we will take a small break now and then we will see the plasma, because, that is what we are here to study the course title. If you remember, it is inductively coupled plasma atomic emission spectroscopy. So, we should study plasma. We will study that in our next session.

Thank you very much.