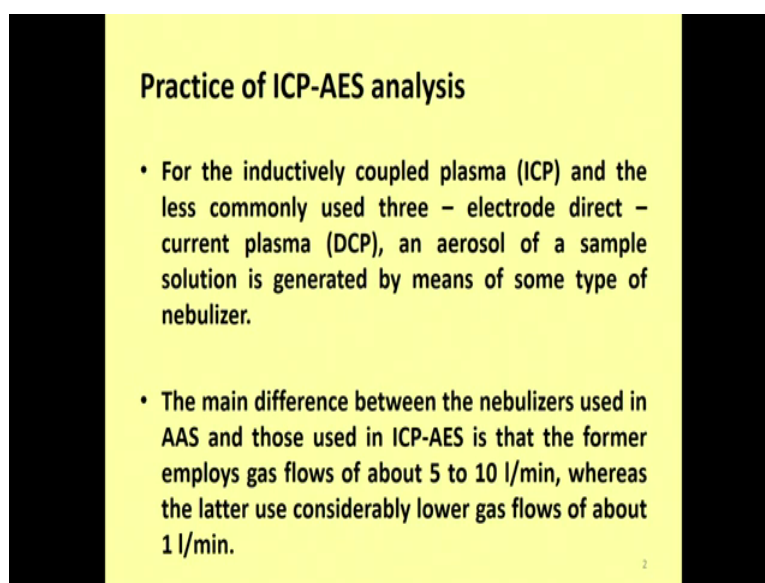


Inductive Couple Plasma Atomic Emission Spectrometry (ICP-AES) for Pollution Monitoring

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Lecture – 18 **Practice and Applications of ICP AES I – Nebulizers**

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Practice of ICP-AES analysis

- For the inductively coupled plasma (ICP) and the less commonly used three – electrode direct – current plasma (DCP), an aerosol of a sample solution is generated by means of some type of nebulizer.
- The main difference between the nebulizers used in AAS and those used in ICP-AES is that the former employs gas flows of about 5 to 10 l/min, whereas the latter use considerably lower gas flows of about 1 l/min.

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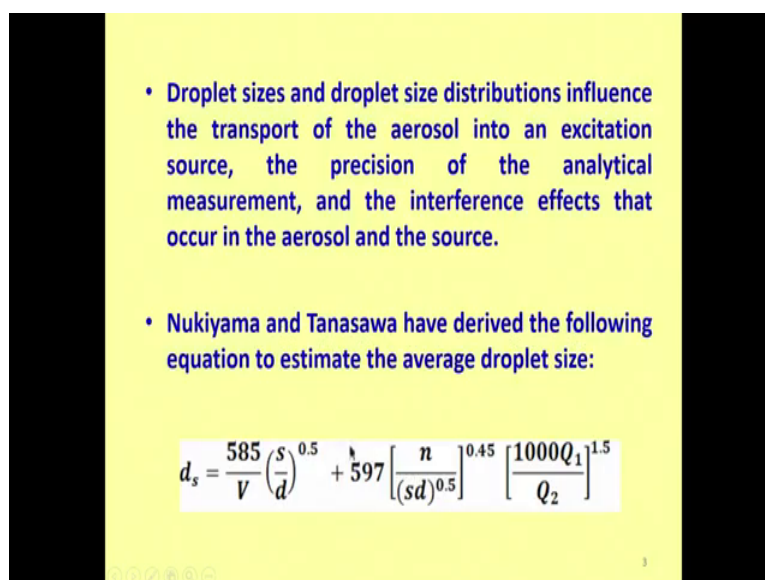
So, how do we practice on ICP a suppose you are being given an instrument, what all you should be knowing what you should be doing how the sample should be prepared and all that we will have a small discussion. Now for the ICP and the less commonly used 3 electrode director DC plasma that is the direct current plasma, what is required is an aerosol, I have explained to you number of times the role of the aerosol generated by means of some type of nebulizer. So, nebulizer design is a special requirement of a spectrometer Deepali yeah. So, the main difference between the nebulizers used in s, and those used in ICP is that the former employees gas flow of 5 to 10 liters per minute, and ICP requires about 1 liter per minute, this point I have already covered in my previous session.

So, the droplet sizes and droplet size distribution assumes a very big, important role in all ICP AES determinations is not it. Suppose the droplets are very small there is more efficiency of the error aerosol and it gives you a higher signal if the nebulizer is not that

good and not able to produce the aerosol, then what is what happens is many of the bigger droplets drain away, they do not enter the plasma nor do they tell you nor is it useful for measurement also. So, the understanding of the droplet size, and size distribution becomes very important in ICP, because apart from the normal expectation of an instrument over, they over a period of time the performance of the nebulizer comes down.

So, we have to clean the nebulizer as well as ICP torch number of times, whenever we want to determine high solids, and samples containing high solids or even otherwise also.

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- Droplet sizes and droplet size distributions influence the transport of the aerosol into an excitation source, the precision of the analytical measurement, and the interference effects that occur in the aerosol and the source.
- Nukiyama and Tanasawa have derived the following equation to estimate the average droplet size:

$$d_s = \frac{585}{V} \left(\frac{s}{d} \right)^{0.5} + 597 \left[\frac{n}{(sd)^{0.5}} \right]^{0.45} \left[\frac{1000Q_1}{Q_2} \right]^{1.5}$$

So, the distribution droplet distribution is defined by some sort of an equation here, I have written, and Nukiyama and Tanasawa are the people who derived the following equation to estimate the average droplet size. So, here you can see the droplet size is given by d_s that is diameter of the sample, and V is the volume is and the 585 by V multiplied by s by d raised to 0.5, plus 597 n into $s d$ raised to 5 raised to point, the whole thing is raised to 0.45 multiplied by 1000 Q_1 by Q_2 raised to 1.5.

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Where,

- d_s is the median of the ratio of volume to surface area and represents the mean droplet diameter,
- V is the difference in the velocity of the gas and liquid flows to the nebulizer (m/s),
- s is the surface tension of the liquid (dyn/cm), d the liquid density (g/cm^3),
- n is the liquid viscosity (P), and
- Q_1 & Q_2 are the volume flow rate of the liquid and the gas (cm^3/s) respectively.

It is important to realize that this equation applies only to the primary nebulization process, and does not provide an estimate of the size of the droplets after secondary or tertiary nebulization. The equation indicates that with increase in the pump rate of the solution the droplet – size distributions will shift to larger diameters.

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So; obviously, it is a highly mathematical equation, and in this equation d_s is the median of the ratio of volume to surface area, I think it is important for us to determine the average median means average average ratio of volume to surface area that is d_s that represents, the mean droplet diameter, and V is the difference in the velocity of the gas, and liquid flows to the nebulizer ok..

That is meters per second units are in meters per second, and s is the surface tension of the liquid that is dynes per centimeter d is the liquid density, and n is the liquid viscosity that is sample viscosity, and Q_1 and Q_2 are the volume flow rates of the liquid, and the gas respectively the units are in centimeter cube per second. So, in this equation we have defined d_s that is droplet size mean in droplets, and then V is the difference in the velocity of the gas, and liquid flows s is the surface tension of the liquid d is the density n is viscosity Q_1 and Q_2 are the flow.

That means, the quality of the droplet size distribution is governed by several factors, and those factors are volume to surface area ratio, viscosity, temperature, and then the volume flow rates all these things are important in obtaining a good droplet size distribution. So, this equation applies only to the primary nebulization process, and does not provide an estimate of the size of droplets after secondary or tertiary nebulization.

Usually the whenever sample is to be introduced, the first crop of aerosol is primary, and after that part of it gets the operated part of it gets into solid particles and aerosol all the

concentration etcetera will keep on varying, but the equation what I had shown you just now, it represents only the primary nebulization. So, it does not provide an estimate of the size of the droplets after secondary or tertiary nebulization, we have to understand that..

So, the equation indicates that with increase in the pump rate of the solution, the droplet size distribution will shift to larger diameters. So, what does it mean, the suppose I increase the pumping rate do, I really increase the aerosol concentration not necessarily ok. So, it it may increase the pumping rate, but the size distribution will also shift to larger diameters; that means, efficiency will come down the sample introduction should be as less as possible in the nebulizer.

So, generally if a solution is injected directly into the ICP, sometimes I had shown you that sample can be introduced directly into the ICP, or it can be introduced as vapor, or it can be introduced as solid aerosol etcetera that is something like a mist ok, the nebulizer job is to convert a sample solution to an aerosol, and it is importance arises from the fact. That it is generally recognized as a large source of error, and be in ICP, AES.

So, nebulizers can leak they can block, and they can be maladjusted because if you take a look at the nebulizer, there will be a small bead that breaks their liquid coming in into small small droplets. So, the performance varies with the viscosity of the solution temperature, and state of the electrostatic earth connection, and the presence of surface active agent this is nothing, but a surfactant which you use normally to reduce the viscosity of the sample. So, that the viscosity is reduced the aerosol concentration becomes better.

So, surfactants are also like detergents, they produce foam and things like that, and the liquid moves smoothly, suppose you want to determine lead in blood blood does not flow. So, nicely so, what do we do we normally add the triton x hundred a surfactant to the blood sample, and then make it flow smoothly, and into the nebulizer and into the plasma. So, that is why we feel.

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Generally, if a solution is injected directly into an ICP, the plasma will be extinguished. However, since the plasma will tolerate an aerosol (mist), a nebulizer is used to convert a sample solution to an aerosol, and its importance arises from the fact that it is generally recognized as a large source of error in ICP-AES measurement. Nebulizers can leak, block, and be maladjusted. Their performance varies with the viscosity of the solution, the temperature, the state of the electrostatic earth connection, and the presence of a surface-active agent in the solution.

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It is very important to use a surface acting agent, in the solution unless the viscosity is very low. Just like water if it is water we do not, add if it is a blood sample urine sample etcetera, we have to add some sort of a surfactant agent to the sample ok.

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Most nebulizers create an aerosol that contains droplets ranging from very small to greater than $100\mu\text{m}$ in diameter. Spray chambers are designed to filter out the larger droplets and allow the finest fraction to be transported into the ICP.

The transport efficiency of most nebulizers is 0.5 to 1.5 percent, i.e. only a small percentage of the solution entering a nebulizer reaches the excitation source; the bulk flows to drain. Higher efficiencies can be realized if the sample solution is pumped at a low rate to starve the nebulizer, but the amount of solution (and analyte) reaching the source is reduced, and the emission signals are decreased. Higher efficiencies are claimed for ultrasonic nebulizers.

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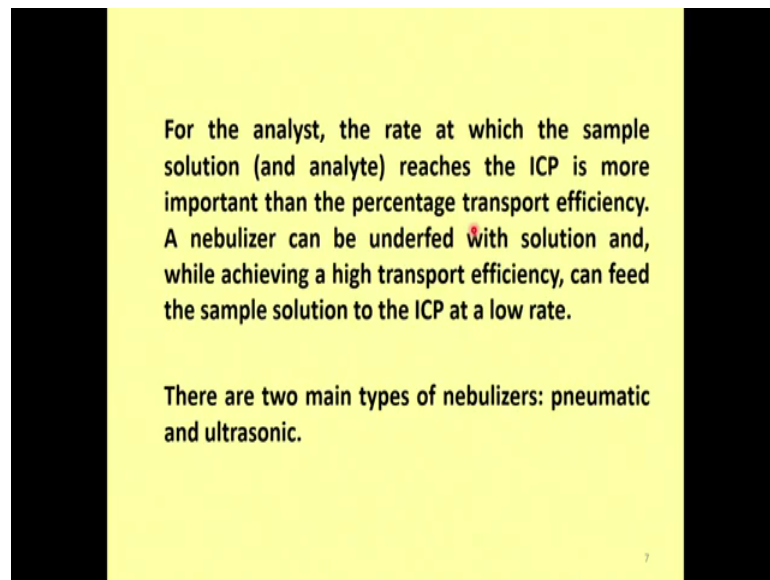
Most nebulizers create a aerosol that contains droplets ranging from very small to greater than 100 micrometer in diameter ok. So, the point is the spray chambers are designed to filter out larger droplets, and they should fall on their own back into the system, or it should be drained out completely not into the sample again, but somewhere else.

So, they allow the finest fraction to be transported into the ICP that is important the smallest size mist needs to be carried into the plasma, that is why we several nebulizer designs are available, and we will take a look at them. So, shortly the transport efficiency of most of the nebulizer is again 0.5 to 1.5 percent not more than that that is a very small percentage of the solution entering a nebulizer reaches the excitation source, the bulk flows into the drain as usual as expected.

So, high if you want to increase the efficiency the sample solution has to be pumped at a very low rate very very important concept in all ICP. So, please do not forget that the sample must be pumped at very slow slow rate flow rate, and the nebulizer must be starved; that means, there should not be too much solution in the nebulizer. So, the amount of solution reaching the source is reduced, but aerosol becomes more. So, reaching the source is important concept in all ICP, AES and the emission signals are decreased, if you give a bigger droplets because they all just flow down the drain.

So, higher efficiencies are claimed for ultrasonic nebulizers, usually ultrasonic nebulizers do not waste their sample. There are they now question of bigger droplets or smaller droplets etcetera everything gets converted into a mist. So, for the analyst, if you are a not a k electrical engineer or a chemical engineer or something, you want to just do the analysis the rate at which the samples solution reaches, the ICP is more important than the percentage transport efficient this is the bottom line. So, the sample should be as less as possible that enters the plasma.

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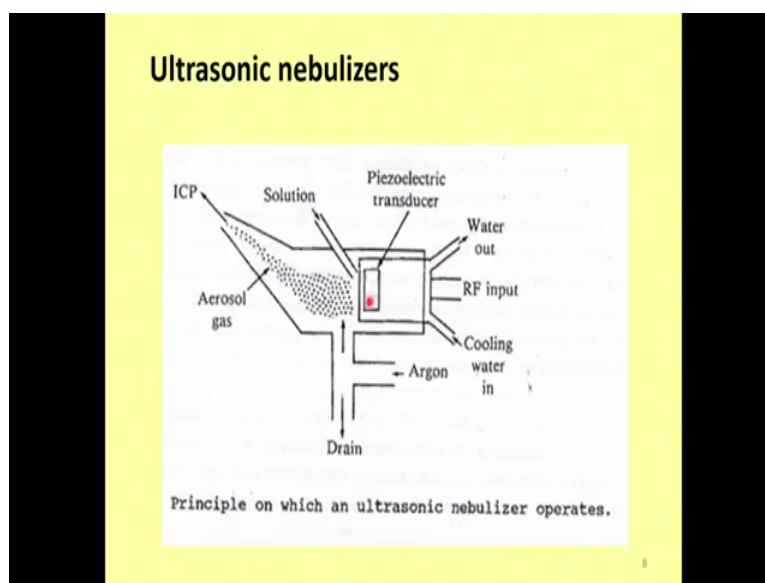


So, a nebulizer can be underfed; that means, it should be starved with solution, and while achieving a higher transport efficiency, it can feed the sample solution to the ICP at a low rate. There are two types of nebulizers: one is pneumatic and another is ultrasonic. So, as I explained to you, ultrasonic is a special equipment by itself; you have to buy whenever you want to buy an ICP instrument here, to buy the sample nebulizer also.

So, normally pneumatic nebulizers are provided along with the equipment, but if you want to want ultrasonic nebulizer with higher efficiency, and better sensitivity, you have to tell the factory people the suppliers to give you a special ultrasonic device sampling device; they will ask you whenever you want to buy an instrument, they will ask you what type of nebulizer you want.

So, the ultrasonic nebulizers are nothing, but a very simple piezoelectric contains a very simple piezoelectric transducer like this figure shown here.

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Here I have a sample solution is coming here, the transducer is here, the moment the drop liquid droplets enter here, the liquid gets converted into a spray, and there is a water out that is a cooling system. So, cooling water in and cooling water out r f input is there. So, the mist that comes out after heating this inner plate, and I have argon coming from the left side here, and then from the mist there are bigger droplets, they fall down the drain, and then aerosol gets carried into the plasma that is through the plasma torch. So, this aerosol goes into ICP. So, pneumatic nebulizers are quite a few.

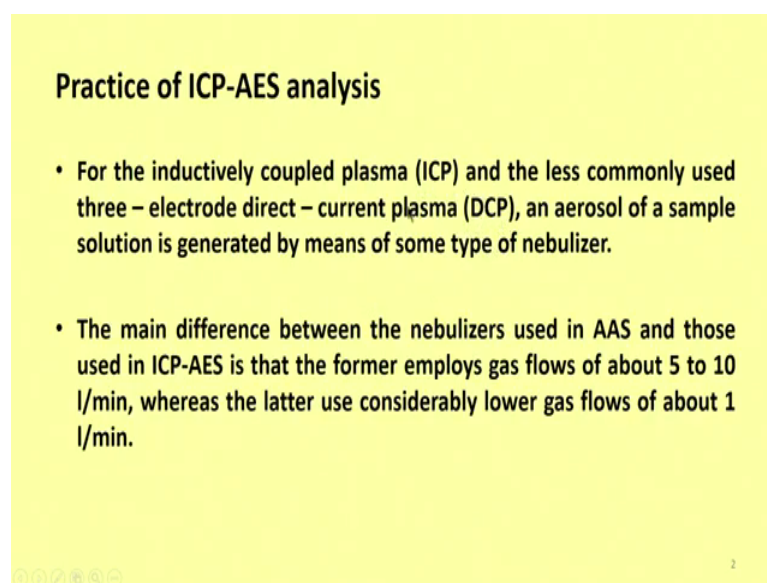
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- ### Pneumatic nebulizers
- 1) Concentric nebulizer, e.g. the Meinhard nebulizer
 - 2) Cross - flow nebulizer
 - 3) Babington - type nebulizer
 - 4) Glass - frit nebulizer
 - 5) Grid nebulizer, and
 - 6) Jet - impact nebulizer.

For example concentrate there are about 5 things, I have listed here one is concentric nebulizer that is known as meinhard nebulizer, after the scientist who developed it, and then there is cross flow nebulizer, then there is babington type nebulizer, if they again it is the name of the scientist, and you can even use a glass frits, and pass the liquid through that and then you can use grid nebulizer or jet impact nebulizer these are different kinds of equipment to produce the sample in the nebulized form ok.

Now we will discuss a little bit about the different kinds of nebulizers that we will take it up in the next class. So, thank you very much, I wish we will be able to conclude the course in the next 2 or 3 sessions. So, all the best greetings to you. We were discussing the practice and applications of ICP AES for chemical analysis. So, I had shown you a couple of slides, in this maybe up to ninth slide.

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Practice of ICP-AES analysis

- For the inductively coupled plasma (ICP) and the less commonly used three – electrode direct – current plasma (DCP), an aerosol of a sample solution is generated by means of some type of nebulizer.
- The main difference between the nebulizers used in AAS and those used in ICP-AES is that the former employs gas flows of about 5 to 10 l/min, whereas the latter use considerably lower gas flows of about 1 l/min.

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So, I will quickly go through the what we had done in the last class only from the point of view of ICP analysis. So, for the ICP or DCP aerosol of a sample is generated by means of a nebulizer, and this nebulizer is different from ICP AES in that the former employs gas flow of only about 1 AES employs 5 to 10 liters per minute whereas, the ICP requires only about 1 liter per minute.

Then we for efficient analysis we need an aerosol. So, the droplet size, and droplet size distribution generated from the sample into an aerosol, and that is to be introduced into

the excitation source that is the plasma, the precision of the analytical instrument interference effects etcetera etcetera occur in the aerosol and the source.

So, this is the equation for the estimation of a drop size droplet size, and that is we have covered already this is the diameter, this is the velocity, this is the drop diameter, and yes is the surface tension η is liquid viscosity Q_1 and Q_2 are the volume flow rates of the liquid and the gas. So, we have to optimize all these parameters to obtain good efficiency; that means, the velocity, viscosity, and the surface tension..

So, all these parameters need to be adjusted in such a way that the detection or determination is optimum. So, it is important to realize that this equation applies only to the primary nebulization processes, and does not provide an estimate of from the secondary and tertiary nebulization. So, the equation indicates that increase in the pumping rate of the solution, droplet size distribution will shift to larger diameter; that means, you should not be pumping more and more liquid to get the better sensitivity, it does not work that way ok.

So, if a solution is injected directly plasma gets extinguished. So, it , but it tolerates an aerosol, and the nebulizers job is to generate the aerosol we take a look at the nebulizer, but nebulizer is a consumable item. So, the normally what happens is in nebulizers, can they can leak, they can block, these dissolved solids can block the nebulizer affecting the efficiency.

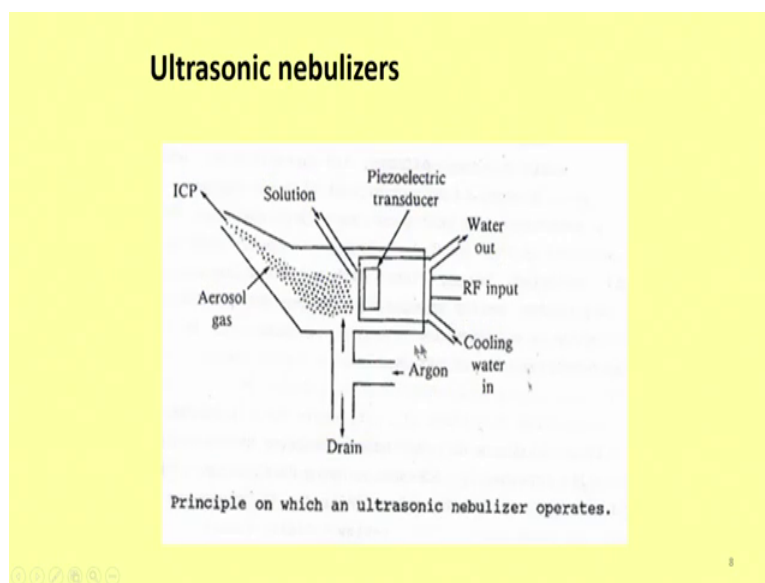
And they can mal they can be maladjusted the impact bead, and other things they could be maladjusted. So, it is very important for us to see that nebulizer is working very very efficiently all the time whenever we want to do the chemical analysis. So, the nebulizer performance varies with the viscosity of the solution temperature, and state of the electro static earth grounding, and the presence of surface active agent in the solution.

So, I had explained to you that in the last class, we do need to add some surfactants to make the samples to make the samples more easy for flowing so, that the droplet size can be controlled precisely. So, most of the nebulizers create an aerosol, they containing droplets about 100 micrometers spray chambers are designed in such a way that bigger droplets on their own gravity, they fall down and it is wasted.

So, the percent efficiency of the nebulizer is always about point 5 to 1.5 percent that is a very small percentage of the sample that goes into aerosol, is the into nebulizer is actually converted into the aerosol. So, we have to live with that there is not much we can do about it, but it is enough to get us detection limits of the order of about 0.1 p p m or below that also..

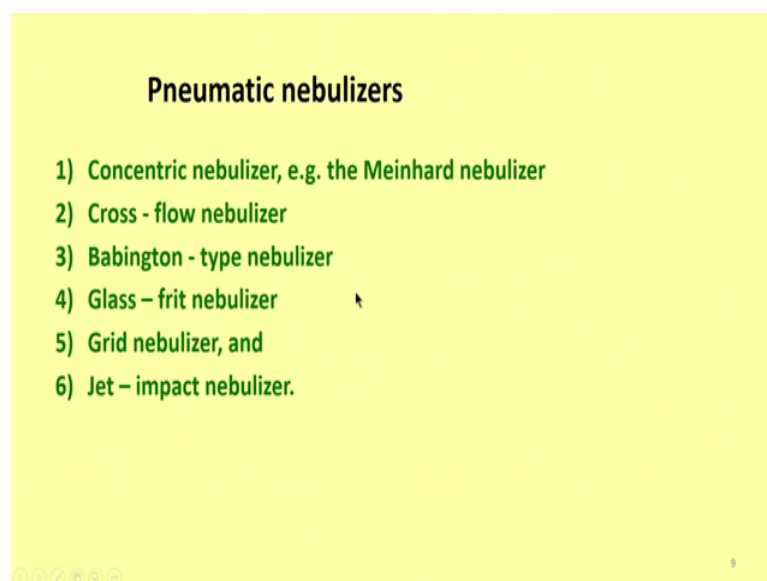
So, the for the analyst, the rate at which the sample solution that is analyte, reaches the ICP is more important than the percentage of transport efficiency; that means, rate should be very uniform, and that gives you better detection limits. So, a nebulizer we can under feed with the solution, and while achieving a higher transport efficiency by introducing lower feed, we can feed the sample all to the ICP also at a very low rate in general, there are two two main types of nebulizers one is pneumatic, and another is ultrasonic.

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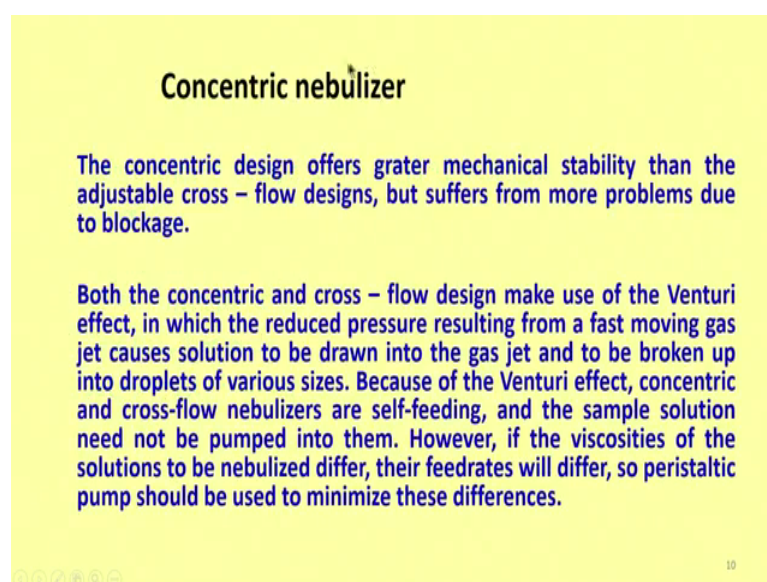
This I had shown you knew, this is the ultrasonic nebulizer, we have a piezoelectric transducer solution coming here, hits it and then goes into forms an aerosol, and bigger droplets fall into the drain, where as argon is coming from the side ok.

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So, pneumatic nebulizers there are quite a few around, and concentric nebulizer that is known as Meinhard nebulizer, name of the scientist cross flow table, either Babington type glass frits or grid nebulizer, and jet impact nebulizer. Among these Babington nebulizer and Meinhard nebulizers are usually the most employed, and available in the commercial instruments.

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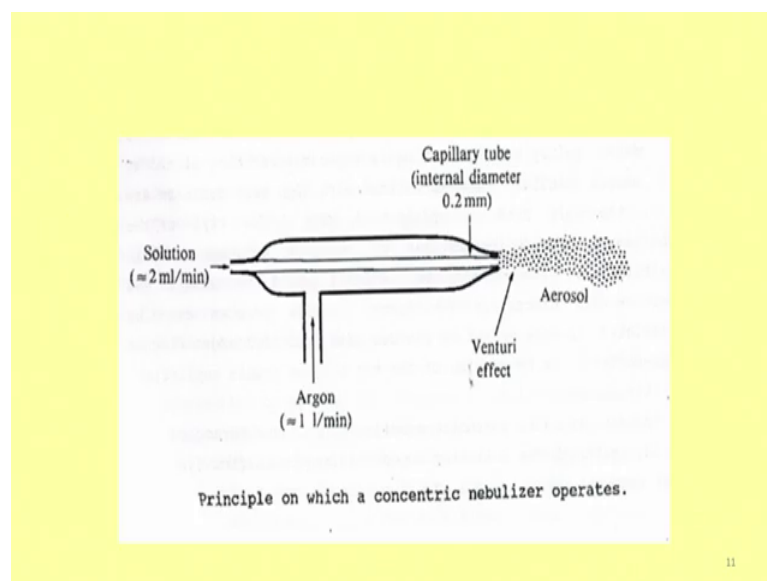


So, the concentric nebulizer up to this point we had covered earlier in my last class. So, now, we are going to discuss the concentric nebulizer. So, this is nothing, but a very

simple arrangement, this we have seen earlier that the figures also we have seen earlier, but essentially it is important to know that the cross flow design makes use of venturi effect, in which the reduced pressure resulting from a fast moving gas jet, causes the solution to be drawn into the gas jet, and carried away.

This is a very simple very simple arrangement, you want to carry anything what you need is a strong gas flow. So, that it will carry automatically anything that comes in it is pathso the venturi effect concentric, and cross flow nebulizers they are all self feeding; that means, you just switch on the argon the material will be sucked into the peristaltic pump, and into the nebulizer, and into the plasma automatically. But if the viscosities of the solutions differ, then the feed rates also will differ. So, what we need is a peristaltic pump to be used to minimize these differences.

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So, this is a concentric nebulizer system solution is coming here, approximately about 2 ml per minute, and then capillary tube is here, 0.2 mm, argon comes here venturi effect, and then this argon will going it pulls the liquid also, and an aerosol forms ok.

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Cross-flow nebulizers

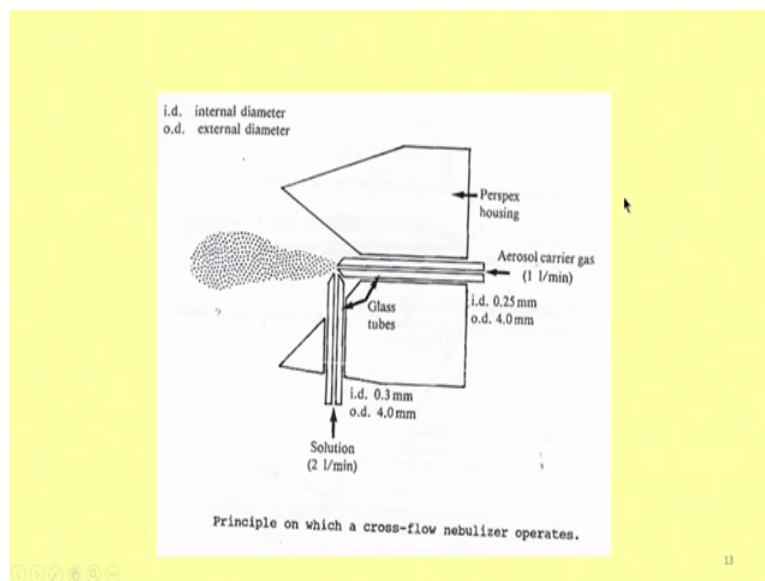
Although the cross-flow design is more tolerant of solutions with high salt contents. Both systems are subject to periodic blockage by stray particulate matter, and to tip blockage as a result of salting out. Such effects tend to occur in solutions in which the total salt content is greater than 1 percent.



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So cross flow nebulizers, here what happens?

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This is more tolerant with the dissolved solids. Suppose you want to determine the iron content in blood, or thallium in blood, or lead in blood. So, most of the samples contained dissolved solids, quite large quantities, sometimes if it is a seawater base you would know that the salt content would be approximately 3.5 percent that is 35000 p p m, and in that you want to determine few elements at p p m, 1 p p m, 2 p p m like that.

So, you can imagine the ratio of 1 p p m of the analyte to 35000 p p m of the remaining unnecessary salts. So, such things such salts can block the nebulizer edge..

So, this is a cross flow nebulizer solution is coming here, organ is coming here, and then it forms an aerosol. So, the i d of this internal diameter is approximately 0.25 m m and o d is about four m m. So, you can imagine how small it could be total outer diameter itself is 4 m m; that means, the radius will be approximately 2 m m, and inner diameter that is the capillary will be of the order of about 0.25 millimeter. So, it is a very good high quality engineering job, and this is a Perspex housing, this is another perfect Perspex housing, and the glass tube is fitted in between these two and connected to the aerosol ok.

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Babington-type nebulizers

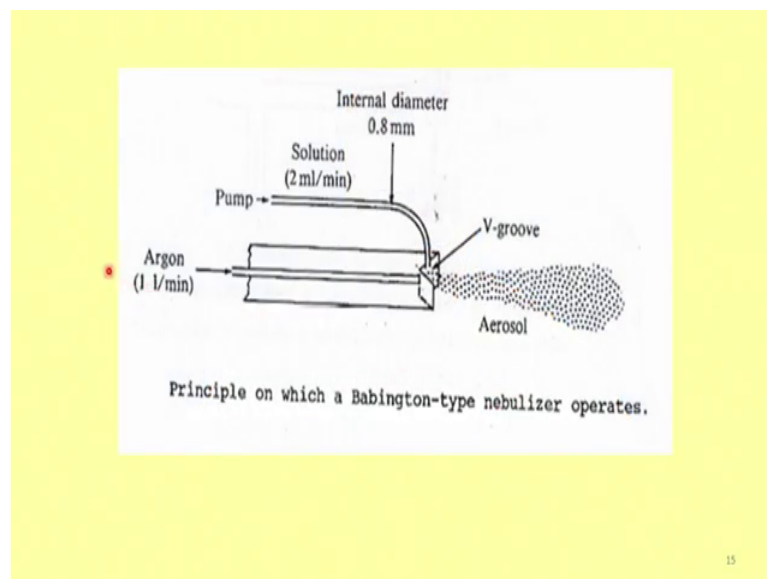
Tip blockages are minimized in the Babington-type nebulizer which is suitable for nebulizing solutions of high salt content (10 percent sodium or more) and for slurries of solid powders. In Babington's design, solutions poured over a hollow sphere with a hole in it through which the nebulizing gas issued in a jet. In 1966, Babington applied for U.S. patent, which was granted in 1969. he was subsequently granted four more patents.

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Now, the another type is Babington type nebulizers, the tip blockages are normally minimized in Babington type nebulizers. So, this is advantageous with because, the tip can tolerate dissolved solids. So, the if you want to analyze blood sea water urine say any of the biological materials with high salt content, what you should be doing is use a Babington a type nebulizer. So, whenever you want to buy an equipment you will be, they will ask you what type of nebulizer you want Babington order a cross flow nebulizer like that, and the beauty of this Babington type nebulizer is it can hold up to 10 percent of the solids dissolved solids. So, the analysis becomes much more simpler in ICP AES compared to atomic absorption spectrometer.

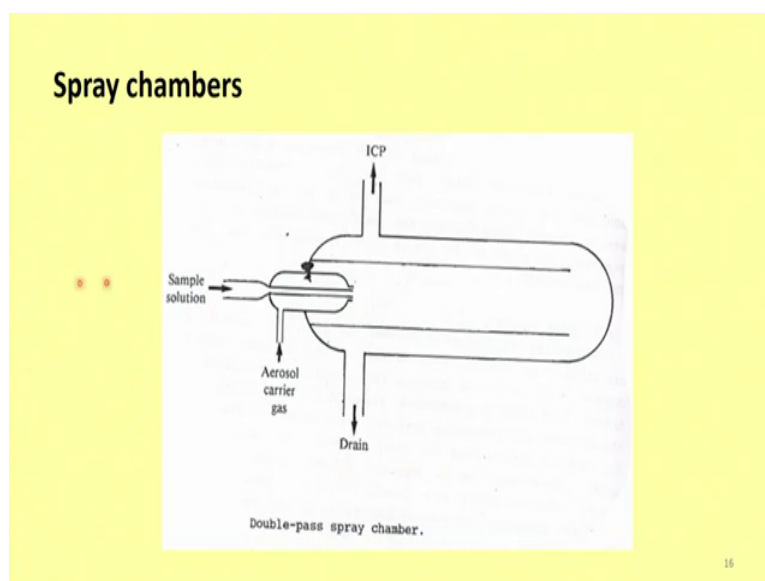
So, the solutions in Babington's design the solutions are poured over a hollow sphere, usually the sample when it comes it hits a ball ok, the the ball it has got a hole in that through which the nebulizing gas also passes through. So, as a it passes through a jet only continuously. So, this was in 1966 arranged arrangement he got a patent for that and subsequently he was awarded 4 more patents, for the designs of the ICP in sample introduction systems..

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So, this is the Babington type nebulizer here, we have an argon sample and a solution is coming here, there is a wedge here ok. This gas passes through, this wedge sample comes into the wedge from there, because the gas is moving, and because of the Bernoulli effect the aerosol is generated.

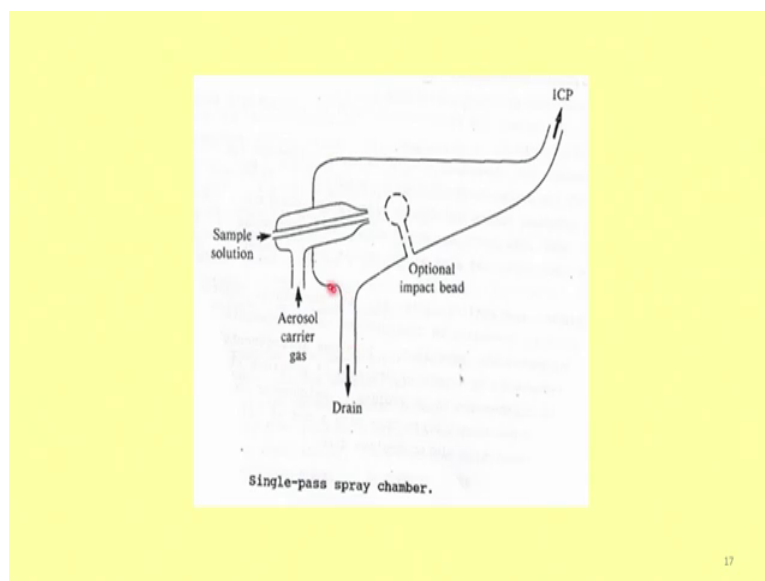
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So, spray chambers are essentially, what is a spray chamber is a box in which aerosol carriers sample solution, and everything is held there, and part of the it is arranged in such a way that the aerosol gets carried up upwards, and the bigger droplets fall downwards. So, that is known as a spray chamber look at this slide.

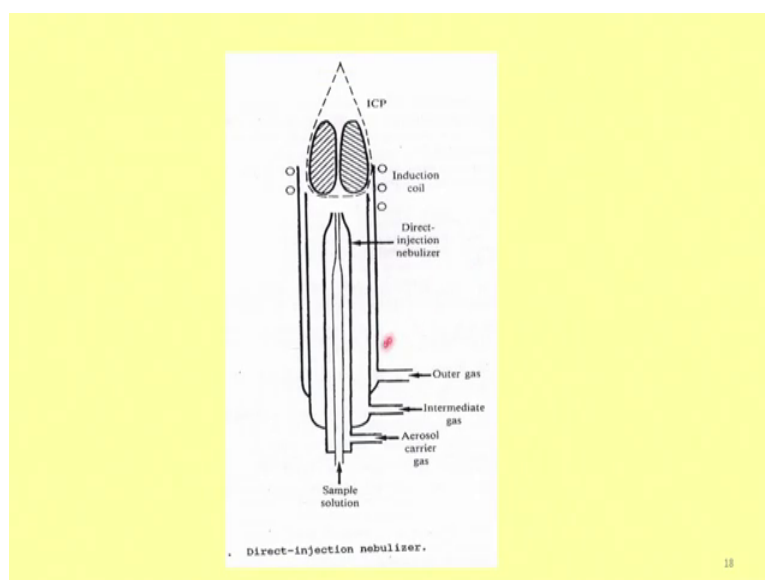
ah Here I have a double pass spray chamber, one is sample solution is here, aerosol is here, and then both of them are coming here, and then it is going to form an aerosol here, in this aerosol once it comes out, the mist this is like a cylinder you know hollow cylinder tube, it is like a tube. And once it comes out of this the whole area above, and below this concentric tube will be filled with aerosol and droplets. So, in ICP aerosol will go up for into the plasma whereas, the bigger droplets are allowed to fall into the drain.

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So, then we have a single pass spray here, what is happening, the sample is coming here, aerosol is carrier gas is coming it is going to impact the bead that is fixed here. So, again because of this kind of design, whatever are the heavy droplets will slide down slowly, and then fall into the drain, and only the aerosol will be going up. So, this is a single pass spray chamber, different types of nebulizers are always there.

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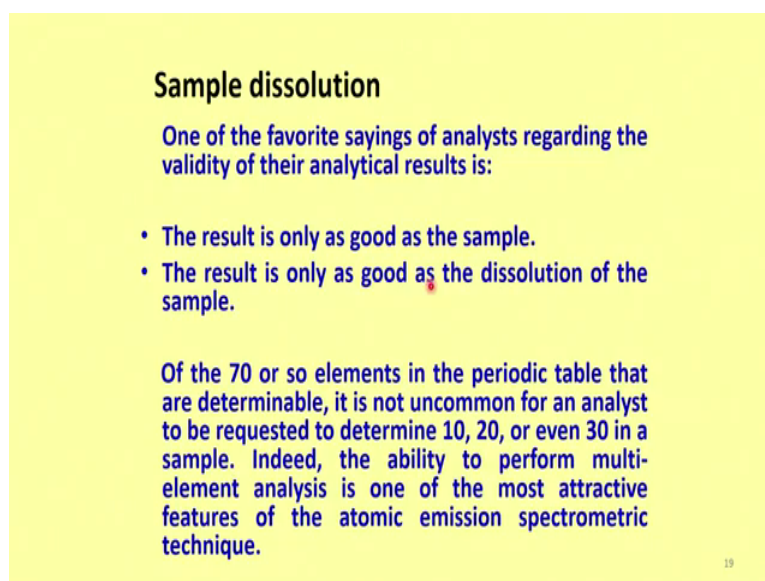


So, this I think you are familiar now, with the different types of direct injection nebulizer, I have shown you this figure number of times, and here what is happening sample

solution is in the concentric tube in the innermost outer next to that is the argon aerosol, and then we have an outer gas that is again argon, and then intermediate gas..

So, there is a complete gas movement in the all the 3 concentric tubes and then sample gets converted into aerosol here, at the edge, and then this itself will serve as a nebulizer, and then the aerosol will normally enter, the plasma that is a very simple arrangement. So, what we learnt. So, far is how to introduce the sample and different designs ok.

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Sample dissolution

One of the favorite sayings of analysts regarding the validity of their analytical results is:

- The result is only as good as the sample.
- The result is only as good as the dissolution of the sample.

Of the 70 or so elements in the periodic table that are determinable, it is not uncommon for an analyst to be requested to determine 10, 20, or even 30 in a sample. Indeed, the ability to perform multi-element analysis is one of the most attractive features of the atomic emission spectrometric technique.

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Now, I want to take you to another realm of another realm of analysis. So, that is sample dissolution normally most of the time, if you 99 percent of the time actually, it is the sample in the liquid form that gets into the ICP. Now the some of them may be I had a indicated to you that it can be introduced as a vapor, or solid itself, I can make a spray and then introduce it, but sample resolution becomes a very great requirement, especially when you are handling different types of samples including minerals etcetera, you cannot make solid aerosol out of mineral it becomes very difficult, if it is milk powder or something like that, the aerosol solid powder which is very light and fluffy, that can be made into aerosol very easily, but if the sample is a rock, and I will powder it or it is coal, or some other hard material, then it becomes very difficult to resolve the sample.

So, a little bit of chemistry knowledge is required if one wants to do the chemical analysis using ICP, because that is the whole crux of the problem, the correct analysis is always important in chemical analysis.

In this respect I want you to understand these two principles look at this slide now. The result what we in all analytical scientists say this sentence, the result is only as good as the sample ; that means, if your sample is good if the sample is representative, if the sample is uniform, if the sample, is within the acceptable measurement, the result will be as good as that..

So, sampling becomes a very very important aspect of ICP analysis also, but this sentence is applicable to all chemical analysis as far as accuracy, and the quality of analysis is concerned, and on the same lines I can also say that the result is only as good as the dissolution of the sample; that means, if the your dissolution is correct, then the analysis becomes very simple. So, normally there are about 70 or so, more elements in the periodic table are determined by ICP now a days.

So, it is not uncommon when people want to say, I want to analyze about 20 elements in a given sample. Suppose it is a mineral they want to know, what are the more important contents of the metals in the mineral. So, if you want to determine 20 or 30 elements in a mineral, it becomes very important that all the 20 elements must be dissolved is not it. So, the ability to perform multi element analysis is one of the most attractive feature of atomic emission spectrometry technique.

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The larger the number of elements that must be brought into solution, the more difficult is the dissolution procedure.

Unfortunately, there is no universal solvent or universal dissolution method. A knowledgeable chemist is needed with a wide experience of sample types and dissolution procedures. Contrary to popular opinion, neither aquaregia nor hydrofluoric acid will dissolve everything. In fact, if silicon is to be determined, hydrofluoric acid has to be treated with some respect, not only because any contact with this acid or its vapor has painful consequences, but because of its ability to convert silicon into gaseous silicon tetrafluoride.

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So, normally what happens is the, larger the number of elements that must be brought into solution, the more difficult is the dissolution procedure. Suppose you want to

determine only iron in a metal sample, or in a the in a water, or in leaf sample you want to determine only iron. So, it is very easy for us to dissolve the take a leaf powder, dry it powder it, put it in nitric acid all the iron will go in solution.

But that kind of analysis is not possible, whenever we want to do multi element analysis, because the dissolution process itself is very different for different elements for example, silicon silica it does not dissolve in nitric acid, gold does not dissolve in nitric acid, it will dissolve only in a (Refer Time: 37:31). So, suppose in an hour you want to determine how much of gold is there how much of iron is there, you put nitric acid only iron will dissolve gold will not dissolve..

So, your analysis would be completely wrong; that means, it is imperative for you to dissolve, as much of the sample as possible using different techniques, because the same solution will not the same solvent will not dissolve all the materials. So, a knowledgeable chemistry is needed in such chemical analysis. So, there are a wide number of dissolution procedures, you can take a look at any analytical science book, and there also there are also published reports available how to dissolve different kinds of samples.

So, for example, if I want to dissolve a silicon, then I had to use hydrofluoric acid I can not to use anything else. So, the problem becomes you cannot do it in glass, because it will glass also will be attacked by hydrofluoric acid. So, if you want to determine silicon, you have to do it in plastic bottle that is polythene..

So, like that there are different considerations to be taken with a pinch of salt that if somebody says he has resolved everything in nitric acid, they do not it would not work it may work, if you keep it for a very long time, but normally the demands on the analyst are such that, and the results are required within half an hour, 1 hour within 2 3 days like that.

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Dry ashing techniques

These methods can be used for large batches of samples, but there can be problems involving the loss of certain volatile elements. These problems can be eliminated or reduced by the use of temperature-programmed furnaces.

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So, the dissolution process itself is a tricky thing. Still we will go through a little bit ashing techniques. So, there are dry ashing techniques; that means, you just keep on heating the sample powder it, heat it, and then the volatile elements will just come out of the sample so, that you can introduce into the plasma.

So, these problems they, but apart from that, certain volatile elements will be lost forever in dry ashing techniques. So, these problems can be eliminated or reduced by the use of temperature program furnaces. So, first I take the sample heat it to 100 degrees water will evaporate, then take it to 400 degrees organic material will evaporate, take it to 600 all types of biochemical, and other organic basis will go to will dissolve coal sample it will burn off like that, and then you can they can be raised to 1000 degrees leaving only the metal oxides in the ash, which can be dissolved using nitric acid or any other techniques.

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Wet ashing techniques

Wet ashing techniques using oxidizing acids give rise to fewer problems involving the loss of elements. Nitric acid used alone is generally effective for most organic materials, but a wide variety of acid mixtures is used. The most common and effective mixture consists of nitric and perchloric acids, but it can be dangerous to use without knowledgeable supervision. Violent explosions have occurred when perchloric acid is heated with any sample containing carbon but, in the presence of adequate nitric acid, the risk is minimized.

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So, the compared to that wet ashing is the more is more preferable technique. So, here what we do is we use oxidizing acids that is nitric acid mostly nitric acid perchloric acid, we can use and then bromine, we can use hydrobromic acid etcetera, these things give rise to fewer problems involving loss of elements; that means, volatile materials instead of getting volatile they dissolve..

So, nitric acid is 99 percent of the time nitric acid is used for most of the organic materials to dissolve, and burn off and oxidize, but a wide variety of a acid mixtures are also used. Sometimes it is important for us to use a mixture of nitric acid, and hydrochloric acid sometimes sulfuric acid, and nitric acid like that, but if you use sulfuric acid many of the salts will form sulfates, and solubility of sulfate is much less compared to nitrates, because nitrates of most of the elements will dissolve in water..

So, the perchloric acid also we can use, but a perchloric acid dissolution is a specialized process, and it could be dangerous, if you do if you do try to dissolve without precautions. So, violent explosions normally take place whenever we are we take perchloric acid, and then try to heat it in an in an attempt to dissolve explosions take place, and all these things have been recorded, and they are available for those interested in the analysis.

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Low temperature ashing techniques

These techniques, which use an induction furnace or an oxygen combustion system, are slow and the apparatus is relatively expensive.

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It is better to spend some time it is better to spend some time studying the dissolving techniques dissolution techniques, low ash temperature ashing technique is another one here, what we do is we do it in a power bomb, you know you must have done experiments in your physics to determine the calorific value..

So, there what you do is put a sample inside a sealed vessel, and then heat it, and then it forms carbon dioxide or whatever it is, and then the sample will be dissolved. And so, low temperature it will be under pressure. So, these techniques which use an induction furnace or an oxygen combustion system, they are usually slow and the apparatus is relatively expensive, but such things are available for about 20 to 25000 rupees power bombs, and Teflon bombs etcetera, they are available. So, a bomb is nothing, but a cylinder in which the sample is put, and sealed, and then pressurized and then the chemical reaction takes place only around 100 to 150 degrees 165 maximum.

Nowadays there are a few systems where 1 to 220 degree centigrade also we can go, but all the liquid in the sample will be evaporated, and it becomes slightly hazardous to open it. So, one has to be a little careful whenever we want to do low temperature ashing techniques, and the hot acid they attack is again, it could be dangerous, if you are not careful any acid for that matter, and if it is hot acid damage will be more..

So, but we can take a sample put it in a beaker cover it with a watch glass, and then heat it and dissolve it, and if it is a silicon or something, we can take a polythene bottle a beaker put a chuff, and other things it can be dissolved at higher temperature.

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Hot acid attack

The next approach would be a hot acid attack. Normally, for both cold and hot acid dissolution, a glass beaker covered with a watch-glass would be used, but polythene or Teflon, i.e. poly-tetrafluoroethylene (PTFE), beakers are necessary when hydrofluoric acid is used to dissolve silica. If the solution is evaporated to dryness to remove the excess hydrofluoric acid, silicon is lost as the volatile silicon tetrafluoride.

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So, only thing is for silica, and all you have to use hydrofluoric acid ok. So, if the solution is evaporated to dryness to remove the excess hydrofluoric acid, silicon is also lost as the volatile silicon tetra fluoride. So, it is very difficult to do the analysis of silica, especially if we want to do hydrofluoric acid treatment, one has to be extremely careful. So, that the analysis are dependable.

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Acid digestion under pressure

If a hot acid attack at atmospheric pressure fails, the next step could be acid attack under pressure using PTFE screw-top bottles (moderate pressure) or dissolution autoclaves such as the Parr 'bomb' (high pressure). Fernando has compared fusion and simple acid dissolution with a Parr bomb technique using a mixture of nitric, hydrochloric, and hydrofluoric acids at 180° C to dissolve steel samples for the determination of Al, B, Ti, Mn, Si, Mo, Cr, Ni, P, and Sn by DCP-AES. A dissolution bomb consists of a screw-top container of high-purity material such as PTFE (marketed commercially as Teflon, Polythion, Halon, Hostafion, Fluon, etc.) or glassy carbon, surrounded by a compact screw-top casing made of stainless steel or aluminium alloy.

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Now, again another system that is acid digestion under pressure here, what happens if a hot acid attack at atmospheric pressure fails ok; that means, you try to dissolve the sample in a in a beaker containing hot acids, but as I told you it may not be soluble in hot acids also..

So, the next step could be acid attack under pressure that is power bomb, and Teflon bombs. we can use polytetrafluoroethylene PTFE Teflon, they are all they all come with screw type you know screw it, and then it becomes airtight, and then power bomb also Fernando with a power bomb technique used a mixture of nitric acid hydrochloric acid, and hydrofluoric acid also at 180 degrees which is sort of a record , but for what elements, it was used it was used for aluminum, boron, titanium, manganese, silicon, molybdenum, chromium, nickel, phosphorous, and tin by DCP is direct current plasma AES.

So, a dissolution bomb basically it consists of nothing, but two parts one part is the sample container, second part is just screwed, and the screw top casing is also made that is made of the stainless steel, or aluminum alloy which should be very stable.

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At temperatures in the region of 170°C (the maximum permissible temperature for the use with PTFE) the reaction capacity of acids and oxidizing agents increases and most samples, irrespective of whether they are organic or inorganic, dissolve in a relatively short period of time. If glassy carbon vessels are used, temperatures up to 220°C can be used.

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So, at temperatures in the region of 170 degrees centigrade the maximum permissible temperature that is the 1. The reaction capacity of the acids, and oxidizing agents increases multifold, and most of the samples irrespective of whether they are organic, or inorganic, they dissolve in a relatively short period of time. So, if glassy carbon vessels are used we can go up to 220 degree centigrade no problem there, because carbon does not burn.

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Summary: materials and methods of dissolutions for inorganic materials

- (a) Acid digestion
Ferrosilicon metal, sulphide ores, phosphate ores.
- (b) Acid digestion and microwave heating
carbon-in-pulp and resin-in-pulp, manganese ores, tantalum-niobium and steel alloys, coal, fly ash, oil shales, biological materials.
- (c) Sodium peroxide fusion
Andalusite, chromium ore, ferrochromium metal and slag, ferrotitanium metal and slag, manganese ores, anode slimes, noble-metal matte-leach residues, lead-tin alloys.
- (d) Lithium metaborate fusion
Ferromanganese metal and slag, vanadium ore, ferrovanadium, silicates, beach sand.

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So, easily at 220, here I want to summarize our discussion on the dissolution techniques . So, basically what you want to do, if you want to dissolve a Ferro silicon material, or sulphide ore or a phosphate ore ok, then as a simple acid digestion will work again it depends upon what elements you want to determine. Second type is acid digestion, and microwave heating nowadays the microwave digestion units, are available plenty in the in the country.

And of course, we are not making them in India we are underdeveloped country as far as scientific instruments are concerned anyway, but such things can be bought, and the sample can be used manganese, ores, tantalum, niobium steel alloys, coal, fly ash, oil shales, biological material. So, many things you can use with microwave digestion technique, there also here to heat it, but only through microwave digestion; that means, again you need a power bomb or a Teflon bomb, put the sample hate it, but heating is done by microwave digestion, and that can be very fast, normally acid digestion takes about 2 1 and a half to 2 hours.

Whereas microwave digestion, if you can afford it will take only 10 minutes maybe 15 20 minutes into a whole thing will be over. So, and nowadays in any good laboratory microwave digestion units are a must ah, if your result output is higher ok. Then we have sodium peroxide fusion. So, for ores what we do normally is we use sodium peroxide to dissolve the course. So chromium, or ferrochromium metal slags, ferrotitanium metal, and slag manganese ores anode slimes, then noble metal matte leach residues lead, and tin alloy. So, many alloys we can use sodium peroxide fusion. And another aspect is lithium metabolite fusion.

So, here also ferromanganese, and slag, vanadium, ferrovandium, silicates, and then beach sand, if you want to analyze all these things can be used it.

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Sample introduction

Barnes estimates that 90 percent of samples are introduced in a liquid form, 8 percent by electrothermal vaporization, and 2 percent by other techniques, including direct insertion and slurry nebulization.

For many AES systems (e.g. DCP and ICP) the most common means of introduction is some form of nebulizer.

Gaseous samples can be introduced by volatilization or by a hydride-generation technique. Apart from the use of nebulization, samples in liquid form can be introduced by electrothermal vaporization or by flow injection.

Powdered samples can be introduced by powder aerosol injection.

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We will continue our discussion, when we want to introduce the sample now because so far I have taught you about the sample dissolution techniques. Now we can discuss about the sample introduction in the next session.

Thank you.