Trace and ultra trace analysis of metals Using atomic absorption spectrometry

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Lecture - 37
Technology and Applications (II)

Dear students, I think we have come almost near the end of our discussions on the atomic absorption spectrometry, and today I will be concluding our discussions. Last class we were talking about the methods nomenclature and techniques, we will continue that. And then we will also discuss a little about method supplications etcetera.

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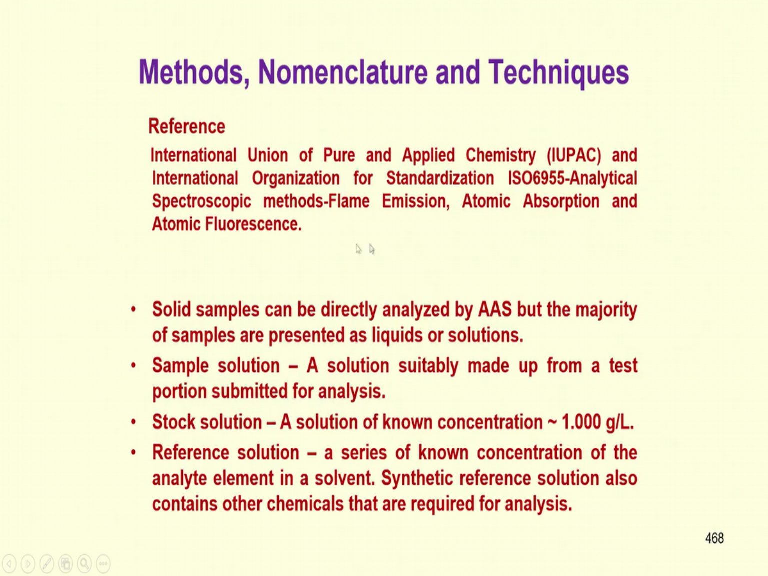

Methods, Nomenclature and Techniques

Reference

International Union of Pure and Applied Chemistry (IUPAC) and International Organization for Standardization ISO6955-Analytical Spectroscopic methods-Flame Emission, Atomic Absorption and Atomic Fluorescence.

- Solid samples can be directly analyzed by AAS but the majority of samples are presented as liquids or solutions.
- Sample solution – A solution suitably made up from a test portion submitted for analysis.
- Stock solution – A solution of known concentration ~ 1.000 g/L.
- Reference solution – a series of known concentration of the analyte element in a solvent. Synthetic reference solution also contains other chemicals that are required for analysis.

What are the different application areas, we will discuss and then we will close our discussion on atomic absorption. So, we were discussing about the methods nomenclature and techniques. Reference is the IUPAC- International Union of Pure and Applied Chemistry and the International Organization of Standardization- ISO6955. You will find more details in these two references.

Now, here we have already discussed about this solid samples that can be analyzed by AAS etcetera, but then during the in the nomenclature we have discussed about sample solution. What it means? A solution suitably made up from a test portion etcetera, stock solution is 1 gram per liter that that can keep for about 2 or 3 about 6 months approximately depending upon the stability of the element at ppm level. This is 1 gram per liter means 1000 ppm. So, reference solution is a series of known concentration of the analyte element prepared from the stock solution. That means, to prepare the calibration curve we need reference solutions. We dilute the stock solution two different concentrations. Sometimes we add other chemicals that are present in the sample to reduce the metrics effects.

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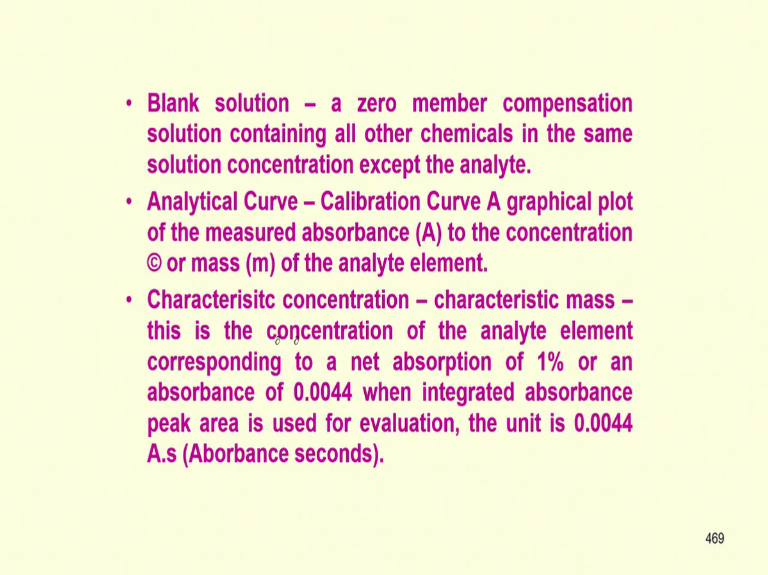

- Blank solution – a zero member compensation solution containing all other chemicals in the same solution concentration except the analyte.
- Analytical Curve – Calibration Curve A graphical plot of the measured absorbance (A) to the concentration © or mass (m) of the analyte element.
- Characterisitc concentration – characteristic mass – this is the concentration of the analyte element corresponding to a net absorption of 1% or an absorbance of 0.0044 when integrated absorbance peak area is used for evaluation, the unit is 0.0044 A.s (Aborbance seconds).

So, we also have a blank solution which does not contain the analyte element. And it is a 0 member compensation solution containing all other chemicals in the same solution except the analyte. So, analytical curve is the plot of absorbance and versus concentration of the reference solutions. So, that is known as analytical curve and it is also known as calibration curve.

Then we defined a quantity known as characteristic concentration. Characteristic mass we can also define for atomic absorption with graphite furnace. And this is the concentration of the analyte element corresponding to a net absorption of 1 percent or an absorbance corresponding to 0.004 when integrated peak absorbance. Peak area is used for evaluation the unit is 0.004 absorbance seconds, it is not the absorbance. So, in most of the atomic absorption methods you will see that the characteristic concentration is normally displayed in the cook book or manual or in the computer etcetera. So, these are the characteristic concentrations prepared from purest solutions under the strict laboratory conditions.

So, if you want to know whether the instrument is in perfect condition for analysis or not what you should be doing is- we have to prepare a calibration standard corresponding to this characteristic concentration. And then see that the absorbance is as prescribed in the cook book, ok.

So, this is a very important concept of atomic absorptions spectrometry.

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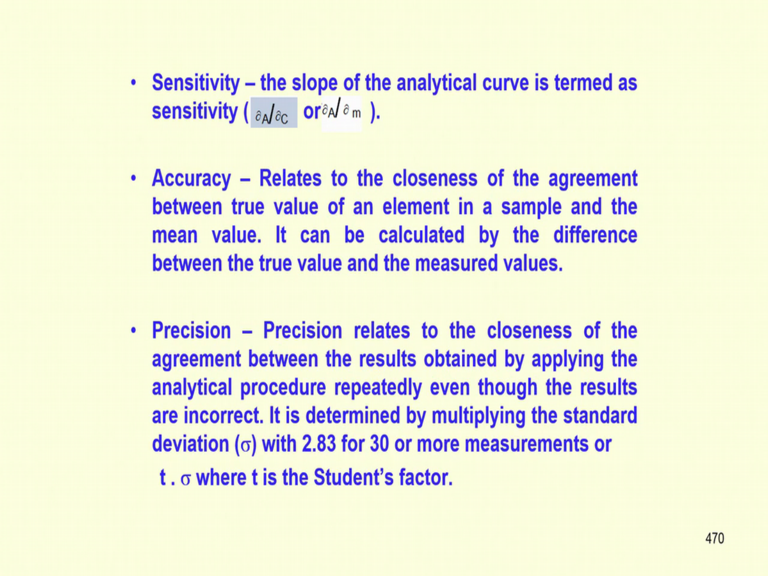

- **Sensitivity – the slope of the analytical curve is termed as sensitivity ($\partial A/\partial C$ or $\partial A/\partial m$).**
- **Accuracy – Relates to the closeness of the agreement between true value of an element in a sample and the mean value. It can be calculated by the difference between the true value and the measured values.**
- **Precision – Precision relates to the closeness of the agreement between the results obtained by applying the analytical procedure repeatedly even though the results are incorrect. It is determined by multiplying the standard deviation (σ) with 2.83 for 30 or more measurements or $t . \sigma$ where t is the Student's factor.**

Then we have also defined what is known as sensitivity. Sensitivity is the slope of the analytical curve that is delta A by delta C or delta A by delta M. So, the minimum absorbance change for a known concentration is the sensitivity. So, higher the sensitivity lower is the determination limit you can go for the any particular element.

Then we wanted accuracy: accuracy, relates to the closeness of the agreement between the true value of an element in a sample and the mean value of what you have measured. So, it can be calculated by the difference between the true value and the measured value. So, precision relates to the closeness of your measurements, if everything is alright your precision may be alright, but there could be a biased error with respect to the accurate value.

So, one has to be careful that even if you get of very good precision the accuracy may be off if there is a systematic error in the determination. Normally, we will determine the precision by multiplying this is the standard deviation sigma with 2.83 for 30 or more measurement. That means, here to measure the same thing, same analysis you have to do the same analysis 30 times and then take that mean, prepare the standard deviation find out how much it is multiplied by 2.83 for 30 or more determinations.

Or if the sample is less than 30 we have to multiply it the sigma with a factor t, then were t is known as the student’s factor, ok. So, this t data you will get it in the standard text books.

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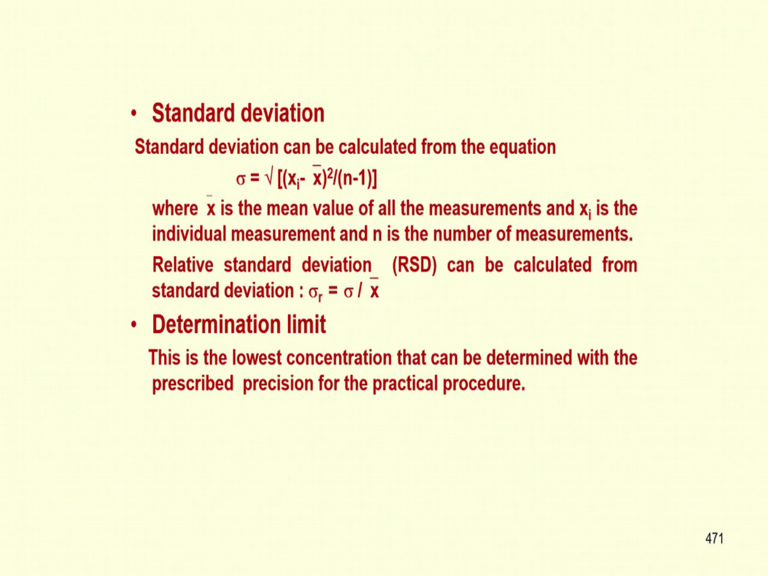

- **Standard deviation**

Standard deviation can be calculated from the equation

$$\sigma = \sqrt{[(x_i - \bar{x})^2/(n-1)]}$$

where $\bar{x}$ is the mean value of all the measurements and x_i is the individual measurement and n is the number of measurements.

Relative standard deviation (RSD) can be calculated from standard deviation : $\sigma_r = \sigma / \bar{x}$

- **Determination limit**

This is the lowest concentration that can be determined with the prescribed precision for the practical procedure.

And then we have to define now standard deviation. So, what is standard deviation? The standard deviation can be calculated by filing out the difference between the mean value and the measured values here to square it divided by the total number of experiments minus 1 and take the square root. Mathematically it can be expressed as sigma square root of x i minus x bar whole square divided by n minus 1; where x is the mean value of all the measurements and x i is the individual measurement and n is the number of measurements.

So, another factor relative standard deviation it can be calculated by sigma r is equal to sigma divided by x bar that is standard deviation divided by the mean value. And the determination limit is the final check whenever you are doing an atomic absorption spectrometry that is approximately for 0.2 normal absorbance; what is the concentration of the anlyte you need.

So, the lowest concentration if you can determine that you will find out that the lowest concentration that can be determined with the prescribed precision for the practical procedure. So, this is a very important concept. And if you know this amount of nomenclature you will be able to do most of the atomic absorption spectrometric analysis yourself without in being in dependent.

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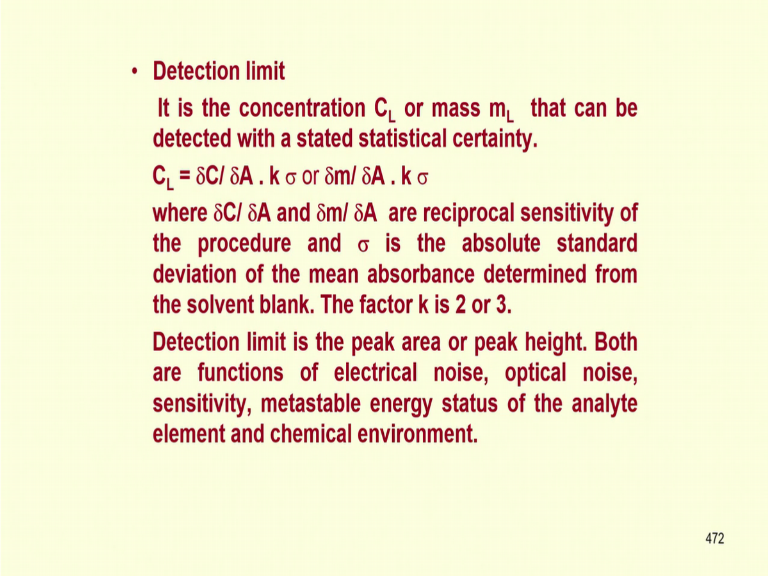

- **Detection limit**

It is the concentration C_L or mass m_L that can be detected with a stated statistical certainty.

$C_L = \delta C/ \delta A \cdot k\,\sigma$ or $\delta m/ \delta A \cdot k\,\sigma$

where $\delta C/ \delta A$ and $\delta m/ \delta A$ are reciprocal sensitivity of the procedure and σ is the absolute standard deviation of the mean absorbance determined from the solvent blank. The factor k is 2 or 3.

Detection limit is the peak area or peak height. Both are functions of electrical noise, optical noise, sensitivity, metastable energy status of the analyte element and chemical environment.

And now, we want to determine the detection limit: defined the detection limit. But there is a difference between determination limit and detection limit. So, detection limit is the concentration C L or mass m L that can be detected with a stated statistical certainty. So, C L is given by delta C by delta A multiplied by k sigma or delta M by delta A multiplied by k into sigma where delta C by delta A and delta M by delta A are the reciprocal sensitivity of the procedure and sigma is the absolute standard deviation, of the mean absorbance determined from the solvent blank. Now the factor k is usually 2 or 3; you can choose either one and state here detection limit whenever you want to develop a method or report it in the journal.

So, detection limit is the peak area you can determine find out the detection limit either by the peak area or peak height, both are functions of the electrical noise, optical noise, sensitivity, metastable energy status of the analyte and chemical environment. So, each method has got a detection limit. So, it is not the standard theoretical detection limit that can be obtained using very pure solutions: that is not the detection limit.

You can define detection limit for the standard then it will work as standard detection limit. That is use for measuring the atomic absorption to find out whether the instrument is in optimum working condition or not.

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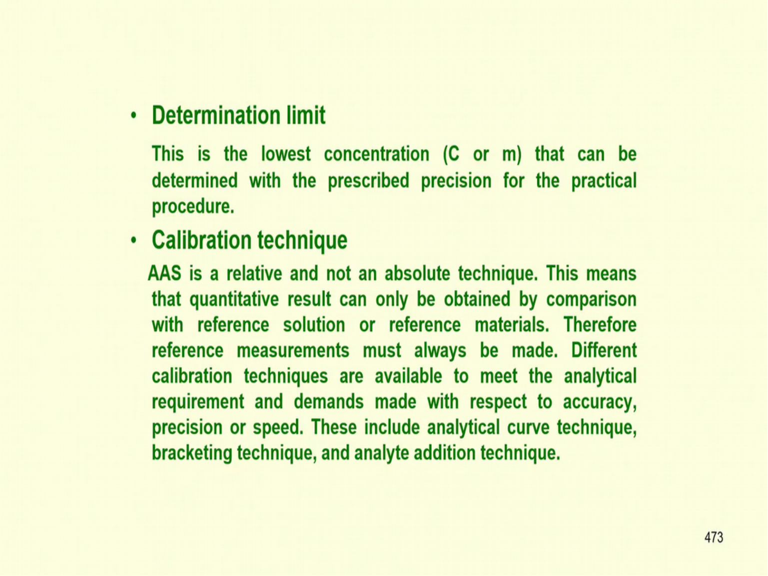

- **Determination limit**

  This is the lowest concentration (C or m) that can be determined with the prescribed precision for the practical procedure.

- **Calibration technique**

  AAS is a relative and not an absolute technique. This means that quantitative result can only be obtained by comparison with reference solution or reference materials. Therefore reference measurements must always be made. Different calibration techniques are available to meet the analytical requirement and demands made with respect to accuracy, precision or speed. These include analytical curve technique, bracketing technique, and analyte addition technique.

Determination limit is the concentration that can be determined with the prescribed precision for the practical procedure. So, there is not much ambiguity in that. And then now we will discuss about the a little bit about calibration technique. So, AAS as I have been telling you; AAS is a relative technique and not an absolute technique. This means that quantitative result can only be obtained by comparison with standard solutions or reference solutions or reference materials. Whenever you want to determine any particular element in a matrix lot of people, you do not know what is the standard reference material.

So, there are international agencies which will analyze a given sample in a matrix by different methods, by different laboratories, by different people in different countries, collate the data and give you a near true value of the substance. That is known as reference material. A standard reference material is available for sale in the market, we can buy that and whenever you want to analyze any unknown sample first you should be doing the standard reference material. And see how much you are getting, whether you are getting the analysis in the range prescribed in the standard reference material.

So, it is important for you to buy standard materials references. Now what is the standard reference material? If you look at the literature or data bases you will find that there is a standard reference materials for sea-water analysis, and then it will be for alloy, it will be for oil, metal in oil, and then there will be metal in oil for atomic absorptions especially for wear metals. Similarly, there are number of standard reference materials available for plant issues, etcetera. And these things can be bought depending upon your requirement. Even coal and other things cement there are lot of standard reference materials available which are marketed by the company's manufacturing atomic absorption or by the company's associated with the manufacture of standard reference materials.

So, we coming back to these different calibration techniques are available to meet the standard reference analytical requirement and with the demands made with respect to accuracy precision or speed. These include analytical curve technique, bracketing technique, and analyte addition technique. This I had taught you when I was doing a course on spectrophotometry. You can refer to that and get more details about the calibration.

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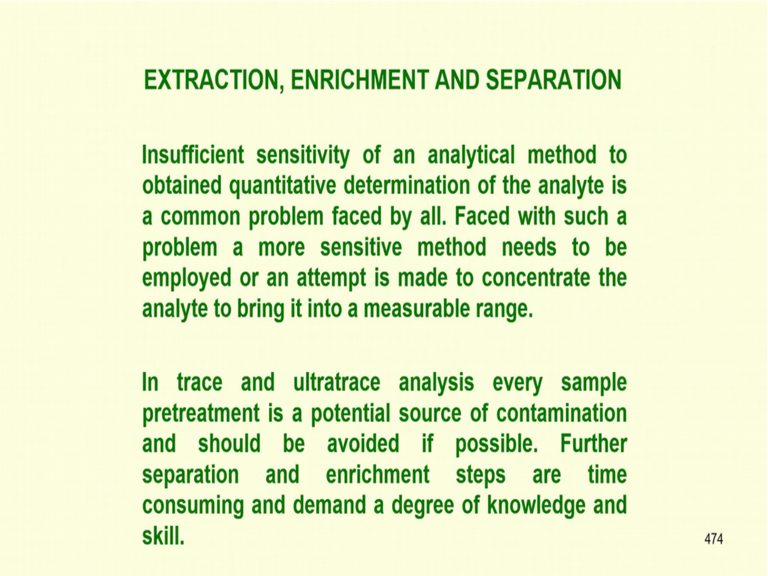

EXTRACTION, ENRICHMENT AND SEPARATION

Insufficient sensitivity of an analytical method to obtained quantitative determination of the analyte is a common problem faced by all. Faced with such a problem a more sensitive method needs to be employed or an attempt is made to concentrate the analyte to bring it into a measurable range.

In trace and ultratrace analysis every sample pretreatment is a potential source of contamination and should be avoided if possible. Further separation and enrichment steps are time consuming and demand a degree of knowledge and skill.

So, basically what we want to talk about the calibration is you plot your absorbance versus concentration curve and then determine your unknown also. Refer the unknown absorbance data to the concentration. Then you can also do single element: one standard and one your sample try to co relate there can be a bracketing technique: that means two known concentrations here to make sure that your analyte is within the absorbance of the two known concentration standard reference. So, like that there are different ways of doing the calibration and completing the analysis.

Now that completes about the nomenclature, I want to discuss with you for about 10 minutes about the extraction, enrichment and separation, because this is part of the atomic absorption analysis. Basically nobody wants to determine at a metals in standard solutions. The application of science and technology is always whenever there is a sample to be analyzed it will be either in matrix or sometimes in very high purity materials you may want to determine the impurities. So, the analyte element most of the time it is in parts per million or parts per billion or parts per trillion level, unless it is end over.

Now, atomic absorption always concentrates on ppb ppm and parts per trillion levels. So, there is the problem of analytical method is how low you can go for the determination of an ailment in analytical method. So, basically it is the common problem faced by all analytical scientist about the insufficient sensitivity. The insufficient sensitivity is basically a problem of the analytical method that needs to be employed or an attempt is made to concentrate the analyte. Whenever the sample is in very low quantities you will not be able to get a signal. Then what are the other ways for us to complete the analysis? I will have to concentrate it, that is known as enrichment.

So, in trace one is the enrichment and second is the analysis one as to also treat the sample to bring it into solution. So, in trace and ultra trace analysis every sample must be treated to dissolve it a bring it into solution. Now whenever we want to work on parts per million or parts per billion level there is always the problem of contamination. This contamination we have to be very very careful it may come from your hands, it may come from your shirt, it may contamination can happen from your puppets Burnett’s etcetera if you do not clean them there will be contamination. Sometimes there may be a contamination from an unknown source during transport or during sample collection everywhere.

So, each and every step in a chemical analysis is a potential source of contamination. So, one has to be extremely careful whenever we want to separate a sample before analysis-whenever we want to enrich a sample before analysis. And this requires a little degree of knowledge and skill. So, that is the training we normally impart for all the chemists working in parts per billion ultras and ultra trace analysis. We teach them how to reduce the kind of errors from contamination.

So, coming back to this what are the ways of enriching: one is extraction enrichment and separation.

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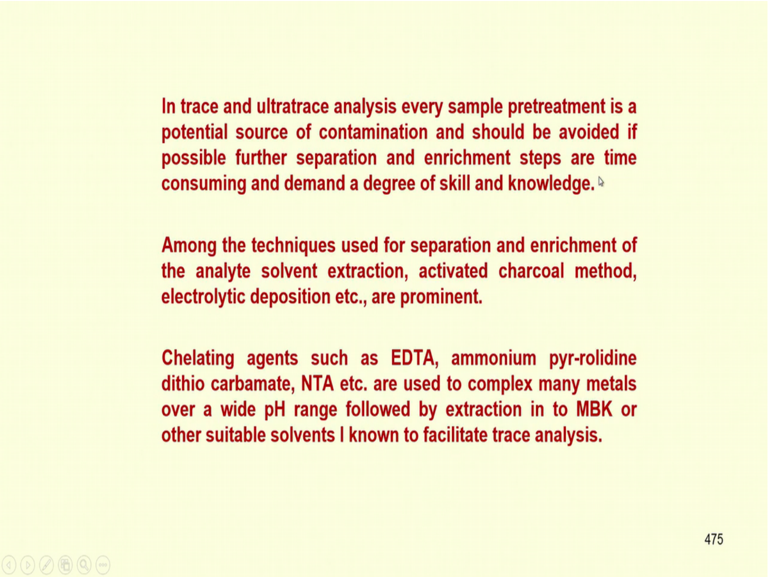

In trace and ultratrace analysis every sample pretreatment is a potential source of contamination and should be avoided if possible further separation and enrichment steps are time consuming and demand a degree of skill and knowledge.

Among the techniques used for separation and enrichment of the analyte solvent extraction, activated charcoal method, electrolytic deposition etc., are prominent.

Chelating agents such as EDTA, ammonium pyr-rolidine dithio carbamate, NTA etc. are used to complex many metals over a wide pH range followed by extraction in to MBK or other suitable solvents I known to facilitate trace analysis.

So, there are certain methods which are normally used. The techniques used for separation and enrichment are the solvent extraction, activated charcoal method, electrolytic deposition, and several other related techniques are usually employed. And sometimes we want to extract the sample using EDTA, though we complex them, ammonium, pyr-olidine, dithio carbamate, is another chemical which complexes with several metals in trace elements. Nitrilotriacetic acid is another one.

And these things are used to complex many metals over a wide pH range followed by extraction into MIBK or other suitable solvents known in the trace analysis, ok.

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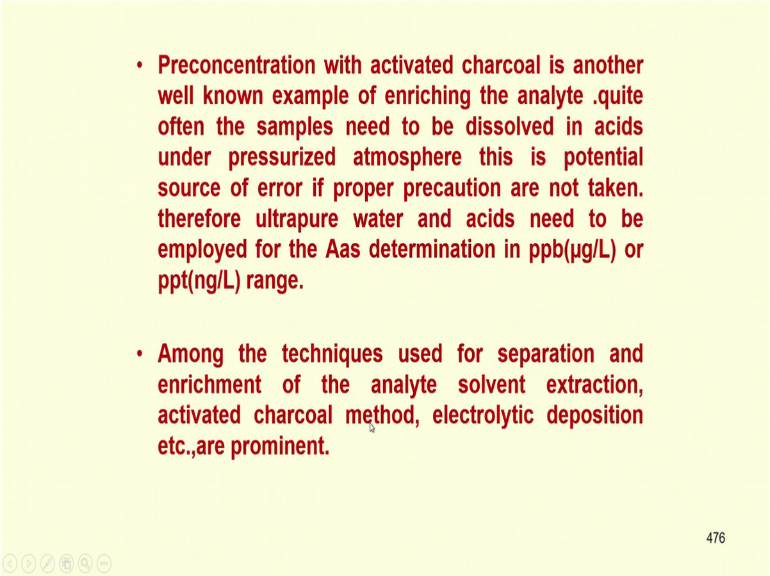

- Preconcentration with activated charcoal is another well known example of enriching the analyte .quite often the samples need to be dissolved in acids under pressurized atmosphere this is potential source of error if proper precaution are not taken. therefore ultrapure water and acids need to be employed for the Aas determination in ppb(µg/L) or ppt(ng/L) range.
- Among the techniques used for separation and enrichment of the analyte solvent extraction, activated charcoal method, electrolytic deposition etc.,are prominent.

So, pre concentration with activated charcoal is another well known example of enriching the analyte, quite often the samples need to be dissolved in acids. And then if take all the precautions, the analysis will be proper otherwise there will be some sort of contamination that is expected. And among the techniques used for separation and enrichment of the analyte solvent extraction activated charcoal method electrolytic deposition are more prominent.

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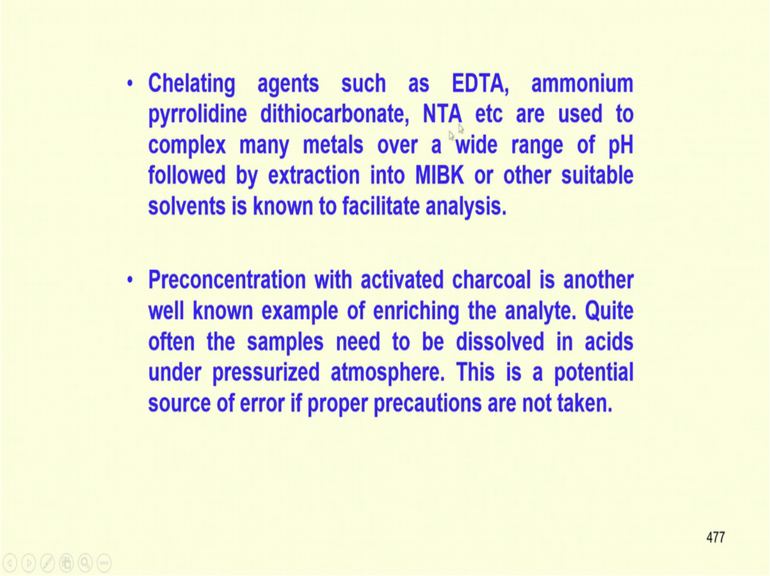

- Chelating agents such as EDTA, ammonium pyrrolidine dithiocarbonate, NTA etc are used to complex many metals over a wide range of pH followed by extraction into MIBK or other suitable solvents is known to facilitate analysis.
- Preconcentration with activated charcoal is another well known example of enriching the analyte. Quite often the samples need to be dissolved in acids under pressurized atmosphere. This is a potential source of error if proper precautions are not taken.

And chelating agents EDTA, ammonium, NTA are used, pre concentration is another method.

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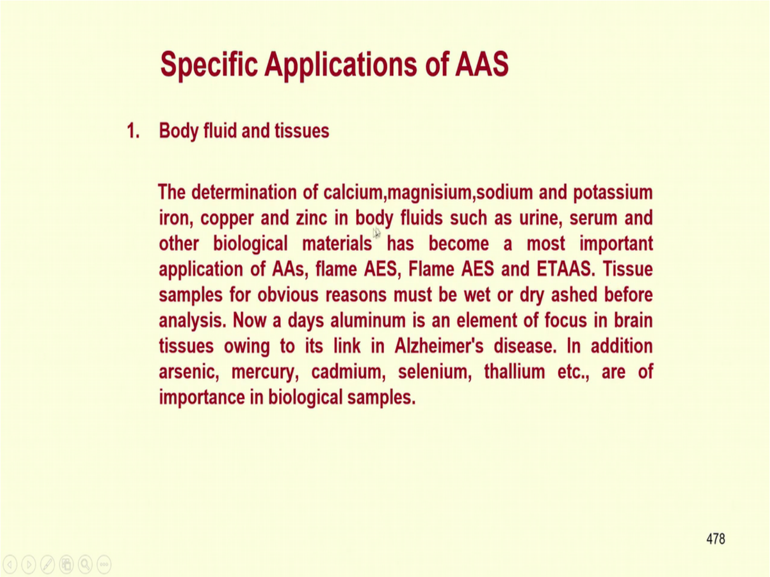

Specific Applications of AAS

1. Body fluid and tissues

The determination of calcium,magnisium,sodium and potassium iron, copper and zinc in body fluids such as urine, serum and other biological materials has become a most important application of AAs, flame AES, Flame AES and ETAAS. Tissue samples for obvious reasons must be wet or dry ashed before analysis. Now a days aluminum is an element of focus in brain tissues owing to its link in Alzheimer's disease. In addition arsenic, mercury, cadmium, selenium, thallium etc., are of importance in biological samples.

And then specific applications now I want to discuss with you that is- the determination of elements in various areas. One is body fluid, in most of the time I want you to understand that the atomic absorption method is used for the elemental analysis; 99 present of the time. So, wherever you find metals it will be required for analysis. So, in body fluids, issues, kidneys, brain, blood, hair so many not only in humans, but also in plant issues and animal tissues etcetera we want to determine many elements. And agree cultural scientist would like to determine many aliments in the plants, routs, leaves etcetera. And the urine serum and other biological materials, the atomic absorption is the method for the determination of the elements.

So, tissues samples for obvious reasons must be wet or dry ashed before analysis. Nowadays aluminum is an element of focus in brain because of Alzheimer’s disease. In addition arsenic, mercury, cadmium, selenium, thallium, etcetera are of importance in the biological samples.

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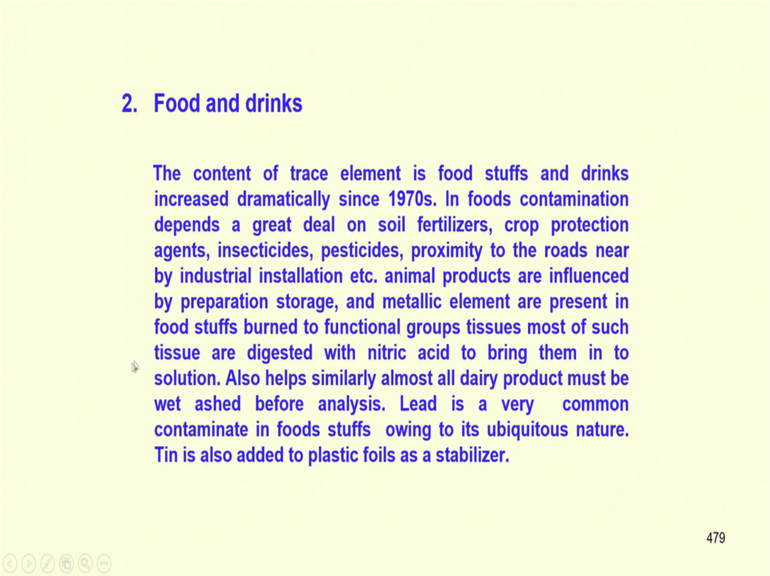

2. Food and drinks

The content of trace element is food stuffs and drinks increased dramatically since 1970s. In foods contamination depends a great deal on soil fertilizers, crop protection agents, insecticides, pesticides, proximity to the roads near by industrial installation etc. animal products are influenced by preparation storage, and metallic element are present in food stuffs burned to functional groups tissues most of such tissue are digested with nitric acid to bring them in to solution. Also helps similarly almost all dairy product must be wet ashed before analysis. Lead is a very common contaminate in foods stuffs owing to its ubiquitous nature. Tin is also added to plastic foils as a stabilizer.

So, second stage is the second area where maximum amount of atomic absorption in analysis is being done is food and drinks. You know there so many foods which we eat: there may contaminate quite often, whenever you read news paper you will see that food poisoning is one of the main causes in the people’s health. If it is in large kill lot of people fall sick, but if it is in ppm level many elements need to be determined. Especially the elements like lead, selenium, mercury such elements, arsenic, fluoride many such elements are usually in the required to be determined in parts per million or parts per billion level.

So, the content of trace element in the food stuffs and drinks increased dramatically in the 70s. Contamination depends a great deal on the soil fertilizers, crop protection agents, insecticides, pesticides all these things can be contaminated with metals, ok. Animal products are there and the concentrations are influenced by the preparation storage, and metallic elements are present in the food stuffs. So, it helps similarly almost all dairy products like milk, cheese, curds, butter, etcetera, chocolates.

A very important concept for making them acceptable to all human beings is lead. Lead has to be absent; of course it is a little difficult because it has become ubiquitous in nature. And tin is also added as plastic foils which are used for making the packing. So, the requirement of metal analysis in food and drinks is a very important concept.

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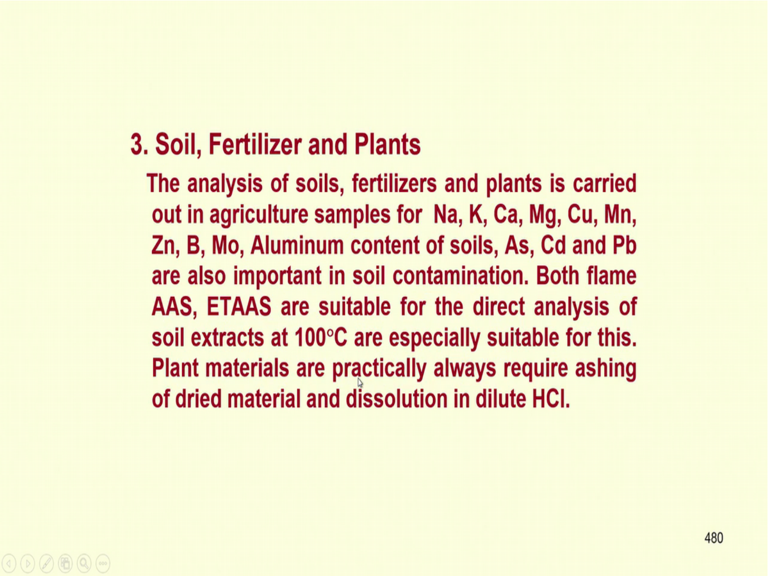

3. Soil, Fertilizer and Plants

The analysis of soils, fertilizers and plants is carried out in agriculture samples for Na, K, Ca, Mg, Cu, Mn, Zn, B, Mo, Aluminum content of soils, As, Cd and Pb are also important in soil contamination. Both flame AAS, ETAAS are suitable for the direct analysis of soil extracts at 100°C are especially suitable for this. Plant materials are practically always require ashing of dried material and dissolution in dilute HCl.

Third is soil, fertilizer and plants. The analysis of soils, fertilizers and plants is carried out in agriculture samples for sodium, potassium, calcium, magnesium, copper, manganese; you name think of the elements the analysis is required, zinc, mercury, boron, many of them are micro nutrients.

So, it arsenic cadmium leads are pollutants. So, 90 percent of the elements that we come across in day to day foods are in the agriculture either as micronutrients or as pollutants or carcinogenic hazardous elements. So, both flame and ETAAS- Electrothermal Atomic Absorptions are suitable for direct analyses of the soil extracts at 100 degree centigrade are especially suitable for plant materials.

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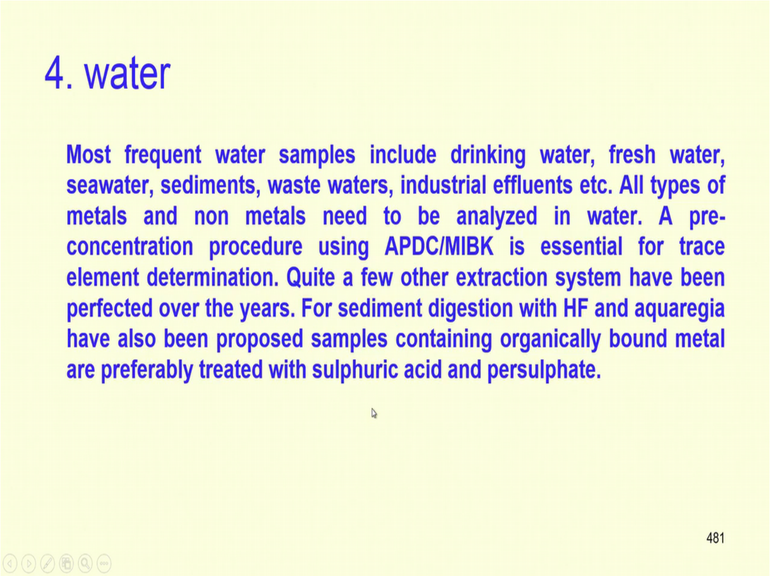

4. water

Most frequent water samples include drinking water, fresh water, seawater, sediments, waste waters, industrial effluents etc. All types of metals and non metals need to be analyzed in water. A pre-concentration procedure using APDC/MIBK is essential for trace element determination. Quite a few other extraction system have been perfected over the years. For sediment digestion with HF and aquaregia have also been proposed samples containing organically bound metal are preferably treated with sulphuric acid and persulphate.

So, usually they require dissolution in the hydrochloric acid because most of the plants are easy to analyze by dissolving in it seal.

And the next largest area of interest is water: drinking water all over the world very important. Then there are fresh water available; you may like to do the quality control for fresh water, sea water, sediments waste water, industrial effluents name it see what are lot of people want to analyze. So, all types of metals and non-metals are need to be analyzed in water.

So, a preconcentration procedure using APDC or MIBK is essential for trace elements determination. So, quite a few elements need extraction and enrichment. So, one has to be very careful when you want to determine the organically bound metals, because they are not usually determines straight away because they will give the flame a typical color. So, you may think that- oh it is not there, but definitely it will be there.

So, it is important for us to oxidize most of the organic compounds in the samples by using sulphuric acid and persulphate. So, detail methods are available in atomic absorption books and cook book also, sometimes teach you about the water analysis.

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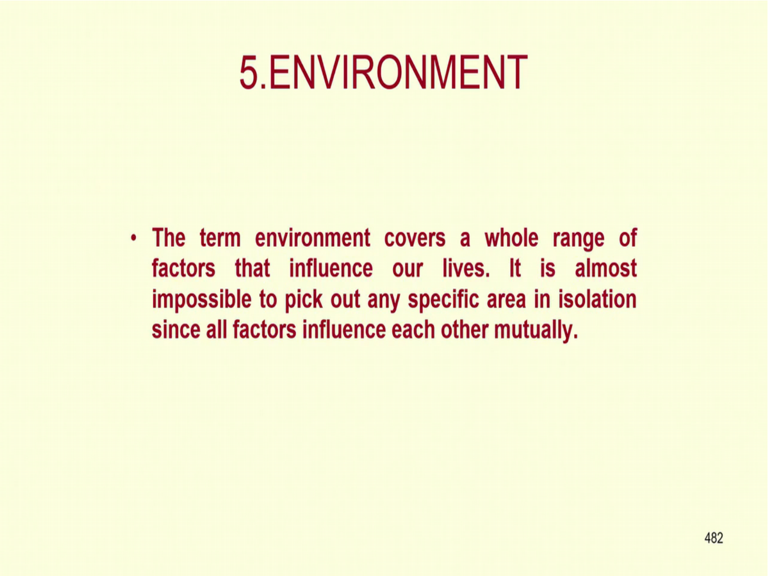

5.ENVIRONMENT

- The term environment 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.

So, next largest area of application is environment. So, the term environment 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.

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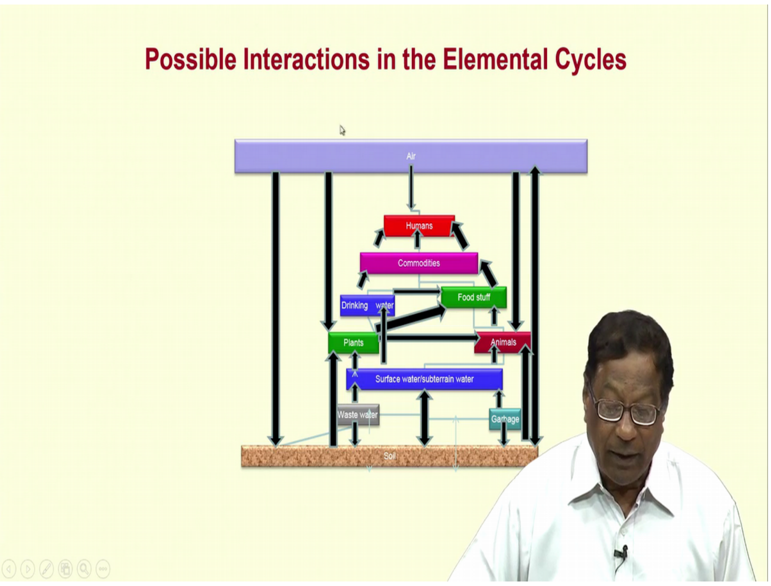

Possible Interactions in the Elemental Cycles

You may see this figure: in the figure what I have drawn is this is air, this is soil at the bottom, and then this is air, this is soil, and then in between are humans, commodities, drinking water, food stuff, plants, animals, surface water, subterranean water, waste water, and garbage.

So, there is an interaction at almost all levels between the different contributors. So, the importance of atomic absorption as a prefer technique for a element analysis in the environment cannot be over emphasized. It is a must if you want to determine the elements in the environment.

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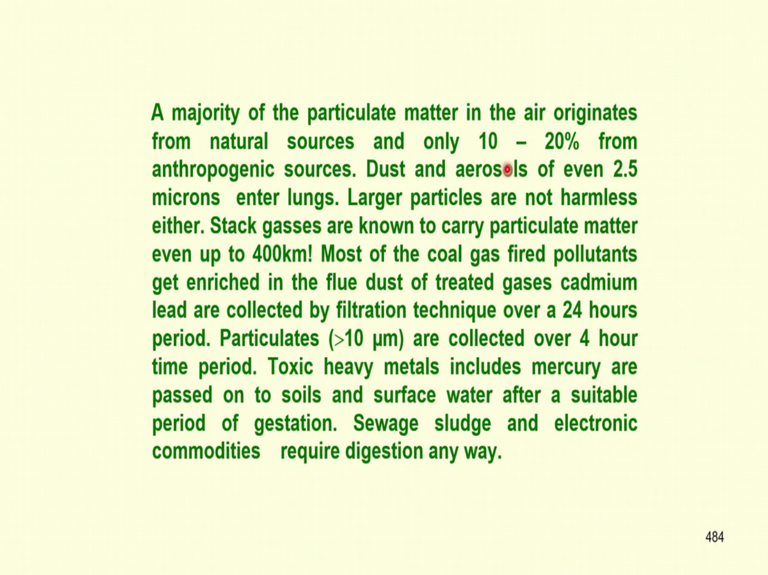

A majority of the particulate matter in the air originates from natural sources and only 10 – 20% from anthropogenic sources. Dust and aerosols of even 2.5 microns enter lungs. Larger particles are not harmless either. Stack gasses are known to carry particulate matter even up to 400km! Most of the coal gas fired pollutants get enriched in the flue dust of treated gases cadmium lead are collected by filtration technique over a 24 hours period. Particulates (>10 μm) are collected over 4 hour time period. Toxic heavy metals includes mercury are passed on to soils and surface water after a suitable period of gestation. Sewage sludge and electronic commodities require digestion any way.

So, a majority of the particulate matter in the air originates from natural sources and only 10 to 20 percent are from anthropogenic sources. Dust aerosols 2.5 microns they enter the lungs larger particles are not harmless either. So, stack gases are known to carry particulate matter up to 400 kilo meters. And most of the coal gas fired pollutants get enriched in the flue dust of the treated gases, and cadmium and lead are normally collected by filtration techniques over a 24 hours period.

We like to collect the particulates over 4 hour period, time period if the pollution is heavy otherwise you can go for 24 hour sample collection. So, normally heavy metals including mercury are passed on to soils and surface water after a suitable period of gestation, sewage sludge, electronic commodities, etcetera they also require digestion any way.

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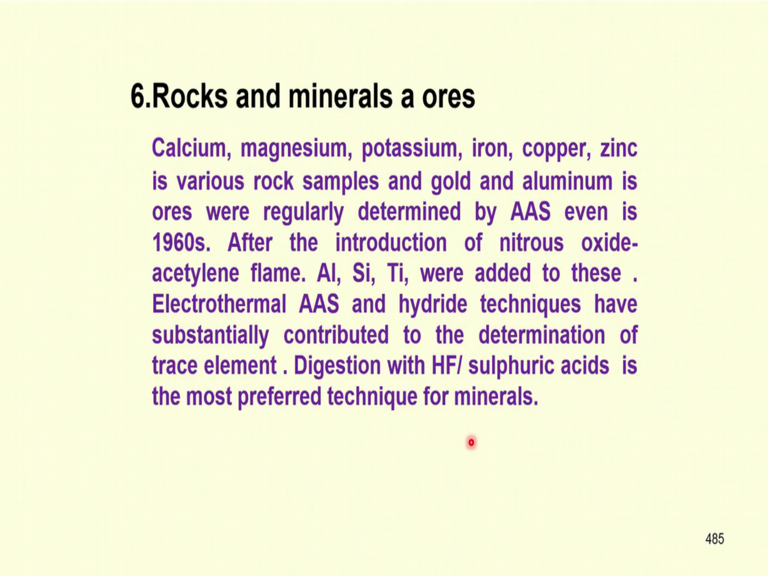

6.Rocks and minerals a ores

Calcium, magnesium, potassium, iron, copper, zinc is various rock samples and gold and aluminum is ores were regularly determined by AAS even is 1960s. After the introduction of nitrous oxide-acetylene flame. Al, Si, Ti, were added to these . Electrothermal AAS and hydride techniques have substantially contributed to the determination of trace element . Digestion with HF/ sulphuric acids is the most preferred technique for minerals.

So, next comes this rocks and minerals. Most of the rocks, ores minerals need to be analyzed because we want the metals for our day to day life; nearly 53 elements we come across in our day to day life. And especially in terms of whenever we are using computers etcetera, but even otherwise we are using lot of metals in our day to day life.

And calcium, magnesium, potassium, iron, copper, zinc, etcetera need to be analyzed in rocks. And whenever you want to analyze the metals to consider metal manufacture from the ores atomic absorption is a must. And both flame and electrothermal atomic absorption spectrometry are used for the determination of rocks. Usually digestion with HF and sulphuric acid is the most preferred technique for minerals, ok.

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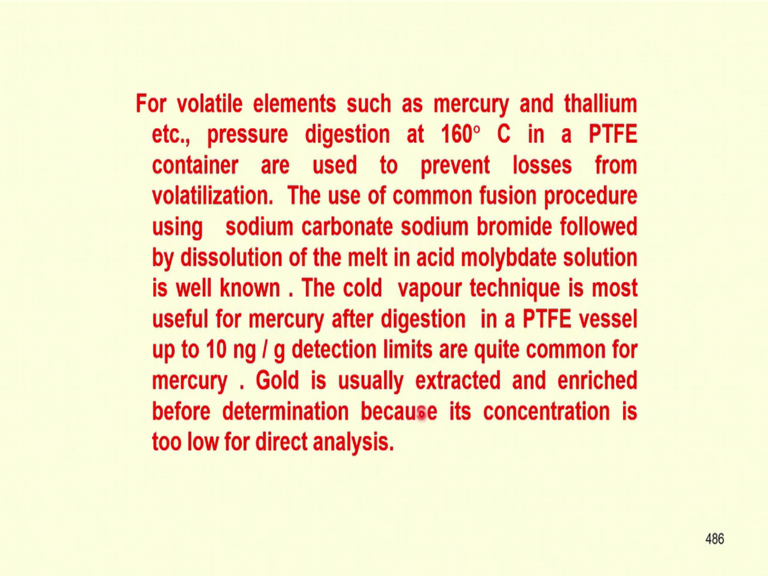
For volatile elements such as mercury and thallium etc., pressure digestion at 160° C in a PTFE container are used to prevent losses from volatilization. The use of common fusion procedure using sodium carbonate sodium bromide followed by dissolution of the melt in acid molybdate solution is well known . The cold vapour technique is most useful for mercury after digestion in a PTFE vessel up to 10 ng / g detection limits are quite common for mercury . Gold is usually extracted and enriched before determination because its concentration is too low for direct analysis.

For volatile elements, we need digestion around 160 degree centigrade. So, do not go more than this. So, use of common fusion procedures is a very recommended procedure for sodium carbonate and sodium bromide etcetera followed by dissolution of the melt in the acid molybdate solution. That is a very well known geological technique.

Cold vapour technique definitely useful for mercury and we use that in a PTFE vessel up to Poly Tetra Fluoro Ethylene that is Teflon- in a Teflon vessel we have to sail it dissolve it and then dilute it, fire at in the atomic absorption to get up to 10 nanogram detection limits are easily obtained and gold also is usually extracted and enriched before determination because its concentration is too low for direct analysis.

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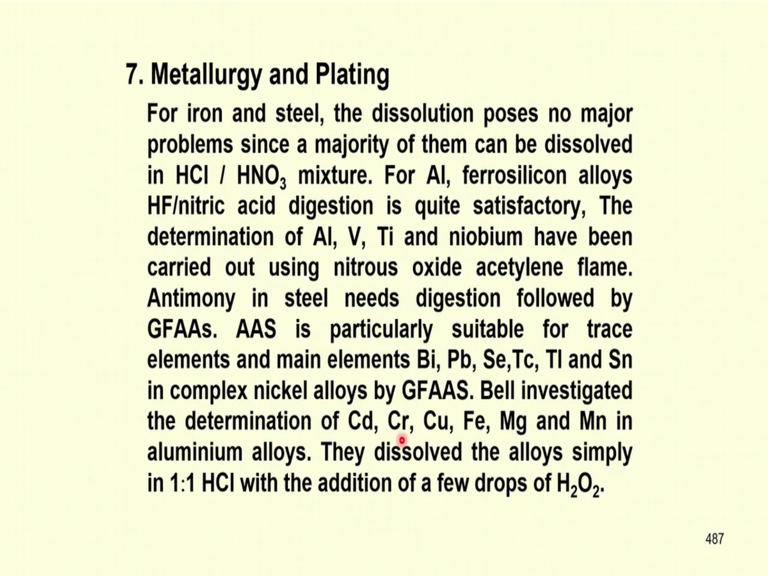

7. Metallurgy and Plating

For iron and steel, the dissolution poses no major problems since a majority of them can be dissolved in HCl / HNO_3 mixture. For Al, ferrosilicon alloys HF/nitric acid digestion is quite satisfactory, The determination of Al, V, Ti and niobium have been carried out using nitrous oxide acetylene flame. Antimony in steel needs digestion followed by GFAAs. AAS is particularly suitable for trace elements and main elements Bi, Pb, Se,Tc, Tl and Sn in complex nickel alloys by GFAAS. Bell investigated the determination of Cd, Cr, Cu, Fe, Mg and Mn in aluminium alloys. They dissolved the alloys simply in 1:1 HCl with the addition of a few drops of H_2O_2.

So, in metallurgy and plating most of the samples need to be dissolved. For metallurgical samples we prefer HCL- hydrochloric acid and or nitric acid. For aluminum ferrosillicn alloys etcetera determination of aluminum, titanium, vanadium, they have been carried out using nitrous oxide flame. Most of the things are refactoring; for most of the refractory things nitrous oxide, but almost every metal requires digestion.

So, main elements like lead, bismuth, selenium, tellurium, thallium, tin, etcetera can be determined by graphite furnace AAS. And Doctor Bell investigated the determination of cadmium chromium etcetera in aluminum alloys. That means, I am just giving you these kinds of data to introduce you to the complications of the atomic absorption analysis before you get into the field.

So, one has to be aware of how to digest a given sample.

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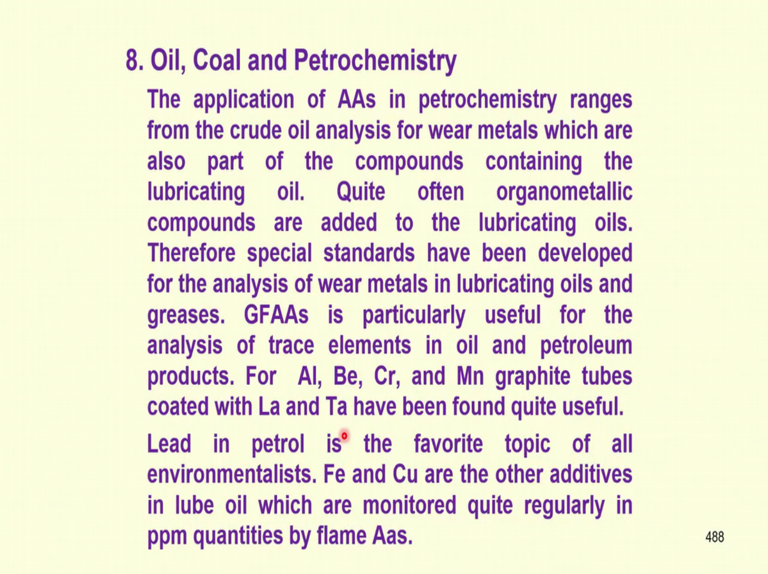

8. Oil, Coal and Petrochemistry

The application of AAs in petrochemistry ranges from the crude oil analysis for wear metals which are also part of the compounds containing the lubricating oil. Quite often organometallic compounds are added to the lubricating oils. Therefore special standards have been developed for the analysis of wear metals in lubricating oils and greases. GFAAs is particularly useful for the analysis of trace elements in oil and petroleum products. For Al, Be, Cr, and Mn graphite tubes coated with La and Ta have been found quite useful.

Lead in petrol is the favorite topic of all environmentalists. Fe and Cu are the other additives in lube oil which are monitored quite regularly in ppm quantities by flame Aas.

Oil, coal and petrochemistry: one of the most important areas for our day to day life. So, the requirement is crude oil analysis for wear metals, because most of the oils contained metals for lubrication. So, lubricating oils need to be analyzed for most of the wear metals and quite often organometallic compounds are added. So, you need the organic de composition of the organic substances and graphite furnace is a prefer technique for atomic absorption of wear metals.

Aluminum, beryllium, chromium, manganese, etcetera graphite tubes are coated with lanthanum and tantalums have been quite useful. But, I have not taught you about this, but I have taught you about pyrolityc coated graphite tube this thing, because that is the most common available electrothermal atomic absorption you lit aware in the market.

Led in petrol is the favorite topic of all the environmentalists. Iron and copper are the other additives in lube oil which are monitored quite regularly in ppm quantities by the flame AAS.

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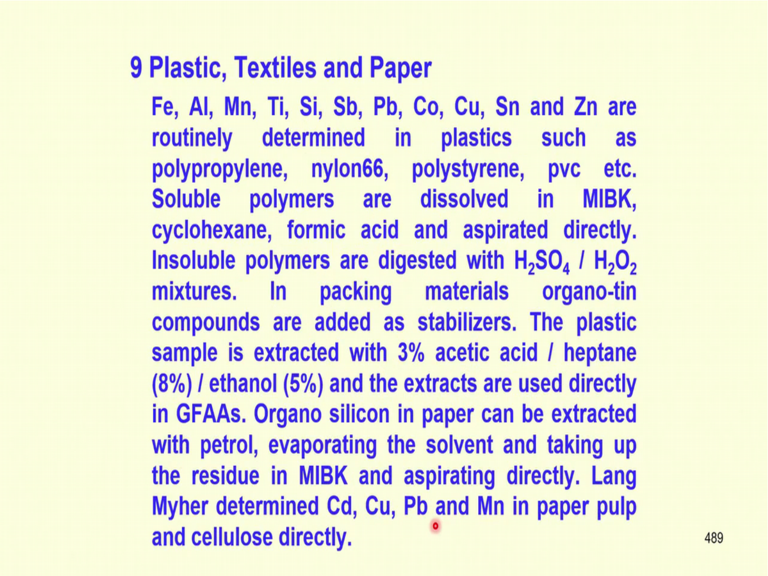

9 Plastic, Textiles and Paper

Fe, Al, Mn, Ti, Si, Sb, Pb, Co, Cu, Sn and Zn are routinely determined in plastics such as polypropylene, nylon66, polystyrene, pvc etc. Soluble polymers are dissolved in MIBK, cyclohexane, formic acid and aspirated directly. Insoluble polymers are digested with H_2SO_4 / H_2O_2 mixtures. In packing materials organo-tin compounds are added as stabilizers. The plastic sample is extracted with 3% acetic acid / heptane (8%) / ethanol (5%) and the extracts are used directly in GFAAs. Organo silicon in paper can be extracted with petrol, evaporating the solvent and taking up the residue in MIBK and aspirating directly. Lang Myher determined Cd, Cu, Pb and Mn in paper pulp and cellulose directly.

So, plastic, textiles, and paper: again another area where lot of elements like iron, aluminum, manganese, titanium, antimony, lead, cobalt, copper, tin, zinc, and many of them are analyzed in plastic such as polypropylene, nylon, polystyrene, pvc etcetera. Soluble polymers are dissolved in MIBK, formic acid cyclohexane you can use aspirate them directly because you make it a better sensitivity, because the organic compounds do burn with exothermic properties. In packing materials organo-tin compounds are assume importance, because they are added as stabilizers.

So, the plastic sample has to be extracted with about 3 percent acetic acid, 5 percent acetic acid etcetera. And these potheads have been standardized and available in the standard text books related to atomic absorption.

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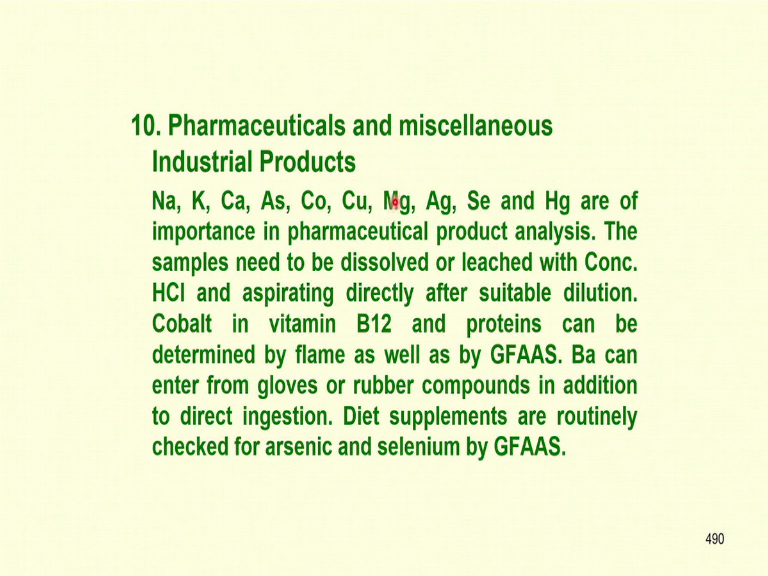

10. Pharmaceuticals and miscellaneous Industrial Products

Na, K, Ca, As, Co, Cu, Mg, Ag, Se and Hg are of importance in pharmaceutical product analysis. The samples need to be dissolved or leached with Conc. HCl and aspirating directly after suitable dilution. Cobalt in vitamin B12 and proteins can be determined by flame as well as by GFAAS. Ba can enter from gloves or rubber compounds in addition to direct ingestion. Diet supplements are routinely checked for arsenic and selenium by GFAAS.

So, pharmaceuticals and miscellaneous industrial products are there: sodium, potassium, calcium, almost every element we need to analyze them either as a pollutant or as a component. So, the dissolution can be very easily done using concentrated hydrochloric acid and aspirating directly after suitable dilution. Cobalt for example: we need to determine cobalt in vitamin B12 and proteins can be determined by flame cobalt can be determined in B12 or proteins. Barium can enter as a pollutant, barium can enter from the gloves or rubber components in addition to direct ingestion. So, direct supplements are routinely checked for arsenic and selenium.

So, this is done by graphite furnace AAS.

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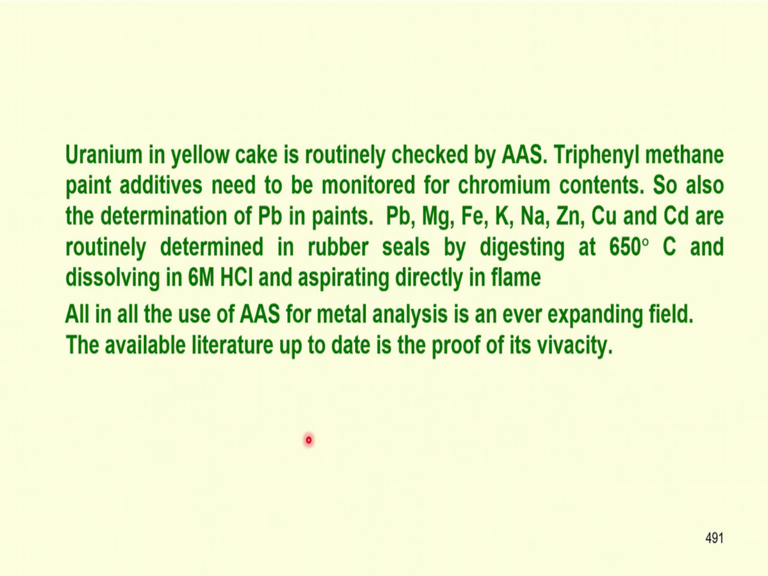

Uranium in yellow cake is routinely checked by AAS. Triphenyl methane paint additives need to be monitored for chromium contents. So also the determination of Pb in paints. Pb, Mg, Fe, K, Na, Zn, Cu and Cd are routinely determined in rubber seals by digesting at 650° C and dissolving in 6M HCl and aspirating directly in flame

All in all the use of AAS for metal analysis is an ever expanding field. The available literature up to date is the proof of its vivacity.

So, uranium in the mineral section: uranium in yellow cake is routinely checked by atomic absorption triphenyl methane paint additives need to be monitored for chromium contents so also the determination of lead. Magnesium, iron, potassium, sodium, zinc, copper, cadmium, etcetera are routinely determined in rubber seals. What we have to do is we have to digest it around 650 degrees and dissolving it in 6 molar HCL and aspirating directly in the flame. So, all in all the use of atomic absorption for metal analysis is an ever expanding field and the available literature up to date is the proof of its soya acid. The open the literature, we will see even last month somebody has determined they have published a paper on atomic absorption analysis of some element or rather in some matrix or the other.

So, I am trying to give you a an overall view of the atomic absorption, spectrometry during the last 33 lectures. And I hope it will be useful for you as a technique for your course work as well as for your future carrier. I wish you all the best. Before I close I want to you to understand this periodic table where all the elements are determined using atomic absorption.

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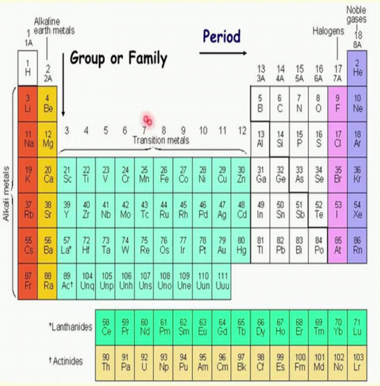
Periodic Table



1 1A	2 2A	3	4	5	6	7	8	9	10	11	12	13 3A	14 4A	15 5A	16 6A	17 7A	18 8A
1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La*	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac†	104 Unq	105 Unp	106 Unh	107 Uns	108 Uno	109 Une	110 Uun	111 Uuu							

*Lanthanides	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
†Actinides	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

On the left side there is sodium potassium alkali alkaline are metals, here are transition metals, and then here are the boron metalloids can be determined, these things need to be determined, this halogens and noble gases usually not, but lanthanides and actinides are determined usually by atomic absorption.

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So, this is the atomic absorption spectrometry. I want to close my lecture with the introduction of this modern instrument, recently introduced into the market. I will not tell you the details, but you can look it up.

And I wish you all a good carrier in atomic absorptions spectrometry. If you have to use it, I am sure you will find the course very useful and I wish you all the best. You need any more information you can contact me.

Thank you very much, all the best.