

IANCAS BULLETIN

TRACE ELEMENT ANALYSIS

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ALLIED SCIENTISTS**

Editorial

The exercise of identification and estimation of elements in the concentration range of parts-per-million (ppm) or lower is called trace element analysis. It is known that trace level impurities change the behaviour and properties of material. The role played by trace elements in influencing bio-chemical processes in human body is not yet completely understood. Apart from this, a lot of valuable information in earth sciences and socially relevant areas, such as, environment, forensic science and archeology is obtained through trace element analysis. These examples, by no means exhaustive, highlight the importance of this discipline which continues to provide challenges, inspite of a variety of analytical techniques developed so far. In this bulletin, the articles provide a comprehensive idea about the philosophy in trace analysis, as well as, introduce analytical spectroscopy and mass spectroscopic techniques and their application in the areas such as material science, earth science and biological sciences.

In addition, description of a kit, developed to demonstrate the concept of half-life to school children as part of our endeavour to popularise nuclear sciences, is included in this bulletin.

I take this opportunity to thank all the authors for their contributions. My sincere thanks are also due to Shri J.K. Samuel for his help in improving the layout of this bulletin.

Looking forward to your comments on this issue and contributions for the future publications,

P.K. PUJARI

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Trace Analysis And Quality Of Measurement



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Analysis of elements ("impurities") at trace and ultra trace levels constitutes a significant component of the compositional characterisation of materials. The other aspect of establishing stoichiometry involves major and minor component analysis with high precision and accuracy. Property based characterisation has the major problem in that, while the characteristics govern the properties, the properties do not fully describe the characteristics; simple examples of this anomaly are resistivity measurements where compensating impurities can give very acceptable value for resistivity while the material by itself is not acceptable. Another such example is the effect of impurities, in addition to Oxygen, on the recrystallisation temperature of Zirconium.

This discipline of trace analysis has (played) a vital role in materials science, where it has helped to understand the role and effect of "impurities" on the behaviour and properties of materials; in environmental science, for understanding the source patterns of pollutants and exposure; in the life science, to understand the role and the effect of trace elements in health and disease; in earth science for resource prospecting and investigations in petrogenesis; in socially relevant forensic science for investigations in toxicology (involving inorganic poisonous), ballistics (to help establish whether the hole has been caused by the passage of a bullet or whether the person has simply fired or handled the weapon or whether there was any firing in the room and the main topic of establishing the commonness of origins of samples found in the scene of crime with those collected from suspects) and finally in the aesthetically pleasing area of archaeology to help establish the

authenticity and the evolution of the technology in the making of these artefacts, both earthen and metallic.

The choice of an analytical technique has been governed by the nature of the sample, concentration level of impurities and their location in surface/depth, preservation of the sample, the quality of results, the turn around time and the cost. Nuclear techniques have (played) a vital role in providing quantitative, multielement, simultaneous and on occasions "nondestructive" results. The most important aspect of the nuclear activation techniques is minimal handling of the sample prior to excitation, thus ensuring the integrity of the sample and post irradiation physiochemical separation prior to radiation measurement for enhanced specificity. These 'unique' features are to a great extent responsible for the role of nuclear activation as a referral method to provide validation support to other analytical techniques.

In all these measurements, the underlying factor is the quality, primarily for drawing definitive inferences and for application to areas like environmental science, where the results have political and socio economic ramifications; the need for such quality assurance cannot be overemphasised. Quality does not necessarily imply that the precision and accuracy have to be the best possible; quality is end use oriented but quality of the analytical measurements should be validated and well understood. Hence our aim should be towards valid analytical measurements.

The problems of establishing the quality of results assume higher significance in ultra trace analysis, and determination of concentration at ppb and lower levels, particularly in small quanti-

ties of samples, where it is rather dangerous to make any generalisation. Only generalisation one can make is that there can be no generalisation! Another guiding rule is that one (analytical) method is no method. It is primarily because, the Chemistry and kinetics are not well understood at such low amounts of elements in solution. In addition, the role of environment, including containers is equally important and there is an absolute need for cross validation of results by more than two independent analytical methodologies.

A classic example of the role of environment and the purity of reagents in the determination of elements is the analysis of glass for lead. The results for such a study carried out at NBS, USA long ago are given in Table 1 as an illustrative example.

One can thus visualise trace analysis and quality measurement consisting of several factors depicted in the Fig.1.

Although there are several options to overcome these problems, the basic approaches are confined to the following:

- a) choice of a proper container and a single container philosophy for minimising the contact with surfaces of container walls.
- b) metal free clean environment, preferably with laminar air flow at the work surfaces;
- c) freshly purified reagents preferably for use on same day.

The purification of reagents constitutes one of most difficult components in ultra trace analysis.

The protocols in respect of methods to be followed for carrying out the analytical measurement

process have been fairly well defined. However, implementation of these protocols, particularly in instrumental methods of analysis, where often times it is not possible to monitor the intermediate steps, has posed problems in obtaining and maintaining the quality of measurements that is otherwise possible using these methods/instruments. Table 2 summarises the factors affecting quality of results in neutron activation analysis.

The international standards like ISO Guide 25 or EN 45000 or GLP have been of immense value in providing valid analytical measurements which in turn have helped proper homogenisation of data, particularly on environmental samples. The need for generating data of known quality is very essential for creating our own national base line data, be it in food stuff or in environment or medicine to help evolve realistic regulatory standards. These standards should not only protect and preserve the environment and population but should also not stifle industrial development which is so essential for providing a good standard of living for people. This concept of environmentally sustainable industrial development is even more pertinent in the changing scenario with respect to globalisation and open market economy, where the analytical sciences, have a vital role in ensuring quality of product ensuring minimum wastage and in turn minimal environmental pollution. To sum up, analytical measurement with adequate quality holds the key to industrial development and a clean environment.

TABLE 1. TRACE ELEMENTS IN GLASS

	Lead found
Initial analysis of TEG standard	330±250
TEG analysis using selected acids	260±200
TEG analysis in class 100 hood	20±8
TEG analysis using special acids in clean room	2±1
{T.J.Murphy, NBS Spl.pub.No.422, p.509 (1976)}	

TABLE 2. QUALITY OF RESULTS

COUNTING STATISTICS	QUALITY OF MEASUREMENT
IRRADIATION	POSITION CHARACTERISATION DIRECT INTERFERENCES GEOMETRY
RADIATION MEASUREMENT	IDENTIFICATION QUANTITATION SPECTRAL BACKGROUND INDIRECT INTERFERENCE SYSTEM BEHAVIOUR
STANDARDS	ELEMENTAL, MULTIELEMENT, MONO, ABSOLUTE
SAMPLE	PREPARATION
PRESAMPLING	!!!

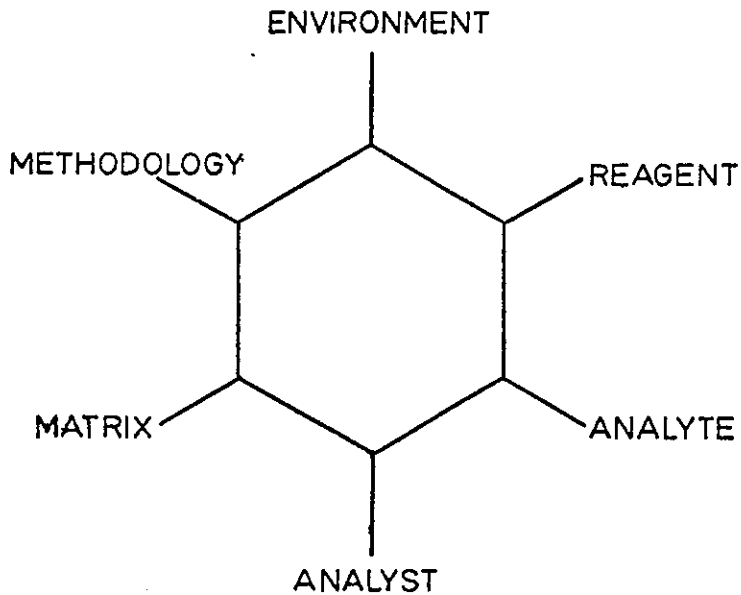


FIG 1

Analytical Spectroscopy For Trace Metal Assay



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In analytical spectroscopy, compositional characterization of a sample under investigation can be easily carried out by identification of wavelengths and measurement of intensities of the spectral lines/bands absorbed/emitted by the constituents of the sample under the influence of external radiation field. However, because of the highly sensitive nature of the techniques, macro-scale determination can very often, cause saturation effects such as concentration quenching, self-absorption, saturation of the detector etc. The conventional techniques in analytical spectroscopy, therefore, offer better performance in micro-scale determinations. The major fall-out of the proficiency in micro-scale determinations is that the spectroscopic techniques can provide suitable experimental procedures to check the purity of highly pure materials. These techniques also play a vital role in the analysis of environmental pollutants. Some of the techniques also enable determination of major and minor constituents of alloys and can be successfully utilized in chemical characterization of special materials.

The analytical spectroscopy has been classified into three branches viz. absorption, fluorescence and emission spectrometry. In what follows, a brief description of the working principles of the techniques used in these three branches is given, followed by their role in various fields.

ABSORPTION SPECTROMETRY

It consists of conventional spectrophotometry and the atomic absorption spectrometry (AAS). Both the techniques are governed by Beer-Lambert's laws in a broad sense. In uv-visible spectrophotometry, extinction coefficient becomes the

measure of the complex species formed by the metal atoms and can be used for quantification at trace concentration levels. The methods used here are highly specific and susceptible to interference due to the presence of other metallics. The IR spectrometry is mostly qualitative and would work at relatively high concentration levels. The advent of Fourier Transform Infra-Red (FTIR) spectrometry has caused a renaissance in this field and has greatly improved the capabilities of the IR spectrometry. The FTIR, now serves as a powerful analytical technique for quantitative determination of various functional groups in chemical reactions.

The atomic absorption spectrometry is based on the atomization of the sample followed by absorption of characteristic radiation by the ground state/low level excited atoms. There are three basic processes involved in the working of the AAS technique: (i) Generation of characteristic radiation of the element of interest (ii) Creation of atomic vapor of the sample and (iii) Detection and measurement of the absorption signal. The block diagram of the experimental set-up is shown in Figure 1.

The source of characteristic radiation is provided by a Hollow Cathode Lamp (HCL) wherein the cathode is either fabricated out of the analyte metal or has a coating of a suitable compound of the analyte. The structural details and mode of operation of the lamp enables one to have sharp line spectrum of the analyte essential for attaining high sensitivity in AAS. The most important step in AAS is the production of ground state or low-lying level atoms of the analyte elements present in the sample. The major thrust, therefore, being

on the atomization of the sample, extensive research has undergone in the two modes of atomization prevalent in AAS technique viz., flame and Electro Thermal Atomization (ETA). In flame-AAS, a solution sample undergoes following steps prior to its atomization using suitable oxidant-fuel combination: nebulization, droplet precipitation, mixing, desolvation and compound decomposition. In ETA-AAS technique, pyrolytically coated high density graphite tubes, cups or cuvettes are used for accommodating micro-litre volumes of sample solutions or milligram amounts of solid samples. These are then heated electrically in a programmed manner to achieve 'Drying', 'Ashing' and 'Atomization' of the sample. The characteristic radiation passing through the atomizer, is collected by a grating monochromator of moderate resolution. A photomultiplier tube placed at the exit slit of the dispersing device receives a specific analytical wavelength and the signal is further processed by a logarithmic amplifier prior to its digital display. The ETA-AAS offers better sensitivity due to improved atomization efficiency and higher attainable temperatures and enables picogram level determinations in some favorable cases while flame - AAS techniques are more precise and can offer precision levels of 1-3% RSD in many cases. In view of the small sample size requirement, high atomization efficiency, prevention of open flame within the critically important facilities and compatibility with solid sampling, ETA-AAS has found easy acceptability in many fields. The drawback of the technique lies in strong interaction of analyte atoms with the carbon walls of the atomizer, leading to poor precision of determinations as compared to that attainable by flame-AAS technique. Platform technique and tungsten wire heating are some of the innovations introduced in ETA-AAS and are aimed at radiational mode of heating of the sample.

The AAS technique is in general, limited in its ability to determine low concentrations of metallics forming stable carbides and refractory oxides, in addition, to being a very specific analytical technique. The non-specific absorbance co-existing with analyte absorbance in some of the systems can be evaluated and analyte signal can be corrected for by using one of the three methods: i) Deuterium lamp continuum ii) Zeeman effect with source or the atomizer in magnetic field and iii)

Smith-Heitje correction. Recent advances in AAS technique in general and ETA- AAS technique in particular, are aimed at improving atomization efficiency, effective application of background correction, advanced analytical software and micro-processor based automation.

Some of the special techniques adopted in AAS include

- (1) Solid sampling for metallurgical and geological samples
- (2) Standard addition technique for miscellaneous types of samples where sample-standard matching cannot be achieved perfectly
- (3) Hydride generation technique for As, Se, Te, Sb, Sn, and
- (4) Cold vapor generation technique for Hg.

FLUORESCENCE SPECTROMETRY

The fluorescence spectrometry as an analytical technique is in vogue for quite some time in the case of few metallics which emit strong visible fluorescence such as fluorimetric determination of uranium. The fluorescence intensity is directly related to the power of the excitation source. The fluorescence technique is, in general, supposed to be more sensitive than the absorption mode because a signal, howsoever small it may be, is detected on a negligibly low background thereby increasing S/N ratio significantly. Of late, it is gaining momentum as a very sensitive spectroscopic technique due to the advent of tunable lasers and effective use of atomic fluorescence spectrometry (AFS). In addition, site selective excitation of fluorescence results in enhancement of fluorescence yield while gating of photomultiplier tubes improves S/N ratio still further. Again, photon collection efficiency (around 5%) being very low as compared to ion collection efficiency (almost 100%), laser ionization-charge detection methods have been used to achieve ultimate limits in sensitivity viz. single atom detection. By a careful choice of the energy levels involved, a single atom can be made to undergo the transition of interest several times during its stay in the laser beam so that the number of fluorescent photons observed is far in excess of the number of atoms present in the system. Obviously, the limit of sensitivity under such conditions is a single atom. Most of the fluorescence based analytical techniques, though attractive have yet to gain acceptability for practical applications due to several reasons such as exorbitant cost of laser instrumentation, intricate

experimental arrangement, spectral and chemical interferences etc. Besides, scattered light and detector background needs to be reduced significantly to improve fluorescence signal. However, laser - based fluorimetry of uranium is by far the most widely used sensitive technique for monitoring uranium in environmental samples.

EMISSION SPECTROMETRY

The emission spectrometry, by far, has served as the main workhorse in analytical spectroscopy. By its very nature, it offers simultaneous multi-element determination and the success of the method depends upon the power and stability of the excitation source. The progress of research for the development of useful excitation sources has gone through the stages of flame, thermo-electric, electrical and plasma sources. The present day Atomic Emission Spectrometry (AES) or Optical Emission Spectrometry (OES) is invariably based on the use of Inductively Coupled argon Plasma (ICP) as the excitation source which offers good sensitivity for most of the metallics, large linear dynamic range and by far, the best precision of determinations attainable by any of the spectroscopic techniques.

The excitation source is an electrodeless argon plasma operated at atmospheric pressure and sustained by inductive coupling to radiofrequency electromagnetic field. Argon gas flows axially through a quartz tube assembly that is surrounded by three or four turns of an induction coil connected to a R.F. generator. The standard frequency of operation is 27.12 MHz while standard forward power is 1-2 kW. Some of the recently installed plasma units work on 40 MHz frequency with consequent improvement in analyte sensitivity. The high frequency, low power operation ensures satisfactory introduction of sample aerosols into the plasma. The high frequency current flowing in the induction coil generates oscillating magnetic fields whose lines of force are axially oriented inside the quartz tube and follow closed elliptical paths outside the tube. Induced magnetic fields, in turn, induce electrons in the gas to flow in closed annular paths inside the quartz space. These electrons (eddy current) are accelerated by the time-varying magnetic field, meeting resistance to their flow such that resistive heating and additional ionization result. A brief tesla discharge provides 'seed' electrons to initiate the process. The plasma forms instantaneously and is subsequently self-

sustaining with temperatures upto 10,000 K. The plasma torch consists of three concentric quartz tubes. The solution is aspirated by a nebulizer system (pneumatic or ultra-sonic) and a fine liquid aerosol is transported up through the central tube and through the toroidal core of the plasma by a flow of argon gas. Thermal isolation of plasma is accomplished by Reed's Vortex stabilization technique by introducing flow of argon/nitrogen gas. This flow cools inner walls of the outer quartz tube and stabilizes and centers the plasma radially. Typical observation height is 15 mm above the top of the induction coils where temperature is around 6500 K and where the argon continuum vanishes thereby reducing the spectral background significantly. The excitation of the analyte atom/ion is achieved by one or more of the three excitation mechanisms: collisional transfer of the excitation energy; energy transfer through metastable states of argon atoms/ions and charge transfer between argon ions and analyte atoms.

The main constraint in achieving better sensitivity by ICP- AES is, the low throughput of the sample due to very poor nebulization efficiency. Further, low tolerance of dissolved solids in essentially solution sampling methods leads to poor relative detection limits. Prior chemical separation of the analytes from a matrix has, therefore, become a pre-requisite to the application of ICP-AES technique to real-life samples. The low nebulization efficiency in ICP-AES can be improved by development of solid sample insertion devices or by combining it with electrothermal vaporization approach of ETA-AAS technique. Such hyphenations within the spectroscopic techniques result in marked improvement in sensitivity and precision otherwise attainable by conventional approach. ICP-carrier distillation approach and ETV-ICP combination developed in the laboratory, have been highly successful in the trace metal assay of nuclear materials. Of the other plasma sources such as DCP, CCP and MIP, DCP alone is known at present for its practical utility for simple aqueous systems. As the sample never senses high temperature of the plasma in DCP, chemical interferences are more prevalent leading to poor reproducibility of analyte determinations. The working principles of ICP and DCP sources are shown in Figures 2 and 3.

In contrast to the near ideal excitation source such as ICP, d.c. arc suffers from poor excitation temperature, poor precision of determinations,

self-absorption effects etc. However, the d.c. arc source offers a distinct advantage over ICP in that it can facilitate selective volatilization and excitation of the analytes leaving behind the major matrix in the electrode crater due to the addition of suitable carrier material to the sample. The technique, commonly known as carrier-distillation technique, enables direct determination of a host of volatile and semi-volatile metallics at ppm concentration levels. The sensitivity of the method largely depends upon the choice and proportion of the carrier while the precision of determinations is governed by the excitation source and detection device. The d.c. arc-carrier distillation technique has a special role to play in the trace metal characterization of nuclear fuels and their base materials.

The high voltage a.c. spark-based AES technique enables determination of major and minor constituents of alloys such as stainless steel, zirconium, aluminum-based alloys etc. The excitation source offers moderately high sensitivity with better precision of determinations as compared to d.c. arc source. A significant improvement in the sensitivity can be achieved by transport of analyte vapors generated in the spark-chamber into ICP by argon carrier gas. The dissociation/excitation of analyte atoms/ions is thus secured by the plasma source.

HYPHENATED TECHNIQUES

As mentioned above, the latest trend in instrumental methods of analysis is to combine two or more analytical techniques into one to derive advantages and to overcome constraints of the individual techniques. Such combinations are aimed at arriving at a 'UNIVERSAL TECHNIQUE' but have so far achieved limited success. Notable combinations commercially produced are ICP-MS, GC-AAS, GC-MS and ICP-AFS. A typical ICP - AFS set-up is shown in Figure 4.

The charge detection methods used in conjunction with lasers and mentioned above combine the advantage of very high selectivity of the laser excitation with the ultra high sensitivity of charge detection. Some of the more established techniques include resonance ionization spectroscopy, laser-ionization/mass spectrometry and optogalvanic spectroscopy. The basic principle of trace analysis by laser ionization is the selective excitation of the required species followed by ionization. The ions

are then detected by collection at an electrode kept at a suitable voltage. In more sophisticated set-ups, a time of flight or quadrupole mass spectrometer followed by suitable ion detectors are used. The main disadvantage of the laser ionization technique caused by non-selective background ions produced out of the matrix, can be overcome by multi-step ionization processes where the laser powers employed are very small. Laser ionization and ion detection for analysis has currently been refined to an extent where a few atoms of a trace component present in various kinds of matrices can be routinely detected. Some of the related techniques include calorimetric methods which make use of the conversion of the absorbed radiation into heat energy. The absorption measurements are made by photoacoustic detection, thermally induced phase shift, thermal lensing and optothermal detection techniques.

As mentioned earlier, let us now examine briefly as to how successfully some of these techniques have been applied in various fields:

Nuclear Industry:

The most important application of analytical spectroscopy in this field is its vital role in trace metal characterization of nuclear fuels and base materials. The trace metallics of relevance to nuclear fuel performance are: Ag, Al, B, Be, Ca, Cd, Co, Cr, Cu, Dy, Eu, Fe, Gd, Li, Mg, Mn, Mo, Na, Ni, Pb, Si, Sm, Sn, Ta, V, W, Zn and Zr. The nuclear fuels and fuel materials of current interest are: UO_2 , PuO_2 , $(\text{U,Pu})\text{O}_2$, $(\text{U,Pu})\text{C}$, $(\text{U,Pu})\text{N}$, $(\text{Al}-\text{U}^{233})$ alloy, $(\text{Al}-\text{Pu}^{239})$ alloy U_3Si_2 , ThO_2 , ZrO_2 and nuclear grade graphite. Based on the nature of the analytes and their analytical requirements in terms of the upper permissible concentrations in the fuel materials, the host of metallics listed above are classified into three groups and analyzed by separate techniques.

I. D. C arc-carrier distillation approach in AES: A group of metallics viz. Al, B, Be, Ca, Cd, Co, Cr, Cu, Fe, Li, Mg, Mn, Mo, Na, Ni, Pb, Si, Sn, Ta, V, W and Zn are normally determined using the above mentioned technique. The most important parameter to be optimized for the success of the method is the choice and proportion of a carrier / carrier combination which would facilitate selective volatilization of the analytes in the presence of the refractory form of the major matrix. The other parameters to be optimized are d.c. arc current, arc gap, axial viewing position of the arc, analytical charge in the electrode crater etc. In

view of the complex nature of the fuel materials, these parameters do vary to an appreciable extent, thereby necessitating development of separate methods for each of the matrices of interest.

II. ICP-AES Technique: The group of the lanthanides, in particular, Sm, Eu, Gd and Dy are the specification elements with stringent specification limits. Further, they are as refractory as uranium/plutonium matrices. The carrier distillation type of analytical approach, therefore, does not work here. The analytes are, therefore, chemically separated, pre-concentrated and then analyzed using d.c. arc/ICP-based AES methods. The ICP-AES offers better sensitivity and precision of determinations. However, in view of the high excitation temperatures available in ICP, tolerance of major matrix in the aqueous phase is extremely low as compared to that in d.c. arc source. As a result additional precautions need to be observed to have a matrix free aqueous solution prior to the analysis by ICP- AES technique.

III. ETA-AAS Technique: The technique, normally offers an in-house independent check on the determination of a number of crucially important metallics otherwise determined by AES technique. These include Ag, Cd, Zn etc. A multifold approach is generally adopted in ETA-AAS which includes direct analysis of sample solutions/solids and analysis of solutions on chemical separation of the major matrix.

The specification limits for the metallics in nuclear fuel materials used in thermal and fast reactors are in sub-ppm to ppm range depending upon the critical nature of the trace metal vis-a-vis fuel performance. By convention, the analytical range for any element should cover at least a factor of two lower and four times the specification limit. This condition is easily met by each of the three techniques described above.

Environmental Analysis

Materials of interest in environmental studies encompass a variety of matrices such as air, water, plant material, animal tissue, dust, industrial and domestic refuse, sewage sludge, sediment and soil etc. Determination of metallic constituents in major, minor and trace proportions of these materials is of immense interest to the environmentalist for reasons of their toxicity to human beings as also their adverse effect on animals and plants. AAS and AES methods have been fully exploited for the analysis of the environmental samples. ICP-AES technique is best suited for the analysis of water

and soil samples whereas analysis of air and biological materials falls within the domain of ETA-AAS. However, cost effective analysis of these samples by either of the two techniques needs prior knowledge of the specific requirements of the analysis.

The very high sensitivity of the AES methods for the determination of Be has found wide recognition while Pb in air is determined by flame- and ETA-AAS methods due to better sensitivity attainable for it in AAS technique. The small sample size requirement of ETA-AAS is of particular interest in air analysis.

Water: In many cases, capabilities of ICP and requirements of water analysis are ideally matched. (1) Water, being liquid, is easy for injection into ICP. (2) Except at very low levels of detection, water does not need chemical pretreatment. (3) Presence of Ca, Mg, Fe, Al etc. does not interfere with ICP-AES analysis. A large number of metallics can be determined in water by ICP-AES either directly or on pre-concentration. However, the analytical requirements of analysis such as Ag, As, Bi, Cd, Co, Hg, Pb, Sb, Se and Te in water samples are not met by ICP-AES techniques even after pre-concentration as reported by American data. Sea water and other saline waters are faced with certain problems. Different types of nebulisers claim varying degree of tolerance towards the salt content.

Domestic and Industrial Refuse: The heterogeneity of the samples in this category of materials is well known. The elements of primary interest are the common toxic elements such as Ag, As, Be, Cd, Cr, Cu, Hg, Ni, Pb and Zn. All the concentration of the elements except Be and Cd can be determined by the AAS methods. The potential of ICP-AES however can be beneficially used in the analysis of these materials as it takes care of the sporadic occurrence of high concentration of individual elements due to large linear dynamic range of the technique.

Animal and Plant tissues: The analysis of biological materials falls into two parts. (1) the task of quantitatively releasing a broad range of trace metallic into solution and (2) analysis of the resultant solution. ICP-AES method faces serious Analysis of elements ("impurities") at trace and ultra trace levels constitutes a significant component of the compositional characterisation of materials. The other aspect of establishing stoichiometry involves major or minor component

problems about the detection limits of toxic elements. Pre concentration methods being highly selective, do not help ICP-AES method. The ETA-AAS methods are more convenient and cost effective. The ashing stage particularly helps to get rid of the organic matter. Further, compatibility of ETA-AAS with solid sampling can be beneficially used in the application.

Metallurgical Analysis:

The most commonly used technique is based on the use of various types of high voltage sparks followed by AES. The major and minor constituents of alloys are conveniently determined by this way. The precision of the method can be improved by dissolution of the sample and by using ICP-AES technique. The high sensitivity offered by the technique can be fruitfully utilized by using dilute solutions and avoiding the problems, if any, of spectral interference and of sample transport due to high solid content. A combination of spark and ICP is proving to be very ideal and some commercial set-ups are available. The technique

avoids dissolution of the sample and thus improves sample transport efficiency significantly.

The solid sampling approach in ETA-AAS has also been explored for real samples and has resulted in good success. The most important condition to be met is the very small particle size preferably of 400 mesh coupled with weighable amount of the sample aliquots.

The ICP-AES method is also used successfully for the chemical characterization of some of the special materials such as superconducting compounds where stoichiometry plays a vital role. The high precision of the method helps in improved reliability of estimates.

In conclusion, spectroscopic techniques offer a comprehensive analytical approach in various fields. The analytical capabilities of the conventional techniques are greatly improved with the advent of plasma sources and high powered tunable dye lasers while hyphenated approach is aimed at achieving the best of the both worlds.

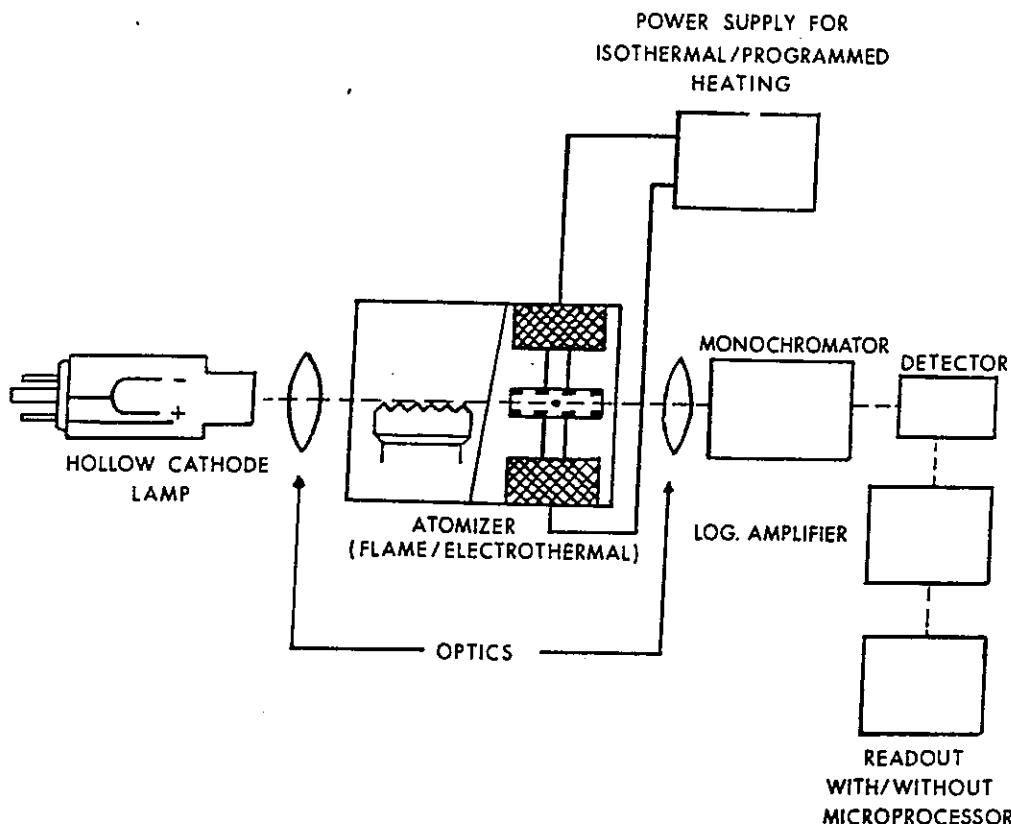


FIG.-1. BLOCK DIAGRAM OF ATOMIC ABSORPTION SPECTROMETER.

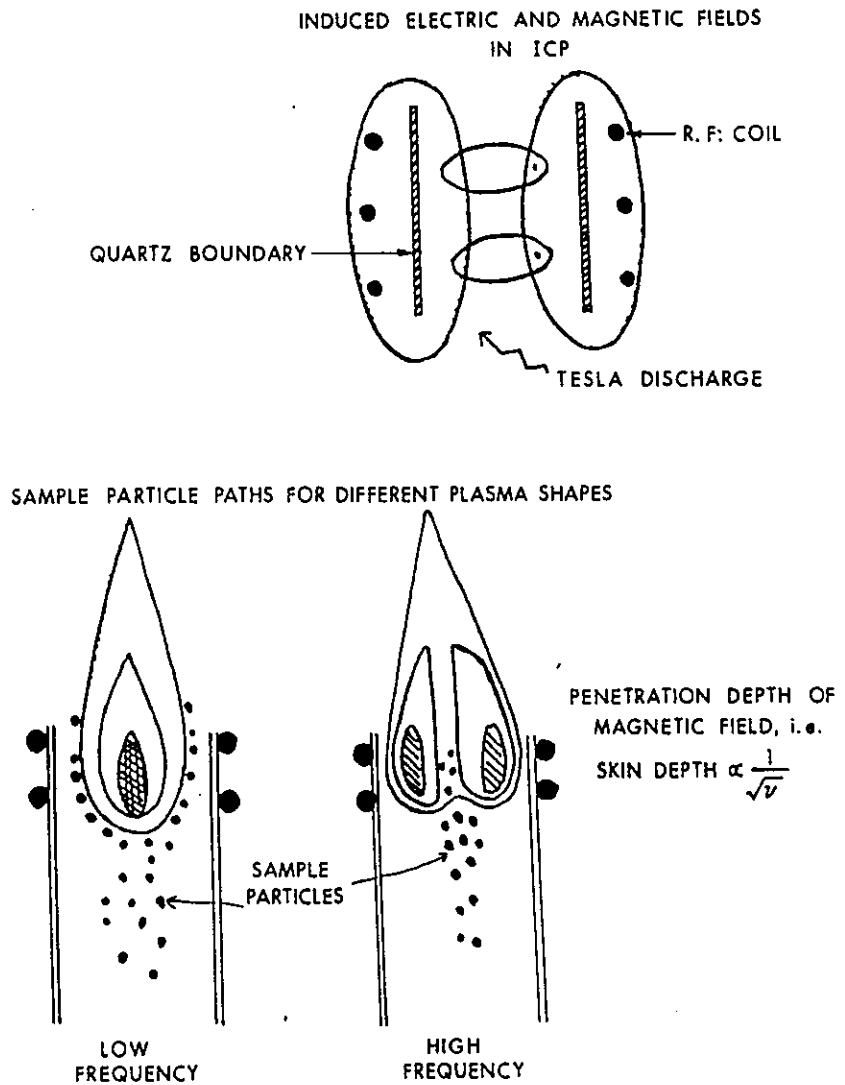


FIG. - 2. WORKING PRINCIPLE OF ICP.

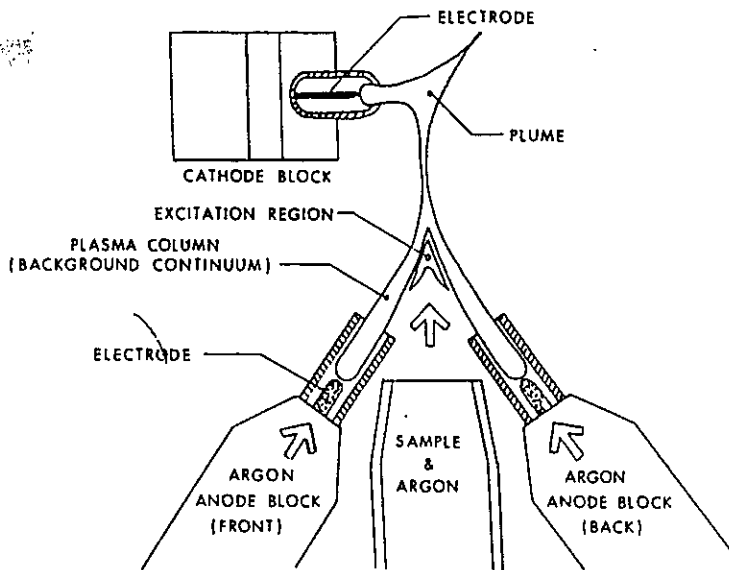


FIG.-3. A TYPICAL DCP CONFIGURATION.

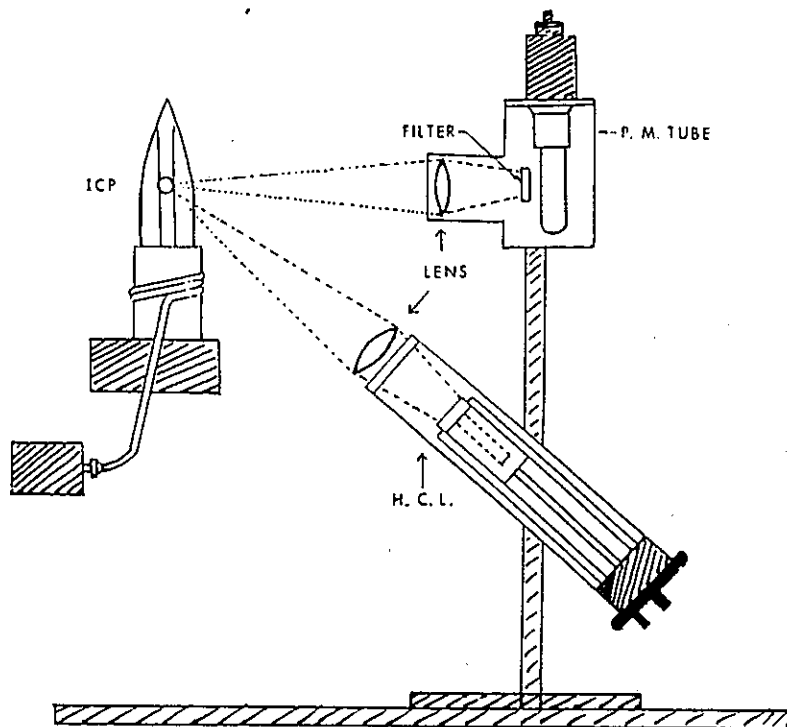


FIG.-4. A TYPICAL ICP-AFS SET-UP.

Atomic Mass Spectrometry In Biological And Environmental Sciences



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1. INTRODUCTION

1.1 WHY ELEMENTAL DETERMINATION IS REQUIRED?

Determination of trace elements in biological and environmental samples is required for many reasons. With the rapid industrialisation and increasing demand of electricity, there is a need to monitor the environment e.g. soil, water and air for carcinogens, pathogens and mutagens. Coal based thermal power stations occupy a key position in electricity production in our country and release fly ash to the atmosphere. This fly ash contains almost all the naturally occurring elements at trace levels. The analysis of coal for trace elements is required to predict its environmental impact with respect to heavy elements (e.g. Pb, Hg, Cd, As). Nuclear power reactors utilising U, Pu fuels demand the determination of actinides as well as of fission products (e.g. Sr-88, Sr-90, Tc-99 etc.) which are by-products in the nuclear fuel cycle.

There are many other industrial sources which may contaminate the environment with toxic metals. For example, lead (Pb) is released to the atmosphere due to its prolonged use in paints, as an anti-knocking agent in petrol and due to the presence of Pb smelters and refineries. The use of chromium (Cr) salts in leather industry for tanning of hides can lead to the pollution of the nearby well waters. Cr exposure can also occur due to chrome plating and manual arc welding of stainless steel. The combustion of municipal, chemical and medical wastes leads to metals (e.g. Cd) in the environment.

Different trace elements present in the environment can enter the human biological system and are known to have important implications in human health from the toxicological point of view. For example, minamata disease due to mercury (Hg) compound and a syndrome called "itai-itai" characterised by severe bone pain and osteomalacia due to Cd are well documented in literature. Pb present at trace levels in the blood affects the intelligence level in the growing children.

On the contrary, some trace elements are known to have important nutritional and clinical effects. For example, iron (Fe) binds, transports and releases oxygen in the body; copper (Cu) and nickel (Ni) are essential for several enzyme systems; Cr is involved in important biochemical processes such as glucose metabolism and the action of insulin. Selenium (Se) deficiency has been related to the Keshan Disease, an endemic cardiomyopathy primarily affecting young children and women of child bearing age. Compounds/salts of some of the elements like lithium, titanium, gallium, tellurium and platinum are beneficial to health through their pharmacological actions.

Studies on the trace elements are, therefore, required to answer the nutritional questions and to understand their bioavailability to humans as well as to establish their safe and toxic limits. For example, absorption and metabolism of calcium (Ca) is currently of great importance because of the wide spread incidence of metabolic bone disease osteoporosis. Though such studies in the past have been done using radioactive isotopes of different trace elements, more and more researchers are switching over to the use of enriched stable isotopes in healthy individuals particularly in in-

fants and pregnant/lactating women which are the subjects of prime importance.

1.2 DIFFERENT ANALYTICAL TECHNIQUES USED:

Conventionally, the most important information required for any element in biological and environmental samples is its concentration. A variety of analytical techniques are available and are being developed/used for this purpose. These include flame and flameless (also known as electrothermal or graphite furnace) atomic absorption spectroscopy (AAS), neutron activation analysis (NAA), sub-stoichiometry isotope dilution analysis, electrochemical methods like anodic stripping voltammetry etc. These methods are extremely useful for determining various elements at trace to ultra trace concentrations and have been playing important role.

As with any analytical technique, each of these methods has its own limitations like matrix effects etc. Some of these are single element techniques which are costly and generally require several sample preparation steps before carrying out the measurements. Some elements such as I and Te in coal are seldom determined because of the high cost and lack of convenient methodologies. Standard reference materials (SRMs) and interlaboratory intercomparison experiments are commonly used to validate the developed methodologies and check the reliability of the data. Needless to say, it is important to control the blank levels of the trace elements from the working environment, reagents, apparatus and personnel during the experimental procedure.

1.3 DATA REQUIRED ON TRACE ELEMENTS:

In addition to concentration values, the data on the isotopic composition of the trace element are also required. Most of the time, this information is not available from any of the above listed analytical techniques. At times, it can be obtained for some of the elements with great difficulty with poor precision and accuracy which may not meet the needs of the experimenter e.g. in any experiment using enriched stable isotope as a tracer.

The other information desirable for trace element is its speciation. Since the toxicity and absorption-excretion of any element depends upon its physical and chemical properties e.g. oxidation state, organic vs inorganic form, speciation studies

on trace elements are gaining increasing importance. Several metals such as Cr, As, Sn, Hg and Pb are well known for their different toxicities based on their specific chemical forms. For example, methyl-Hg is more toxic compared to inorganic Hg. Thus there is a need to use an analytical technique which can provide data on the concentration, isotopic composition and speciation of trace element in the sample.

1.4 NEED FOR MASS SPECTROMETRY:

Mass spectrometry is a powerful analytical tool for trace elemental determination in biological and environmental samples. The technique provides high sensitivity, holds the potential of quantitation with high accuracy, can give high throughput for screening purposes and is recognised as a reference and definitive analytical technique. It can provide data on the isotopic composition and concentration of the element. Mass spectrometry coupled with gas chromatography (GC), high performance liquid chromatography (HPLC) and supercritical fluid chromatography (SFC) can be used to obtain information on speciation of the element. Sometimes, mass spectrometry alone in conjunction with intelligent analytical chemistry can also be used to obtain information on speciation of some of the elements.

The use of a stable enriched isotope as an internal standard in the isotope dilution methodology for determining the concentration of the trace element obviates the need of quantitation recovery of the analyte from the sample. This quantitative recovery is difficult to achieve, at times, particularly when dealing with volatile elements. The use of isotope dilution mass spectrometry (IDMS) makes the results independent of the chemical yield or recovery of the element. In addition, the matrix effects are not important when IDMS is employed for concentration determination since the data on the change in the isotope ratio of the same element need to be measured experimentally

2. WHAT IS A MASS SPECTROMETER?

A mass spectrometer consists of an ion source for the production of ions (positive or negative, singly or multiply charged), an analyser for resolving these ions into various mass to charge (m/z) ratios, a detector and an on-line data acquisition and processing system. The ion source, the analyser and the detector are kept in high vacuum

(pressure 10⁻⁸ torr or less) by using a combination of rotary pumps, mercury or oil diffusion pumps, ion-getter pumps and turbo molecular pumps. High vacuum is essential to increase the mean free path of the ions and reduce their scattering by residual gas molecules. A sample introduction system is provided either externally to the ion source or is incorporated as an integral part of the ion source.

The ion sources commonly used in atomic mass spectrometry for trace elements determination in biological and environmental samples are inductively coupled plasma source and thermal ionisation or surface ionisation source. Other sources used are spark source, glow discharge source, secondary ion source and field desorption. These ion sources are provided in the dedicated systems for elemental analysis and have led to the development of various types of atomic mass spectrometry viz. thermal ionisation mass spectrometry (TIMS), inductively coupled plasma source mass spectrometry (ICPMS), spark source mass spectrometry (SSMS), glow discharge mass spectrometry (GDMS) and secondary ion mass spectrometry (SIMS) etc. Gas chromatography-mass spectrometry (GCMS) with electron ionisation/chemical ionisation (EI/CI) source and fast atom bombardment source mass spectrometry (FABMS) are the other two techniques which utilise the organic mass spectrometers easily available to many of the laboratories. The different types of mass spectrometric techniques are discussed below in the order of popularity with which they are being used for biological and environmental samples.

3. INDUCTIVELY COUPLED PLASMA SOURCE MASS SPECTROMETRY (ICPMS):

Inductively coupled plasma source mass spectrometry (ICPMS) depends upon the use of an rf induction field to generate a high temperature Ar plasma at atmospheric pressure into which the liquid sample is injected. The ICPMS instrument consists of a nebuliser (ultrasonic or pneumatic), an inductively coupled plasma torch, a plasma sampling orifice, ion extraction interface, a quadrupole mass filter and a pulse-counting detection system. Samples are usually introduced into the ICP in the form of aerosol generated by nebulising an aqueous solution of the sample at 1 mL/min. A small portion of the nebulised sample (1 to 3% for pneumatic nebuliser and 10% for

ultrasonic nebuliser) is swept into the plasma torch by a rapid stream of argon gas (10 to 15 L/min). In the atmospheric pressure ICP, the aerosol is subjected to a reaction zone having a gas temperature of about 5000K where the aerosol is atomised and ionised. The plasma gas containing the ionised sample flows into the mass spectrometer high vacuum chamber via a sampling orifice consisting of a sample cone and a skimming cone. The region between the sampling orifice and the skimmer orifice is maintained at a pressure of about 1 torr. The mass spectrometer region containing the ion lenses, the quadrupole analyser and the electron multiplier detector is at a pressure of about 10⁻⁵ torr. In this region, the ions are collected and focused into the quadrupole analyser. Ions of selected m/z leave the mass analyser and are deflected into the detector. Generally a channeltron (continuous dynode) multiplier is used in the pulse counting mode. Because of the low abundance sensitivity of the quadrupole systems used, the ability to measure accurately the low abundance ion adjacent to the major abundant ion is limited.

A high resolution double focusing ICPMS instrument with multi-collector detector has recently been introduced. Flat topped peaks obtained using the magnetic sector improve the accuracy and the use of a multicollector allows simultaneous isotopic measurements thereby eliminating plasma instability considerations and allowing high precision measurements. This instrument holds the potential of providing high precision and high accuracy data comparable to those obtained by TIMS with the advantages of simpler sample preparation and reduced analysis time.

The salient features which make ICPMS attractive are versatility of direct solution introduction, the large sample throughput, the high precision, increased dynamic range and the ability to perform isotope dilution. The multielement capability of ICPMS makes other methods like TIMS (discussed below) less attractive unless any possible increase in precision is justifiable. Some of the limitations of ICPMS include isobaric interferences from the singly charged and doubly charged atomic ions from concomitant elements and polyatomic molecular interferences due to the matrix composition introduced into the plasma as well as from argon, water and their reaction products in the plasma. In addition, non-spectral interfer-

ences due to matrix effects lead to suppression (sometimes enhancement) of the ion signal and severely affect the results. It is generally agreed that the total solid content of the analytical solution should be kept below 0.2% for continuous nebulisation. Mass discrimination, instability, drift of the ion signal and memory are the other problems which need be investigated in ICPMS. Different ways have been suggested to minimize/overcome these problems. These methods are based on internal standard (single or multiple) addition, standard addition, matrix matching and isotope dilution.

ICPMS has been used for determining trace elements Li, Fe, Co, Cu, Zn, Br, Rb, Sr, Mo and Cs in reference serum and in normal human serum. In was used as an internal standard and a matrix matched blank solution was prepared to subtract the apparent concentrations (spectral interferences) at the isotopes chosen for analysis. Multielement analysis of biological samples viz. bovine liver (NIST SRM 1577), IAEA certified reference materials (IAEA CRM H8 Kidney and IAEA CRM H4 animal muscle), IAEA mixed human diet H9 and human serum has also been reported. Accurate measurements of Li, Mg, Fe, Cu, Zn, Br and Se in biological fluids have been done for human metabolic studies. Dietary availability of different elements Mg, Fe, Cu, Zn and Se have been studied by using enriched stable isotopes as tracers. Zn absorption in infants and fractional absorption of Fe during pregnancy in women have also been studied using enriched stable isotopes as tracers.

The hyphenated technique of LC-ICPMS is the most popular technique for elemental speciation. For example, reversed phase LC, ion pair LC and ion exchange chromatography with ICPMS have been used for the separation and detection of AsO_3^- , AsO_4^{3-} , monomethyl arsenate, dimethyl arsenate and arsenobetaine species in dog fish muscle, urine wine and club soda samples with detection limits of 50 to 300 pg. Urine and water samples have been analysed for Pb speciation using reversed phase and ion pair LC at 0.2 to 3900 pg detection limits. Gas chromatography and supercritical fluid chromatography have also been used with ICPMS and microwave induced plasma MIPMS (using He instead of Ar) for elemental speciation.

ICPMS is gaining popularity for the determination of long-lived radioactive nuclides in the environmental and biological samples. For example, Tc-99 and Np-237 in the environmental soil sam-

ples and Th-232 and U-238 in biological samples were determined by this technique. In the latter, Bi-209 and Tl-205 (100 ng/mL) were used as internal standards to compensate for the non-spectral interference arising from matrix elements in sample solution. Detection limits of 3 and 1 pg/mL in solution were reported for Th and U, respectively. ICPMS has also been used for determining Pu-240/Pu-239 ratio in environmental samples since this ratio is useful to discriminate the source (nuclear facilities or from nuclear explosion testing) of Pu contamination in the environment. For example, Pu-240/Pu-239 ratio is 0.04 to 0.06 in the weapon grade Pu and the global fall-out Pu has a ratio of about 0.18.

Laser ablation (LA) with pulsed Q-switchable Nd-YAG laser is being used as an alternative sample introduction method for solids into ICPMS. As the solid is not dissolved, little or no sample preparation is necessary. In the case of powders, these are pressed into a pellet using a binder (e.g. boric acid) and milder ablation conditions are used than for solids. The precision of LA-ICPMS is much worse than that of conventional ICPMS due to signal fluctuations. The LA-ICPMS technique is very useful for the fast semiquantitative survey analysis of completely unknown samples. This technique is being tried as a complementary to d.c. arc optical emission spectrometry (d.c. arc OES) and X-ray fluorescence (XRF) spectroscopy for soil samples due to its superior throughput and sensitivity. Memory effect is stated to be a drawback of LA-ICPMS which necessitates the introduction of a cleaning step. LA-ICPMS has also been used for the multi-elemental analysis of whole coal. Detection limits of 0.003 mg/g for U and 0.4 mg/g for Se were reported.

4. THERMAL IONISATION MASS SPECTROMETRY (TIMS):

In a thermal ionisation mass spectrometer, a small drop of the solution containing sub-microgram to a few microgram amounts of the element is loaded on a suitable high purity metallic filament (Re, Ta, W, Pt) and the ions are produced by resistively heating the filament to achieve thermal ionisation. Single filament as well as multiple filament (double and triple) assemblies have been used for vaporisation and ionisation. Most of the time, singly charged positive monoatomic ions e.g. Mg^+ , Pb^+ , U^+ , Pu^+ etc. are employed. Sometimes, the singly charged positive molecular ions

are used to (i) circumvent the isobaric interferences (e.g. monitoring of oxide ions for heavy lanthanides in the presence of light lanthanide elements) (ii) reduce the extent of isotope fractionation and mass discrimination between the isotopes in the instrument (e.g. Li_2BO_2^+ instead of Li^+ for Li, Cs_2BO_2^+ instead of Na_2BO_2^+ for boron) and (iii) expand the range of elements amenable to TIMS (e.g. S as AsS^+). For the last couple of years, singly charged negative ions (atomic and molecular) have also been employed. The use of negative ions has been shown to (i) improve the sensitivity (by two orders of magnitude for B monitored as BO_2^-), (ii) eliminate the isobaric interferences (e.g. in Re-187/Os-187 using ReO_4^- and OsO_3^- ions, respectively) and (iii) widen the applicability of TIMS to non-metals and other elements (e.g. for halogens, Pt, Se etc). Using positive and negative ions, the technique is referred to as PTIMS and NTIMS, respectively. TIMS is a single element and at the most oligoelement technique and works well for actinides, lanthanides, alkalis and alkaline earth elements. Coupled with isotope dilution (ID-TIMS), it has the potential of providing the concentration data with the highest precision and accuracy and is therefore used as a reference and definitive analytical technique. The commercial TIMS instruments available these days are based on the use of extended geometry magnetic sector analyser or quadrupole analyser. The detectors generally used are secondary electron multiplier (SEM), single or multiple Faraday cups and the ion counting system (for extremely low ion currents from low abundant isotopes). The optimisation of different instrument parameters and the data acquisition and processing are carried out by an on-line computer. Presently, internal precision values of better than 0.01% can routinely and easily be achieved on isotope ratio data. Since the extremely high precision of magnetic sector based TIMS instrument is not justified for concentration determination of trace elements in biological and environmental applications where errors in sample handling and preparation stage overshadow the high precision achievable, the quadrupole based systems suffice for day-to-day requirements of trace elements work in these samples.

Moore and Machlan from National Institute of Standards and Technology NIST (formerly known as National Bureau of Standards NBS), USA were the first to report in 1972 high accuracy determination of Ca in blood serum by ID-TIMS using Ca-44 as an internal standard. Since then, ID-TIMS has been used for determining the concentrations of Li in blood plasma and urine, B isotope ratios in plant materials, K in serum, V in oyster tissue, citrus leaves, bovine liver and human serum, Zn in brain tissue of rats, Pb in fresh and canned pineapple, and Pb in diet, feces, blood, urine,

facial hair and atmosphere. Picogram quantities of uranium in urine of workers at the nuclear facilities have been determined.

TIMS has been used to study the mineral metabolism in humans by using enriched stable isotopes of Mg, Ca, Zn, Cu, Fe and Mo. Extensive studies have been performed on the kinetics of Ca absorption in humans using stable enriched isotopes of Ca as tracers (oral and IV). TIMS has also been employed to determine Pu-240/Pu-239 isotope ratio in the environmental samples.

TIMS is also invaluable for identifying the pollution source. Enriched rare-earth isotopes were proposed and used to tag emissions from multiple sources of fossil fuel combustion. As an example, enriched rare-earth isotopes Nd-148 and Nd-150 have been used to tag fly ash particles for studying dry particle deposition. Enriched isotopes of samarium (Sm-149 and Sm-150) have been used to tag the diesel fuel burned by (i) the city bus and truck fleet and (ii) residential heating oil, respectively. The tracers were converted into their oil-soluble organometallic chelates (tetramethyl heptane dione chelates) prior to mixing with oil. Picogram amounts of the tracers collected on quartz fibers were measured by TIMS, after spiking with Sm-152, to tag the particulate emissions from these two sources.

5. GAS CHROMATOGRAPHY MASS SPECTROMETRY (GCMS):

GCMS depends upon the formation of thermally stable and volatile metal chelates. It makes use of the commercial organic mass spectrometers available to many of the laboratories and is based on the ionisation by using 60 to 100 eV electrons from an incandescent filament in an electron impact (EI) source. The double focusing sector based mass spectrometers or the quadrupole based systems can be used. There have been several problems limiting the use of GCMS for trace elements analyses. These include the lack of recognition of suitable chelating agents, memory effect or carry-over effect during sequential analyses of samples of widely varying isotope ratios and poor precision and accuracy of isotope ratio data. In addition, the contributions of the different isotopes of C, N, S etc. present in the chelating agent need be accounted for, particularly when studying the enrichments in different samples followed by tracer administration (intravenous I.V. or oral). These problems have been solved for many of the

trace elements and suitable chelating agents have been recognised. The advent of fused silica capillary columns compared to the previously used packed columns has enhanced the sensitivity and separation efficiency of different metal chelates. Further, the introduction of bench-top GCMS systems equipped with auto-sample injector have increased the speed of analysis.

There are a number of advantages of GCMS approach over the other mass spectrometric techniques. Intensity ratio measurements are done in a mass range where the contributions from background are small and in many cases, the isobaric interfering elements are eliminated since various metal chelates have different retention times. Mass discrimination effects are fewer because the isotopic ions used for mass spectrometric analyses have smaller relative mass differences. An elaborate and time consuming protocol of filament degassing and heating is required in TIMS to keep the isotope fractionation effects in the ion source small, whereas no such procedure is necessary in GCMS allowing a considerable larger sample throughput (5 to 10 fold). When performing isotope dilution experiments using a spike (internal standard), the concentration of the trace element can be calculated by employing both the molecular ion and fragment ion peaks thus enhancing the confidence in the concentration data.

Isotope dilution GCMS methods have been validated for a number of elements viz. Ni, Cr, Pt, Cu, Se, Co, Cd, Pb, Hg and Te. A variety of thermally stable and volatile chelating agents have been identified for these elements.

6. FAST ATOM BOMBARDMENT MASS SPECTROMETRY (FABMS):

FABMS also sometimes called as particle induced desorption mass spectrometry is attractive because it requires little or no sample preparation and may be performed with a conventional high resolution mass spectrometer normally used for organic analysis. The former feature is especially important for studies of mineral nutrition and metabolism which often require analysing many samples and the latter is attractive because it does not require a mass spectrometer specifically designed for isotope ratio measurements. FABMS has thus the advantage of easy availability and offers good sensitivity for some of the elements like Mg, Ca, Fe, Zn etc.

In FABMS, 2 to 5 microlitre of the solution is placed on the probe tip (stainless steel, copper or gold) and dried in a stream of air. Sample probe is then inserted into the vacuum chamber. A beam of high energy atoms (e.g. Xe at 7 to 8 keV) is used to desorb the ions from the surface of the sample. Since the process is not selective, many different atomic species are produced from a complex matrix such as plasma or urine. It is therefore essential to use a high resolution (4000 or more) mass spectrometer. The desorbed or sputtered ions are accelerated and mass analysed in the usual manner. Precision values of about 1% RSD have been achieved by FABMS. However, to arrive at the accurate value for the isotope ratios, it was found essential to employ bracketing standards prepared by mixing natural standard and enriched isotope solutions. Some of the limitations of FABMS include interference due to metal hydride ions at some masses, manual introduction of the samples and the requirement of a high degree of operator skill and attention. Although FABMS cannot replace TIMS or ICPMS, it certainly provides a favorable compromise between the sample preparation time and the achievable precision.

FABMS has been reported for the determination of Mg, Ca, Fe and Zn isotope ratios in urine, plasma and fecal samples.

7. OTHER MASS SPECTROMETRIC TECHNIQUES:

A number of other mass spectrometric techniques have been used for trace elements in biological and environmental samples. Field desorption mass spectrometry (FDMS) has been used for alkali metals and alkaline earth elements. Secondary ion mass spectrometry (SIMS) has been used for Li, Ca, Mg and Te in biological samples as well as for localisation studies. The process used is to bombard the solid sample with energetic primary ion beam (a few keV) which not only causes ionisation but also leads to sputtering of the sample. The secondary ions generated are used for mass spectrometric analysis.

Glow discharge mass spectrometry (GDMS) has been reported for Pb and Pt at ppb levels in urines of patients receiving cancer chemotherapy with cis-platin. Several NIST certified fly ashes after mixing with high purity Ag powder for electrical conductivity and pressing into a pin form have been studied using the VG 9000 double focusing magnetic sector GDMS for evaluating the

viability of this technique. Accuracies varying from 5% to 25% for matrix to trace elements using the previously determined matrix independent calibration factors (relative sensitivity factors) have been reported. Spark source mass spectrometry (SSMS) has been evaluated for the analysis of plant (orchard leaves) and biological tissue (bovine liver). In this technique, a radiofrequency spark is generated between the two conducting electrodes in a double focusing mass spectrometer. Lasers and accelerators have also been used and have led to the evolution of resonance ionisation mass spectrometry (RIMS) and accelerator based mass spectrometry (AMS), respectively, for achieving extremely high sensitivity unsurpassable by the mass spectrometric techniques discussed above and for measuring low isotope ratios. RIMS has been used for the determination of Fe, Cu and Cr in biological samples. It has been developed and reported for determining extremely small concentrations of Sr-90, Tc-99, Np-237 and Pu-239 in environmental samples. AMS has been reported for the measurement of Al-26 and Ca-41 in biological samples. These two techniques (RIMS and AMS) are quite fascinating in view of their potential of providing the ultimate in sensitivity, but are being pursued presently in a limited number of laboratories around the world due to the complexity and high cost involved.

8. ATOMIC MASS SPECTROMETRY FACILITIES IN INDIA:

In addition to the highly skilled manpower requirements, one of the most important limitations of the mass spectrometric techniques is the high capital cost (ranging from a few tens of lakhs to about one crore of rupees) needed for setting up these systems. It may be noted that many of these facilities are available in the country. For example, TIMS instruments are available at BARC, Bombay; IGCAR, Kalpakkam; AMD, Hyderabad;

NGRI, Hyderabad etc. ICPMS are available at IGCAR and NGRI. SSMS is available at BARC and SIMS is being used at IGCAR and at NPL, Delhi. FABMS facility exists in the system available at CDRI, Lucknow. A number of laboratories in India use GC-MS for different purposes. These different facilities available in the country have been compiled in a Directory of Mass Spectrometers published under the auspices of the Indian Society for Mass Spectrometry (ISMAS). The interested readers can contact the author of the article for further information.

9. CONCLUSIONS:

It is beyond doubt that TIMS is a "gold standard" and provides the best precision and accuracy for isotope ratio data despite its slow speed and rigorous sample purification requirements. This would be the only method of choice when low enrichments are to be measured for extended periods of bioavailability studies or for environmental purposes which demand the highest precision. Since interelemental interactions have recently attracted great interest, ICPMS holds the potential of fulfilling the need for multielemental studies at trace levels. The number of laboratories using ICPMS for determining the isotope ratios and concentration of trace elements is ever-increasing and is currently the leading mass spectrometric method in biological and environmental sciences. Laser ablation for solid sample introduction in ICPMS is useful for fast semiquantitative survey analysis of completely unknown samples. FABMS and GCMS are useful viable alternatives to a large number of laboratories due to the non-availability of dedicated inorganic mass spectrometers like ICPMS, TIMS, GDMS etc.

Demonstration of half-life with ^{137m}Ba activity

Introduction : The half life period of ^{137}Cs is 30 years and that of the daughter, ^{137m}Ba , is 2.55 minutes, a convenient radionuclide to demonstrate the concept of half-life experimentally. At higher level the concepts of secular equilibrium can also be explained. Since, ^{137}Cs is a cow for the ^{137m}Ba activity, this experiment can be repeated with a reasonable gap of about half an hour. Ion exchange procedure⁽¹⁾ involved in the experiment for separation of the daughter activity is simple and clean.

Experiment :

Aim : To separate the ^{137m}Ba from ^{137}Cs and to follow its half life period.

Instrumentation and chemicals : Ion exchange column (dia around 5 mm to 1 cm and height from 10 to 30 cm), ammonium molybdo phosphate (AMP), asbestos, Ammonium nitrate, nitric acid, standard flasks (100 or 250 ml), distilled water, wash bottle, transfer pipettes, syringe, beakers, counting tubes, NaI(Tl) scintillation detector (of any volume and preferably a well type), associated electronic accessories (high voltage, pre-amplifier, amplifier, single channel analyser and scaler-timer) and linear or semi-log graph papers.

Procedure :

1. Solution-1: Prepare a standard solution of ammonium nitrate (1 N) (about 100 ml).

2. Solution-2: Prepare 0.1 N ammonium nitrate solution in 0.5 N nitric acid (about 100 ml)

3. Mix Ammonium molybdo phosphate and fine powder of asbestos is in 2:1 proportion and soak in solution-1.

4. Load the above paste in the ion exchange column to about 2cm height. Load about 500 bq of ^{137}Cs activity in 1 ml of solution-1. Wash the column with solution-1 (about 10 ml).

5. Elute the daughter activity of ^{137m}Ba using solution-2 and collect in a counting tube. Seal the counting tube with a parafilm.

Counting : Check the electrical connections of the NaI(Tl) counter. Put the mains 'on' and increase the high voltage to ~900 volts. Take a spectrum of standard ^{137}Cs and fix the appropriate base line and window width for the 662 KeV gamma peak. Note the background counts for 200 sec. Place the counting tube containing the eluted solution in the well of the detector. Note the time

and count the sample for 20 seconds. Follow the decay by counting the sample as a function of time. Record your readings as shown in the table given below. Plot the background subtracted count rate as a function of time on a linear graph paper and find half life of ^{137m}Ba . If semilog paper is available plot the background subtracted count rate as a function of time. From the slope, half life is calculated.

Reference

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Table : Settings of the counter and readings

High voltage:800 V	Base line voltage:4.2V
Window width:2 V	Counting time:20 sec.
Background:1600/200 s.	Background/20 s:160

Time Min.	Count /20 s.	Bkgd subtr. count/20 s.
0.0	2006	1846
0.5	1756	1596
1.0	1584	1424
1.5	1343	1183
2.0	1194	1034
2.5	1083	923
3.0	947	787
3.5	862	702
4.0	801	641
4.5	738	578
5.0	642	482
5.5	577	417
6.0	473	313
6.5	383	223