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Lecture No. #16

Toxicology and heavy metals in the environment, time and again, I have been talking about toxicology, I have been talking about environment, and the pollution that the metals have caused. In the previous lecture, we had seen, which are the nine notorious heavy metals.

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And today, we will proceed with some more of the information that is related to heavy metal contamination.

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Environmental toxicology - it is a very important topic which an analyst must know and understand, in order to be able to be an efficient analyzer for metal determination. Two important sources of pollutants affecting the environment are: discharge of industrial pollutants and automobiles. These are two major issues from where the pollution actually comes in. One is that the industrial affluent sometimes is just left untreated and it is run into the soil or into the water body, and the other one is from the automobile. Liver and lung diseases resulting from vehicular pollution affect people leaving in the urban areas. Modern agricultural practices lead to the saturation of soil and water with very dangerous chemicals, such as pesticides and fertilizers.

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What are the environmental toxins?

Heavy metals, pesticides, chlorinated hydrocarbon or PCBs which I have already covered (polychlorinated biphenyls), poly-aromatic cyclic hydro carbons, plastics, many industrial chemicals which lead to the environmental degradation. So, you see, these are the broad scale of environmental pollutants and there would be many more, but I have just listed a broad list of heavy metals, pesticides, chlorinated hydrocarbons, poly-aromatic hydrocarbons, plastics and many other industrial chemicals.

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What does environmental degradation lead to?

Now, let us understand this whole process. Health condition of individuals is affected. Genetic and harmonic hormonal changes caused by the toxins take place. Harmful effects of toxin on immune system and nervous system takes place. Cardiac, respiratory and other disorders because of indoor and outdoor pollution are the main reasons that cause environmental degradation.

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Metals as pollutants - even in the previous lecture, we had seen that, the 9 notorious heavy metals were the main toxins or the main pollutants, but there are other metals also, and any metal which is present in larger quantity can exceed the limit and be in the category of a toxin.

Heavy metals such as Iron, Manganese, Zinc, Chromium, Copper, Nickel, Arsenic, Lead, Mercury and cadmium are the nine ones, of which, the last three have no biological significance or beneficial use, and are extremely toxic. So, among the extremely toxic metals are: Lead, Mercury, and Cadmium. Metals are not biodegradable. Air, soil, and water have varying amounts of toxic heavy metals.

So, you see that they do not biodegrade in the system, whether it is environmental system or biological system, and they are present in air, soil and water. More susceptible are regions where inorganic chemical industries using metals are concentrated, and the most dangerous area where one would find metal toxicity is the area where there are industries which are related to in organic compounds.

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Contributors to metal pollution Tanneries Mining belts and metal smelters Textile and dyeing houses Steel cities Collieries Sites of Coal based thermal power houses Ganga delta-acts as sinks for a variety of metals received through sewage, industrial effluents and accidental spills.

Contributors to metal pollution – now, which are the industries that are related to, or, are the cause for creating metal pollution? Tanneries, mining belts and metal smelters, textile and dyeing houses, steel cities, collieries, sites of coal based thermal power houses. Ganga delta-acts as a sink for a variety of metals received through sewage, industrial effluents and accidental spills.

So, I gave you a list of huge list of industries. Because in industries, at some step of the processing, some material is being used, and unfortunately, in our country, the rules have not been laid down by the Government in a very stringent manner; as a result, not every industry is treating their affluent. And the untreated affluent, when it is run into the Ganges or any other nearby river, it actually causes a lot of pollution in the water that has been flowing in that river, and what? Even the sewage water, industrial affluent, and sometimes the accidents fill, add on to the pollution problem.

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In destructible poison - even a small concentration is capable of disrupting the body's normal metabolic function. Now, what happens? When the metal enters our body or any other pollutant, for that matter, it could be PCB or it could be pesticide or it could be poly aromatic hydrocarbon, when they enter the biological system, they do not find a way to get out of the biological system. As a result, they keep on bio accumulating in the system, and as a result, it becomes is as a toxin in a particular organ. Heavy metals are in the air we breathe, the food we eat, and the water we drink.

So, can we avoid heavy metals? We really cannot avoid because we need to breathe, we need to eat and we need to drink water. Heavy metal pollution can remain dormant for a very long time and then surface with full force. What happens? When a small amount, trace amount of toxin gets into our body, it does not show any adverse effect or any disease that appears to be appears to be appearing but, over a period of time, due to bio accumulation, this gets accumulated and reaches a threshold limit, where it starts interfering with the metabolic activity of the cell and that is where it starts creating or becomes a cause of a disease.

Analysis of heavy metal, thus becomes very impetrative because in order to know whether it has reached the threshold level, what is the kind of levels of each of these heavy metals in environmental sample.

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It is important to have a very distinct protocol of testing. Analysis of heavy metals and trace metals can be done very efficiently by means of a very efficient and full proof method, which is called Atomic Absorption Spectrometer or AAS and a very similar kind of another instrument which is called Inductively Coupled Plasma spectrometer ICP. Sample preparation is an important part of the analysis. Time and again, I have been emphasizing on the fact that sample preparation is very important and very crucial. Acid digestion by oxidizing acids is the routine procedure. However, stubborn samples are digested in specialized microwave digesters with combination of acids or by first ashing and then acid digestion.

So, we have seen in the previous lectures, how these focused microwave digesters are required, to sometimes digest the stubborn samples of the metals that need to be acid digested. Sometimes, a programmed procedure has to be applied where, a variety of acids are added one by one, in order to completely digest the sample.

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Atomic absorption - in atomic absorption, the flamed functions to convert the sample aerosol into atomic vapor which can then absorb light from the primary light source which is a Hollow cathode lamp (HDL) or Electrodeless discharge lamp (EDL).

In this, what happens? Sample is first dissolved. The metal is first converted into metal ion and this is now in the solution form. The solution is then converted into an aerosol. You must have seen these spraying machines; they convert the liquid into an aerosol; so, similar type of aerosol is produced through a nozzle, and then this aerosol is then passed through a flame. In the flame, it takes that acts as a primary source of energy, and that is then converted into the metal zero state; from the ionic state, it becomes metal vapour.

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Other Flame Mode The nitrous oxide –acetylene flame has a maximum temperature of about 2900 degree and is mainly used for the elements which form refractory oxides. It is also used to overcome chemical interferences that may be present in flames at lower temperature.

Air acetylene flame is preferred flame for the determination of approximately, 35 elements. The temperature of air acetylene flame is about 2300 degrees centigrade. So, you see that, at that temperature, the air acetylene flame provides the energy for the convergent of the metal ion to the metal zero state. Other flame mode - the Nitrous oxide acetylene flame has a maximum temperature of about 2900 degrees and is mainly used for the elements which form refractory oxides. Now, normally, air acetylene would be applied as a flame, but in case of certain elements where they have a tendency to form oxides in the flame, there is this nitrous oxide acetylene flame which has a further more higher temperature, as compared to the air acetylene flame, and that is particularly used for aluminum.

It is also used to overcome chemical interferences that may be present in flames at low temperature. So, sometimes, when there are chemical interferences, even that helps because Nitrous oxide acetylene flame is always at a higher temperature, and this prevents all the interferences to be withered off.

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Choice of Nitrous oxide flame is mainly for elements, as I mentioned a little while ago, for Aluminum, Boron, Barium, Molybdenum, Strontium, Silicon, and Titanium.

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Comparison of analytical techniques - if we try to see that how does an AAS vis-a-vis an ICP work, there must be some advantage in each one of them and there must be some disadvantage in each one of them. It is always a very scientific proof that no single method is the ultimate method. There has to be an edge over when there are scientific advancements; it comes from necessity point of view. Now, if we try to look at the

working of the ICP, in ICP, instead of an air acetylene flame, there is a plasma plane which is created by Argon gas. So, the Argon gas which is used is very costly, and so the speed at which the analysis can be compared. In AAS, analysis can be done only one by one, one element at a time, whereas in ICP, multi elements are analyzed.

Even the sensitivity is moderate in terms of AAS, but in the case of ICP, it is highly sensitive, and thus it is good interferences. Very few interferences are experienced while working with AAS; however, there are spectral interferences when we are doing multi element analysis in ICP. When it comes to cost, relative cost is moderate in the case of AAS, but in ICP, the cost of analysis is very high. So, one has to make a choice. As an analyzer, one has to choose which one is more sensitive, where is it required, at that point of time, the cost effectively is not taken into account. But when one has to do large number of samples, I think the answer is AAS.

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If one looks at a pictorial diagram of an AAS machine, this is a hollow cathode lamp and that provides the energy and there is a flame. There are lenses to focus the energy and it goes through the monochromator and then to the detector. And then, from the detector, it goes to the amplifier, and then, the results are read out. This is like a pictorial diagram of how, the source of light and the lenses and the flame are in conjunction in an AAS machine.

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Standard preparation – now, since both ICP AA and AAS are calibration methods, one needs to have a standard as a reference, and against that standard, how these samples will fair, whether it will be above the that grade or whether it will be below that grade; so, we need to have a scale; a standard is like a scale and against which it is measured.

Standard solutions to be prepared from stock solution purchased from certified stock standard meant for calibration. There are companies who supply standards stock solution and they are used for calibration purposes.

For example, if I have to analyze Copper or Chromium, I will buy from the company, a stock solution of 1000 PPM of Copper and Chromium separately, and use it by diluting it at the time of analysis. Alternatively, stock standards can be prepared directly from the reagent grade chemicals. However, it is not always necessary that one needs to buy the chemical all the time; one can even prepare the stock solution. Presence of dilute acid that is 0.1 percent to 1 percent in many solutions lengthens our life of standard; the standards must be preserved with a little amount of acid, so that they are stabilized.



Limitation of flame atomic absorption sensitivity - as I said, every process has its advantages as well as disadvantages. Here, we will discuss the limitations of flame AAS. Although flame AA is very rapid and precise method of analysis, where determinations of analyte concentrations in milligram per litre are done routinely, which means it is PPM. However, the need for trace metal analyses at micro gram per litre, and even sometimes, sub micro gram per litre calls for a more sensitive technique.

Now, as I said, when analysis has to be done at PPB or PPT level, AAS is not the solution. Why? because the sensitivity is only up to the PPM level and it cannot analyze trace elements. This limitation can be improved by improving sample efficiency by constraining analytes atom to the light part for a longer period of time, although some modifications have been brought about in AAS, so that trace quantities also can be analyzed; however, it is not as sensitive as ICP.

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Other techniques - that cold vapor mercury technique, specifically meant for mercury analysis, is the only metal which can exist as atom at room temperature. So, it can be measured without heating sample cell. This is a very special technique, only meant for mercury; another technique is hydride generation technique. Samples are reacted in an external system with the reducing agent, usually, sodium borohydride; gaseous reaction products are then carried to a sampling cell; the volatile hybrids are then heated in a sample cell.

Now, here, I would like to draw your attention that, these this hydride method is particularly used for arsenic and many other such transition metals, where they have a tendency of having variable oxidation state. In order to bring them to the same oxidation state and to convert them to same hydride, it is then this hydride which is very volatile and analyzed. So, the total arsenic can be analyzed from this. Arsenic 3 and arsenic 5 are all converted in to one oxidation sate's hydride, and that hydride is analyzed.

The third type of technique is graphite furnace. Instead of air acetylene furnace or instead of flamed furnace, this is a furnace; as the name suggests, it is not a flame; it is a furnace and the furnace is made out of graphite, which gives even higher temperature for the sample to be facing, this higher temperature getting volatilized. Most advanced and widely used and it is highly sensitive sampling technique.

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Trace metals in soil - how can trace metals be analyzed in soil? In soil, in salt affected soil, metal ions are accumulated in the form of soluble salts near the soil surface. Excessive concentration of metals can be associated with naturally occurring ore deposits, but more usually, are the results of human activities. Leaching of metal is favored by a high rain fall and where soils are coarse textured.

Now, I would like to draw your attention, that metals are not evenly dispersed in the soil. When there are soils which have salt, it will come to the soil surface. Sometimes, excessive concentration of metals will occur because they have been in like deposits in definite pockets, and this could be due to the dumping by the human activities, or metals can be leached to rainwater into the groundwater because there is acid rain. And due to the acidified action of the rainwater, the metals are digested, and leaching takes place and they enter the ground water.

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Trace metal poisoning - the cations of metals like Arsenic, Barium, Led and Silver, even if present in trace amounts, have toxic effects. We all know that silver is a very good anti-microbial activity substance.

The main sources of arsenic are: rodenticides, fungicides and insecticides. Barium are rodenticides, and for led poising are: paints, leaching of glazed tiles, use of lead pipes and batteries. Silver poising are from photographic laboratory waste.

You see, so, these are the sources which cause the metal poisoning. For arsenic, it can come from the poison that is created for rats or fungicides or insecticides. Barium again is a compound which is used for rat poising; that is called rodenticide. And Lead can come from paints, leaching glazed tiles, use of lead pipes, and so on, and silver poisoning can come from silver photographic laboratory waste because a lot of silver nitrate is being used there, and untreatedly it is flown into the a waste water.

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Chromium poisoning - time and again, I am talking about Chromium because it is a very very crucial poisoning and it has really caused a lot of devastation in the whole of tannery area. Chromium poisoning enters the entire environment through the natural as well as anthropogenic sources. The major anthropogenic sources of Chromium include: burning of oil and coal, pigments, oxidants, catalysts, refractory materials, Chromium steel, tanneries and fertilizers. So, you see, these are the major sources that mankind or anthropogenic causes, or sources have been created by mankind, and it has we are responsible for it because we have not taken care of the waste, and that has caused Chromium poising.

Chromium is also a component of coal, fly ash, urban dust, and industrial effluents. You will be very surprised to know that the coal that is used in thermal power creates huge amount of fly ash, and this fly ash is also a major source of Chromium poisoning. With this, we have come to an end of the main pollutants that are derived, but the story does not end there. Chromium still has a long long story and in need to dedicate some more time to Chromium.

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What is Chromium? Chromium is mined as chromite ore. Chromium compounds are widely used in industry and the valance state dramatically affects toxicity and chemical properties. Just yesterday, I was telling you that Chromium III is not toxic, if it is within the limit; however, Chromium VI species is highly toxic even in trace quantities. So, what? Does it mean that the same metal can be in oxidation state, less toxic than the other oxidation state which is highly toxic?

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Why Chromium and valence matters? Chromium metal is at 0 valence; bivalent Chromium that is chromous chloride, chromous sulphate; trivalent - the most prevalent form in the environment because of reducing condition, Chromium 4 and Chromium 5 are found as transition products. And the most notorious is the Chromium VI; it is highly reactive and because of its high oxidation state, it has a great reactivity also. These are the various oxidation states of Chromium.

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Industries that contribute to Chromium compound and its toxicity - anodizing agencies, color television picture tube manufacturing agency, Copper etching, glass working, lithography, metal plating, metal working, oil purification, photoengraving, photography, portland cement use, stainless steel grinding, textile production and welding. You will see, that these many industries apart from tanneries.

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How does the average person get exposed to? Primarily through food; about 90 percent of Chromium which we get affected with, is through food channel. Some exposure comes from drinking water. Air exposure is significant, except near the industrial sources like chromate chrome plating facilities, cooling towers, emissions from power plants and waste disposal. These are other localized areas which can cause air bond Chromium species to get into our system.

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Occupations that may involve Chromium exposure include metal plating operations; people who are working in these occupations are getting affected by Chromium VI; painters get affected by Chromium III and Chromium VI; workers involved in the maintenance and servicing of copying machines and disposal of some toner powders from the copying machines are exposed to Chromium VI.

Battery makers are exposed to Chromium VI species; candle makers, dye makers are exposed to Chromium III and Chromium VI; dye makers use Chromium VI; printers use Chromium III and Chromium VI; rubber makers use Chromium III and Chromium VI, and so, they are exposed to both the species. Cement workers are exposed to Chromium III and VI. Industrial workers near cooling towers have been exposed to a Chromium VI. So, you see that, there are varieties of occupations, where they are directly exposed to these levels.

Let me tell you, that Chromium III under the oxidizing conditions and under the air conditions are easily converted to chrome VI. So, the chrome III which is less toxic can become more toxic under the moisturous condition and under conditions where oxidations can be facilitated.

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Higher than normal levels of Chromium can from: landfill sites with Chromiumcontaining wastes; sometimes, lot of industrial dumps are put as landfills. Cement producing plants because cement contains Chromium. Industrial cooling towers that previously used Chromium as a rust inhibitor also can be a cause for high levels of Chromium. Waterways that receive industrial discharges from electroplating, leather tanning and textile industries can also be a causative for Chromium levels to be high, busy roadways because emissions from automobiles, brake lining, and catalytic converters contain Chromium. So, all these can create higher and higher levels of Chromium than the normal level of Chromium, that would normally exist in the air and water and soil.

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Now, Chromium is a deadly carcinogen or necessary element, is a debatable issue. It is both; Chromium III is necessary to maintain blood glucose level; however, Chromium VI is classified as a known carcinogen. So, you see that one of the species is our friend and the other species is an our enemy.

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Ingestion - gastric contents rapidly reduce Chromium VI to Chromium III. During this reduction process, severe erosion injury to the stomach can occur. Even small ingestions of dichromates have resulted in hemorrhagic gastroenteritis and even death. Thirteen accidental ingestions reported – seven of them to be fatal. So, you see how it reacts in our biological system.

When we ingest Chromium species by accident through food chain, what it does? It starts reacting in the body system. The chrome VI then gets reduced to chrome III, and during this reduction process, it causes injury in the stomach and hemorrhage takes place, and as many as 13 from 7 out of 13 are fatal. That causes death. So, you see how dangerous it is. It is not only a known carcinogen, but it is also death causing, by this kind of internal hemorrhage. What about effects on the skin? We also know that Chromium VI causes dermal allergy.

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It is an irritant and sensitizer. Chromium VI compound cause skin ulcers or chrome holes commonly seen in nasal septum; not only in the nasal septum, but also on the skin. When chrome VI effects or it reacts, its starts forming some kind of ulcers or blisters, and so on. May be a culprit in housewives' eczema; it can also be that if the housewives are using, it can cause eczema or dermal ulcers.

Once sensitized, mostly they stay sensitized, and Chromium VI salts are quickly absorbed. So, that that is even worse, as compared to the reactivity, solubility, and the absorption, chrome VI has all the notorious properties.

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How does it affect the lung? It can induce asthma. Chrome VI is known to cause lung cancer. There have been several medical studies, and it has been proven time and again that chrome VI is responsible for lung cancer. Chromate compounds that are in solution are insoluble are more potent. Zinc chromate is the most potent chromate found in industrial setting, particularly in the paints which are used for aircraft. So, chromates are the source through which, you know, it is inhaled, and when it reaches the lung, it gets set into the lung, and there it causes the cancerous activity or acts as a carcinogen.

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Poisoning (Ingestion) - no emesis if ingested may be corrosive if Chromium VI is not present. Absorb ascorbic acid administered orally if Chromium still is in stomach can help digestion, or dilution with milk or water can also help. Gastric lavage removal or Chromium VI weighed against perforation can also happen. Chelation therapy may not be very effective in this case. So, once the poisoning has taken place, how can one help by taking certain compounds to be able to reduce the effect of chrome VI.

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Poisoning in dermal - irrigate with water, look for chrome VI burn damage, and treat appropriately. Topical application of 10 percent ascorbic acid or of a barrier cream containing 2 percent of glycine and 1 percent of tartaric acid has proved beneficial. So, if there is a dermal poisoning caused by Chromium, one can use a combination of glycine and tartaric acid, or simply ascorbic acid and 10 percent of ascorbic acid; if it is applied on the skin, it can help.

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When it is a cause that is caused by inhalation, it is the air should be made clear; if respiratory distress is taking place, oxygen should be provided. Observe carefully, the signs of pulmonary edema.

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Drinking water limits – now, since it is such a crucial and critical and toxic substance, EPA has, that is the environmental protection agency, has setup a maximum level of Chromium of chrome III and chrome VI in drinking water as 100 microgram Chromium per litre. According to EPA, the following levels of Chromium III and Chromium VI in drinking water are not expected to cause effects that are harmful to health. For children, particularly, if it is 1400 microgram per litre for ten days, and if they are exposed, it does not cause any bad effect. For children, if it is 240 microgram per litre for even longer term exposure, it does not cause any harm. For adults it is 840 microgram per litre for longer term exposure, and it was found that it did not cause any ill effect. Similarly, 120 microgram Chromium per litre for lifetime exposure for adults is also same.

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EPA for soil cleanup goals - the USEPA region 9 soil residue residential USEPA region 9 soil residential preliminary remediation goal showed that chrome III at 100000 milligram per kilogram chrome VI chrome 3 at 210 milligram per kilo gram and chrome I alone only 30 milligram per kilogram can be allowed. Chrome III is the predominant form in soil, but a 1 is to 6, chrome VI is to III ratio is sometimes used for soil cleanup.

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OSHA limits - the occupational exposure limits for an 8-hour workday, for 40 hour workweek are: 500 microgram Chromium per cubic meter for water soluble chromic salts and 1000 microgram Chromium per cubic meter for metallic Chromium, and the levels for Chromium trioxide that is the chromic acid and other Chromium VI compounds in the work place should not be higher than 52 microgram Chromium for chrome VI for any period of time. OSHA is proposing lowering of chrome VI standard to 1 microgram per meter cube.

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Biological monitoring is, therefore, very essential.

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