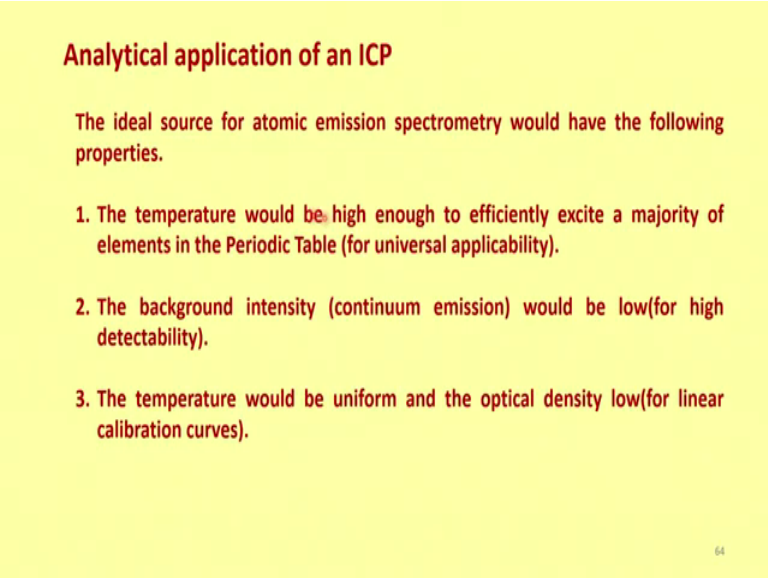
Inductive Couple Plasma Atomic Emission Spectrometry (ICP-AES) for Pollution Monitoring

Dr. J R Mudakavi
Department of Chemical Engineering
Indian Institute of Science, Bangalore

Lecture – 21

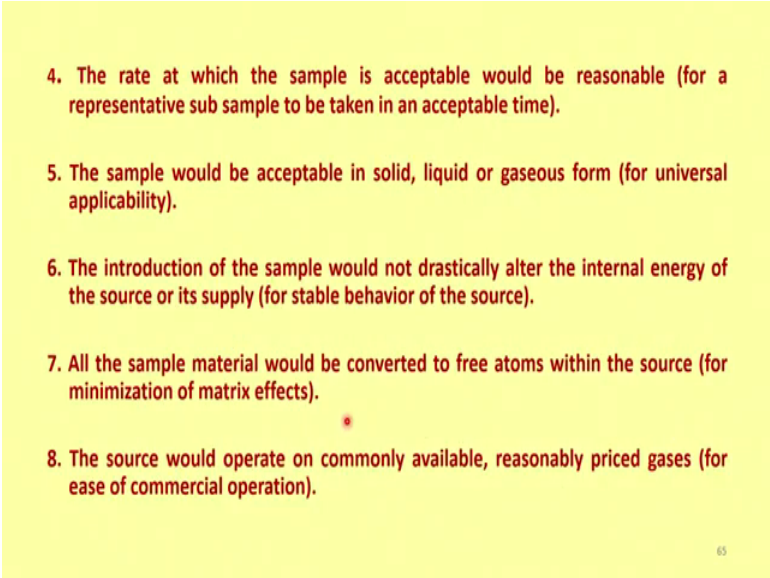
Practice and Applications of ICP AES – IV – Chemical analysis

(Refer Slide Time: 00:15)



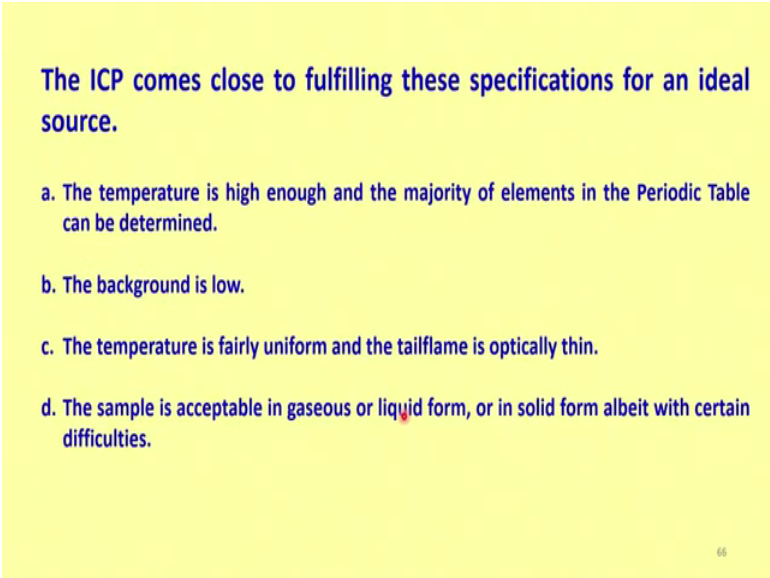
So, the ideal source for atomic emission spectrometry should have the following properties, one is temperature should be high enough ; that means, the plasma should be very stable ok. the temperature should be high enough for all the elements you want to analyze must be excited to the next higher energy level that is what it means that is that is a universal applicable principle. So, second thing is background intensity should be as low as possible for high detectability, the temperature should be uniform and the optical density should be low for linear calibration curves.

(Refer Slide Time: 01:04)



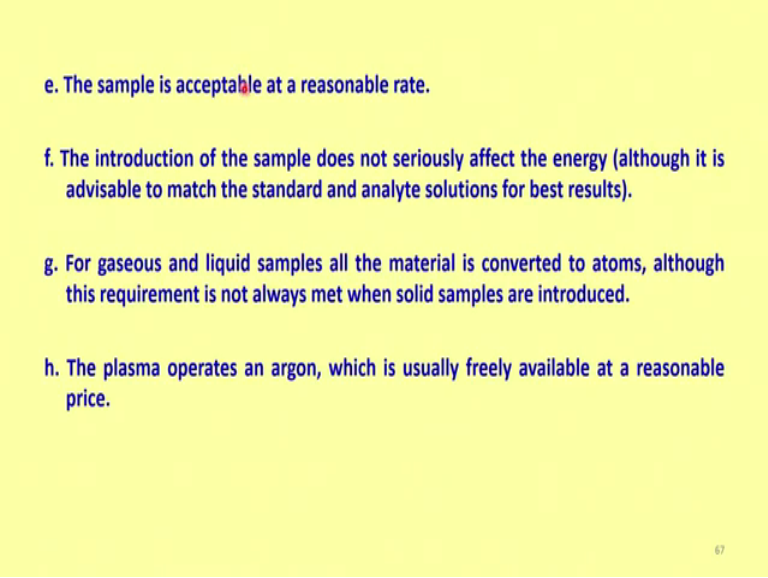
So, the rate at which the sample is acceptable should be reasonable; that means the representative sub sample it should be taken in an acceptable time within the time it takes to transport. So, the sample should be acceptable as solid liquid or gaseous forms introduction of the sample should not drastically alter the internal energy of the source that is plasma source or it supply the; that means, the plasma should be very stable. All the sample material should be converted into free atoms within the source, and the source would operate on commonly available reasonably priced gases that are argon only as far as our experience is concerned.

(Refer Slide Time: 01:50)



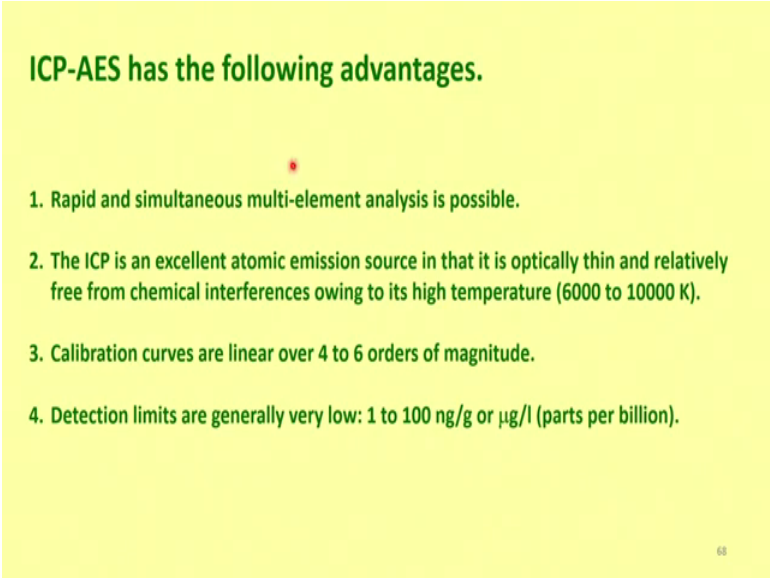
So, the ICP comes close to fulfilling these specifications for an ideal source, because the temperature is high enough and majority of the elements can be determined background is really low because the ICP optically it is almost transparent the plasma, the temperature is fairly uniform and the tail flame is optically thin; that means, not much emission coming from the tail flame that background would be very less sample is acceptable in all the forms ok.

(Refer Slide Time: 02:20)



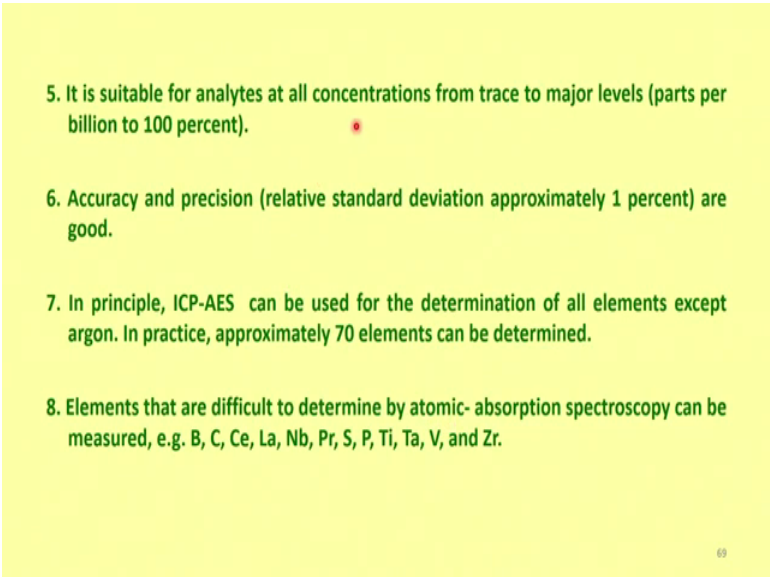
And the sample input through the peristaltic pump is acceptable at a reasonable rate the introduction of the sample does not seriously affect the energy, for gaseous and liquid samples the material is converted into atoms and the plant operates on the argon which is freely available at a reasonable price.

(Refer Slide Time: 02:45)



So, it has the advantages one is rapid and simultaneous multi element analysis it is an excellent source of atomic emission that it is optically thin, calibration curves are linear over 4 to 6 orders of magnitude also. Detection limits are very low the 1 to 100 nano grams or microgram per liter that is parts per billion.

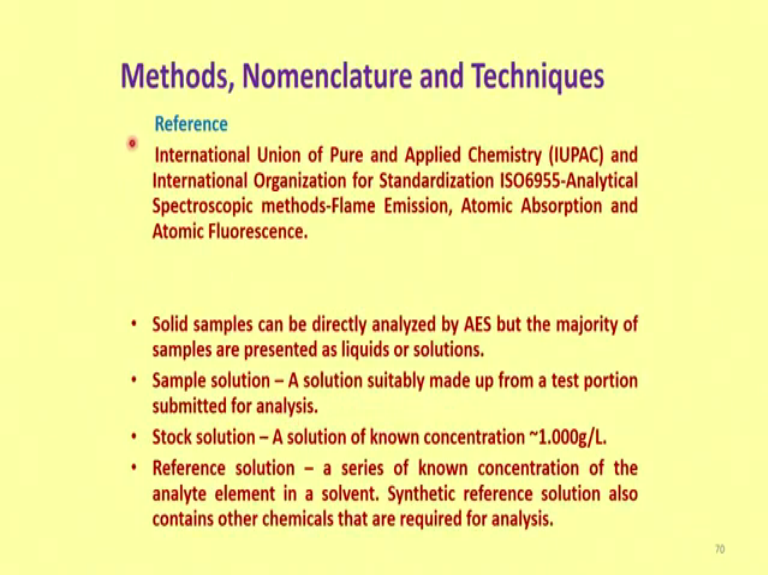
(Refer Slide Time: 03:12)



And it is suitable for analyses at all concentrations from trace to major levels, accuracy and precision are very good in principle ICP-AES can be used for the determination of all elements except argon that is understandable isn't it. So, in practice practically about

seventy elements can be determined using ICP-AES with 1 single source that is plasma. So, elements that are difficult to determine by AAS can be determined easily for example, boron carbon, cerium lanthanum, these are rare earth elements and then actinium elements and then many of them are refractory elements like titanium tantalum vanadium zirconium etcetera.

(Refer Slide Time: 04:01)



So, now I want to talk to you about the a little bit about the analytical aspects, because any chemical analysis must follow certain analytical rules and these are for analytical scientists these are all a sort of understood, but for students it is better to understand a little bit about the fundamental principles of chemical analysis.

So, here we talk of several several systems and I to define, I want to define certain solution certain terms for your easy reference, because whenever we talk of chemical analysis the technical terms we normally use technical jargon should not be confusing to nonprofessionals for example, many of you who are taking this course may be students or may be officials may be you know professionals, but not trained in analytical science, but you may need the results anyway. So, it this is the reason.

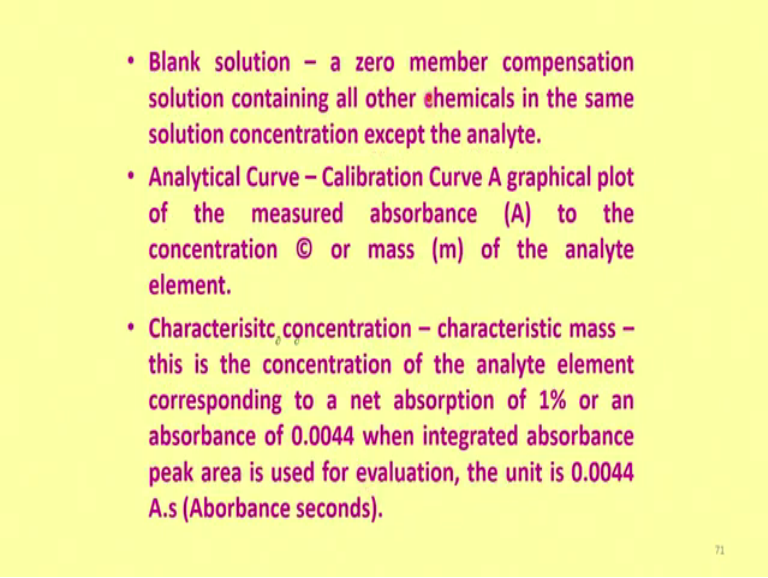
So, the reference what I am giving you is the international union of pure and applied chemistry that is IUPAC, you can see the slide now and international organization for standardization that is ISO 6955 that this defines the analytical spectroscopic methods for flame emission atomic absorption and atomic fluorescence. So, the solid samples can

be directly analyzed by AES, but the majority of the samples are presented as liquids as solutions. Now what is a sample solution it is a solution suitably made up from a test portion of the sample submitted for analysis; that means, it is the solution to be aspirated into the ICP.

What is a stock solution a solution of known concentration from which the dilutions are made to prepare the calibration standards ok, then comes reference solution these are what we prepare known concentrations from the stock solutions.

So, from the stock solution is suppose you have 1 PPM, here and 1 gram per liter that is approximately 1 milligram per milliliter that is 1000 PPM, but you don't need 1 thousand PPM you may need only 1 PPM, 10 PPM, 50 PPM. So, these concentrations, these solutions prepared from the stock solution are known as reference solutions. So, a series of known concentration of the analyte element in a solvent is known as reference solution it may contain the matrix elements also ok.

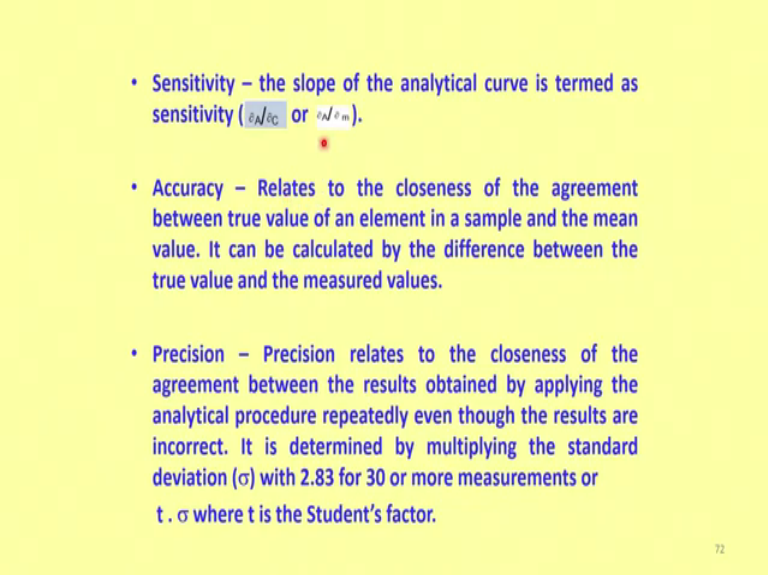
(Refer Slide Time: 07:00)



So, a blank solution, so blank solution is a 0 member compensation solution containing all other elements that is matrix matching in the same solution, but it does not contain the analyte. So, blank solution should be having 0 concentrations of the analyte and analytical curve. So, what it means it is the calibration curve or a graphical plot of the measured absorbance or emission or to the concentration or mass of the analyte sample.

So, it is the, this is the curve what you need for chemical analysis interpretation of the results. So, what is a characteristic concentration or characteristic mass? So, this refers to the concentration of the analyte element corresponding to a net absorption or emission of 1 percent or an absorption absorbance of 0.044, when integrated absorbance or peak area is used. So, the we can take the almost the same for emission ICP-AES also ok.

(Refer Slide Time: 08:18)

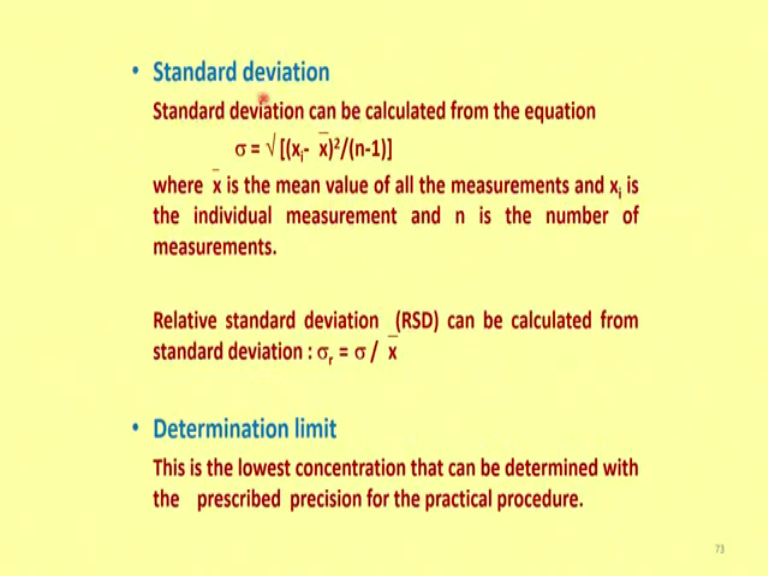


So, sensitivity, so it is the slope of the analytical curve that is termed as sensitivity it is delta a by delta c or delta a by delta m c delta c is the concentration delta a is the absorbance or emission. So, change in the emission or absorption with respect to concentration or mass is the know is known as the sensitivity. So, for good sensitivity change should be large for small concentration change. So, accuracy, accuracy relates to the closeness of the agreement between the true value of an element in a sample and the mean value usually true value is not determined is not determinable, but mean value is determinable.

So, it can be calculated by the difference between the true value and the measured value there will be some slight difference, and thus difference should be as low as possible compared to the true value and mean value. So, precision, precision relates to the closeness of the agreement between the results obtained by applying the analytical procedure repeatedly suppose you do three typical, three different analysis using the same set of conditions if the results match then we say results are very precise.

But the results it does not mean results are correct ok, because the same error can could have been carried out in carried out in all the three samples. So, a precision does not guarantee accuracy, but precision means the system is perfect. So, it is determined by multiplying the standard deviation sigma with 22.83 for 30 or more measurements or t dot sigma t into sigma, where t is the students factor you should look up a little bit about students factor in your analytical books to find out what is exactly the student factor is student is the name of the scientist.

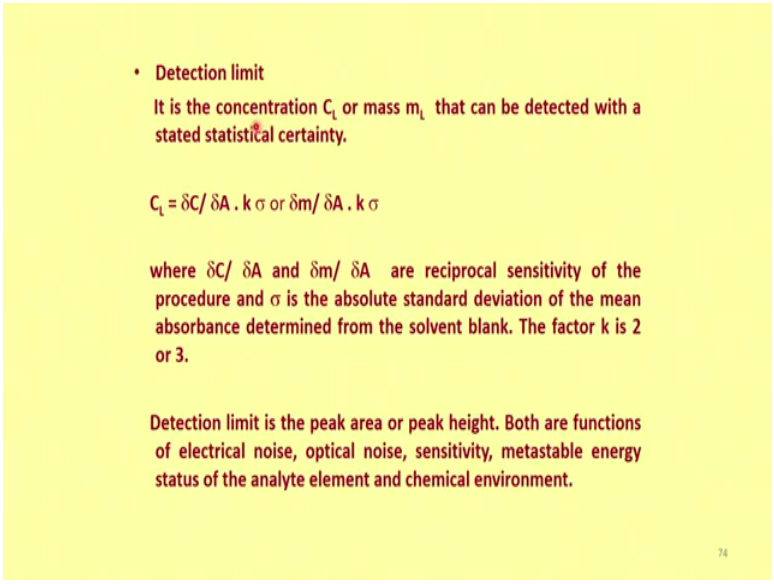
(Refer Slide Time: 10:42)



So, we also have some of these terms, so you come across regularly that is standard deviation it is given by square root of x y minus x bar whole square divided by n, where x bar is the mean value of all measurements and x i, the individual measurement n is the number of measurements in standard deviation what we mean is the actual analytical value is spread over the mean value plus or minus some number ok. So, the it is a very important concept in all analytical measurements.

So, relative standard deviation is can be calculated by dividing standard deviation by the mean value ok. So, the determination limit this is the lowest concentration that can be determined with the prescribed precision for practical procedure; that means, not detected it is determined; that means, quantitative a determination is involved here not just the present yes or no it's not that type ok.

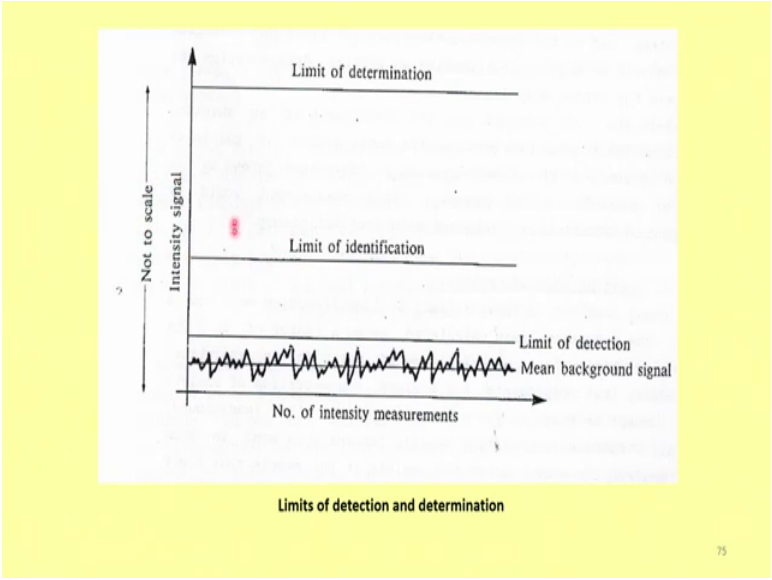
(Refer Slide Time: 11:56)



So, detection limit is delta c by delta a into k dot sigma or delta m by delta a into k dot sigma where k is the factor of k is 2 or 3, and sigma is the absolute standard deviation. So, the detection limit 1 what I have shown you earlier in the table are these numbers ok. So, it is the detection limit can be measured either using peak area or peak height that is the emission line spectrum both are functions of electrical noise, optical noise, sensitivity metastable energy status of the analyte element, and the chemical environment; that means, that is matrix matching.

So, the detection limit can vary for different systems I hope you are understanding, what I am trying to tell you are the different analytical aspects jargons, what we normally come across. So, it should be evident to you that the reliability of a measurement depends upon all these factors detection limit standard deviation relative, standard deviation and all that slope sensitivity we should be able to determine all these things.

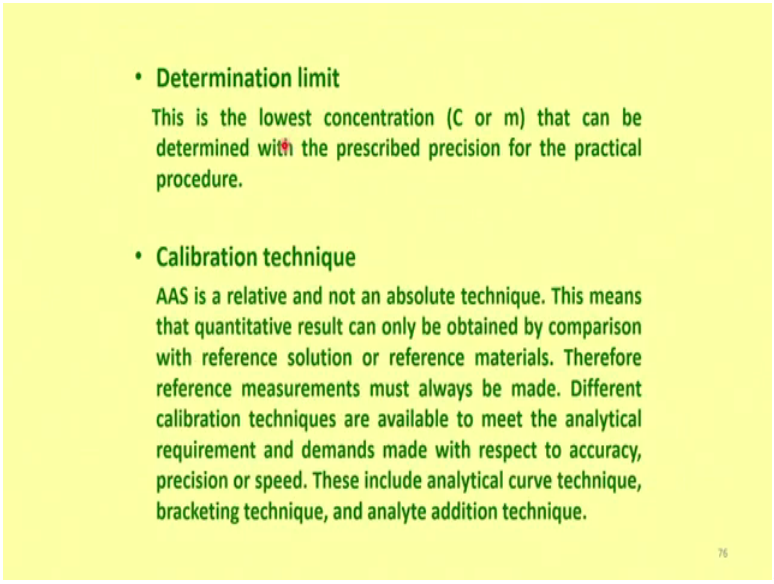
(Refer Slide Time: 13:23)



So, I have a figure here for you that makes a difference here for example, this is the mean background signal ok. Here is the intensity signal number of counts this is without putting anything your sample, the signal goes like this and above the three times about this the average value of the mean background signal is the limit of detection and intensity signal limit of identification.

So, we can say if you get a signal around this level I think there may be element, element maybe there, but to make it sure that the element of analysis is there we have to go to a higher level that is known as limit of identification. So, if you get a reading like this it means the element is definitely there ok, and if you how much is there is gives you the limit of determination. So, above this if you get a reading anywhere around this region the determination is possible. So, you have to understand that this is not done according to scale because I will have to define all the k sigma and 2.3 student t factor and all those things ok.

(Refer Slide Time: 14:52)

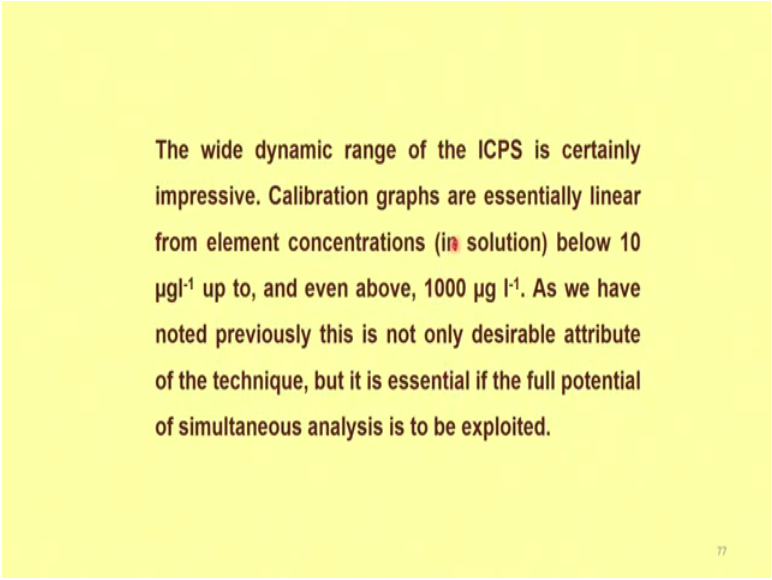


So, the determination limit that can be determined with the prescribed precision for the analytical procedure.

And now I will tell you a little bit about calibration technique. So, AAS is the relative technique and not an absolute technique, AES also is a relative technique, but not an absolute technique this means that quantitative result can be obtained by comparison with reference to solutions or reference materials therefore, reference measurements must always be made different calibration techniques are available to meet the analytical requirement and I have also told you that internal standards need to be employed in AES.

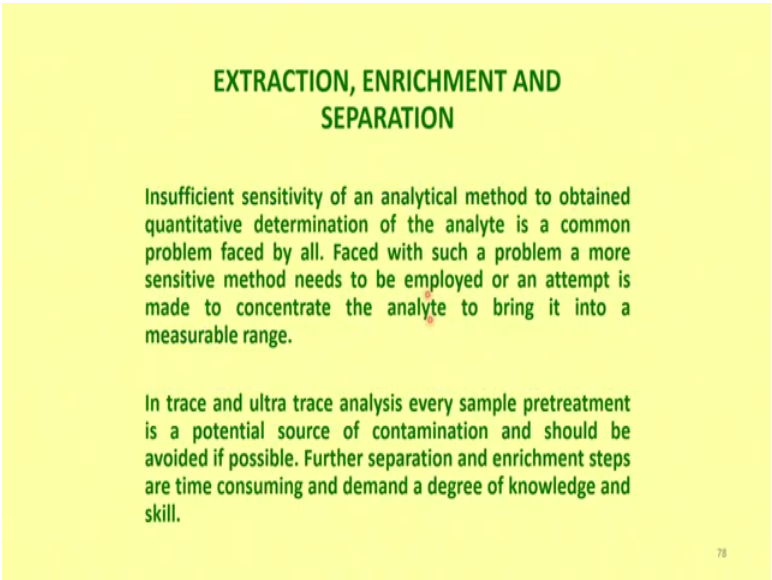
So, the analytical curve technique bracketing technique and light addition technique all these things can be employed to determine the concentrations of the samples.

(Refer Slide Time: 15:47)



So, the wide dynamic range of ICPS is certainly impressive calibration graphs are essentially linear below 10 p p m, and even up to 1000 p p m that is stock solution itself can be measured if the sensitivity is low. So, as we have noted previously this is not only desirable attribute of the technique, but it is essential for us if the full potential of simultaneous analysis is to be exploited.

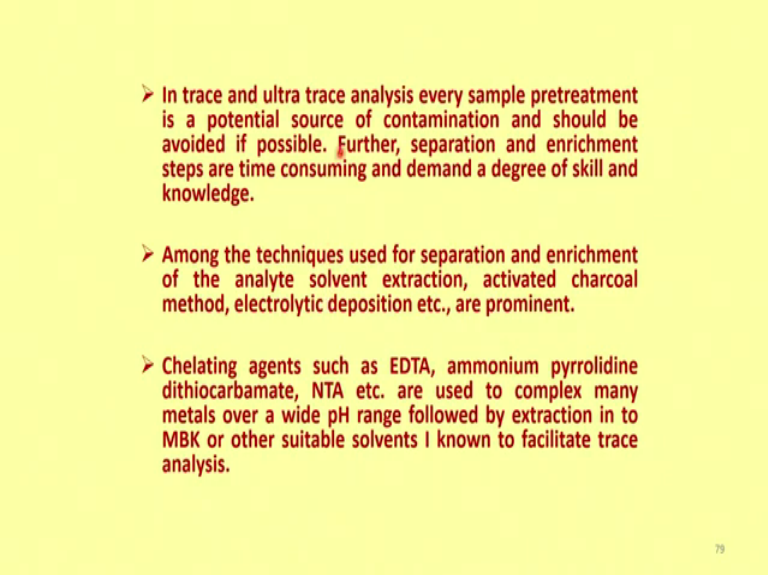
(Refer Slide Time: 16:18)



So, sometimes what happens is there we need to extract and enrich the sample and separation. So, in sufficient sensitivity is 1 of the reasons faced with such a problem a

more sensitive method needs to be employed in trace and ultra-trace analysis every sample pretreatment is a potential source of contamination, we have to be very careful. And if separation and enrichments are time consuming they do demand a degree of knowledge and skill this is where the chemical ingenuity of the person performing the chemical analysis comes into play.

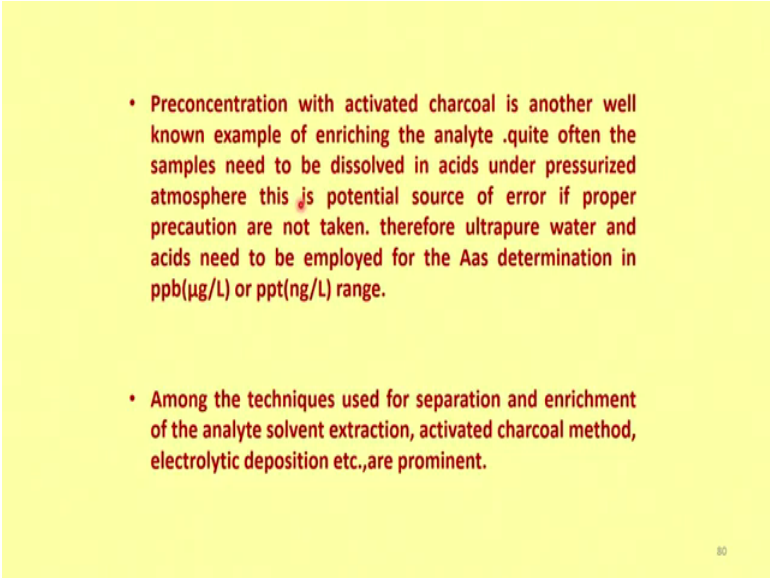
(Refer Slide Time: 16:59)



So, in trace and ultra-trace analysis every sample source is a sample pretreatment should be a source of contamination as far as possible we try to avoid that is the reason we try to give it a introduce the sample as it is. So, among the techniques used for separation and enrichment of the analyte solvent extraction activated charcoal method, the electrolytic decomposition etcetera are prominent I will not go into details of these.

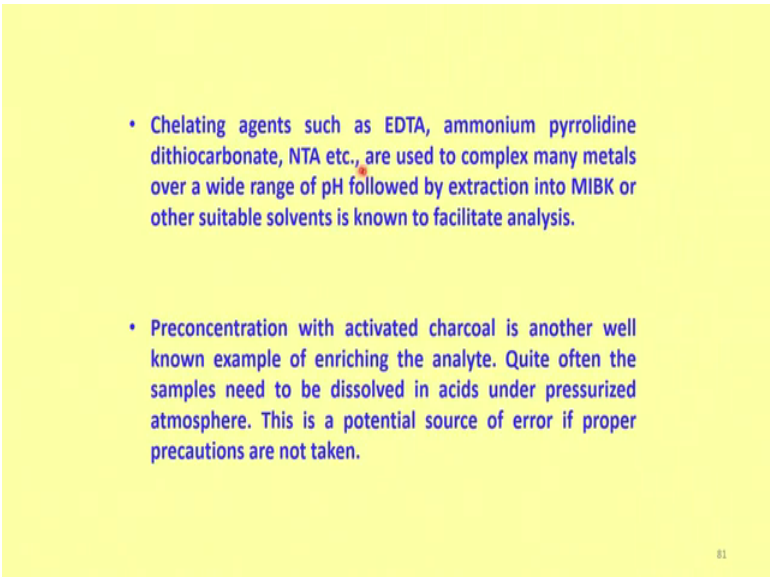
But these things are available in the literature and the reference books ah. So, we also use chelating agents such as EDTA, ammonium pure lead in diethyl carbonate in nitrile or try a stick as it etcetera these are used to complex many metals over a wide pH range followed by extraction into MMIBK, or methyl ethyl ketone or any other solvent known to facilitate trace analysis.

(Refer Slide Time: 18:00)



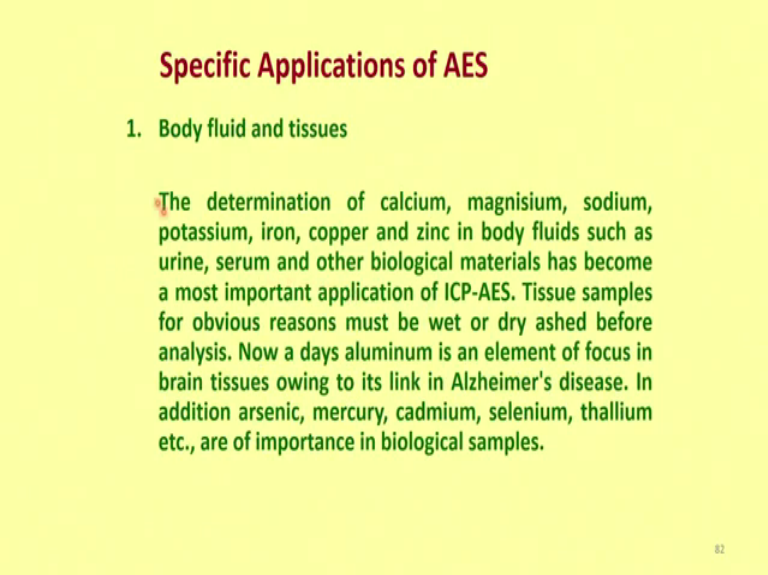
So, pre concentration with activated charcoal is very well known example of enriching the analyte quite often the samples need to be dissolved in acids, and their pressurized atmosphere this is also a potential source of error any sample treatment for that matter can be a potential source of error, if we do not take the proper precautions. So, ultra-pure water and acids need to be employed for the analysis as well as in parts per million or parts per trillion level it is for AS as well as ICP, among the techniques used for separation and enrichment of the analyte sample solvent extraction etcetera are prominent.

(Refer Slide Time: 18:41)



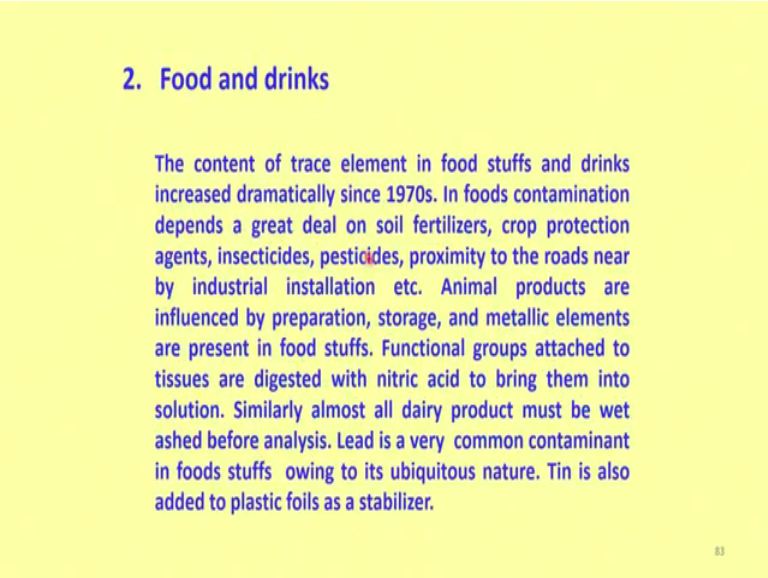
So, chelating agents I have already referred to that and pre concentration with activated charcoal.

(Refer Slide Time: 18:51)



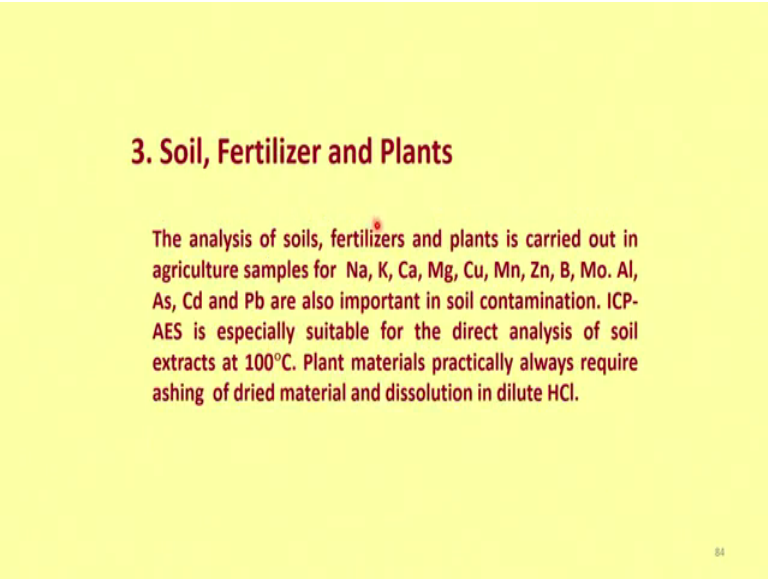
Now, I will spend some time about specific applications of atomic emission spectrometry ok. So, here a here is a list of about ten areas the determination of calcium magnesium sodium potassium metal body fluids and tissues. So, tissue samples must be wet and dry ashed, before analysis nowadays aluminum is also an element of focus in the brain tissues owing to Alzheimer’s disease in addition in biological applications body, fluids, arsenic mercury, cadmium, selenium, thallium, etcetera are of importance.

(Refer Slide Time: 19:34)



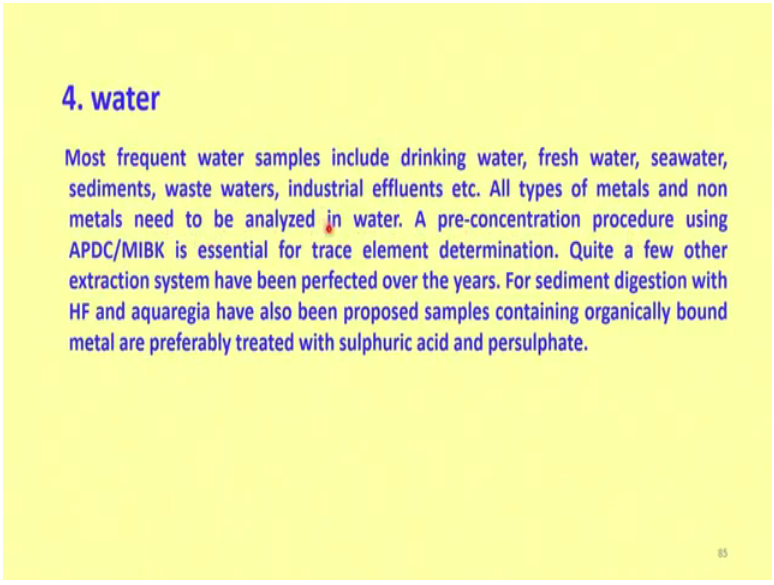
So, in food and drinks we have animal products as such as ghee butter etcetera cheese preparation storage and metallic elements are present in many of the foodstuffs. So, functional groups attached to tissues they need to be digested with nitric acid they have to decompose basically nitric acid does that job and almost all dairy products must be wet ashed, before analysis lead a very common contaminant in foodstuffs great emphasis is being laid on the their analysis of lead tin is also added to plastic foils.

(Refer Slide Time: 20:15)



So, soil fertilizer and sodium potassium calcium magnesium copper manganese zinc boron all these elements arsenic cadmium lead, all these are of importance in the soil analysis for using ICP AES.

(Refer Slide Time: 20:34)

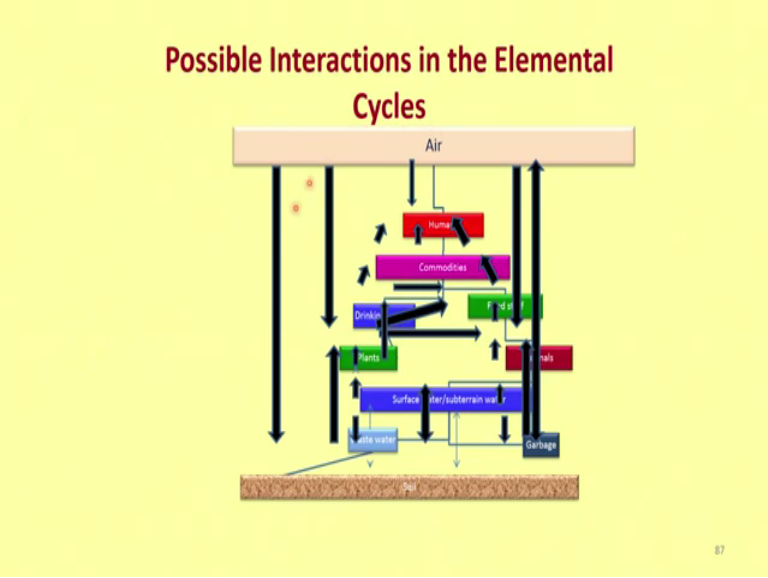


So, water we determine almost all elements in water and sometimes you use APDC and MIBK for concentrating the elements of interest. So, many other extraction systems have also been perfected over the years the details are available in the standard textbooks. So, for sediment digestion, we need HF and aquaregia HF for silica and aquaregia for difficult to dissolve the samples metals.

(Refer Slide Time: 21:09)

And in the environment it covers a whole range of factors that influence our lives it is almost impossible to pick out any specific area in isolation since all factors influence each other mutually.

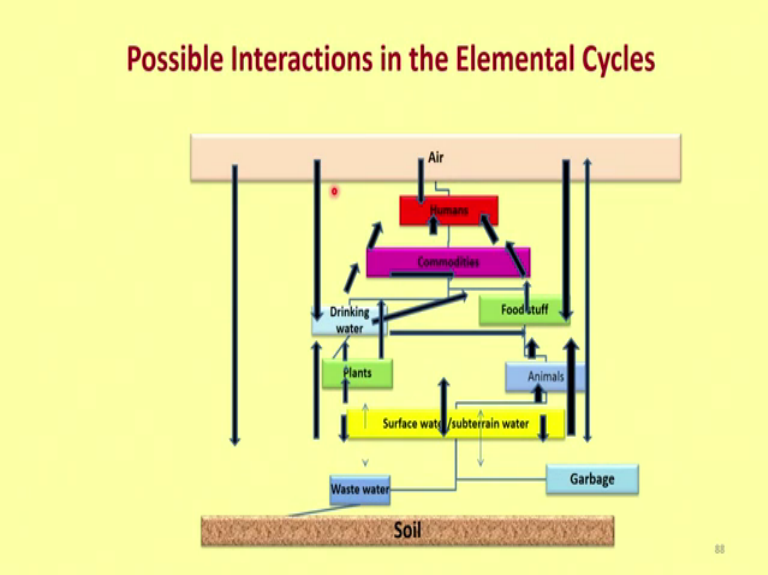
(Refer Slide Time: 21:26)



So, here is a list of possible interactions and in the general word. So, for example, you can see that many of the these are all equilibrium reactions from the air we have humans we breathe in and take the elements and then commodities, they are their drinking water foodstuff plants animals surface water and subterranean water waste water garbage, and

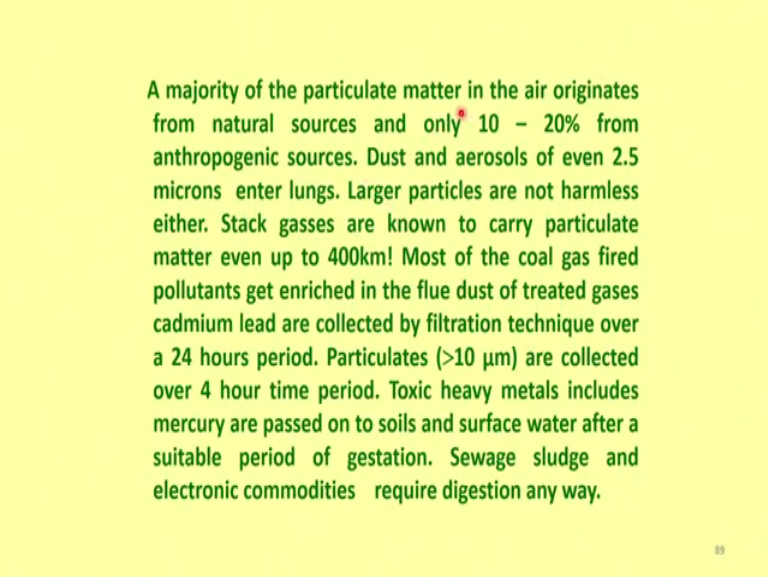
soil I suggest you study this cycle very carefully, because I may ask you in the examination what kind of interactions are possible in the environment.

(Refer Slide Time: 22:09)



So, this is a same picture I had drawn it slightly better, so that if your understanding should be proper

(Refer Slide Time: 22:18)

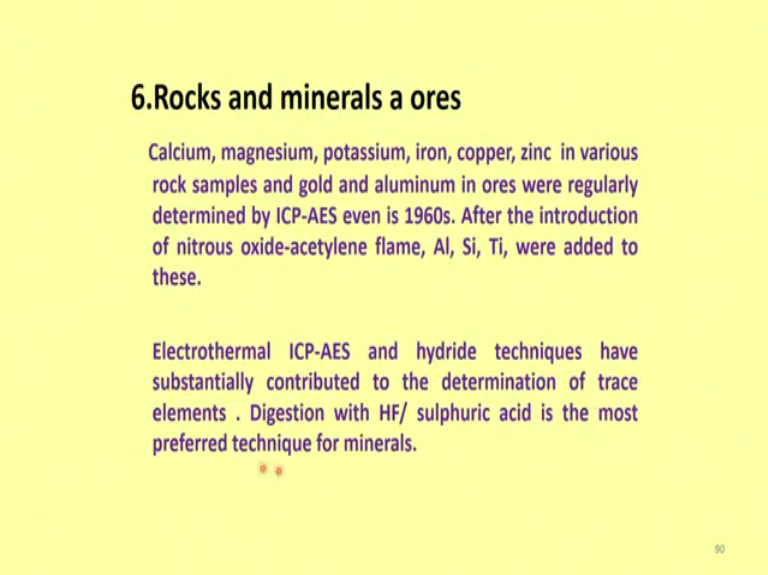


So, a majority of the particulate matter in the air originates from natural sources dust and aerosols of 2 point 5 micron size enter our lungs they deposit in our lungs and they are not harmless either they are very harmful. So, stock gases are known to carry particulate

matter even up to four, stack gases up to 400 kilometer, suppose you have a factory that is spewing out smoke the smoke components can be carried out up to 400 kilometers away also.

So, the air pollutants are normally found everywhere you cannot escape the polluted air. So, most of the coal gas fire pollutants get enriched in the flue dust treated gases cadmium and lead are collected by filtration techniques to determine in the effluents or emission gases particulates are collected over 4 hour time, and sometimes 6 hours, sometimes 24 hours depending upon the requirement and toxic heavy metals including mercury are passed on to soils surface water etcetera and sewage sludge and electronic commodities require digestion anyway.

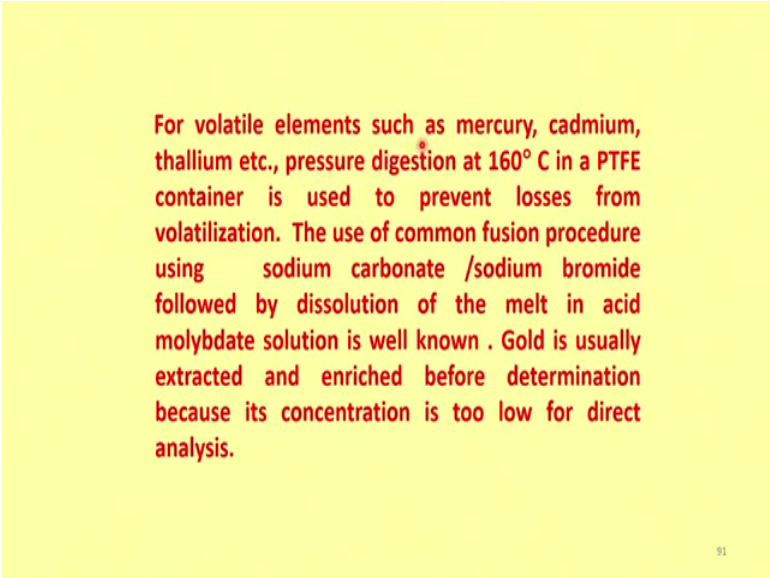
(Refer Slide Time: 23:44)



I have already covered what kind of digestion we should be doing the using power bomb and other method wet ashing, techniques, etcetera, anyway digestion is a very important concept in almost all atomic emission techniques.

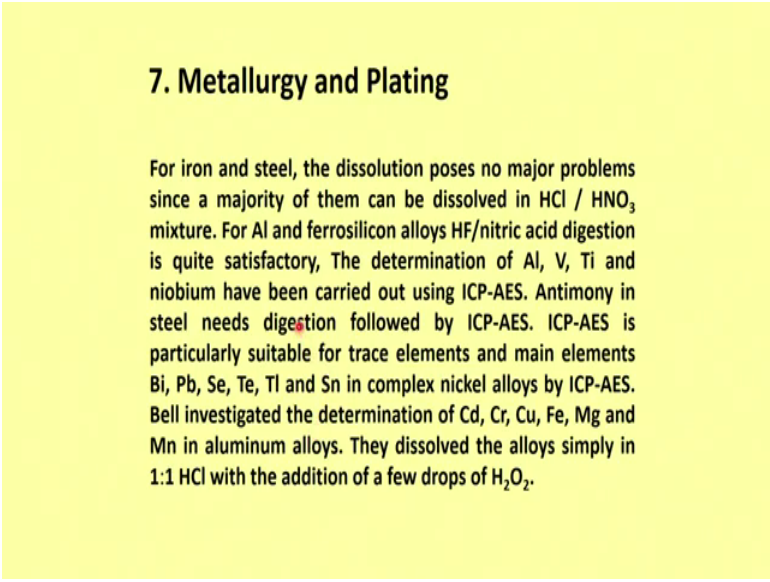
So, calcium in rocks and minerals of course, ICP was developed mainly for the analysis of rocks and minerals in ores. So, calcium magnesium potassium iron copper zinc etcetera in various rock samples gold aluminum platinum many of these elements have been used and ICP AES, and hydride techniques have substantially contributed to the determination of trace elements. So, digestion with HF and sulfuric acid is the most preferred technique for minerals.

(Refer Slide Time: 24:34)



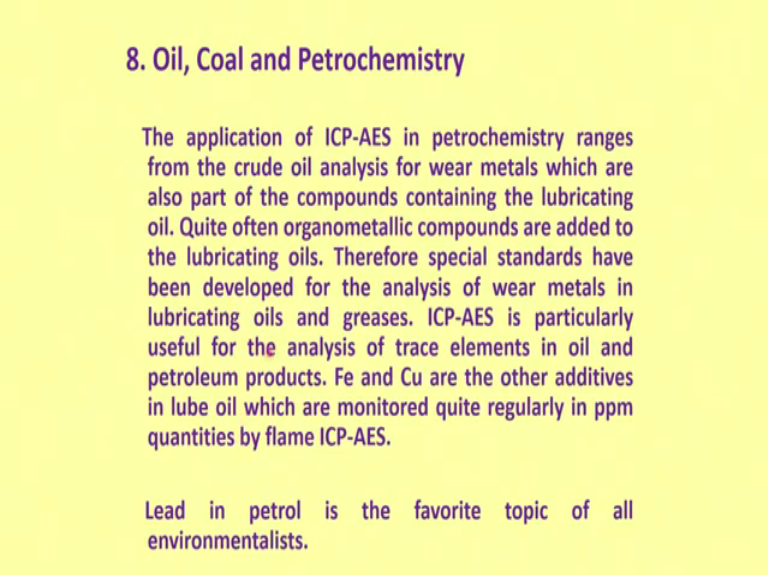
For volatile elements such as mercury cadmium etcetera what we need is pressurization using power bomb the use of common fusion procedure using sodium carbonate, sodium bromide followed by resolution of the melt in acid the molybdate solution is well known. You can look up the details whenever you there is a need for you to analyze by ICP dissolution. So, gold is usually extracted and enriched before determination because of its because its concentration is too low for direct analysis

(Refer Slide Time: 25:14)



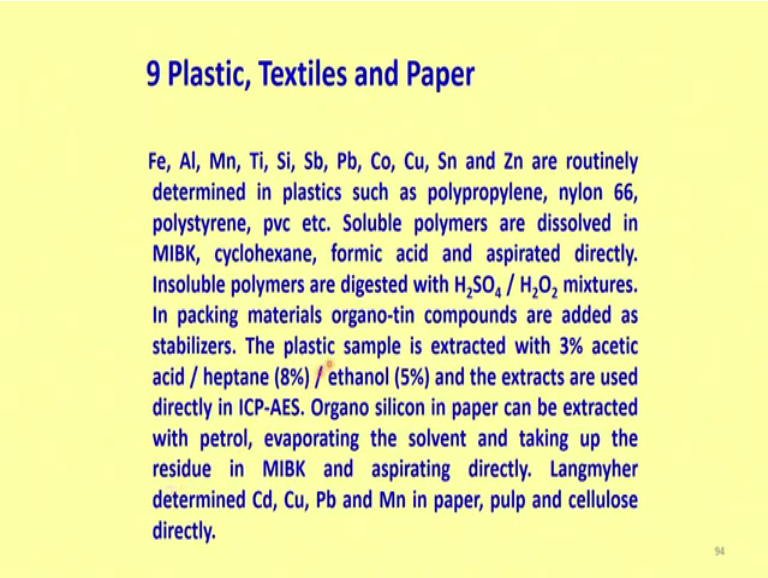
And metallurgy and plating aluminum vanadium titanium chromium niobium and all these elements are usually in a determined especially, if you want to determine plating solutions HCI HNO, 3 treatment is a fairly suitable technique. So, ICP AES, is suitable for trace elements bismuth lead selenium tellurium then thallium maintained in complex nickel alloys and bell has investigated, the determination of chrome cadmium chromium copper iron magnesium in aluminum alloys they dissolve the alloy simply in 1 is to an HCI not more than that with the addition of few drops of H 2 O 2.

(Refer Slide Time: 26:02)



So, oil coal and petro chemistry I have already covered quite a lot in wear metals and it is particularly useful for the elements of trace analysis in oil, and petroleum products iron and copper are the additives in the lube oil which are monitored quite regularly in p p m quantities by flame ICP flame or ICP AES, lead in petrol is the favorite topic of all environmental analysts

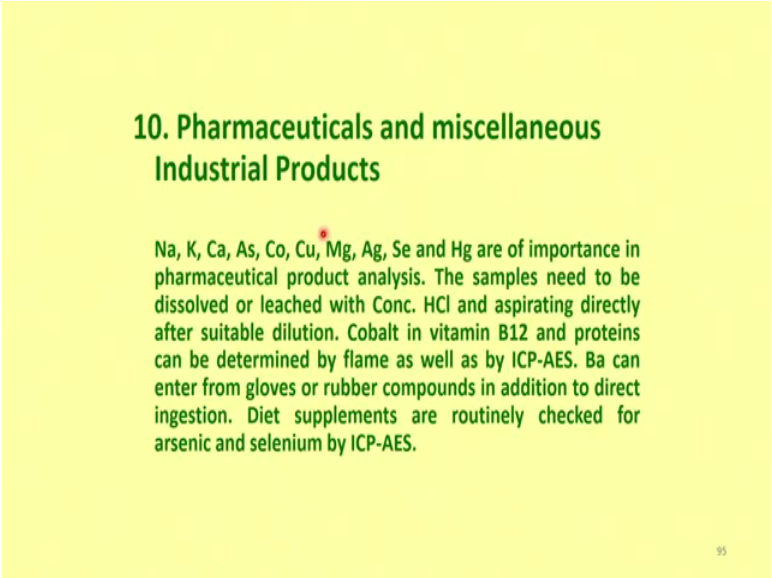
(Refer Slide Time: 26:31)



Plastic paper and textiles required iron aluminum manganese titanium silicon sanctimony plate tin zinc, and many of these things are determined in plastics nowadays and the polypropylene nylon 66 polystyrene PVC, all these polymers are dissolved in MIBK cyclohexane formic acid etcetera and aspirated directly.

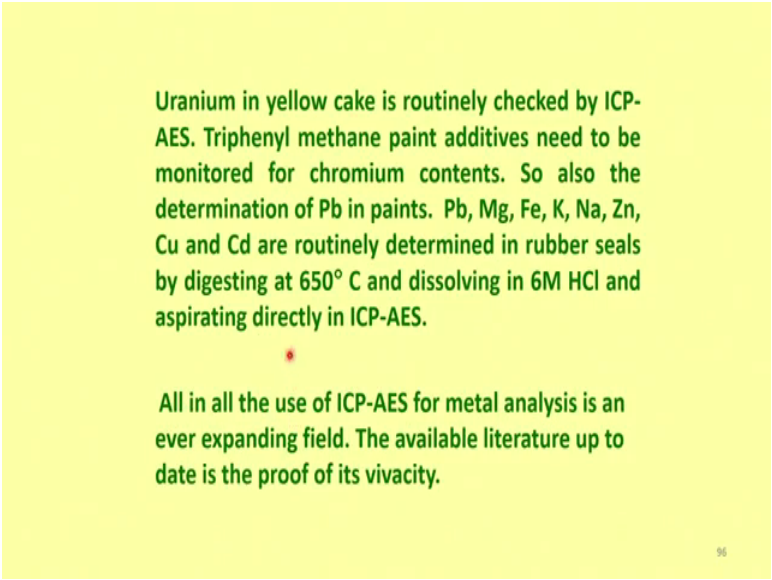
So, insoluble polymers are digested they need to be digested anyway and bring them in solution packing materials may contain organotin compounds, and as stabilizers and metal plastic, sample is extracted with three percent acetic acid and heptane ethanol etcetera and the extracts are determined directly in ICP AES, that is why I keep on telling you that matrix matching is a very important concept in ICP AES, otherwise there is no way we can determine such elements in such low concentration zones for example, langmuir has determined cadmium copper lead, and manganese in paper pulp cellulose such small the concentration should be less than parts per trillion anyway that is why their work in such matrices is very well known.

(Refer Slide Time: 28:00)



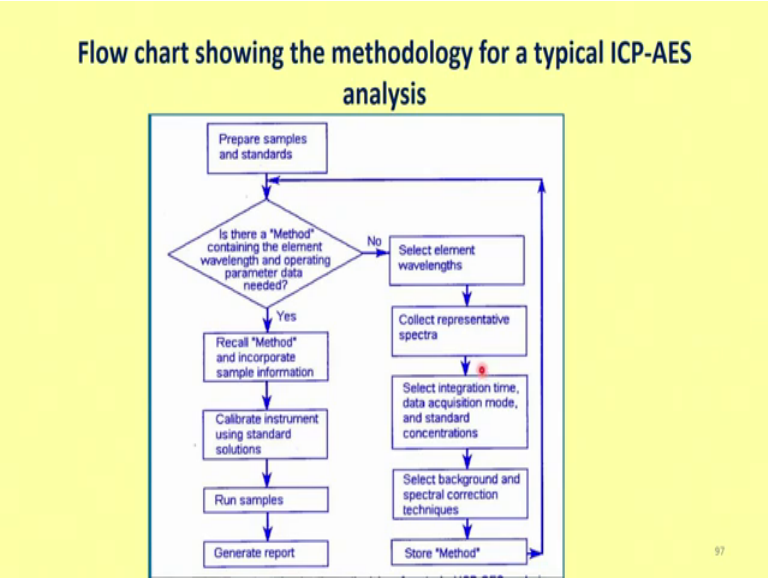
So, pharmaceuticals miscellaneous products industrial products quite a few elements are of importance sodium, potassium, calcium, arsenic, cobalt manganese, air silver, etcetera, the samples need to be dissolved or leached in concentrated HCI, and aspirated directly cobalt in vitamin b twelve and proteins can be determined by the flame AAS as well as ICP AES, barium can enter from the glows or rubber components in addition to direct ingestion. So, direct diet supplements are routinely checked for arsenic and selenium.

(Refer Slide Time: 28:38)



So, uranium in yellow cake is usually determined by ICP AES, and the these are the radioactive elements know. So, many other elements like lead magnesium iron potassium cadmium copper are routinely determined in rubber sales radioactive elements, and many of these things ICP AES is the panacea the available literature up to date is the proof of its vivacity only.

(Refer Slide Time: 29:11)



So, here is a typical flow chart showing the methodology for a typical ICP, how do you go about actually doing the analysis first prepare the samples and standards and then find out is there a ready-made method for measuring the wave length and for measuring the concentration. If it is there you have to tell the computer to recall the method and put all the parameters in place and then you aspirate your calibrated, samples using standard solutions and then run the samples generate the report. So, this is how the normal scheme of chemical analysis using ICP AES run.

So, suppose there is no method then what do you do then we will have to select the element find out, what are the elements find out the select elements and then collect the representative spectra select integration time data acquisition mode and standard concentrations etcetera, select the background store the method and then go back to developing a method using this technique come back here.

(Refer Slide Time: 30:27)

So, this is how an atomic ICP AES looks nowadays it can be it is a it can be put on a bench top and it is a very simple instrument to operate. But of course, I am not showing you the gas arrangement that is argon gas arrangement etcetera on the right side you can see the plasma here very there is a toroidal space and the sample, comes through from the bottom and the plasma is that area is somewhere here this is only a blow up of that.

So, I would like to thank you for your attention during all these ten plus 1 lectures during all these lectures and I hope I have given a sort of preliminary introduction to the technique of ICP AES. So, if you need more information you can refer to the textbooks and other reference material I have already taught you, I have already told you and if you need any additional information or any help you can always contact me and my details I have given in the first lecture of this course, so I wish you all the best.

Thank you very much and may god bless you.