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

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Lecture – 20
Instrumentation for ICP AES -VIII-Instruments

Greetings today we are discussing about the analytical applications of ICP AES. And as I have explained to you in the last class the applications of atomic emission spectroscopy are found in almost all spheres of human activity including inorganic analysis for metals and sometimes metalloids sometimes non-metals also to some extent.

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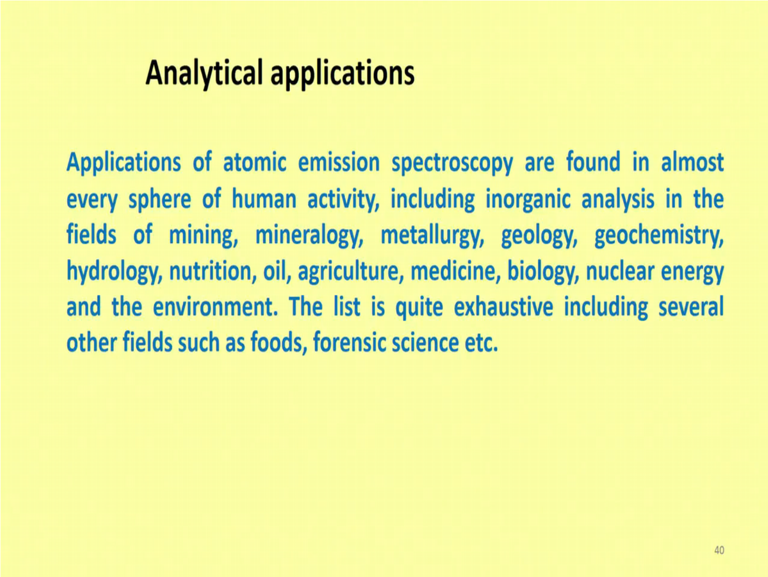

Analytical applications

Applications of atomic emission spectroscopy are found in almost every sphere of human activity, including inorganic analysis in the fields of mining, mineralogy, metallurgy, geology, geochemistry, hydrology, nutrition, oil, agriculture, medicine, biology, nuclear energy and the environment. The list is quite exhaustive including several other fields such as foods, forensic science etc.

So, the applications include mining mineralogy, metallurgy, geology, geochemistry, hydrology, nutrition, oil analysis, agriculture, medicine, biology, nuclear energy and the environment. The list is still continuing it is more exhaustive that include several other fields also such as food forensic sciences etcetera.

Normally what we expect is the we expect inductive couple plasma ICP analysis. Almost to replace a atomic absorption spectrometry as a regular routine analytical tool for the determination of metals. So, I will quickly take you through some of these applications and I think we will be able to cover a little bit about the dissolution techniques.

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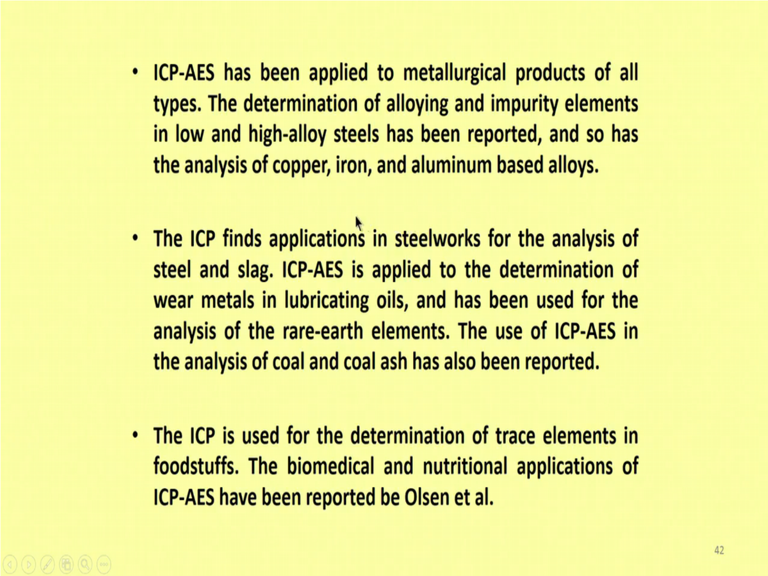

- ICP-AES has been applied to metallurgical products of all types. The determination of alloying and impurity elements in low and high-alloy steels has been reported, and so has the analysis of copper, iron, and aluminum based alloys.
- The ICP finds applications in steelworks for the analysis of steel and slag. ICP-AES is applied to the determination of wear metals in lubricating oils, and has been used for the analysis of the rare-earth elements. The use of ICP-AES in the analysis of coal and coal ash has also been reported.
- The ICP is used for the determination of trace elements in foodstuffs. The biomedical and nutritional applications of ICP-AES have been reported be Olsen et al.

So, ICP AES has been applied to the metallurgical product of all types alloys impurity elements and high alloy steels etcetera have been reported chemical analysis that is why that is what I mean. And so, so also is the analysis of copper aluminum and other aluminum-based alloys. So, it finds applications in foundaries steel work for the analysis of steel and slag.

So, it is apply to the determination of wear metals in lubricating oils and has been used for the analysis of rare earth elements, especially in lubricating oils what we normally expect is that the we use ball bearings then those ball bearings are mixed with lubricating oil sometimes greases etcetera. Now what happens is during the operation the metal ball bearing metal dissolves or it gets damaged and the metal elements will enter into the oil. So, that is known as wear metal. So, wear wear metal so; that means, ball bearings wear it is a very common phenomenon, but oil gets contaminant. And so, it is important for us to determine the metal ions in the oils especially lubricating oils.

So, the use of ICP AES in the analysis of apart from this the coal and coal ash also been reported. So, the it is used for the determination of trace elements in foodstuffs, biomedical applications, nutrition applications etcetera, have been reported by Olsen et al

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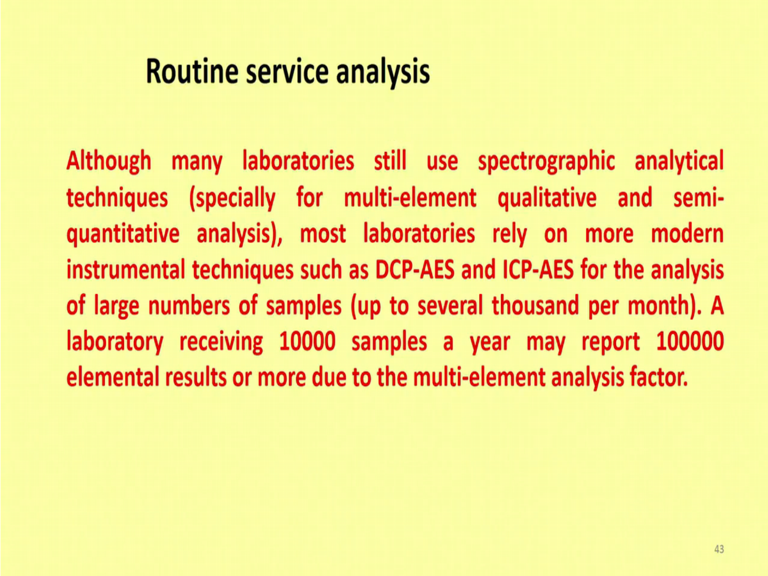

Routine service analysis

Although many laboratories still use spectrographic analytical techniques (specially for multi-element qualitative and semi-quantitative analysis), most laboratories rely on more modern instrumental techniques such as DCP-AES and ICP-AES for the analysis of large numbers of samples (up to several thousand per month). A laboratory receiving 10000 samples a year may report 100000 elemental results or more due to the multi-element analysis factor.

So, for routine service analysis what we normally do is although, multi element and sequential both of them we normally follow and the more modern instrumental techniques are direct current plasma AES and ICP AES for the analysis of large number of samples for multi element analysis DCP AES is much better. And there are reports that a laboratory receiving about 10000 samples per year may report 100 thousand elemental analysis or more due to multi element analysis factor alone.

So, it is a very powerful technique especially if the requirement of metal analysis is continuous and regular it is much faster than atomic absorption also, because nowadays even though there are multi element analysis possible with atomic absorption. It has not reached the same efficiency like ICP AES. So, that is what it advance so I am going to list some of the advantages of claimed for higher power plasma that is less acceptability to ionization interference, it is less acceptable to carbon deposits.

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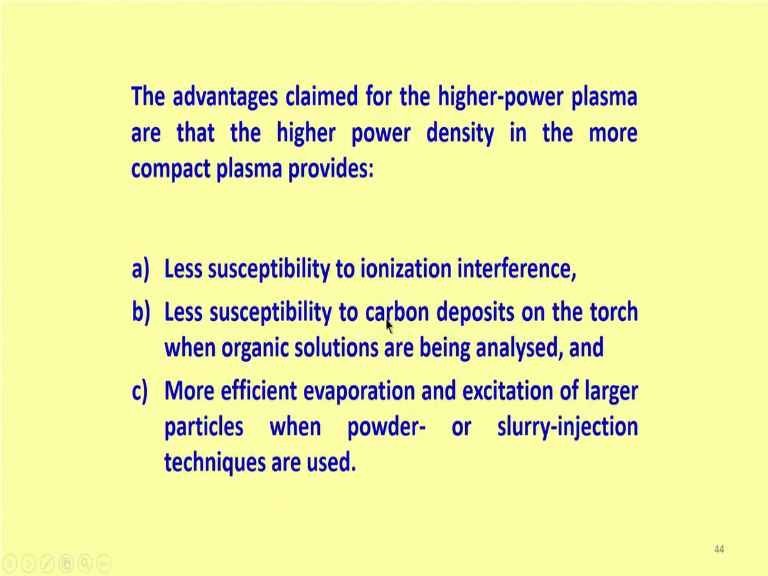

The advantages claimed for the higher-power plasma are that the higher power density in the more compact plasma provides:

a) Less susceptibility to ionization interference,
b) Less susceptibility to carbon deposits on the torch when organic solutions are being analysed, and
c) More efficient evaporation and excitation of larger particles when powder- or slurry-injection techniques are used.

On the torch when organic solutions are being analyzed because hardly carbon will deposit whatever carbon is there it will just burn off and so the carbon deposits due to organic solutions are very less and efficient evaporation and excitation of larger particles, when powder or slurry injection techniques are used these are the some of the advantages ok.

Now, the ICP still fall short of ideal excitation source, you know there are certain problems still with ICP; that means, it is not a penatia for all chemical analysis. So, Thompson there is a comment by scientist called as Thompson is a in comparison with what we went before; however, it is astonishing achievement as far as ICP AES is concerned. So, it ranks with the greatest discoveries in analytical science; that is what it means.

So, he highlights a need for still rapid multi element solvent extraction systems that would enable trace analysis to be selectively stripped away from the matrix elements. So, if we are able to do that and if we are able to pre-concentrate we should be able to do much more especially with respect to toxic elements in the air like beryllium, arsenic and all selenium like that many of the elements are there. So, a considerable effect in purely chemical ingenuity is called for here.

Now it is not a question of instrument, but for chemical ingenuity. So, ICP is only a tool that will help us achieve that.

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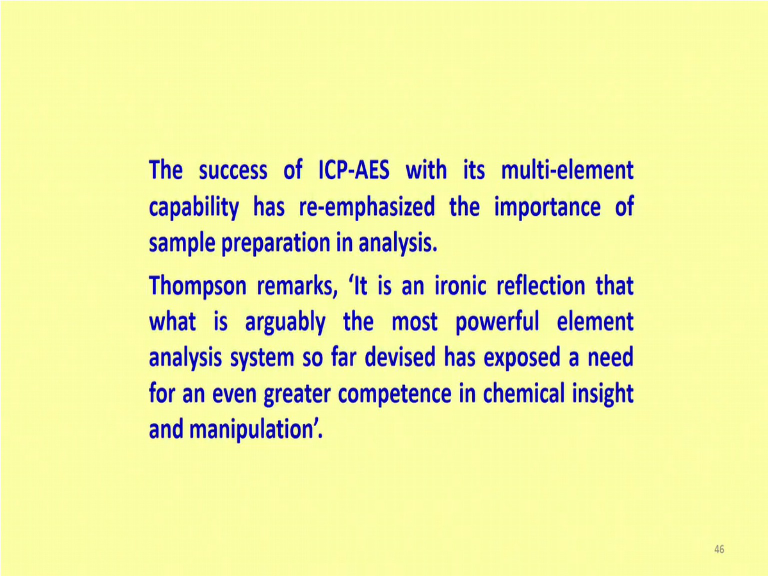

The success of ICP-AES with its multi-element capability has re-emphasized the importance of sample preparation in analysis.

Thompson remarks, 'It is an ironic reflection that what is arguably the most powerful element analysis system so far devised has exposed a need for an even greater competence in chemical insight and manipulation'.

So, the success of ICP AES with it is multi element capability has reemphasized the importance of sample preparation. in my last slide I said it requires chemical ingenuity what is that chemical ingenuity we need to reemphasize the importance of sample preparation. So, basically Thompson remarks it is an ironic reflection that what is arguably the most powerful element analysis technique so far devised has exposed a need for further even greater competence in chemical insight itself.

So, you cannot really divorce analytical capability from chemical ingenuity to ICP, an chemical analysis that is what it means basically, we want both great instrumentation and great chemical ingenuity still there is scope. So, that is one of the reasons why there is so much of work and reports on ICP AES applications in the world today. may be another 10 years all a atomic absorption systems would have would be replaced by ICP I will not be surprised at all, every laboratory every university would be having an ICP AES system.

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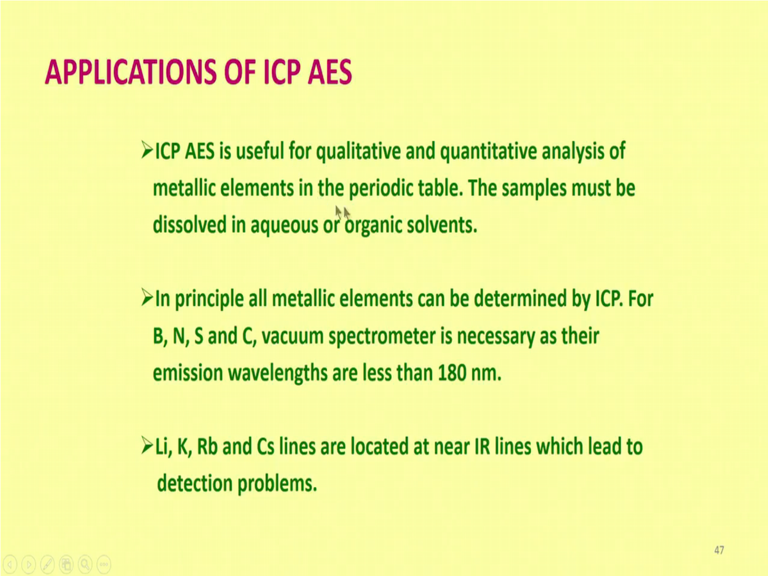

APPLICATIONS OF ICP AES

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

So, the applications of I a s ICP AES now I am talking only about ICP AES not DCP AES also. So, it is useful for qualitative and quantitative elements this is like your university examination. If I say list the advantages of ICP AES you should write this, ICP AES is useful for qualitative and quantitative analysis for this samples must be dissolved in aqueous or organic solvents.

Number 2 in principle all metallic elements can be determined, but for boron nitrogens sulfur and carbon vacuum spectrometer is necessary, why because there emission lines lie below 180 nanometers; that means, the normal sources like tungsten etcetera are not useful we have to go for now UV, normal UV optics will not work we need a vacuum spectrometer.

So, it is little difficult even now. So, some line some elements like lithium, potassium, rubidium and cesium lines are located near IR lines. See generally what we expect is the emission lines we have to follow to determine the elements some of them are visible range, some of them are in UV range, some of them are in vacuum ultra-violate range still higher energy, some of them are near infrared also. So, so the lines emission lines of the elements like lithium potassium, rubidium and cesium they are located near IR lines and there the energy of the electromagnetic radiation is.

So, less so the detection problems may sometimes arise. So, this still there are opportunities for other instruments like sodium, potassium, lithium etcetera to use flame atomic emission or atomic absorption also.

So, chemical analysis with ICP what is required is we measure the electrical signal in the from of counts. So, you plot the count versus concentration analyte concentration. So, more than 70 elements have been determined by ICP at various wavelengths and the data is recorder to 3 decimal places 0.001 p p m 0.005 p p m, like that up to that level chemical analysis with accuracy can be obtained using ICP. So, this is necessary because it has been observed that for each elements several wavelengths may overlap.

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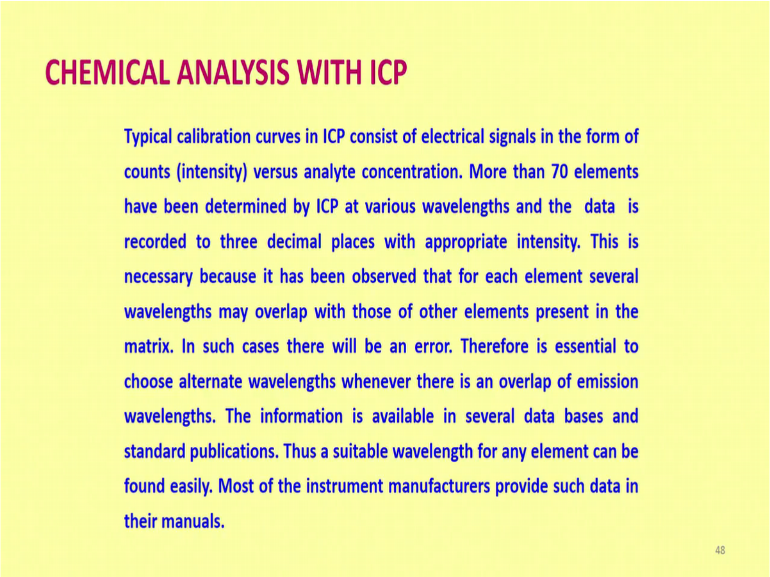

CHEMICAL ANALYSIS WITH ICP

Typical calibration curves in ICP consist of electrical signals in the form of counts (intensity) versus analyte concentration. More than 70 elements have been determined by ICP at various wavelengths and the data is recorded to three decimal places with appropriate intensity. This is necessary because it has been observed that for each element several wavelengths may overlap with those of other elements present in the matrix. In such cases there will be an error. Therefore is essential to choose alternate wavelengths whenever there is an overlap of emission wavelengths. The information is available in several data bases and standard publications. Thus a suitable wavelength for any element can be found easily. Most of the instrument manufacturers provide such data in their manuals.

So, it is important for us that other elements should not interfere with the determination of other elements our analyte, because many emission lines still match with the analyte element.

So, it is essential to choose sometime alternate wavelengths whether whenever there is an overlap of emission wavelengths. This information is available in several data bases, manufacturers manuals, and other Google you can just look up whenever you want to you need to analyze any chemical analysis any metal you can see what are the other elements present along with the sample whether their emission lines match or not if they match go for another wavelength if they do not match you are safe ok.

So, usually the selection of analytical line depends upon the intensity. So, minimum concentration maximum intensity is what we aim for that is what gives us higher sensitivity, but other concomitant elements present in the sample for example, if you want to determine cadmium in cadmium in sea water there will be sodium potassium magnesium and 1000s 100s of other chemicals will be there. So, psi in such matrix the other elements should not be emitting at the same wavelength.

So, calibration plots what we normally do is we do not do the calibration plots with only your standards, but take the matrix without your analyte element and then add it to add your standard samples plot it as if it is there. So, that matrix effect do not interfere they are anald by using this it is a great analytical technique very simple very straightforward 90 percent of the chemical analysis people use this techniques automatically.

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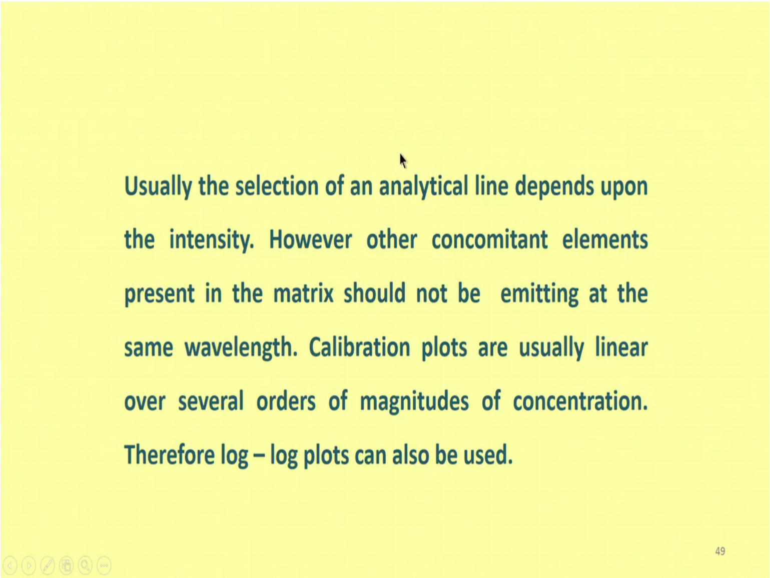

Usually the selection of an analytical line depends upon the intensity. However other concomitant elements present in the matrix should not be emitting at the same wavelength. Calibration plots are usually linear over several orders of magnitudes of concentration. Therefore log – log plots can also be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

So, if you are a student of analytical chemistry you would automatically know what is basically matrix and then as per as possible you prepare the standards in the same matrix. Suppose you want to determine molybdenum in oil it is a wear metal wear metal is one in which from which bearings are made. So molybdenum in oil if you want to determine; so, you take the oil itself as the blank.

So, whatever is there in the oil will take care of the matrix effect, you want to determine cadmium in sea water take sea water itself as a solvent and then whatever is there in every sea water sample will be there and you can be we will be should be able to analyze without a much problem. So, normally log log plots can also be used because if the intensity is very high you will not be able to use ordinary graph paper, but you can use log log plots nowadays computers help quite a lot in sorting out some problems, because you can with the same data you can do normal plotting x y log x log y or log x and y something like that you can always plot and get it on the on your computer screen. So, these are the typical curve calibration curves in ICP AES.

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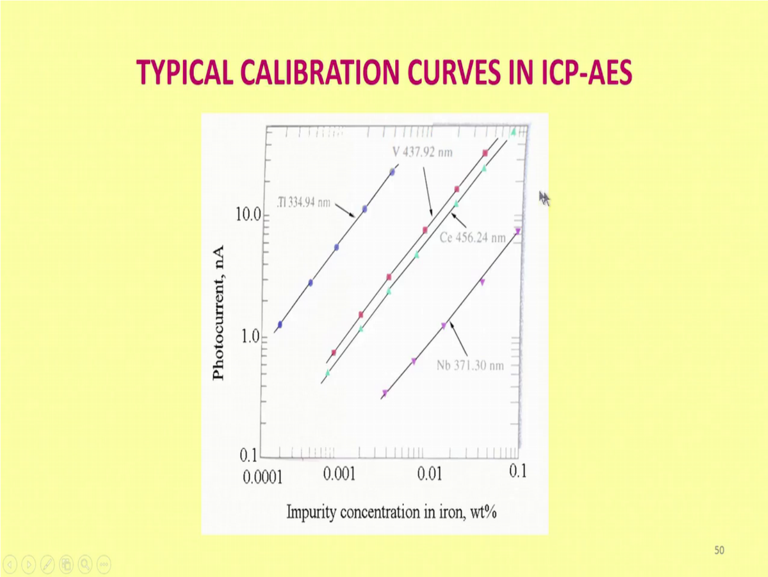

TYPICAL CALIBRATION CURVES IN ICP-AES

Here you can see that the I am showing you the first one is vanadium ok. Hm this is analysis of metals in iron that is weight percent. So, we have analyzed titanium using 334.94 nano meter you can see the plot of concentration from 0.00 0001 up to 0.00 that fall somewhere here up to 0.02 or something like that ok.

So, the next one is the red one here is vanadium and next one is serum and this is niobium. So, in iron all these elements can be determined by dissolving an iron sample and then subject it to ICP AES.

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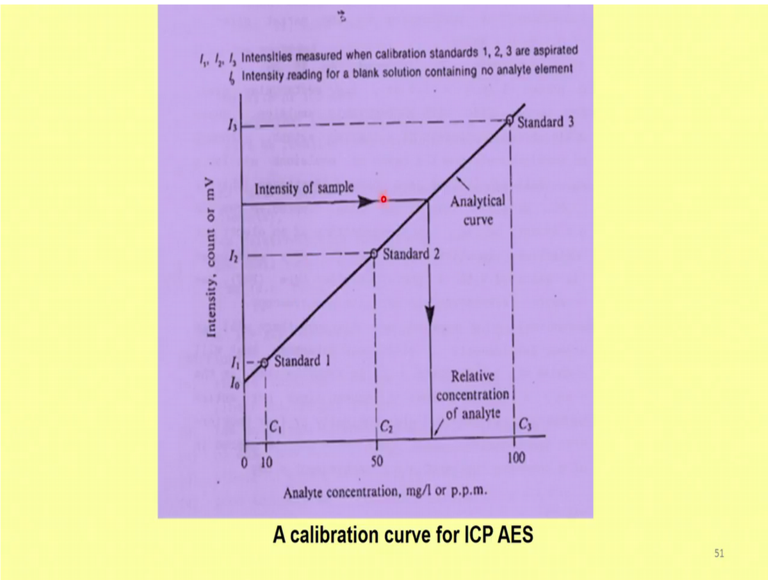

A calibration curve for ICP AES

So, this is how we do the plot here I plot intensity or count on my count or millivolts that is the photon response and analyte concentration is here on the x axes; that is 10 p p m 50 p p m 100 p p m. I told you this is order will be it will be linear over several orders. So, write from 0.0 write from 0 p p m I can go up to 1000 p p m also depending upon.

So, I prepare standards from 10 p p m, 50 p p m, 100 p p m, 1000 p p m still I should be able to get a linear curve and my unknown sample wherever it fits I should be able to determine. So, that is the beauty of ICP AES.

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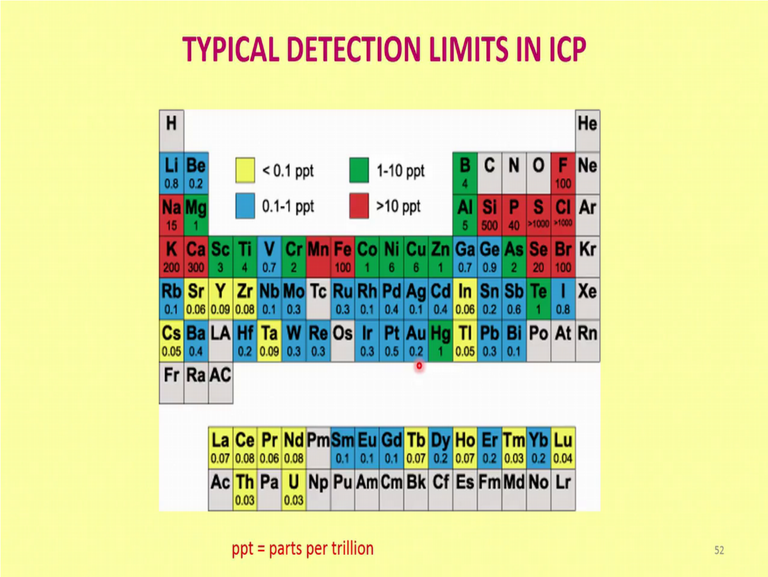

TYPICAL DETECTION LIMITS IN ICP

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

H																	He
Li 0.8	Be 0.2											B 4	C	N	O	F 100	Ne
Na 15	Mg 1											Al 5	Si 500	P 40	S >1000	Cl >1000	Ar
K 200	Ca 300	Sc 3	Ti 4	V 0.7	Cr 2	Mn	Fe 100	Co 1	Ni 6	Cu 6	Zn 1	Ga 0.7	Ge 0.9	As 2	Se 20	Br 100	Kr
Rb 0.1	Sr 0.06	Y 0.09	Zr 0.08	Nb 0.1	Mo 0.3	Tc	Ru 0.3	Rh 0.1	Pd 0.4	Ag 0.1	Cd 0.4	In 0.06	Sn 0.2	Sb 0.6	Te 1	I 0.8	Xe
Cs 0.05	Ba 0.4	LA	Hf 0.2	Ta 0.09	W 0.3	Re 0.3	Os	Ir 0.3	Pt 0.5	Au 0.2	Hg 1	Tl 0.05	Pb 0.3	Bi 0.1	Po	At	Rn
Fr	Ra	AC															
		La 0.07	Ce 0.08	Pr 0.06	Nd 0.08	Pm	Sm 0.1	Eu 0.1	Gd 0.1	Tb 0.07	Dy 0.2	Ho 0.07	Er 0.2	Tm 0.03	Yb 0.2	Lu 0.04	
		Ac	Th 0.03	Pa	U 0.03	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	

ppt = parts per trillion

So, typical detection limits in ICP are point I am showing you from the periodic table yeah whatever is yellow here are determined determined using about 0.1 p p t ok. that is the detection limits and then blue are 0.1 to 1 p p t parts per trillion, that is 10 raise to minus 12 grams that is absolute.

And greenish ones are one to 10 parts per trillion, red ones are more than 10 parts per trillion that is p p t and these gases CNO etcetera they are not much interested right now, but more than 10 p p t are elements like silicon, prosperous, sulfur, selenium metalloids ok. And some of them are you can even do manganese iron, calcium, sodium, potassium etcetera.

So, if you take a look at this periodic table normally you will get an idea of how much is the detection limit without even performing the analysis. So, that you can prepare your standard this table helps you to prepare the standards for the chemical analysis using ICP. So, many of these elements are present in the environment also. So, the for-pollution control environmental pollution control we need to know these detection limits

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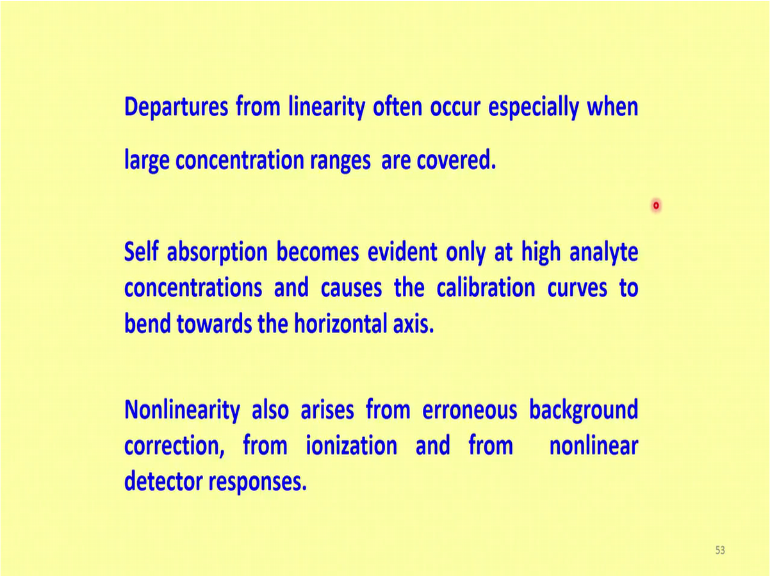

Departures from linearity often occur especially when large concentration ranges are covered.

Self absorption becomes evident only at high analyte concentrations and causes the calibration curves to bend towards the horizontal axis.

Nonlinearity also arises from erroneous background correction, from ionization and from nonlinear detector responses.

So, do we have always a linearity? Answer is no because linearity is always expected for very low concentrations normally, but the whenever large concentration ranges are covered we do see some departure from the linearity when; that means, the counts will not be exactly proportional to the concentration.

So, what do we do? The way scientific way of solving a non-linear problem is use the treat the response that is number of counts as binary equation, instead of m x plus y is equal to m x plus c. You write y is equal to a x square plus b x plus c or you can write cubic this thing also if your try to fit in the data in that the linearity can be again reestablish.

So, it is not just y is equal m x plus c, but there are other algorithms you can use in ICP to get linear curve. So, but why does non-linearity occur at all. So, the answer is self-absorption you can see this slide now self-absorption becomes evident. Only at high analyte concentrations and causes the calibration curves to bend towards the horizontal axis.

So, this leads to non-linearity, nonlinearity also arises from erroneous background correction sometimes background correction is a very tricky one and it also arises from ionization and from non-linear detector responses also. So, these are normally this kind of nonlinearity there will be powerful algorithms in the computer attached to the attach to the ICP AES.

So, you should be able to apply different algorithms to fit the data to obtain linearity. So, if m x plus c looks somewhat y is equal to m x plus c looks somewhat non-linear you can try a x square plus b choose another polynomial see whether it becomes straightforward, but the for this reason suppose you are able to you are not able to get the linearity then, what do we do? There is analytical technique trick what do we do is we use an internal standard like iron.

So, you add a little bit of iron as an internal standard determine the iron in that sample. So, if your iron analysis is correct then you assume that your whole analysis is correct, because you know how much of iron you put and if that is matching all other element should automatically match because it is only the emission ok.

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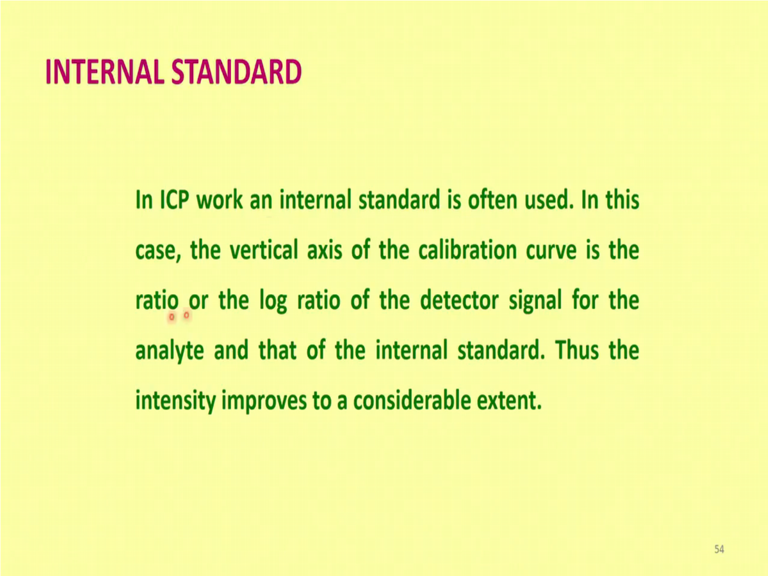

INTERNAL STANDARD

In ICP work an internal standard is often used. In this case, the vertical axis of the calibration curve is the ratio or the log ratio of the detector signal for the analyte and that of the internal standard. Thus the intensity improves to a considerable extent.

So, the ICP work in internal standards the vertical axis is the ratio of the log ratio or the log ratio of the detector signal and that of the internal standard also. So, the intensity improves to a considerable extent if you use an internal standard. I am going to ask you a question if you are going to take an examination in this subject in the on this topic. So, please go through some of the reference books what I had already taught, I had already indicated earlier and it should be of great help to you in your future courier also if you will be working with ICP AES ok.

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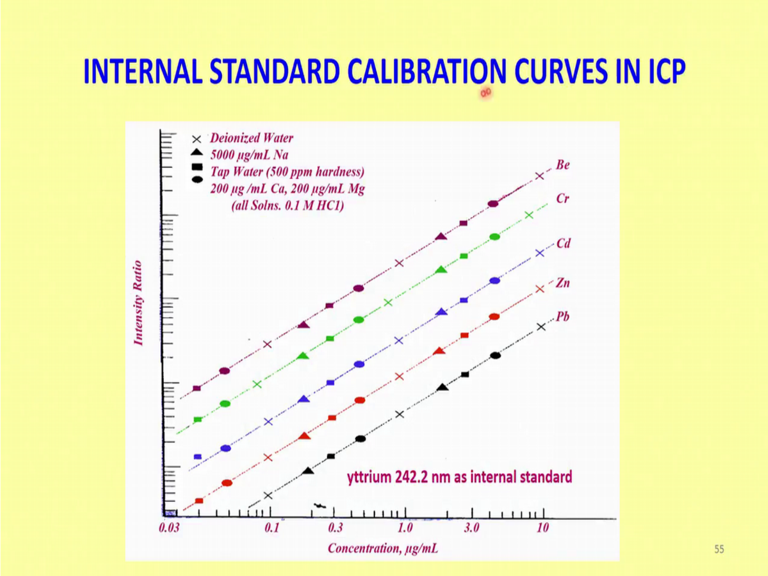

INTERNAL STANDARD CALIBRATION CURVES IN ICP

yttrium 242.2 nm as internal standard

So, these are the internal standards calibration curves some of them I am going to show you. For example, this one is deionized water lead and here yttrium 2 4 was added as internal standard and yttrium was measured at 242.2 nano meter. of emission wavelength, but what we have determined is beryllium, chromium, cadmium, zinc and lead. We are used determine the these elements in deionized water another matrix is up to 5000 milligram per m l of sodium and this is tap water approximately 500 p p m hardness. And this one the round one is 200 milligram it contains calcium, magnesium and all other solutions.

So, again this lied gives you the importance of matrix matching ok. So, you can see it is for each element for different matrix different concentration are different intensity ratios are obtained for the same concentration. So, please study this table this figure carefully and try to understand it is also given in scoog

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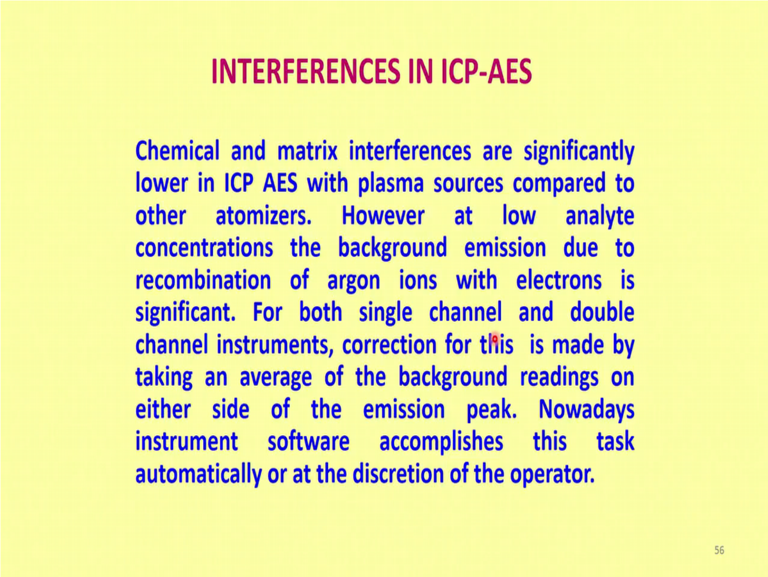

INTERFERENCES IN ICP-AES

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

So now we discuss a little bit about interferences in ICP AES. So, what we do is chemical and matrix interferences are significantly lower this we have to understand with ICP AES; however, at low analyte concentrations background emission can be very high, isn’t it? It makes sense, that if you want to determine parts per trillion element in any given sample background could be anything because we want to do the matrix matching.

So, for both single channel and double channel instruments correction for the background is very important; that means, whatever is the background you have to subtract it from the actual analyte signal, that is what it mean. So, background correction is a very important part of ICP AES. Nowadays instrument software does accomplish this task automatically at the or at the discretion of the operate sometimes operators ingenuity also helps in sorting out some of the problems.

So, in interferences in ICP AES we are going to discuss that many of them are given in the literature also. So, we can classify them as spectral overlap including continuum and background radiation.

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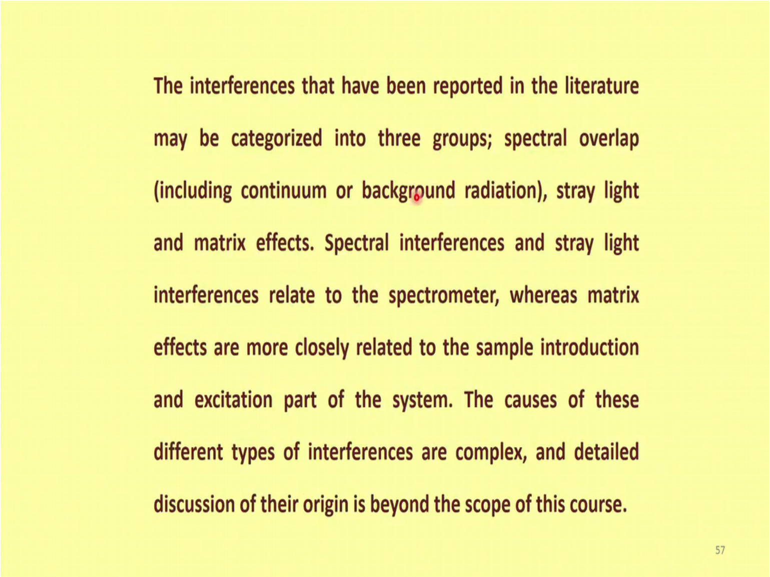

The interferences that have been reported in the literature may be categorized into three groups; spectral overlap (including continuum or background radiation), stray light and matrix effects. Spectral interferences and stray light interferences relate to the spectrometer, whereas matrix effects are more closely related to the sample introduction and excitation part of the system. The causes of these different types of interferences are complex, and detailed discussion of their origin is beyond the scope of this course.

Sometimes stray lights is also introduce it is interferences and matrix effects. So, we have already discussed matrix effects quite a lot and spectral interferences and stray light interferences relate to the spectrometer whereas, matrix effects are closely related to the sample introduction, and sample excitation part of the system. So, the causes of these different types of interferences are very complex.

And a detailed discussion is beyond the scope of this course, but I can refer you to some of the research papers and review papers which area available in analytical sciences generals you can go through them, whenever you feel like you have to learn more about that ok.

So now I am going to discuss with you a little bit about spectral interferences. And I have to tell you that or rather I do not have to tell you that spectral interferences are always possible in ICP analysis because emission spectra of many elements are numerous and quite a few match with each other therefore, it is preferable to have a knowledge of other matrix elements that is number 1.

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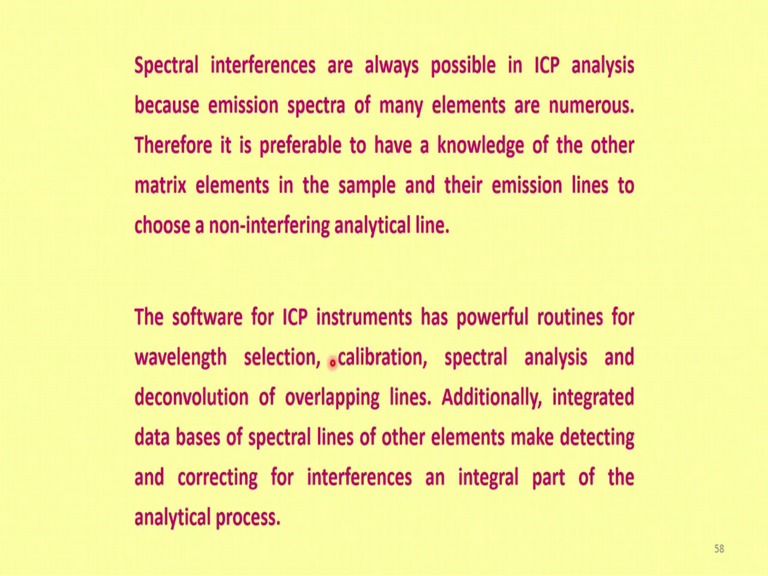

Spectral interferences are always possible in ICP analysis because emission spectra of many elements are numerous. Therefore it is preferable to have a knowledge of the other matrix elements in the sample and their emission lines to choose a non-interfering analytical line.

The software for ICP instruments has powerful routines for wavelength selection, calibration, spectral analysis and deconvolution of overlapping lines. Additionally, integrated data bases of spectral lines of other elements make detecting and correcting for interferences an integral part of the analytical process.

Number 2 the software has powerful routines for wavelength selection calibration spectral analysis and deconvolution of the overlapping lines the computer will take care of it most of time if you know the system. So, additionally integrated data bases of spectral lines for elements for detecting and correcting for interferences is an integral part of the analytical process.

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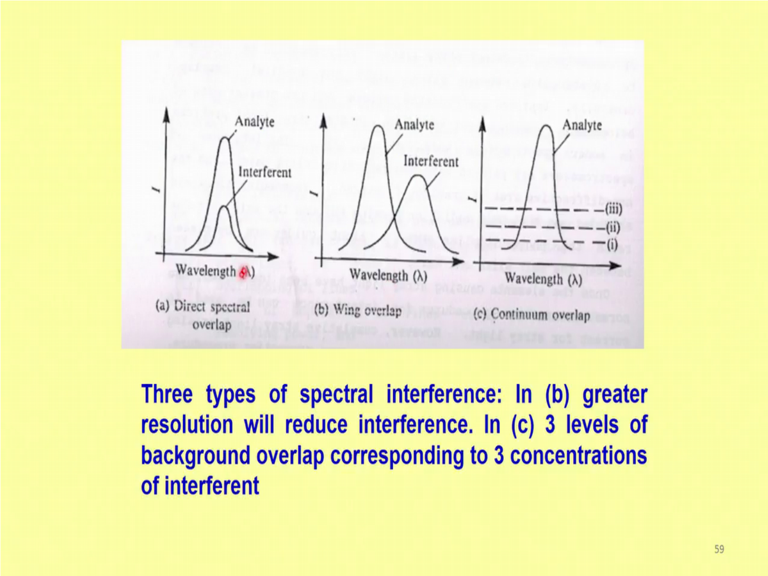

(a) Direct spectral overlap

(b) Wing overlap

(c) Continuum overlap

Three types of spectral interference: In (b) greater resolution will reduce interference. In (c) 3 levels of background overlap corresponding to 3 concentrations of interferent

So, here I am showing you some of the interferences spectral interferences. You can see part a here the interferent is there analyte is here on the above, but you have to your suppose to subtract this the interferent this much of emission said to be subtracted from the total area of the analyte. Here it is the spectral system interferent is totally inside the emission spectrum. So, this is known as direct spectral overlap.

And if you see the middle one a small portion of the interferent is accounted by the detector most of it is not accounted by the detector. So, I should be able to correct this is known as wing overlap and the next one is continuum overlap, there is 1 2 3 these this is this has nothing to do with this sample, but it has something to do with the matrix.

So, 3 types of spectral interferences here also we have to suppose to subtract the 1 2 background up to this level. So, the actual signal is only what is above the dash lines. So, here I am giving you 3-line levels of background correction overlap corresponding to 3 concentrations of the interferents.