

Trace and ultra trace analysis of metals Using atomic absorption spectrometry

Dr. J R Mudakavi

Department of Chemical Engineering

Indian Institute of Science, Bangalore

Lecture – 01

Course Introduction

Dear students, it is my pleasure to address you in another MOOC course on Trace and ultra trace analysis of metal ions using flame and flameless atomic absorption spectrometry. Basically what we want to achieve in this course; is to determine the metal ions, why we want to determine the metal ions? The point is; so, why do we want to determine the metal ions in the environment?

Basically, man has been on this planet born and brought up and living on a diet of no metals; that means, ever since man has appeared on the surface of the earth, most of the time the environment was very pure. If you look at the formation of the earth geological evidence etcetera, you would know that long long back earth and other planets are formed by sun and then they are all revolving around each other, slowly the earth cooled and as it cooled, the water vapor condensed and then because of temperature again it evaporated and then again cooled, again it rained and rained and rained and strained like that for millions of years.

So, whatever was on this surface of the earth before the man appeared; most of the metals and other materials had washed away into the sea, where they were diluted to a large extent. So, initially when the life forms appeared on the face of the earth, we the most of the life forms were born and nurtured on a diet of no metals because the concentration of the metals in the sea was very less except for sodium, potassium, magnesium, chloride, sulfate etcetera.

So, when man has appeared on the surface of the earth; again there were no metals on the surface of the earth and the only metals available where sodium chloride, salts or some salts like sodium chlorides of magnesium sulfate etcetera and then the water was available. Water was a solution of mineral salts ponds etcetera, but as you know clean water should not have any dissolved salts at all.

Now, when we talk of metal ions; we also mean metal salts because most of the metals in a solution are in water or in other aqueous solutions are in the form of salt and these salts are ionized. So, when the man has been brought up on a diet of no metals over a period of time and when we think of present times, we are using nearly 50 percent of the metals in the periodic table in our day to day life.

For example, if you look at a computer; a normal computer which we have very much accustomed; it will contain about 53 metals, our mobile will contain gold, platinum, palladium, indium, lead, chromium all these metals and so on. These life forms, once the lifetime of such utilities are over; they are discarded and then thrown here and there all of them will get corroded and the corroded metals will enter into our soil and then from the soil, we will grow the crops and the cows eat the crops and animals eat the crops, we eat the crops and it forms a chain where metal ions are being circulated in our body.

Now, as I told you if we are born on a diet of no metals; we should not have any metals at all, but so many metals are coming and unlike organic foods, which do not contain metal salts they are excreted without much problem, but metal salts have a problem of getting accumulated in our body. So, many metals which we are not accustomed to are getting accumulated in our body and then the metal salts will interfere in the physiological processes leading to unnecessary complications.

Further than that, we also for our modern living we do mining and then we take the metals make them into jewelry, metals and then plastics, chairs, furnitures and so many other articles and which will end up after their useful life on the soil or in the water. So, metal ions are one of the most dangerous elements in our ecosystem which are not biodegradable. So, this brings me to the discussion on the application of science and technology.

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Application of science and technology for improving quality of life on earth is an evolutionary ongoing process. The pace of adoption has been increasing at a break neck speed in recent years.

Adoption of SKT for human comforts such as food, clothing, housing, medicine, travel, entertainment etc. is a very visible process.

However the same advances can also be used to solve myriad problems confronting humanity. Such examples include medicines for diseases, pollution control etc.

So, in the modern times what we expect is the application of science and technology for improving quality of life on the earth it is an evolutionary ongoing process. The pace of adoption has been increasing at a breakneck speed in recent years. Adoption of SKT for human comforts such as food, clothing, housing, medicine, travel, entertainment etcetera it is a very visible process to all of us and the use of science and technology for such materials as an aftermath; what happens is the materials used will take the form of unwanted material which has to be discarded or treated or reused.

So, the problem of modern science is that; the same advances that have made our life very comfortable are also making that fair life uncomfortable for us when their useful life is over. So, what we want to do is we use the same technology, use to solve the myriad problems confronting humanity. So, such examples includes include medicines for diseases, pollution control etcetera, so in the same problem many of the modern problems associated with our lifestyle are solved by inventing the medicines, tablets and then other comforting materials; for example, AC's to make a room comfortable like that all these things are the problems or the benefits to the modern society and the same thing can be used to mitigate the environmental problems.

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Fundamental Science such as atomic and molecular structure has made rapid strides in the last century and currently are able to understand the atomic and molecular structure of elements and compounds in terms of electronic and nuclear structure when they undergo chemical reaction.

Atomic and molecular Spectroscopy is a science which is an offshoot of the structural changes occurring during electronic and nuclear transitions. Over the years spectroscopy has grown into a very powerful tool for the identification and quantitation of chemical compounds. The same can also be used to follow the progress of chemical reactions.

So, fundamental science such as atomic and molecular structure has made rapid strides in the last century and currently we are able to understand the atomic and molecular structure of the elements and compounds in order to in terms of electronic and nuclear structure when they undergo a chemical reaction.

So, why should we understand these things at all the question comes because when we understand the structure of the atoms, structure of the element, structure of the compounds, structure of the environment, structure of the earth, structure of the planets, structure of the astronomical bodies; we will be able to lead a better life. So, on the micros level; we need to understand things around us and the smallest particles that influence our lifestyle we have to understand. So, we want to know the structure of the atoms and molecules etcetera, so atomic and molecular spectroscopy is a science that deals with it; it is an offshoot of these structural changes occurring during electronic and nuclear reactions.

So, in general whenever a substance undergoes a change in its structure; it could be on the core that is in the nucleus or it may be in the electronic cloud around the atom. So, most of the spectroscopic techniques address this problem of identifying the changes in the nuclear and electronic structure in the reactions, so over the years spectroscopy has grown into a very powerful tool for the identification and quantitation of chemical

compounds, the same can also be used to follow the progress of chemical reactions because that is what exactly we want to do in most of the scientific pursuits.

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Environmental pollution is defined as the temporary or permanent changes occurring in our surroundings such as air, water and land which affect the quality of human life, temporarily or permanently.

Since last sixty years environmental pollution has been posing major threat to the survival of humanity and other plant and animal life of our planet.

So, environmental pollution which is an offshoot of our life that we define it as the temporary and permanent changes occurring in our surroundings and; what are these surroundings? These surroundings are air, water and land; which affect the quality of human life; it may be either temporary or permanent. Since last 60 years; environmental pollution has been posing major threat to the survival of humanity and other plant and animal species in our planet. One reason is the lifestyle that brings a variety of compounds in our day-to-day life and the second is the population explosion, which leads to increase the use of the resources and which in turn leads to increased discordance, increased wastage of the materials.

So, all these increased discarded materials will affect the quality of life in one way or another and the only media which we know in general which affect the quality of life is our the air we breathe, the water we drink, the food we eat and the soil in which we live. So, this is the basic requirement of any environmental pollution control program.

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Technically Environmental pollution is thought to originate from dust, chemicals and their reactions and microbiological Species such as bacteria, viruses, algae, fungi etc.

Technically localized pollution is caused by the:

- (i) Variation of BOD and COD in water bodies by the chemicals and petrochemicals.
- (ii) Atmospheric emissions.
- (iii) Decomposition of organic matter in air and water or land
- (iv) Retrievable loss of metal ions in the environment.

Now, technically the environmental pollution problem is thought to originate from dust chemicals and their reactions, microbiological species such as bacteria, viruses, algae, fungi and many other microorganisms.

Basically, we define a localized pollution the quite often we are suffering from the degradation of the quality of the environment locally. So, the localized pollution control how does it look like; when do we say a localized pollution has occurred in Bangalore or in Lalbagh or in Delhi; whenever there is no good air to breathe, whenever there is Diwali; in the whole country comes out alive with crackers and that increases the dust pollution, so but it is a temporary phenomena. So, like that the pollution could be temporary phenomena; arising out of our activities over a localized area because everybody everywhere does not celebrate Diwali with crackers, so it could be localized.

So what are the parameters we look forward; to say a certain localized area is polluted, that is we see the variation of BOD and COD in water bodies by the chemicals and petrochemicals. So, we want to know what is the biochemical oxygen demand or chemical oxygen demand in water bodies, if the biochemical oxygen demand and c o d are increasing then we say water bodies are polluted.

So, whenever we see dust particles in the atmosphere; we say atmospheric emissions are more, so we have to take action to mitigate the atmospheric emissions. For example, industries may let out a lot of smoke and dust and particles and gases into the

atmosphere, but that also leads to localized problems because once the pollutants enter into the atmosphere, they get dispersed.

So, when the dispersed concentration of the pollutant decreases beyond a certain level to a certain level; we do not feel the discomfort, so that is again a localized phenomena. Then there is a decomposition of organic matter in the air or water and water or land. Whenever things decompose they emit foul smell, we are all used to their foul smell in several of our cities, towns, localities etcetera; again it is a localized pollution and then we have another form of pollution that is retrievable loss of metals in the environment; this is a serious problem.

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While it is true that pollution causes a variety of maladies, it is also possible to at least partially remedy the situation by physically and chemically removing the offending chemicals. Therefore the procedure for environmental pollution control involves:

The determination of the pollutant and the extent of pollution
(ii) Technical intervention
(iii) Post intervention evaluation

Fortunately it is possible to employ molecular spectroscopy to qualitatively and quantitatively determine the pollutants in a matrix. For monitoring also the spectroscopic methods offer a simple solution which is fast, reliable and cost effective.

Because, whenever there are metals in the environment, we have the problem of adjusting; the life for all life forms must adjust to increased metal ion pollution. Sometimes what happens, if there is a increase in the pollution level; animals especially they can migrate and go and live in some other areas, but man cannot do that; if you are living in Bangalore and then Bangalore is polluted, you cannot go to some other place because of several other economic and non economic reasons.

So, man is bound to a locality by his profession, by his work needs, by his work ethics etcetera whereas, animals do not have such a restrictions; so, they can avoid the localized the pollutions. Now, while it is true that pollution causes a variety of maladies; it is also possible to at least partially remedy the situation by physically and chemically removing

the offending chemicals. Therefore, the procedure for environmental pollution control that involves the determination of the pollutant; how much pollutant has come? What is the extent of pollution? And how what exact measures we take to intervene technically to remove the pollutant and then it is also possible to estimate how much has been removed that is post intervention evaluation.

So, the basic idea of pollution and pollution control is involves three steps; that is first is estimate the pollution, second is technical intervention followed by post intervention evaluation. So, fortunately it is possible for us to employ the science and technology; especially the molecular spectroscopy to qualitatively and quantitatively determine the pollutants in a given sample. So, what do we mean a sample? It may be air sample, it may be water sample, it may be a soil sample; we call it in general; a matrix. So, this matrix which is not made of the elements which should not be there for example, any material which contains extraneous materials to be used for analysis is known as matrix.

So, for monitoring also the spectroscopic methods offer a simple solution which is fast reliable and cost effective.

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Environmental analytical Science aims at developing methodologies, instrumentation and or mathematical correlations and models that predict the environmental fate of new and existing chemical compounds. It presents in a concise form the most important properties relating to chemical reaction and the amount of substances present. A thorough knowledge of the environmental analytical chemistry greatly helps to measure the extent of environmental pollution monitoring which in turn can be adopted to pollution control .

Now, we are going to study environmental analytical science in this course and what it aims is at developing methodologies, instrumentation and or mathematical correlations and models that predict the environmental fate of the new and existing chemical compounds, it presents in a concise form the most important properties related to the

chemical reaction and the amount of substances that are present will be drawn as a conclusion. So, a thorough knowledge of the environmental analytical chemistry or science greatly helps us to measure the extent of environmental pollution damage; which in turn can be adopted for pollution control.

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The majority of the compounds are colourless and hence not amenable for spectrophotometry. Fortunately it is possible to convert them into coloured compounds by reacting them with suitable chromophores. As of now more than 1,00,000 compounds can be made to undergo chemical reactions to produce coloured compounds on an average more than 30 million spectrophotometric measurements are made daily worldwide. Another advantage of spectrophotometry is that the procedures can be easily automated with little or no manual intervention.

Now, the majority of the compounds in this world are colorless; especially the chemicals and hence they are not amenable for spectrophotometry. Spectrophotometry is a science which deals with the color of a substance, so color of a substance is related to concentration. Now in here, today we are talking in this course we talk about metal ions, metals and the fortunately; it is quite possible to convert them into color compounds by reacting them with suitable chemicals.

So, more than 100000 compounds can be made to undergo chemical reactions to produce color compounds and on an average more than 30 millions spectrophotometric measurements are made daily worldwide, I am talking about spectrophotometry now; that is the science of absorption of light in the determination of metal ions. So, another advantage of spectrophotometry is that procedures can be easily automated with little or no manual intervention.

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Heterocyclic Chemistry and Analytical Chemistry today are rapidly changing subjects whose almost frenetic activities are attested by the countless research papers appearing in established and new journals and by the proliferation of monographs and reviews on all aspects of the fields. The interdependence of these two major branches of chemistry has resulted in the resurgence of UV-visible spectrophotometry due to the enhanced selectivity and sensitivity of the method by choosing appropriate heterocyclics to react with the target species. Consequently, majority of this research has been transferred in the last two decades to the field of Environmental Analytical Chemistry.

Now, there are other ways of looking at it, when we say heterocyclic; chemistry and analytical chemistry today are rapidly changing subjects, where most frenetic activities are attested by countless chemical research papers, they appear in established and new journals and by the proliferation of monographs and reviews on all aspects of fields. The interdependence of these two major branches of chemistry has resulted in the resurgence of spectrophotometric technology.

Now in spectrophotometry, we look at enhance the selectivity and sensitivity of the method; selectivity means the method should be applicable to a particular component, irrespective of what other compounds are there and sensitivities I must be able to determine minimum amount of the pollutant and that is the characteristic concentration that can be determined using a spectrophotometer technique.

Now, we are not talking about spectrophotometric technique here because we are talking about spectroscopic technique; that is atomic absorption spectrometry. Still, I would like to inform you of the structure of the atom and compounds for metal ions so that as per a more powerful technology is available to us as a branch of environmental analytical chemistry; to determine the metal ions. So, any colored substance we can any color substance we can do by spectrophotometry; what about metal ions they are many of them are not colored.

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This course has therefore been designed to give you an insight into this aspect of pollution control by incorporating several Scientific disciplines, which includes:

- (i) Atomic and molecular structure.
- (ii) Molecular spectroscopy- basics.
- (iii) Instrumentation for spectroscopic instrumentation.
- (iv) Practice of spectrophotometry , fluorescence, Phosphorescence, turbidimetry and Nephelometry etc.
- (v) Molecular Spectroscopy for pollution monitoring.

So, we need some other technique which is not dependent upon the with color reaction. So, that is spectroscopy atomic absorption; that means, any atom which absorbs a radiation; if it kept the characteristic of an element, we should be able to follow the absorption of radiation by the element and we should be able to determine them.

So, this course has therefore, being designed to give an insight into this aspect of pollution control by incorporating several scientific disciplines. Now these disciplines include atomic and molecular structure, this we have to study anyway atomic and molecular. So, if we do not know the structure of an atom how are we going to study the changes in the atomic structure?

So, it is a basic important aspect of atomic and molecular structure that we should learn about the atomic and molecular structure and then molecular spectroscopy basis of molecular spectroscopy and basis of atomic spectroscopy that we have to learn and then we will learn about the instrumentation for spectroscopic equipments and then we will learn the practice of spectrophotometry; fluorescence to some extent phosphorescence and we will not study turbidimetry and nephelometry.

But we will study the atomic absorption and then molecular spectroscopy; also we can study use the same atomic absorption technique for studying the molecular changes in a given substance that is in the form of an ions that will be in direct determination; not

direct determination. So, these aspects we are going to study in our course on atomic absorption spectroscopy.

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ATOMIC AND MOLECULAR STRUCTURE

The concept that the matter is built up of tiny discrete particles traces its origin to ancient Hindu scriptures such as Vedas. The description of atom and electrons and molecules known as paramanus, anu and kana has permeated the Indian social milieu since 2000 B.C. However it was John Dalton 'the father of modern atomic theory' who provided the first scientific hypothesis of the structure of the atom in 1802. He suggested that the matter is composed of tiny real particles called atoms which are indivisible, cannot be created or destroyed. Atoms of each pure substance are identical in nature, weight, size and other properties. Atoms of one pure substance differ in weight and other characteristics from those of other substances. Further he suggested that union of atoms in definite numerical proportion results in chemical combinations.

So, let us start looking at atomic and molecular structure and this is still we are still learning in the introductory stage, we look at atomic and molecular structure. What it is made up of? All of us know from our high school days and college days that the concept of the matter is made up of small tiny particles; discrete particles and they are known as atoms and even in our Hindu scriptures such as Vedas and Puranas etcetera, they refer to the descriptions of atoms and electrons and molecules they were known as anu, paramanu and kana.

Paramanu means smallest structure; capable of independent existence, anu is smallest structure of a compound of an element that is capable of independent existence and kana is the smallest structure of a compound. So, ever say right from our Vedic times; we were aware that all the atoms, all the materials were made up of atoms and anus and paramanas and kanas. However, modern scientist John Dalton; he is 'the father of modern atomic theory' who provided the first scientific hypothesis of the structure; of the atom as we know it today. That was in 1802, but we are still studying it, we have not finished the requirement of knowing the atom fully; he suggests, what he suggested is that the matter is composed of tiny small particles called as atoms, he said atoms are

indivisible, they are not you cannot cut them into still smaller species that was in 1802, we know now that we can cut the atoms also into different species.

So, what else he said atoms of one pure substance differ in weight and other characteristics from those of other substances; that means, atoms of one element should be different from other elements, which we know is wrong now, but in 1802, it seemed to be the most logical thing to do and further he suggested that union of atoms in definite numerical proportion results in chemical combination, this is a universal truth. For example, water is made of two elements hydrogen and oxygen; they are combined in definite proportions to form water and that is the compound.

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Subsequent developments in science led to the expansions of atomic theory and experimental data generated by a number of workers such as Michel Faraday, Rutherford and other peers with the discovery of the electron, X-rays, radioactivity, nuclear reactions and subatomic particles. It is now widely recognized that atoms are composed of several types of ultimate particles, some capable of independent existence outside the atom and some others capable of existing momentarily outside the atom or inside.

So, like that we also take a look at subsequent developments in science that led to the expansion of atomic theory and as the lot of people started working on the atomic structure; experimental data generated by a number of workers such as Michel Faraday, Rutherford and other Niels Bohr and other peers with the discuss; subsequently they worked on the fundamental particles, discovery of electron was made, X-rays were found, radioactivity was found, nuclear reactions were identified and subatomic particles were found and to be existent and now it is widely recognized that atoms are composed of several types of ultimate particles.

Some capable of independent existence outside the atom and some others capable of existing momentarily outside the atom or inside the atom, inside the atom; What we

mean? We mean is nucleus outside the atom means just outside the nucleus where electrons are revolving around it and then some particles are generated due to chemical reactions which may have momentary existence, but may not be capable of independent existence.

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Among the atomic components only three particles namely electrons, protons and neutrons are recognized as stable particles.

The stable particles : Electrons, protons and neutrons

Electrons are made up of small but energetic negatively charged particles whose existence was proved by Sir J.J Thompson. Electrons are fundamental particles of all substances.

So, among the atomic components only basically there are three particles namely electrons, protons and neutrons; they are recognized as stable particles. So, electrons are made of small, but energetic negatively charged particles and their existence was proved by J.J Thompson, they are fundamental particles of all substances which negates the John Daltons theory.

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Electrons impart negative charges to objects in their paths and get deflected in applied electrostatic or magnetic fields. Further it was shown that they cause ionization in gases, expose photographic plates, yield X-rays against suitable targets. These particles were named as electrons in 1897, by Sir J.J. Thompson. Thompson evaluated the ratio of the charge to mass (e/m) for the electron from different sources and showed them to be identical having a charge of -4.8029×10^{10} and an atomic mass of 0.0005486 AMU (1.6603×10^{-24} g).

De Broglie in 1925 advanced the theory that the electrons also possess wave properties such as reflection and diffraction. This formed the theoretical basis of extra nuclear structures of the atoms.

So, electrons impart negative charges to objects in their paths and get deflected and applied electromagnetic and magnetic fields. Further, it was shown that they cause ionization in gases, expose photographic plates, the yield X-rays against suitable targets, when you take the electrons and bombard them on metals, you get X-rays and these particles were now known as electrons. The fundamental particles that generate these things are known as electrons and he evaluated the ratio of the charge to mass that is known as e by m; e is electronic charge and m is the mass for the electron from different sources and showed them to be having identical in all elements, they have a charge of 4.8029 into 10 raised to 10 s s minus and then atomic mass of 0.0005486 atomic mass units.

Because we do not know the exact weight, we call them AMU and they after Avogadro's number was found out, we know that the mass of atomic k of an electron is 1.6603 into 10 raised to minus 24 grams. So, De Broglie in 1925 advanced the theory that the electrons and protons also possess wave properties; that means, the electrons do not just move around like a heavy particle, but they also move as electrons and as reflection and diffraction, they also move as waves like this.

So, the waves can be diffracted and then reflected if they fall on a reflecting surface, they can be thrown back in the opposite directions and this form the basis of extra nuclear structure of the atoms. We will study more of it in our next class.