

**Editorial**

*Atomic spectroscopy is one of the oldest and well-established analytical methods. Spectroscopy is the measurement and interpretation of electromagnetic radiation absorbed, scattered or emitted by atoms or molecules. Absorption and emission of light is associated with changes in the characteristic energy states of interacting chemical species. Spectroscopy is used to identify the interacting species and also to obtain quantitative information.*

*By 1913, detailed and precise data were available concerning the light given off by atoms, although mechanics of the atom were not well understood. For years field of optical spectra had been the subject of diligent experimental research. Bohr's model of atom in 1933, explained characteristic emission and absorption spectra. Since then rapid progress is made in spectroscopic measurements both as a tool of research and for analytical measurements. Today, spectroscopy is an interdisciplinary branch of science and it finds applications in many branches of science like biology, geology, environment and nuclear science and technology. In the last century, rapid progress was made in spectroscopic instrumentation mainly due to the improvements in the detection technology and excitation sources, advent of lasers and evolution of computer technology. The potential of spectroscopy for analytical measurement is well known and most of the researchers use one or more of the spectroscopic techniques in the day-to-day research. In view of the vast progress made and wide range of applications, an attempt is made to bring a thematic bulletin on Analytical Spectroscopy encompassing the various facets of developments and applications. Dr. M.D. Sastry, Guest Editor of this bulletin, is a renowned spectroscopist, and has meticulously chosen the experts and topics for this bulletin. I thank Dr. Sastry and all the authors for their contributions.*

*Although it is impossible to cover all the aspects of the theme, I am hopeful that this issue will be of interest to both, the beginners and the experts in the field of spectroscopy.*

**A.V.R. Reddy**

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## ***From the Secretary's Desk***



*Greetings to the members!*

*Today, or even more in the future, there is the strong demand from Industry, medicine and research for analytical techniques, which allow the determination of absolute quantities of trace elements in the femtogram or even attogram range. Given the breadth of spectroscopy as a topic, it is not possible to cover the subject in its entirety. Hence it is intended to bring out this bulletin on 'Analytical Spectroscopy' to serve scientists who are interested in staying clued-up of activities and innovations captivating the chosen field. The objective and approach of this bulletin is to bring out the underlying principles and practices that govern the analytical aspects using spectroscopic techniques. The compendium of the 9 focal point articles symbolizes a wide swatch of topical areas of interest in the broad-spectrum of spectroscopy. The articles can be used to exemplify the many facets of the subject besides the questions that most textbooks address.*

*Dr.M.D.Sastry, one of the prominent spectroscopists in the Department of Atomic Energy has put versatile effort as a guest editor for this issue on "Analytical Spectroscopy". The articles contributed by renowned scientists are expected to assist the creative teacher in adding personality and depth to the field of Analytical Spectroscopy.*

*IANCAS Awards during AGM-2002: The IANCAS-Dr.M.V.Ramaniah Memorial Senior Radiochemist award was bestowed on Prof.Satyaprakash, Dayalbaugh Institute for his life-time contribution in the field of Nuclear and Radiochemistry. The IANCAS-Dr.Tarun Datta Memorial award was presented to Dr.(Ms.) Dalia Nayak, Chemical Sciences Division, SINP, Kolkata for her contribution in the production of carrier free nuclides useful in biochemical applications. The IANCAS-Prof. Arnika Best Thesis award-2001 was presented to Dr.(Mrs.) Aruna Korde, Radiopharmaceuticals Division, BARC for her work on the development of in-vivo and in-vitro Radiopharmaceuticals involving radiolabelling. IANCAS compliments all the awardees. I derive pleasure in including the citations in this issue.*

*Southern Chapter: The request from our members from IGCAR, Kalpakkam to form a Southern Regional Chapter with head quarters at Kalpakkam to provide IANCAS services in that area has been acceded to with the Charity Commissioner approving the inclusion of the necessary byelaws to facilitate the creation of a Regional Chapter of the association.*

*IANCAS plans to bring out a member directory with addresses and members are requested to update their postal and email addresses*

*BRNS has been encouraging and supporting one of the chief activities of IANCAS, namely organizing the National Workshops on 'Radiochemistry and Applications of Radioisotopes'. IANCAS is grateful to BRNS for appreciating the publication of these thematic bulletins with generous grants every year.*

## **Analytical Spectroscopy**

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## FOCUS

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*At the outset, I wish to compliment the Indian Association of Nuclear Chemists and Allied Scientists (IANCAS) for bringing out a Special Bulletin on Spectroscopic Methods. Spectroscopy has come a long way from being a tool of experimental physicists for determination of energy states of electrons in atoms and molecules. It has evolved into a prominent inter-disciplinary science augmenting several aspects of physics, chemistry, biology, medicine and environmental sciences. Many spectroscopic investigations have contributed to areas and activities which IANCAS has been addressing. The contribution of spectroscopy to nuclear and environmental sciences are of fundamental importance and has also led to development of day-to-day analytical and diagnostic tools which have become indispensable. The fundamental aspects of spectroscopy, which contain nuclear information, are: the isomer shift and isotopic shifts of spectral lines and magnetic hyperfine interactions. The isomer and isotopic shifts both arise due to electrostatic interactions of nucleus with finite volume, and hyperfine structure arises due to magnetic hyperfine interaction for nuclei with non-zero spins. High resolution laser spectroscopic techniques have yielded unprecedented data on isomer shifts and their dependence on nuclear shape and volume changes. Some of these aspects are covered in this issue, including resonance ionization and opto-galvanic techniques. The high resolution spectroscopic techniques in solids also gave unique information on electron-nuclear interactions in excited states. The potential of spectroscopy as an analytical tool is too vast and too well-known. The recent trends in total reflection XRF, ICP-MS, ICP-AES and AAS have been covered. In addition to the application to nuclear fuels, their utility for geological and environmental samples and bio-medical samples are exhaustively covered. The instrumental techniques, particularly for analytical applications, are on the fast track, making obsolescence a frequent occurrence. The indigenous efforts in electronic and optical instrumentation, and an update on the instrumental methods included in this issue would serve as useful material for new entrants to analytical spectroscopy, and also for practicing analytical spectroscopists. With this in view, a literature update on ICP-AES and AAS are also included as these are more common techniques practised by analytical spectroscopists. The contributions to this issue have come from different groups working in National laboratories. From a recent experience in conducting an Inter-Laboratory Comparison Experiment for analytical procedures, involving various DAE laboratories, it appears to me that vast potential and scope exists for developing spectroscopic standards, of international acceptability, for various materials, if all laboratories work together towards this goal.*

*It is earnestly hoped that this issue, a collection of contributions from practicing and accomplished scientists in the respective fields, will seed interest in the beginners and serve as an update for experienced workers in the field.*

# Optical Spectroscopy for Nuclear Sciences : Glimpses of Perspectives and Frontiers



*Dr. M.D. Sastry obtained his Ph.D. In Physics in 1968 from IIT, Kanpur and worked as a postdoctoral research associate at University of British Columbia, Vancouver, Canada, University of Newcastle Upon Tyne, England and University of Leeds, England, before joining Radiochemistry Division, BARC in March 1973. His main areas of interest are solid state spectroscopy of actinides and analytical spectroscopy for trace metallic assay of nuclear fuel materials. He has worked extensively on electron paramagnetic resonance (EPR) spectroscopy of metal ion complexes in condensed matter, radiation damage using EPR TSL correlation and structural phase transitions. He has built-up facilities for photocaustic spectroscopy of solids and investigated a number of plutonium compounds. He is currently head of the Spectroscopy Section of Radiochemistry Division, BARC.*

## Introduction

Traditionally spectroscopy is directed at the elucidation of electronic structures of atoms and molecules, and its growth coincided and accelerated with the growth of quantum mechanics in the early part of 20<sup>th</sup> century. Bohr's model [1] of atom, resulted in a neat expression for the energies (in wave number units) of light quanta emitted (or absorbed) by an atom, due to transitions of electrons between different stationary states. This is given by

$$\bar{\nu} = Z^2 R (1/n_f^2 - 1/n_i^2) \quad (1)$$

where  $n_i$  and  $n_f$  refer to the principal quantum numbers of initial and final states,  $Z$  is the atomic number of the element and  $R = 2\pi^2\mu e^4 / ch^3$ , called Rydberg constant ( $\mu$ =reduced mass). This expression implicitly conveys that the spectral line contains the fingerprint of the element emitting the radiation and its mass through  $Z$  and  $\mu$  respectively and hence can be used for identifying the elements and their isotopic species. This was the basic reason for using spectroscopy as a tool for identification of chemical elements. In fact, the discovery of helium in the spectrum of sun, and of deuterium in the laboratory are a few classic examples of the beginning of analytical spectroscopy, in addition to

the discovery of Fraunhofer lines in the solar spectrum at the time of total solar eclipse.

Over the last eighty years or so, spectroscopic measurements leading to a complete description of electronic structure of atoms and molecules, made significant impact on physical, chemical and biological sciences and also formed the basis for understanding a number of aspects of stellar and interstellar space. This is evident from the work being done using the Hubble-space Telescope [2]. In the normal laboratory investigations, a great revolution occurred in spectroscopy with the advent of lasers and the development of intense tunable lasers. The synchrotron radiation facility has brought yet another revolution as it serves as an intense source for the UV and X-ray studies of highly excited atom and the electronic structure of solids.

Over the last few decades the development of spectroscopic techniques were primarily focused on two aspects.

- (i) Improving the resolution to a very high degree.
- (ii) Improving the photon detection sensitivity, optimizing both intrinsic and extrinsic factors i.e. improving the detection technology.

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**TABLE 1. The interactions experienced by electrons in a multielectron atom, and the relevant spectroscopic methods.**

Interaction term in the Hamiltonian	Effect of the interaction	Spectroscopic methods used to investigate the interactions.
$= - (\hbar^2/2m)\nabla^2 + Ze^2/r$	Hydrogenic atom, the electron is characterized by $n$ and $\ell$ quantum numbers.	X-ray methods, Photoelectron/deep level spectroscopy
(electron-electron repulsion + spin-orbit + hyperfine interactions) $e^2/r_{ij} + 3\mathbf{L}_{ij} \cdot \mathbf{S}_{ij} + A \mathbf{I} \cdot \mathbf{J}$	Russel Saunder States, the lowest state (Hund's rule) has minimum e-e repulsion (The hyperfine term $A \mathbf{I} \cdot \mathbf{J}$ gives rise to $F = \mathbf{I} \oplus \mathbf{J}$ )	High Resolution Laser Spectroscopy of atoms
$+ eV_{\text{cryst.}}$	Crystal (ligand) field effects acting on $ L, S, J\rangle$ states. This term is absent for free ions/atoms	Absorption and fluorescence in solids in UV-visible region. Absorption in crystal field states for a given $ L, S, J\rangle$ manifold is in IR region.
Electronic Zeeman + Hyperfine + Nuclear Zeeman interactions	Lifting of degeneracy of $ M_s, M_I\rangle$ a given $ L, S, J\rangle$ manifold	Resonance methods : EPR in microwave region, and NMR/NQR in radiofrequency region (for ground states) High resolution Laser Spectroscopy (FLN, etc.) for crystal field and hyperfine effects in solids, both in ground and excited states

The former one is most important for elucidating all the interactions that can be experienced by electrons in atoms/molecules. The high resolution spectroscopic techniques of atoms and molecules in gas phase made enormous progress in the last 30 years. The effects due to Doppler broadening could be avoided using elegant saturation spectroscopic techniques such as Lambdip, and two photon absorption [3]. These methods have been proved to be invaluable in the study of nuclear properties through hyperfine interactions [4]. A recent and most remarkable [5,6] outcome of these endeavours, is laser cooling and Bose-Einstein condensation of alkali atoms ( $10^3$ - $10^5$ ).

Some of the high resolution laser spectroscopic techniques in gas phase (discharge tube or flame), with special reference to resonance ionization and resonance absorption detected by change in discharge current (optogalvanic spectroscopy) are

discussed by B.M.Suri [7], in this issue. High resolution laser spectroscopy techniques made impressive impact even in the case of electronic spectra of ions in solids [8-10]. These are fluorescence line narrowing (FLN) and hole burning and optical-microwave/r.f. double resonance techniques [11] enabling the detection of hyperfine interactions in the ground and excited states. Table 1 lists all the interactions experienced by a multielectron atom, both in gas phase (free atom) and in solid matrix subjected to (crystalline) electric and magnetic field. The different spectroscopic methods used to elucidate these interactions are also given.

The development of instrumentation, including more recent advances in detection systems are presented in two articles in this issue, and an update on the analytical instrumental techniques are discussed by Page [12]. The present article is confined to some of the aspects not covered in other



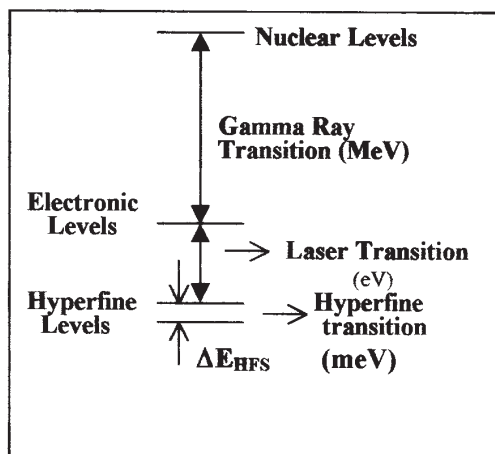


Fig. 1 Laser-Nuclear interaction, The hyperfine interaction is the link which couples together the electrons and nucleus of an atom, and thus provides a means by which laser radiation can probe and orient the nucleus. Another important interaction, the isotope shift, is due to the nuclear mass and charge distribution [4]

articles. In high resolution spectroscopy, those aspects which utilize electron-nuclear hyperfine interactions, are presented, as it extends spectroscopic investigations to the areas of interest to nuclear physicists and chemists. In this subsection, illustrative examples both from gas phase and solid state spectroscopy are presented. In the case of analytical spectroscopy, photothermal techniques only are presented, as it has the uniqueness where in the sample under investigation itself primarily acts as the detector and it can be optimized to improve the detection sensitivity.

### High Resolution Techniques for studying Hyperfine Interactions

#### Gas Phase

Electron-nuclear hyperfine interactions of stable nuclei have long been investigated using optical spectroscopy. With the improvements in high resolution spectroscopic methods, such studies could be extended to even shorted lived nuclides resulting in extremely useful data on isotope/isomer shifts, nuclear spins and moments. The intense

optical fields provided by lasers enabled the production of nuclear spin polarized beams and targets. In many of the experiments a combination of high resolution laser spectroscopic methods for selective excitation of atoms, together with nuclear radiation detection were gainfully employed. Many of these aspects were discussed in an article by Feld [4]. Fig.1 gives the schematic representation of the electron-nuclear interactions that can be investigated. Atomic fluorescence following selective excitation and saturation spectroscopic methods such as Lambdip techniques were used to resolve the hyperfine levels. Typical values for line width, obtained, were of the order of a few MHz. Atomic beam laser optical pumping methods were also found to be extremely sensitive and yielded a wealth of data on long chains of radioactive isotopes of alkalis. Optical pumping methods were also used for nuclear orientation, called laser induced nuclear orientation (LINO), and the hyperfine interaction information is obtained by monitoring the anisotropy signal of gamma emission as a function of laser tuning. Since the angular distribution of the induced anisotropy can be sharply peaked and due to very low background count rates, this technique is extremely sensitive. Nuclear orientation induced by Laser Optical Pumping methods were used to measure the isomer shifts of a nuclear excited state in  $^{134}\text{Ba}(10^+)$  [ $t_{1/2}=2.63 \mu\text{s}$ ]. Using optical pumping techniques to get isomer shift data, the relationship between the deformation parameters, quadrupole momenta and isomer shifts for spontaneous fission isomer  $^{240\text{m}}\text{Am}$  were established. The laser induced Nuclear Orientation technique is applicable over a wide range of nuclear life times down to  $\sim 10^{-9}$  sec.

#### Condensed Matter

The solid state spectroscopy of ions (typically trivalent lanthanides), enables detailed study of various interactions between rare-earth ions and the environment. The early work was mainly focused on obtaining their energy levels and transition. This resulted in the classic and indispensable energy level diagram prepared by Dieke and Crosswhite in 1963. By addressing the problem of line broadening, and developing "Non Linear Laser Spectroscopy" including Optical-microwave-radiofrequency multiple resonance techniques, which resulted in resolution increase of  $10^4$ - $10^6$  over conventional

spectroscopy, newer insights are obtained in electron-nuclear hyperfine interactions, energy migration, the structure of defect centres and the nature of inhomogeneous broadening [10,11].

Spectral lines of ions in solids, can be categorized as homogeneously broadened and inhomogeneously broadened. Homogeneous broadening, experienced equally by all ions, is caused by dynamic perturbations, such as lattice phonons or fluctuating nuclear or electron spins. In addition to homogeneous broadening, there is an inhomogeneous contribution to the line width, due to interactions which are not experienced equally by all ions. This is predominant due to static lattice strains inherent in all crystals since they solidify at a finite temperature, and due to the presence of other chemical impurities. In the case of glasses, inhomogeneous broadening is much larger (upto hundreds of  $\text{cm}^{-1}$ ) than in high quality crystals.

The high resolution spectroscopy work in solids, was done mostly using fluorescence line narrowing (FLN), spectral hole burning and coherent transient spectroscopy techniques. In both these techniques a small portion of inhomogeneously broadened line is excited, and its effects are monitored either in emission (fluorescence) or absorption (Spectral hole burning). When a narrow portion of an inhomogeneously broadened line is excited with a narrow band light source, the resulting fluorescence is often quite sharp. The resolution obtained is instrumentally limited and is of the order of 50 MHz, in the case of an interferometric detection. FLN has been used to measure ground state hyperfine splittings in  $\text{LaCl}_3 : \text{Pr}^{3+}$  and  $\text{LaCl}_3 : \text{Nd}^{3+}$ .

In spectral hole burning, as with FLN, a narrow portion of the inhomogeneously broadened line is excited, and the selective depletion of the population is observed by monitoring the bleaching of absorption. This is done by using a probe laser scanning it through the frequency originally excited. Thus, the ultimate resolution is determined by the frequency stability of the laser itself, since the laser filter adds directly to the line width. For single frequency CW laser the filter width is typically 1-2 MHz. In hole burning experiments, the information obtainable depends upon the population reservoir i.e. the states in which the ions that have been

removed from the ground state are stored. The most important population reservoirs for rare earth ions are provided by hyperfine, superhyperfine splittings of the ground state. The data obtained can be comparable to that of radio frequency spectroscopy in resolution with higher sensitivity of optical spectroscopy. Transient hyperfine interaction and nuclear Zeeman effect were observed in  $\text{LaF}_3:\text{Pr}^{3+}$  using hole burning methods [10]. These saturation spectroscopy measurements have immense potential to investigate actinide doped glasses. Some interesting work was reported on  $^{248}\text{Cm}^{3+}$  in fluorophosphates and fluorozirconate glasses [14]. These are relevant to understand the distribution of site symmetries of actinides in matrices used for waste immobilization.

### Analytical Spectroscopy for Nuclear Materials

Trace metal characterization of nuclear materials including U, Pu and Th based reactor fuels and reactor components such as Zircaloy used as cladding material, are among the most important applications of analytical spectroscopy in nuclear industry. B.Gopalan [15] has reviewed the methods followed on a routine basis. A.G.Page [12] has given an update on the relevant instrumental methods. In this article only photothermal and photoacoustic spectroscopy applications for analytical purposes are included, as this important aspect was not discussed by other authors in this issue. More importantly, photothermal spectroscopic methods have the unique distinction that the sample itself acts as a 'detector' and the sensitivity of detection can be enhanced by proper choice of a sample matrix/material having suitable thermal and optical properties. As actinide ions in condensed matter are best suited for photothermal investigations due to the predominant non-radiative relaxation of their electronic excited states, these techniques offer tremendous possibilities for detection and speciation of actinides in condensed phases at low concentrations. Furthermore, these techniques permit spectroscopic studies in opaque or highly scattering materials.

In photothermal methods, the temperature rise in the sample following an optical absorption or changes caused thereof, is detected as a function of exciting wavelength. Such a spectrum contains information about the electronic absorption. The



strength of the signal, being dependent upon the energy deposited in the medium, can be enhanced by increasing the intensity of the source. (This is in contrast with the normal optical absorption spectrometry). Furthermore, the signal intensity contains information both about the optical property of analyte chromophore, and the thermoelastic property of the medium. Therefore, for a given analyte, the signal can be improved by proper choice of the medium. The thermal waves generated by the heat release result in several effects which have given rise to various techniques [16]. These are : Temperature rise (Optical / laser calorimetry), refractive index gradients above and inside the sample (Photorefractive techniques including thermal lensing, probe beam refractive interferometry and deflectometry), and indirect and direct sound waves (Photoacoustics), Among these, laser based photoacoustic spectroscopy and thermal lensing (Probe beam refraction/deflection) techniques are more widely used for getting both spectroscopic and analytical (quantification of the species) information.

By irradiation of an absorbing solution with CW laser, the heat evolved by radiationless processes produces a temperature rise which modifies the refractive index of the medium. This induces the formation of a thermal lens [16] which in most cases is divergent. This fact depends on the sign of the temperature of the refractive index ( $dn/dT$ ) which is negative for most solvents. The formation of divergent thermal lense can be monitored by following the laser beam size of a good TEM<sub>00</sub> mode, of a He-Ne or Ar ion laser. The magnitude of the signal would be larger in media with large negative values of  $dn/dT$  and low thermal conductivity. Most of the common organic solvents, such as bezene and carbon tetrachloride, give good signals compared to water. In the case of Photoacoustic spectroscopy, the photothermal signal is converted to an acoustic signal by chopping the excitation at an acoustic frequency. Laser photoacoustic spectroscopy has been used to speciate and detect U, Np, Pu and Am in natural solution samples in  $10^{-7} - 10^{-8}$  M/L range [17].

A combination of thermal lensing and HPLC could be used to detect 1 ng of Uranium [18]. Photothermal methods, particularly thermal lensing

methods, offer tremendous new possibilities to detect , speciate and map the distribution of actinides ions on any solid surface.

### Summing up

An attempt has been made to give a glimpse of tremendous progress made in optical spectroscopy, with a special reference to nuclear sciences. The improvements in high resolution methods, both in gas phase and condensed matter, helped in accurate measurements of electron-nuclear hyperfine structure parameters. In gas phase, significant data could be generated on isotopic and isomeric shifts of many radioactive nuclides. From this, the systematics of size and shape variations in an isotopic chain could be understood, leading to a better understanding of the nuclear structure. In the case of solids, the high resolution methods helped in getting hyperfine interaction data both in ground and excited states. In the area of analytical spectroscopy, photothermal methods were described as they often provide unique opportunities for actinide speciation and quantification.

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## Recent Trends in Instrumental Methods in Analytical Spectroscopy



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Analytical spectroscopy provides compositional characterization of a sample under investigation by identifying the wavelength and measuring intensity of the spectral line/band, absorbed/emitted by the constituents of the sample under the influence of external radiation field. The precise quantification of constituents, is however, limited largely by the signal saturation effects. Because of the highly sensitive nature of the techniques, macro scale determinations can, very often, cause saturation effects such as concentration quenching, self-absorbance, 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 these techniques can provide the best possible experimental procedures for examining purity of highly pure materials. These techniques also play a vital role in solid state spectroscopy for the quantitative determination of dopants used as probe ions in crystalline host lattices. 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 such as high T<sub>c</sub> superconductors, nuclear fuel materials, cladding and coolants in nuclear reactors etc. The analytical

spectroscopy has been classified into three branches viz. absorption, fluorescence and emission spectrometry. In the present discussion, it is planned to enumerate the advances made in each of these three fields of study and their implications on achieving better performance or on removal, at least partially, the limitations in a conventional approach. Over the years, common emphasis in the R & D studies conducted for these techniques, has been, on introduction of the concept of PC-based operation and consequent development of analytical software. This has resulted in automation of many experimental parameters, precise control on variables, data acquisition and retrieval etc. On the whole, these advances have brought in, an ease of operation thus eliminating the need of a highly skilled operator. Further, personal errors, having been reduced, precision of determinations has improved significantly. In the following discussion, emphasis will be laid on improvements other than this, so that proper evaluation of R & D studies can be carried out.

### Absorption Spectrometry

UV-visible – near IR Spectrophotometry is a well known technique in absorption spectrometry. Being susceptible to interference problems, greater emphasis is placed on providing solutions for the

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same. A major breakthrough in this regard is provided by studying the derivative spectra which would ensure better accuracy though at the cost of sensitivity. Higher order derivative spectra are very often studied in case of complex matrices. The accessories such as fluorescence and reflectance attachments, help in making the basic instrument more versatile while cryogenic facilities enable study of spectra free from vibrational structure. The temperature dependent measurement of absorption spectra help in studying stability of various complexing species as a function of temperature. The conventional IR spectrometry - hitherto a qualitative analytical technique, is largely replaced by Fourier Transform Infra Red (FTIR) spectrometry due to several advantages that the latter offers in extracting quantitative data with greater precision.

The Atomic Absorption Spectrometry (AAS) is based on flame or electrothermal mode of atomization. The common improvement in both the techniques is related with the way the background correction is applied such as high frequency D<sub>2</sub> lamp correction so that loss of signal will be minimum. There are three essential aspects of AAS viz. (i) Generation of characteristic radiation (ii) Generation of atom vapor and (iii) Detection and measurement of absorption signal. Each one of these aspects have undergone significant change for improving performance or for making the AAS technique a versatile one. Standard source of characteristic radiation is Hollow Cathode Lamp (HCL). Single element sources are being replaced by multi-element one. These are then coupled to prism/grating spectrographs fitted with photodiode array [1]. Very significant amount of R&D efforts has undergone in changing over from line source (LS) to continuum source (CS) such as xenon short arc lamps. These are then coupled with Echelle spectrometers fitted with charge coupled devices as detectors. The CS-AAS has definitely bright future as the simultaneity of multi – element detection / determination will have been achieved by it – a distinctly positive feature of atomic emission spectrometry which otherwise scores over the conventional AAS approach [2]. The atom vapor generation through the use of chemical flames has not undergone any qualitative change over the years while electrothermal atomization mode has made

significant progress. The isothermal heating of the graphite furnace has been achieved in both longitudinal and transverse heating modes to prevent condensation of atom vapor at the ends of the furnace. Radiative mode of heat transfer forms the basis for tungsten wire heating as also the platform based heating of samples. The former mode also helps in preventing analyte - carbon reaction and thereby avoiding formation of stable analyte carbides. The analyte-carbon interaction can also be avoided by using high melting point metal sleeving of the graphite tube such as Ta/W sleeving. The pyrolytic coating of the graphite furnace can be preserved over a large number of atomization cycles by using addition of xylene as an intermediate step during atomization of the standards/samples [3]. Such effect is also achieved using argon-methane gas mixture as the environment around the graphite furnace [4]. In hyphenated approach of analysis, the carbon tube atomizer is used mainly as a vaporizer and the vapour/atom stream is transported by argon gas to the inductively coupled plasma for dissociation/excitation processes. The method known as ETV-ICP-AES has best of both the worlds i.e. the limitations of AAS methods are removed and the advantage of better precision and uniformly good detection sensitivity coupled with simultaneous multi element determination capability of ICP-AES, can be easily achieved [5]. The solid sample approach in AAS method has been, by now, well established and it serves as an effective analytical approach for samples difficult to dissolve and wherein dissolution is likely to contaminate the samples with impurities present in reagents used [6]. Extensive literature reports have appeared in the recent past examining, the effect of particle size, inhomogeneity of sample in milligram quantities, difficulties in weighing such small quantities, use of buffer etc. [7,8]. The hydride generation technique which was hitherto applied only to few selected elements has, over the years, been extended to other elements as well [9].

The studies on mechanism of atom formation, activation energy for such a process and studies on signal appearance temperatures have all led to clear understanding of various processes in AAS technique [10].

The absorption of energy does not always result in radiative de-excitation. In many cases, either part or total energy absorbed is released via non-radiative mode. In such cases, the host material gets heated up. The periodic heating up of the material causes pressure fluctuations in the medium. The acoustic signals thus generated if picked up by a piezo- electric crystal/ powerful microphone, can help in characterization of the material under study [11]. The Photo- Acoustic Spectroscopy(PAS) helps in more than one way: the absorption spectrum of an opaque substance can be obtained very effectively; the radiative and non-radiative components of excitation energy can, together, help in determination of energy level structure. The heating up of the system also leads to change in refractive index of the material and thus photo - refraction (PR) can also be the mode of study for energy absorbed. These studies are covered under the broad title of Photo-Thermal Spectroscopy (PTS) and also include thermally induced phase shifts, thermal lensing etc. [12].

### **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 on the power and stability of the source. The progress of research for the development of useful spectral excitation sources has gone through the stages of flame, thermoelectric (D.C.arc, Plasma jet), electric (A.C.Spark) and plasma sources (Electrode system- D.C.plasma, Electrode less plasma - Inductively Coupled Plasma (ICP), Capacitively Coupled Plasma (CCP) and Microwave Induced Plasma (MIP)). The present day Atomic Emission Spectrometry (AES) or Optical Emission Spectrometry (OES) is invariably based on the use of 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 technique [13]. The frequency of operation is generally either 27.12 MHz or 40.68 MHz. Few units are in operation with 56 MHz frequency also. The major constraint in using ICP is, the small solution sample throughput due to the use of conventional nebulizers. Extensive R & D studies

have undergone in improving the sample throughput through these and other nebulizers such as ultrasonic nebulizers. Large-scale studies have been reported, in general, for improving the sample uptake and reducing the wastage. These efforts include solid sample introduction [14], ETV approach [5] and sample aerosol generation through mechanical vibration or spark / laser ablation [15]. These modes of sample introduction ensure almost quantitative transfer into dissociation/excitation source. In case of ETV mode of sample introduction, investigations on sample condensation, if any, on the inside walls of the transport tube have also been reported. These studies reveal conditions under which such a thing takes place. The mode of direct sample introduction into the plasma through the use of electrodes has made some headway and a fully mechanized set-up is now developed which enables raising of the sample containing electrode through the temperature gradient available within the argon plasma [16]. The radio frequency heating up of the electrode beneath the plasma has been successfully exploited to translate gains of D.C.arc-carrier distillation approach into ICP-AES for U/Pu samples resulting in better sensitivity, precision and increased analytical range [17].

The axial viewing of the plasma has been introduced in many of the present day set-ups. This improves signal to background ratio at least by order of magnitude. The problem of self-absorption, however, limits the analytical range for analyte determinations. A critical review has recently appeared in literature, wherein relative merits of axially and radially viewed plasmas have been discussed in detail [18].

A new concept of combining ICP and AAS techniques into a hyphenated approach has been realized in practice. The emission from a hollow cathode lamp is collimated into atom vapour generated in an axial orientation of the argon plasma but the entire ICP luminous part is diverted from reaching the monochromator- detector assembly by suitably arranging the camera lens position. The plasma being at a distance less than the focal length of the camera lens, the entire ICP radiation goes past it as a divergent beam. This results in efficient transfer of the HCL radiation while minimizing the amount of ICP emission reaching the PMT detector



through the dispersion of the background and plasma emission. The high atomization efficiency of ICP helps in gaining better sensitivity while divergence of ICP emission improves tolerance limit of the matrix, specially that of uranium [19]. The signal modulation, r.f. power etc. can be optimized to achieve better detection limits in the presence of the matrix. It is again a step forward in eliminating the limitation of AAS technique and making it a versatile one.

Another hyphenated approach of coupling graphite furnace with capacitively coupled plasma (GF-CCP) promises very attractive Limits Of Detection (LODs) for a number of elements [20].

### Fluorescence Spectrometry

The fluorescence spectrometry as a spectroscopic 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, 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 advent of tunable laser (Laser Induced Fluorescence Spectrometry – LIFS) and effective use of Atomic Fluorescence Spectrometry (AFS). Laser Excited Atomic Fluorescence (LEAF) is a technique, wherein, atomization of the sample is achieved through use of furnace/laser/ICP and the atoms, in turn, are excited by laser. In addition, site- selective excitation of fluorescence results in enhancement of fluorescence yield while gating of photomultiplier tubes improves S/N ratio still further. A laser-based technique developed on these principles has resulted in impressive detection limits for rare earths which are at par or better than those obtained by neutron activation analysis. Such a technique is Selective Excitation of Probe Ion Luminescence (SEPIL) and has made good strides by studying rare earths in  $\text{CaF}_2$  matrix. Again, photon collection efficiency being very low (around 5%) 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, in far excess of the number of the atoms present in the system. Obviously, the limit of sensitivity under such conditions can be extended to a single atom. Laser Enhanced Ionization (LEI) technique used in conjunction with flame for some of the low ionization potential elements fetches very impressive detection limits. Sputter Induced or Laser Ablation aided Resonance Ionization Spectrometric (SIRIS or LARIS) technique and Resonance Ionization Mass Spectrometry (RIMS) offers detection of few hundred atoms in some of the favourable cases. In RIMS approach, the inherent superiority in detection capability of MS is fully exploited. The laser-based spectroscopic techniques have been summarized excellently in a recent review [21]. Most of the laser induced fluorescence and ionization based analytical techniques, though attractive, have yet to gain acceptability for practical application due to several reasons such as exorbitant cost of laser instrumentation, intricate experimental arrangement, spectral and chemical interferences etc. Besides, scatter light and detector background need 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.

The modern day spectroscopic techniques for characterization of materials are summarized in Figs. 1 and 2. Of these, the former represents conventional approach adopted in optical region. Lasers have brought in a qualitative change in the field of both pure and applied aspects of spectroscopy. Appropriately, therefore, laser based analytical spectroscopic techniques are covered separately in Fig. 2. As predicted in a recent review [22], with more powerful elemental detectors (based on both photon and ion measurements), more and more flexible hybrid techniques and more active cross-fertilization with other fields of science, analytical atomic spectrometry has a bright future as it enters the new millenium.

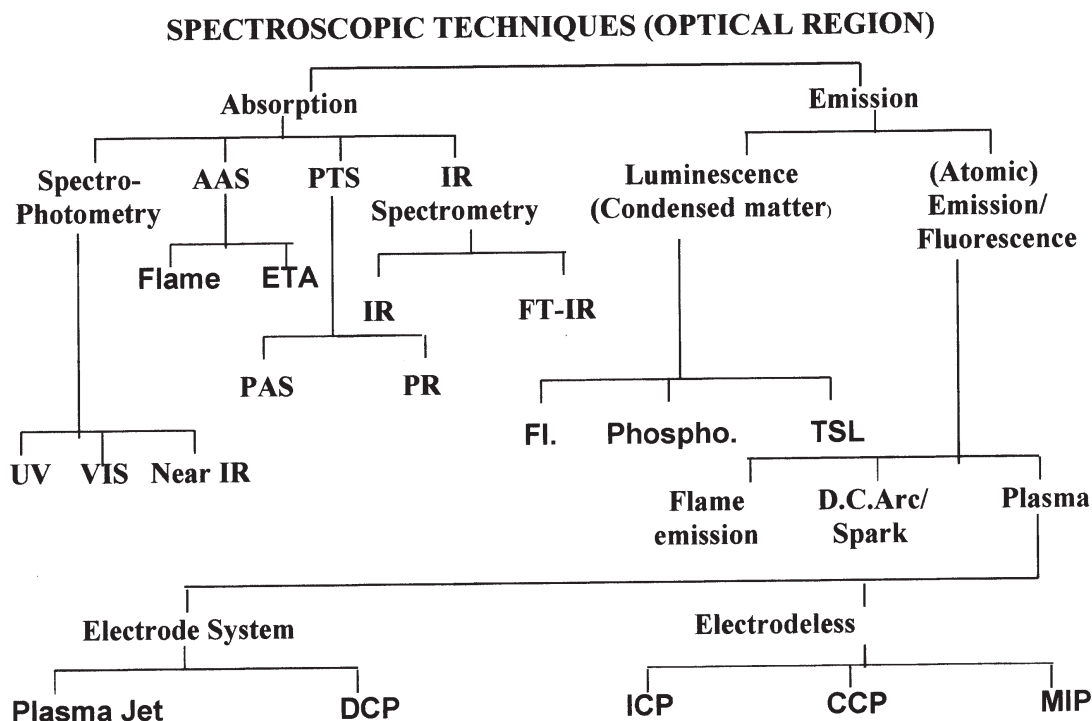


Fig. 1 Analytical spectroscopy (optical region)

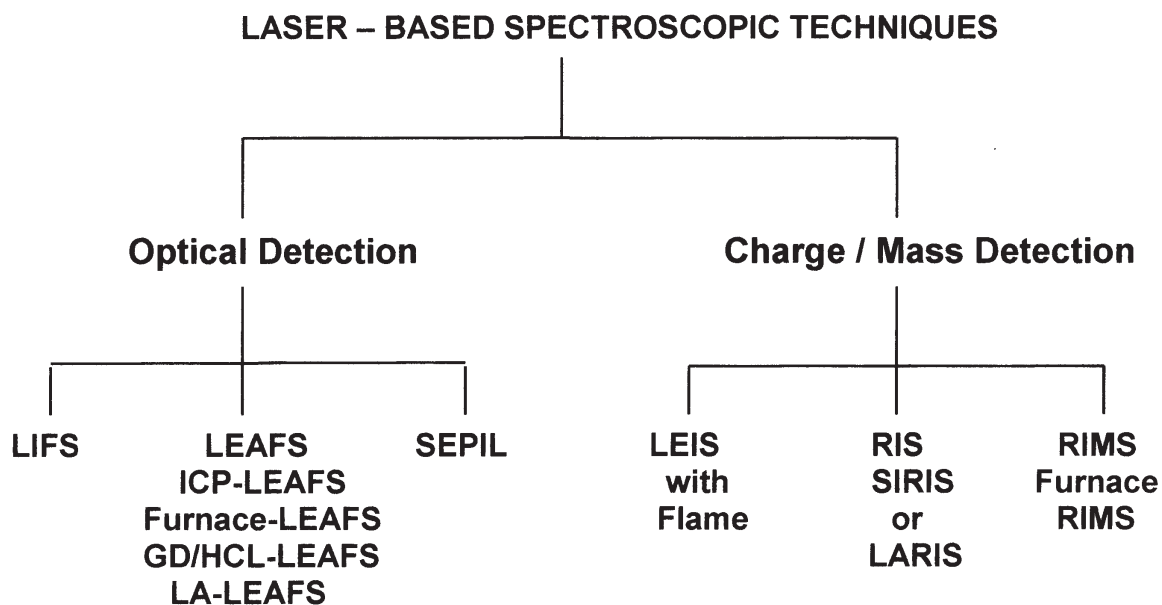


Fig. 2 Laser based analytical spectroscopy

There are other spectroscopic techniques such as electronic Raman and laser Raman spectroscopy which are also used at times for material characterization but their use is not very common and very often the data needs to be corroborated by other techniques. The X-ray based techniques such as XRF, X-ray diffraction and XPES are also prevalent as good techniques in the X-ray spectral region while EPR, ENDOR and NMR techniques work in the micro wave and R.F region of the electromagnetic radiation.

In conclusion, the instrumental update as given above is, an ongoing process and R & D efforts are going on continuously in the field to improve upon the figure of merit and ultimately reach the elusive status of an UNIVERSAL TECHNIQUE [23] - capable of analyzing any material in any form for any element in an interference free manner with the best sensitivity, analytical range and precision.

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# Laser Analytical Spectroscopy – Some Recent Trends



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## Introduction

Last three decades have witnessed tremendous growth in the area of laser spectroscopy and most of it has been driven by applications. One of the most significant applications have been in the area of analytical sciences. Since the advent of tunable lasers, laser powers have continued to increase, line widths of the lasers have decreased and their wavelength coverage also increased. At the same time laser spectroscopic techniques have diversified and technology of detection systems has advanced rapidly. All these developments have given rise to unheard of increase in sensitivity and selectivity as compared to spectroscopy based on classical techniques.

The objective of analytical laser spectroscopic techniques in recent times has been essentially two fold, on one hand, the aim is to simplify the techniques, capable of competing with existing method for achieving certain desired goals and yet be universally acceptable. The second type of thrust has been to address very specific problems demanding certain desired level of sensitivity or/and selectivity. A comprehensive (& exhaustive) review of recent developments is beyond the scope of this article so the aim is to confine to laser spectroscopy of gaseous media (atomic) with particular emphasis on

illustrative examples related to nuclear science and technology.

Beginning with a brief introduction to laser spectroscopy in analytical context, few specific techniques like opto galvanic spectroscopy, resonance ionization spectroscopy and their adaptations to address some very interesting analytical problems will be discussed.

## Laser Spectroscopy : Analytical applications.

A typical analytic laser spectroscopic setup will schematically be as is shown in Fig. 1. Sample preparation is mostly through a furnace, discharge or laser ablation. The sample generates vapor in atomic form which is addressed by suitable tunable laser (one or more than one). Few possible consequences are as depicted. Either the absorbed laser photons are detected, by a PMT, or fluorescence photons are detected by a photomultiplier tube with or without monochromator or detection of photoions by a secondary electron multiplier (or Microchannel Plate) with or without the use of a mass spectrometer, or change in circuit impedance of discharge tube (or a flame) is observed using a CRO (or lockin amplifier or boxcar averager). This article deals with the last two of the techniques.

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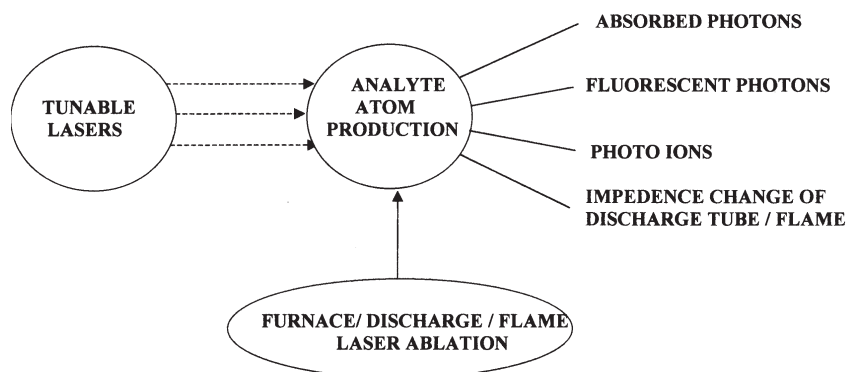


Fig. 1 Laser Analytic Spectroscopy : Some Probable Detection Routes

### Opto galvanic Spectroscopy and Laser Enhanced Ionisation

Opto galvanic spectroscopy makes use of change in impedance of a discharge (or a flame) consequent to resonant absorption of laser photons. Both of them have merits of their own. Ultimate sensitivity of optogalvanic detection in a hollow cathode discharge (HCD) is limited by shot noise while selectivity attainable is dictated by line width of tunable laser employed and absorption width in discharge. This technique has got specific advantages in context of refractory materials as efficient sputtering is possible in HCD. A well designed HCD can also contain moderate level of radioactivity or otherwise the whole process can be performed in a contained atmosphere (e.g. glove box) For various reasons opto galvanic spectroscopy in flames (also called Laser enhanced Ionization) has found more universal acceptance in analytic community partly because of simple adaptation of earlier flame analytic setups. In this adaptation, one of the common procedures is where solid sample is dissolved and aspirated as solution into flame or solution is deposited onto the surface of an ETA. The stages of solid sample and its dissolution almost invariably provides an auxiliary source of impurities affecting the fidelity of analysis.

At present high purity materials are finding an ever growing use in science and technology and demands on purity increasingly being more stringent for semiconductor materials and reagents used in microelectronics and some of the nuclear science

applications. For example admissible level of impurities in some cases is  $10^{-5} - 10^{-7}$  ppm. The sensitivity and selectivity of many commonly used modern analytic methods like inductively coupled plasma mass spectrometry or neutron activation analysis are not sufficient to meet these demands. In many of these techniques detection limit essentially depends upon material content and is degraded considerably in case of samples with complex matrices. This situation motivated the necessity of development of a technique which is direct, highly sensitive, not influenced by matrix, providing a rapid method for analysis of high purity materials with minimum sample preparation. LEI offers itself to fulfill the requirements, in many ways. It is often applied to highly sensitive element determination in liquids and solutions yielding detection limits as low as 10 ppm [1]. Some of the limitations of this technique were

- (i) Low sample utilization factor (0.1 – 0.15)
- (ii) Problems associated with handling micro samples
- (iii) Detection limits in solutions often not better than 10 ppm

For the last few years, extensive work has been done by analytic scientists working on LEI to offer solution to some of these problems. One such promising work uses hybrid ‘Rod – flame’ arrangement in which the micro sample is pulse evaporated from an electrically heated surface of a graphite rod into flame where the analyte is atomized, laser excited and ionized. Schematic of



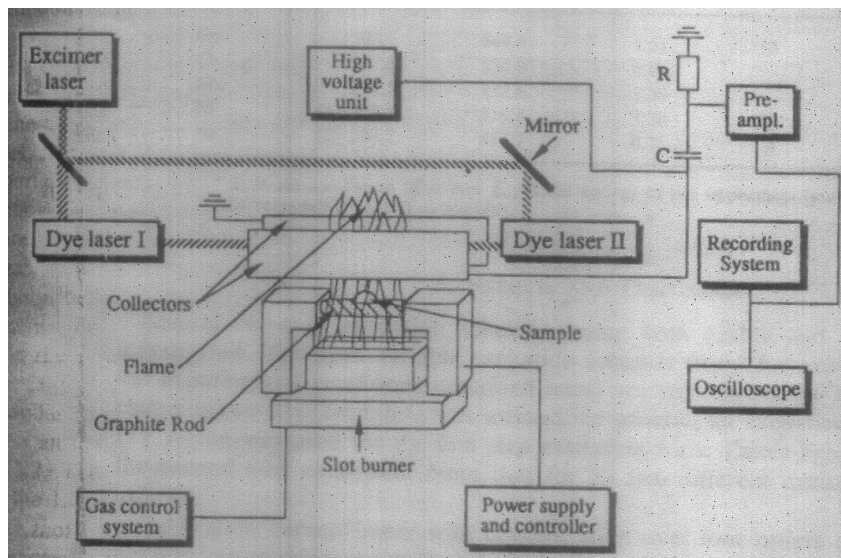


Fig. 2 Experimental Setup for Rod-flame Laser Enhanced Ionization Spectrometer.

such an LEI spectrometer is shown in Fig.2. Temperature of sample evaporation is normally lower than that of atomization therefore rod operates in mild conditions and with practically no ionization background thus increasing the sensitivity of the technique compared to conventional flame set up. Systematic studies and consequent control over matrix interfaces resulted in detection limits  $\sim 10^{-5} - 10^{-6}$  ppm for specific cases of copper in Ge and In in Hg Cd Te respectively.

Similarly another triumph of this technique was trace detection of Co, Cr, Mn & Ni as impurities in two fluorine containing materials  $\text{NH}_4\text{F}$  and  $\text{NaF}$  [2] both with sample in solution as well as solid form and detection limits ranging from 0.8 ng/gm – 0.08 ng/gm could be attained for  $\text{NH}_4\text{F}$  and a little poorer for  $\text{NaF}$  [for Ni and similar ranges for other impurities]. These trace analytic problems were necessitated in context of development of ultra – low loss optical fibers. Many of the fluoride containing glasses were difficult to analyze due to high chemical activity of fluorine atoms which give rise to significant amount of matrix effects and intensive corrosion of analytic devices.

#### Isotopic Analysis : Field Instrumentation

It is quite often in the context of activities related to nuclear science and technology that one

encounters the problem of isotopic analysis. The type of samples required to be analyzed may be from varied sources, e. g. nuclear reactors, fuel fabrication and reprocessing plants, environmental or biological samples etc. The techniques employed depends upon the sample size, level of radioactivity and the extent of sensitivity and selectivity required. Among several conventional techniques employed are decay counting and thermal ionization mass spectrometry.

Decay counting is a technique which is not universally applicable as dependant upon decay life-time, decay mode and fortuitous non interference of energies of decay of the isotopes but in some situations they do prove useful. Thermal ionization mass spectrometry on the other hand is much more universally employed for measuring precision isotope ratios. This technique though offers good precision and is applicable with sensitivity to even long lived samples but does require elaborate sample preparation procedure and is amenable to only laboratory analysis besides being dogged by problem of isobaric interferences. Very often there is a demand for field assessment of isotopic composition with less precision permissible, and this has to be done for a larger number of samples in as small a time as possible.

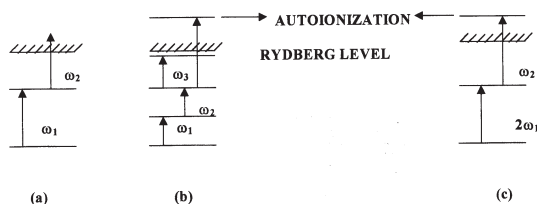


Fig. 3 Some possible resonance ionization schemes involving multi-photon or multi-color excitation

Laser spectroscopy based techniques could in principle offer desired isotope selectivity and requisite sensitivity but about a decade ago one could only dream of a field instrument for this purpose as tunable lasers with appropriate line width (to provide isotope selectivity) were even more cumbersome than TIMS setup itself. But in the last decade or so with rapid developments in the technology of tunable diode lasers such an instrument is within the reach. Young et. al [3] have developed such an instrument for isotopic analysis of Uranium. In this setup they coupled a tunable diode laser of appropriate power, linewidth and spectral range with a hollow cathode discharge for isotope selective excitation of Uranium atoms produced by cathodic sputtering. Opto galvanic detection of discharge atom population allowed  $^{235}\text{U}$  atom identification in depleted, natural and enriched Uranium (metal as well as oxide samples), when excited by well chosen wavelength. Typical power densities used were  $\sim 10 \text{ W/cm}^2$ . They made detailed comparison of result in isotopic analysis with TIMS in terms of precision and accuracy. These measurements with 150mW, 832 nm diode and a demountable type hollow cathode discharge demonstrated easy identification of natural, enriched and depleted samples with a run to run reproducibility  $\pm 8\%$  for this compact field instrument and a good agreement with TIMS could be obtained.

### Resonance Ionisation Spectroscopy

Resonant absorption in atoms followed by further excitation to ionization continuum and the use of ion detectors makes it possible to have another sensitive analytic spectroscopic detection. As technology of tunable lasers developed slowly it

became possible to do RIS of almost all the elements of the periodic table. Depending upon the excitation wavelengths and ionization potential different types of multi step excitation /ionization schemes are employed. Some of the possible schemes are shown in the Fig 3.

Analytical applications of RIS demand that atoms are efficiently converted to ions which are registered with commensurate efficiency. To maximize the ion yield, laser radiation used must meet certain criteria. In case of tunable pulsed lasers, which is the most general approach, the energy fluence of each laser pulse must be high enough to saturate the quantum transition involved. This requirement is quite moderate for allowed atomic transitions, it ranges from  $10^{-6}$  to  $10^{-3} \text{ J/cm}^2$ . But for transition to continuum it is in the range of  $0.1$ - $1 \text{ J/cm}^2$ . This later difficulty of relatively high energy density requirement can be mitigated by proper choice of final excitation / ionization step either to auto – ionization resonance or to a Rydberg state (a state with high principal quantum number) & followed by electric field induced ionization. This way energy density requirement can be reduced by one to two orders of magnitude.

In most practical applications for sake of attaining both isotopic and isobaric selectivity as well as making use of high gain ion detectors like micro – channel plate or channeltrons etc this RIS signal is coupled to a mass spectrometer leading to origin of acronym RIMS - (Resonance Ionization Mass Spectrometer). Additionally for trace analysis problems sample is prepared on a filament, which is heated, on the patterns of TIMS but with a difference – chemistry of sample on filament is so adjusted to release atoms at the cost of any other species (unlike ions in the case of TIMS). Combining such a filament vapor source with RIMS with well chosen three color wavelength excitation /ionization scheme using 5KHz copper vapor laser pumped dye lasers  $\sim 10^6$  atoms of  $^{239}\text{Pu}$  could be detected in an isotope selective manner [4]. Fig. 4 shows a schematic of the experimental set up employed. Additionally the measurement time was  $\sim 2$  hours compared to about 24 hours counting time required in  $\alpha$  spectrometry. Fig. 5 illustrates S/N ratio in detection of  $^{239}\text{Pu}$  using two techniques.

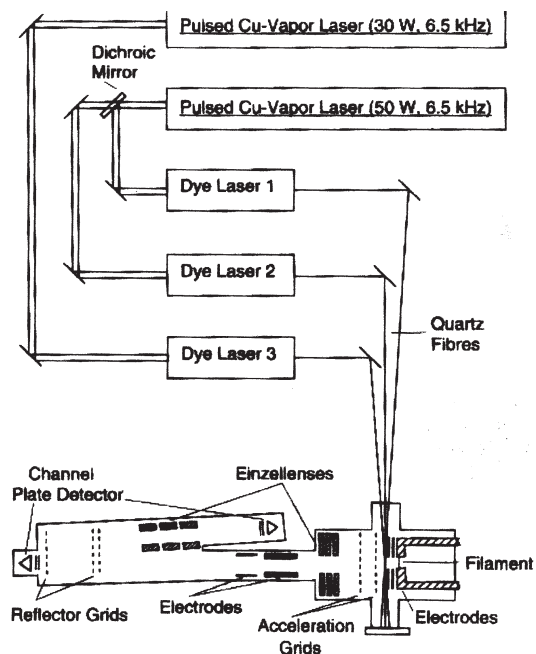


Fig. 4 Experimental set-up for Resonance Ionization Mass Spectrometer

This filament heater based RIMS have been found to be an extremely sensitive and selective trace analysis technique. It competes superbly with some of the traditional trace analysis techniques particularly aimed at long lived radio – isotopes. For example in radiometric detection using alpha spectrometry based on surface barrier detectors for trace analysis, elaborate preparation procedures have to be followed for sake of good energy resolution even then there are limitations in isotopic resolution due to small differences in the energies of lines (e.g. for  $^{239}\text{Pu}$  &  $^{240}\text{Pu}$ ) A practical detection limit of  $10^7$  atoms of Pu with long counting times & moderate isotopic selectivity has been demonstrated with detection of naturally produced  $^{239}\text{Pu}$  in Uranium bearing rocks at level of  $10^8$  atoms per sample using TIMS [5]. In ICP – MS technique isobaric interferences often limit the selective and sensitive detection. Accelerator Mass spectrometry is forging ahead with establishing new low in detection limits with good isotopic and isobaric selectivity. But this is normally too expensive and complicated proposition for many specific tasks.

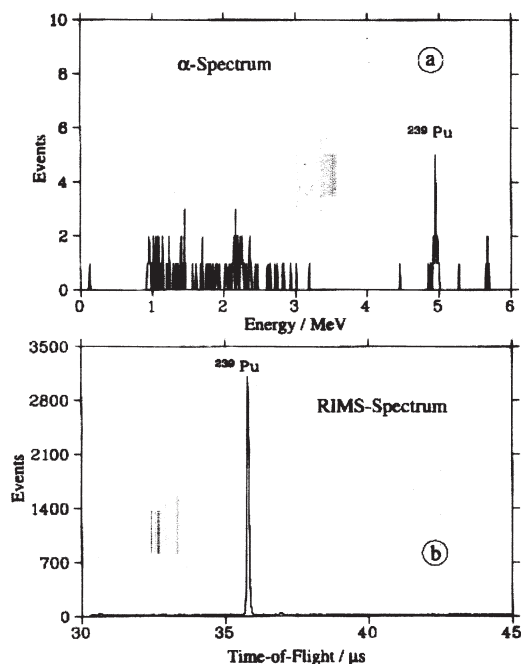


Fig. 5 Comparison of decay counting and RIMS spectrum in detection of  $^{239}\text{Pu}$  also showing the difference in measurement time (about an hour for RIMS and 23 hours for  $\alpha$  counting)

The overall detection efficiency of RIMS using filament based evaporation is mainly limited by poor spatial and temporal overlap of a continuous stream of atomic vapor (average velocity  $10^4$  -  $10^5$  cm/sec) with pulsed laser beams. Despite the use of 6kHz excitation/ionization lasers only moderate temporal (and thus overall efficiency  $\sim 10^{-6}$ ) could be obtained. The highest efficiency of detection using RIMS has been attained by performing atomization (as well as excitation and ionization) within hot cavity [6] where the photo excitation / ionization laser beams are introduced & photo ions are extracted through a small hole. The high efficiency attained is due to large number of times an atom is likely to 'see' the laser interaction region as aftermath of its collisions against hot walls of the cavity. This hot cavity laser interaction is named Laser ion source as it is particularly suited for studies of nuclear reaction products, in a very sensitive and selective way, in accelerators. They have been employed at heavy ion accelerators at GSI [7] and at

CERN [8] for study of short lived isotopes and efficiencies as high as 20% could be observed. Worldwide plans are afoot to upgrade these experimental capabilities employing higher repetition rate tunable solid state lasers, making the system more compact, efficient and rugged.

#### Ultra – High Isotope Selectivity

There are a special class of problems requiring high sensitivity combined with very large isotope selectivity which laser spectroscopy is eminently suited to attempt. One such problem is rapid detection of  $^{89}\text{Sr}$  and  $^{90}\text{Sr}$  which are produced efficiently in fission reaction, have half lives 50 days and 28 years respectively and accumulate easily in bones. Thus it is of significance from environment point of view. This method requires for air samples an isotope selectivity of  $\geq 10^{10}$  to suppress stable strontium isotopes and an overall detection efficiency of  $> 10^{-5}$  to yield statistically significant results as in an air sample of  $1000 \text{ m}^3$  collected in Munich, faraway from Chernobyl, in 1986 where approximately  $10^8 - 10^9$  atoms of  $^{89}\text{Sr}$  &  $^{90}\text{Sr}$ , together with upto  $10^{18}$  atoms of stable Sr were found. The isotope shifts between these two isotopes is  $\sim 100 \text{ MHz}$  and by conventional laser spectroscopic technique it is not possible to reach desired levels of selectivity and sensitivity. The goal could be attained by combining conventional mass separation with collinear fast beam laser excitation.

In this way an artificial isotope shift in the optical resonance line is introduced by the large mass dependent Doppler shift. The fast Strontium atoms obtained after charge exchange are resonantly excited into high lying Rydberg levels in a field free region with a laser beam intersecting the atoms at  $2^\circ$  angle. The excited atoms are subsequently field ionized and ions registered by a particle detector.

The detection limit of the method was tested by measuring synthetic samples containing known amount of  $^{90}\text{Sr}$  in the region of  $10^7 - 10^9$  atoms per sample in the presence of up to  $10^{18}$  atoms of stable Sr [9].  $^{90}\text{Sr}$  was estimated to be  $1.8 \times 10^9$  atoms/sample with variation of 10% demonstrating good reproducibility as shown in Fig. 6. This corresponded to low level of radioactivity  $1.19 \text{ mBq/m}^3$  of air and matched perfectly with radiochemical methods. This method has further scope for improvement for samples from soil, water, etc.

The involved experimental set up is quite specialized and intricate. Thus search is on for alternate methods of achieving high levels of isotope selectivity as well as good sensitivity. More general applicability of such a technique is required in the context of demands on analysis of various radio – nuclides that occur at relative abundances in the range of  $10^{-8} - 10^{-13}$  with respect to other isotopes of the same element. Measurement of the isotopes at

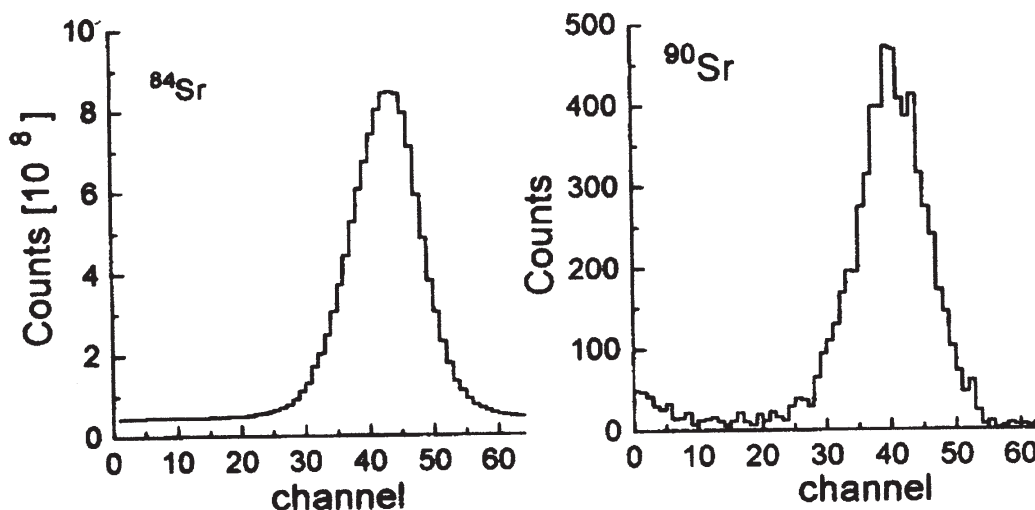


Fig. 6 Results of  $^{90}\text{Sr}$  detection of  $\sim 10^8$  atoms using collinear RIMS



these low abundances is usually beyond the capabilities of pulsed lasers based RIMS which have relatively large line width and thus limit attainable selectivity and because of usually poor duty cycle sensitivity is limited. So narrow line width single mode CW dye lasers in multi – step PI is being proposed to augment the selectivity attainable by mass spectrometers. These CW dye lasers are also being extended and upgraded to incorporate solid state lasers (like semiconductor diode lasers). They have added advantage of good duty cycle but have two main shortcoming – at present stage of technology development they do not cover large spectral range thus presently restricted in number of elements/isotopes of periodic table that can be covered. Additionally for the final ionization step sufficient flux cannot be supplied by present day lasers and is usually implemented with either relatively high power CW CO<sub>2</sub> Laser or Argon - ion laser or also “futuristic” diode array lasers (~ 20w)

Essentially the experiment consists of heating analyte atoms of interest in a narrow graphite tube furnace providing atomic vapor in a mass spectrometer ionization region. A single frequency CW dye (diode) laser is tuned to a resonance of atom starting from its ground state, raising it to a low lying excited state, a second single frequency CW dye laser is tuned to promote the initially excited atom into high lying Rydberg state, the Rydberg state atom is then ionized by a CW CO<sub>2</sub> laser and ions produced are analyzed by a quadrupole mass spectrometer. Graphite tube furnace is self collimating and thus narrow Doppler width (required for high optical selectivity) is attained. Two dye lasers can be counter – propagating to further reduce residual Doppler broadening and optical selectivity can be further enhanced in both resonance excitations (or employing two-photon excitation).

Some of the specific radio – nuclides to which CW – RIMS has been applied are <sup>210</sup>Pb, which is of interest both as an indicator of radon exposure and in microelectronics industry. About 10<sup>-15</sup> gm of <sup>210</sup>Pb could be detected (3σ detection limit is < 3 x 10<sup>-16</sup> gm) in the presence of about few gms of stable Pb [10].

Precision isotope ratio measurements of Calcium isotopes are being actively pursued using

CW RIMS. It is aimed at attaining high efficiency (of sample utilization implying small sample sizes that can be handled), ultra-high selectivity as well as wide dynamic range for reasons of demand of the problem (e.g. expected isotopic abundances and nuclear reaction rates involved). The origin of interest in Ca isotopes is related to several problems of cosmochemistry and medical applications. Medical physicists are interested in transport kinetics of calcium in human body in context of several bone diseases like osteoporosis. Radio-isotope <sup>41</sup>Ca, because of its long life and electron capture decay mode poses negligible radiation threat to patient and can be produced inexpensively in nuclear reactors and should have large dynamic range as there is essentially no background of <sup>41</sup>Ca. The same application by AMS is quite costly and cannot spread over to large number of hospitals, while laser based systems would be smaller, have less expensive instrumentation, higher sensitivity, and provide faster measurements. Similar advantages accrue to cosmochemistry problems related dating and nucleosynthesis studies of meteorite samples, where <sup>41</sup>Ca produced by various cosmic radiations is to be analysed with respect to naturally occurring <sup>40</sup>Ca. Typical sample size expected are 10<sup>9</sup> atoms per gram of rock and ratio of 41 and 40 isotopes encountered in extra-terrestrial sample range from 10<sup>-11</sup> to 10<sup>-13</sup>. Few ppm of <sup>46</sup>Ca in meteorite sample could be detected overcoming isobaric interference of <sup>46</sup>Ti [11] using CW-RIMS (based on diode lasers). There is plenty of scope of improvement in efficiency. Also similar measurements are likely to have wide ranging appeal for several ultra-low isotopic abundance problems.

### Future Outlook

As one reviews the overall current scenario related to laser analytical spectroscopy, it is activated by tremendous developments in laser technology, advances in detector technology and diversification of laser spectroscopic techniques employed. This has resulted in attainment of increasingly higher sensitivity, selectivity as well as simplicity.

For obtaining best sensitivity (in terms of sample size) and moderate to high selectivity (depending on the isotopes) Laser Ion Source using high repetition rate dye lasers is the technique of



choice. So far much work is based on Copper Vapor Laser Pumped Dye lasers but future holds promise with use of diode laser pumped solid state lasers of higher rep rate as well as higher average power. This will enable building up compact and rugged analytic instruments. These or its variations do hold promise for facilitating detection and research of accelerator based reactions (fission, fusion or spallation) producing at low yield species in “super-heavy” region.

Simpler and more elegant techniques of optogalvanic spectroscopy and Laser Enhanced Ionisation in flames have progressed offering very compact alternatives for tasks like isotopic analysis of nuclear materials or handling ppt analysis in complex matrices, in some cases obviating complex instrumentation of TIMS. More can be expected in this field as in LEI, atomization and excitation/ionization steps have been separated, using rod-flame arrangement or laser ablation.

For analytic applications requiring ultra-high selectivity CW-RIMS or resonance Ionization mass spectrometry based on single mode (narrow linewidth) lasers is an elegant, compact and economic alternative (or supplement) to Accelerator Mass Spectrometry based techniques. Tunable single mode diode laser technology is growing rapidly because of appeal of economics and simplicity and it will be possible in near future to cover most of the spectral region of interest enabling CW-RIMS of much of the elements of the periodic table. More innovations in choice of excitation/ionization schemes and techniques can be expected to overcome the limitations of present day diode lasers.

Thus laser spectroscopy and laser technology together will offer unique application specific solutions to various requirements of analytical scientists. While some of the problems cannot be

solved presently by non-laser techniques there are others which are in the form of simpler or more economic alternatives or supplements.

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# Electronics in Spectroscopy Instrumentation



**Dr. S.V.G. Ravindranath** is a graduate in Electronics and Communication Engineering from Osmania University and from the 22<sup>nd</sup> batch of BARC training school. He joined Spectroscopy Division of BARC in 1979 and ever since been working in the field of electronics and instrumentation for the spectroscopic instruments. He obtained his Ph.D. in Electrical Engineering from IIT, Mumbai in 2001. His areas of specialization are: lab automation, design and development of PC based data acquisition and control systems, micro-controller based data acquisition systems, development and application of chemometric techniques. He led his group to develop PC based data acquisition systems for the indigenously developed 22-channel direct reading spectrometer with DC-arc and plasma sources and the sequential ICP-AES. He is currently coordinating the activities of Electronics and Instrumentation group of Spectroscopy Division.

## Introduction

There has been rapid progress for the last six decades in the field of electronics from fragile vacuum tubes to compact VLSI chips. There has been all round impact of this growth in various fields like entertainment, health, science and engineering. Spectroscopic instrumentation is not an exception. The advances in the electronics either directly or indirectly resulted in good light sources, better light detectors and best readout electronics. Unstable light sources got transformed into stable light sources and photographic plates have been replaced by the semiconductor detectors which are electronic counterparts of photographic plates. Manually operated instruments gave way to automated instruments. Manual data processing has become obsolete with the advent of electronic data processing. As a representative case the transformation that took place in the field of atomic emission spectroscopic instrumentation, in the wake of advances in the field of electronics, is briefly outlined in this paper.

## Basic components of an atomic emission spectrometer

A typical atomic emission spectrometer consists of (a) Light source, (b) Sample holder, (c)

Wavelength selector, (d) Light transducer and (e) Signal processor and readout

A block diagram is shown in Fig.1.

In 1860, when Kirchoff and Bunsen published a paper describing the presence of common elements such as Ca, Na and K they built a simple visual spectrometer. In that instrument the human eye played the role of light transducer as well as signal processor. The human brain could take care of signal processing job translating the intensities of the characteristic colors of the elements to their approximate concentrations in the mineral samples. In a visual spectrometer, a glass prism was used as a wavelength selector. Later in the late 1800's and early 1900's photographic emulsions had been introduced as sensors cum recorders. Improved optical configurations for wavelength selection were used. Instrument manufacturers developed micro-photometers to measure the transmission of significant spectral lines recorded on the photographic plates. These instruments were soon recognized as superior to visual spectrometers. Accurate results could be obtained by emulsion calibration.

Perhaps, the direct role of electronics in spectroscopy might have started in the late 1940's,

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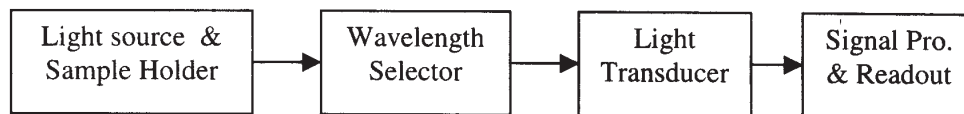


Fig. 1 Block schematic of an atomic emission spectrometer

when several pioneers in universities and industrial research laboratories tried to substitute exit slits and photo-detectors for photographic emulsions. Subsequently these instruments, called as direct reading spectrometers, were made available commercially. Electronic circuits such as integrators, counters were used to process the photo-detector's output so that the line intensity could be directly read as electrical current or voltage without using the microphotometer. Using these values subsequent steps such as calibration and estimation of impurities were carried out manually. Light sources such as dc-arc and spark were employed in these instruments. Though the direct reading spectrometers reduced the spectrochemical analysis time considerably, they were manually operated.

In the last few decades since the development of early direct readers, fields such as light sources, optics, light transducers and electronics have registered significant growth. Inductively coupled plasma (ICP) has established itself as an excellent light source. Motor driven monochromators and polychromatos with holographic gratings provided good spectral resolution. Light sensors such as photomultiplier tubes (PMT), semiconductor sensors such as charge coupled devices (CCD) with high sensitivities improved overall performance of the spectrometers. Compact, efficient and cheap analog and digital electronic circuits helped in implementing the micro-stepping to achieve minute grating movements and to implement the logic to automate the instrument operation. In reality these developments are closely related and interdependent. The role of electronics in the evolution of different constituent parts of the modern spectrometer is outlined in the following sections.

### Light Sources

Several new sources such as glow discharge, hollow cathode lamps, ICP and laser micro probe sources have been invented for atomic emission spectroscopy. A significant resurgence in interest in atomic emission methods has occurred with the invention of plasma sources. The understanding and appreciation of the basic properties of ICP have established it as a reliable tool in atomic emission spectroscopy. In an ICP source a radio frequency (RF) generator provides power for the sustenance of the plasma. Among the experimental parameters, steady RF power level contributes to better performance of the instrument. Impedance mismatch due to certain samples severely affects the power delivered to the plasma torch. Present ICP sources are operated under automatic feedback control mechanism. Such systems classified as servo systems detect a difference between actual and set power level and then feed the difference information to a controlling device which then reacts and causes the difference to become essentially zero. Amplifiers, power supplies, motors and other hardware are important parts of a servo system. Feedback control mechanisms are used in the latest ICP-AESs to maintain at the set values the other experimental parameters such as sample uptake rates and different argon gas flow rates. Thus the combination of feedback control concepts with electronic hardware helped in producing stable ICP sources.

### Wavelength Selectors

Ideally, the output from a wavelength selector would be radiation of a single wavelength or frequency. In reality a band of wavelengths is obtained. A narrow bandwidth provides the selectivity to emission spectroscopy. It is also a requirement for obtaining linear relationship between the optical signal and concentration. Generally prisms and gratings are used as

wavelength selectors. Instruments for emission spectroscopy are of two basic types: sequential and simultaneous multi-channel.

### ***Sequential Spectrometers***

Most sequential instruments incorporate a grating monochromator with a PMT. With these instruments scanning is performed by rotating the grating with a digitally controlled stepper motor so that lines of different wavelengths are sequentially and precisely focussed on the exit slit.

The advent of micro-stepping stepper motors and high resolution optical shaft encoders has made the scanning more precise. At present motors with a micro step of the order of 1/250 or less are available [1]. Micro stepping motors need special electronic hardware for splitting the step into micro time slots. The achievable extent of micro-stepping is limited by the inertia of the motor in responding to small change in phase currents and step angle accuracy. Micro-stepper controller is an electronic hardware to generate required waveforms to cause the micro stepping as well as to make sure that the grating has moved by required amount. These controllers are microprocessor based systems and they can do most of the jobs without external device supervision. They can be operated either from a keyboard or from a digital computer through a standard interface such as serial communication standard RS-232C.

The PMT output is converted to voltage and that voltage is converted to pulse train. The frequency of the pulse train is proportional to the concentration of the analyte. Sequential spectrometers are computer controlled for instrument control, data acquisition and processing. These features are discussed in the signal processing and read-out section.

### ***Simultaneous Multi-Channel Spectrometers***

When analysis is to be performed using analyte lines spread over wide spectral range, sequential instruments spend most of the time moving from one line to another. Analysis time is longer on such instruments. This problem is addressed by the simultaneous multi-channel spectrometers. Such spectrometers use predetermined number of PMTs placed behind exit slits on the periphery of a Rowland circle to sense the line intensities of the

impurities of a sample. Generally, the number of PMTs corresponds to number of elements analyzed on the instrument simultaneously. Compact PMTs are preferred in these instruments as multiple light detectors need to be placed in a limited space. These instruments use holographic gratings for wavelength selection and no grating movement is required as the line intensities are read simultaneously.

In view of the variations in ambient temperature, these spectrometer housings are provided with thermostatic control to maintain inside temperature at a set value within a fraction of degree celsius.

### ***Light Sensors***

PMT is one of the most sensitive light detectors used in the atomic emission spectroscopy. PMTs provide fast response, excellent sensitivity from UV to IR with dynamic range of the order of six decades. Compact PMTs with a diameter less than 1/2" are also available as needed in simultaneous multichannel spectrometers. PMTs need stable low ripple high voltage power supplies. Due to the availability of compact electronic circuits, the dc-dc high voltage power supply, chain of dynode resistors and signal amplifier can be compacted into the base of the PMT. PMTs with completely embedded RS-232C based photon counting systems are also available. These PMTs are operated on an external 5V supply. Such miniaturization helps in minimizing the number of components and connections thereby enhancing reliability as well as compactness of the instruments.

Solid state array detectors are revolutionizing different branches of spectroscopy. These detectors consist of a series of radiation sensitive semiconductor picture elements or pixels. Typical pixel widths are of the order of 10 microns. These pixels convert photons to a quantifiable charge. This charge is transferred to a readout amplifier and later digitized by an Analog to Digital Converter (ADC). Array detectors are the electronic counterparts of the conventional photographic plates. Spectrum in a given band can be stored simultaneously in array detectors. They enable to acquire vast amounts of spectrally and/or spatially resolved data in short periods of time. These are rugged and compact with lower power requirement offer high quantum

efficiency, low read noise and wide dynamic range. Charge coupled devices (CCD), charge injected devices (CID) and recent CMOS detectors are the semiconductor array detectors available. CCDs and CIDs are incorporated in the new generation of emission spectrometers. To operate these detectors additional hardware such as multiplexers, circuits for signal processing, memory and logic circuits are needed. These are not available on chip along with detector hardware with CCDs and CIDs. Detectors based on CMOS technology can incorporate the additional hardware on the same chip housing the detector. CMOS detectors can be very compact and need 100 times less power compared to CCD.

### **Signal Processing and Readout**

Once the analyte line intensity is converted to a proportional electrical signal, the signal processing and readout block takes over. Generally, the detector output is suitably modified and amplified. During analysis when line intensity is very high, the detector sensitivity has to be brought down. Sensitivity of a PMT is controlled by adjusting its supply voltage. In the old instruments the calibration of the instrument is carried out manually. Using the calibration curves, intensity data from the samples are converted to the impurity concentrations. Introduction of the microprocessor based signal processing and read out systems in spectrometers has added significant features in terms of instrument control and data processing. Incorporation of the powerful microcomputers such as personal computers (PC), advances in software technology such as object oriented programming and concepts such as graphic user interface (GUI) have made the modern spectrometers fully automatic, processing power packed and at the same time user friendly.

### ***Analog and Digital Electronics: Data Acquisition System (DAS)***

In principle, an electrometer, which can measure very low currents, is incorporated to measure and display the detector output current. The current readings are used to compute manually the concentrations of impurities in a sample. Such simple analog readout systems are limited by two factors: the dynamic range and resolution. Use of digital version of the electrometer improves only the

resolution. These systems severely limit sampling rate i.e. the number of readings in a second.

Development of a variety of analog and digital electronic circuits contributed to semi-automation of spectroscopic instruments. Electronic components such as operational amplifiers, instrumentation amplifiers, analog switches, analog to digital converters, digital to analog converters, logic gates, counters, microprocessors and microcontrollers are used to develop instrument specific data acquisition system (DAS) hardware. DAS works under a computer control. These systems provide instrument control by monitoring and controlling experimental parameters. They acquire data at required rates with necessary resolution and pass the data to a computer for storage and processing. Several standard protocols are available to link the DAS to a computer. RS232-C and IEEE-488 are the most commonly used interface standards. Computer I/O bus also can be used for interfacing purposes.

Block schematic of a DAS developed in-house by the author and his group for the 22-channel direct reading spectrometer with DC-arc and ICP sources is shown Fig.2 [2]. PMT outputs were given to a bank of integrators in DAS. The charging and discharging sequence of the integrators was coordinated by channel selection and set-reset circuit to achieve 6-decades dynamic range. A 12-bit ADC card with the help of multiplexers periodically converts the outputs of all integrators to digital form. A single PC add-on card provides the required digital I/O for the ADC and channel selection and set-reset circuit. Thus this add-on card forms the link between the PC and the DAS.

With the advances in semiconductor technology such as application specific integrated circuits (ASIC), complete data acquisition system can be placed in a custom designed ASIC. The current trends aim at integrating complete system with data acquisition hardware, data processing hardware and software into a single component viz. system on chip (SOC). SOC technology houses analog subsystems such as opamps and data converters on the same die with the digital circuits. Future spectrometers with such electronic systems will be more powerful, reliable and compact.



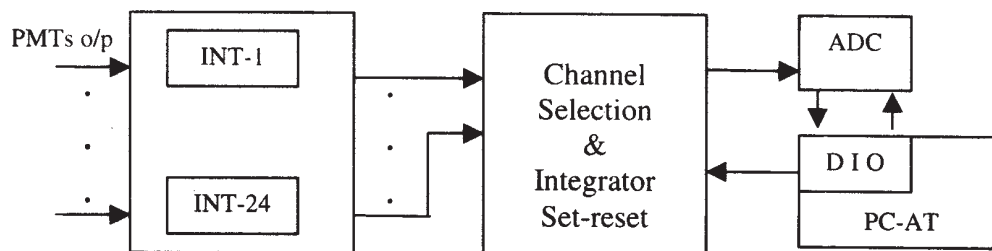


Fig. 2 Block schematic of DAS for the 22-channel direct reading spectrometer

### Computer Hardware

First electronic computer became operational in 1946 in Pennsylvania state university. This computer occupied a large hall, consumed so much power to the extent of dimming the lights in the city and never worked continuously for more than a few minutes. Since then the computer technology has undergone rapid growth rate. Miniaturization in semiconductor technology is the major contributor for this growth rate. Today millions of logic circuits can be etched on a single silicon chip. Advances in computer technology could make present personal computers very compact, less power hungry, fast in computation with millions of operations per second, reliable and yet cheap. Due to low cost and effective, PCs became part and parcel of the present day spectrometers lending instrument control, data acquisition and lot of data processing abilities.

Till late 1980's and early 1990's, computers were used only for off-line data processing. The instrument control and data collection were carried out by simple 8-bit micro-computers. With the advent of PC, both instrument control and data acquisition and processing tasks are carried out by the PC itself. Several components of data acquisition hardware systems such as ADCs, DACs, counters, timers, digital input/output, IEEE-488 controllers and stepper drive controls have become available as PC add-on cards. The PC add-on cards have cut down the system development time considerably.

### Software

Hardware and software are the two technologies that grew simultaneously deeply influencing the growth patterns of the other. Software is a sequence of instructions executed on

the hardware to perform a particular task like putting the light source on in a spectrometer or fitting the concentration versus line intensity data. For the early computers these instructions were written in machine code which comprises of sequences of binary digits 0 and 1. Expert programmers are needed for writing the machine programs, which require complete knowledge of the central processing unit (CPU), the work horse of the computer. Since then several high level programming languages such as FORTRAN, Algol, BASIC, pascal and C have been developed. Essentially, these languages were useful to develop data processing software for scientific and engineering calculations. Instrument control and data acquisition jobs were still done in assembly language, a better version of machine language.

The availability of cheap microcomputers such as home computers and later the personal computers has changed the scenario of programming languages for instrument development. Perhaps BASIC is the first language to incorporate instructions to interact with the computer hardware and provide graphics support. With the advent of PC several versions of BASIC, Pascal and C were developed that support hardware control and graphic instructions. Thus it became possible to develop data acquisition and processing activities from one program and one computer. Programming started growing in to a giant industry catering to the needs of different segments such as business, industry, entertainment, education and so on. It was also the beginning of PC becoming a part of the modern analytical instruments.

User friendly, menu driven and interactive features took place in programming. New programming paradigms such as object oriented programming (OOP) and visual programming have

helped the programmer and ultimately the user greatly. Reusability features of OOP helped for faster and reliable program development. Graphical user interface (GUI) features made the use of computers one of the easiest tasks for an expert as well as a layman. In the field of PC based instrumentation, graphical programming languages such as LabVIEW provide a faster way to program instrumentation, data acquisition and control systems. Most of the modern spectrometers are operated from the terminal itself right from switching on the source to getting the hardcopy of the final analysis results. In most routine applications, the operator of a modern instrument like ICP-AES need not be a professional spectrochemist. If the instructions for calibration, standardization, and analysis of unknowns are followed, one would obtain analysis results as accurate as those obtained by a professional spectrochemist.

The present day PCs are computationally more powerful than the decade old supercomputers and can tackle more complex mathematical computations. They also have large on board memory to hold a huge amount of data for processing. These features helped the spectroscopists to tackle problems such as spectral interference and spectral shift due to instrumental drift. Earlier, lesser sensitive lines were preferred to strong interfered lines as there were no means to extract the analyte signal from the interfering line which would limit the practically achievable detection limits. At present mathematical techniques such as least square methods and Kalman filtering are used to quantify the interference. Pattern recognition and factor analysis techniques are applied to get the number of components and their concentrations without the need for concern about spectral overlaps and interferences. The application of such methods, known as chemometrics, should

prove to be useful for adding smartness and intelligence to the automated spectroscopic instrumentation.

## Conclusions

The role of electronics in spectroscopic instrumentation has undergone a great change from a simple electrometer amplifier to manually measure the low current of the photo-detector output to completely automated data acquisition system. The rapid advances in the field of computer technology in both hardware and software added greater power to electronics in automated instrumentation in terms of speed, intelligence and smartness.

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# Developments in Optics for Analytical Instrumentation



*Dr. R. P. Shukla joined Spectroscopy Division, BARC in the year 1969 and worked in the fabrication, testing of optical components and instruments. He has set up the optical testing facility for checking the high precision optical components. He has also developed the technical know-how of monochromators and spectrographs required for R&D activity of the division. He was involved in the design and development of spectroscopic and analytical instruments required for the identification and determination of ppm level impurities in the uranium matrix. He is presently heading Optics Section of the Spectroscopy Division.*

*Shri Dinesh V. Udupa joined Spectroscopy Division, BARC in the year 1992 through first batch M.Tech orientation course of BARC training school. He is working in the fabrication, testing of optical components. He is in-charge of optical workshop. He was involved in the design and development of spectroscopic and analytical instruments required for the identification and determination of ppm level impurities in the uranium matrix. He is presently working on the development of the periscopes required for inspection of the objects kept inside nuclear reactors.*



*Dr. N. C. Das joined Spectroscopy Division, BARC in the year 1970. He worked in the field of optical design of lenses and optical systems such as night vision camera, projector lenses and collection lens. He also worked in the design and development of various types of anastigmatic monochromators and spectrographs using holographically produced diffraction gratings. He was involved in the development of periscopes required for inspection of materials in nuclear reactors. Recently he has set up the Photoelectron spectroscopy (PES) beam line using the synchrotron radiation source for characterizing the various materials. He is presently heading Spectroscopy Division and is engaged in the various programs of optics, thin films, spectroscopy and high vacuum spectroscopic beam lines.*

## Introduction

The role of optics and spectroscopic instruments for the development of Indian nuclear program was realized well in advance by the forefathers and visionaries of our atomic energy program. This has enabled to establish an optics group for designing, fabricating and testing of varieties of optical and spectroscopic instruments including optical components in Spectroscopy

Division, BARC, Trombay. There is a need to determine the presence of rare earth elements in the uranium and rare earth samples. The analysis of the purity of samples containing rare earth elements is carried out by using the techniques of atomic emission spectroscopy. There is also a requirement to detect various trace impurities in uranium samples with the determination limits in the range from sub ppm to ppm levels. These impurities are determined by optical emission spectrometry. We have

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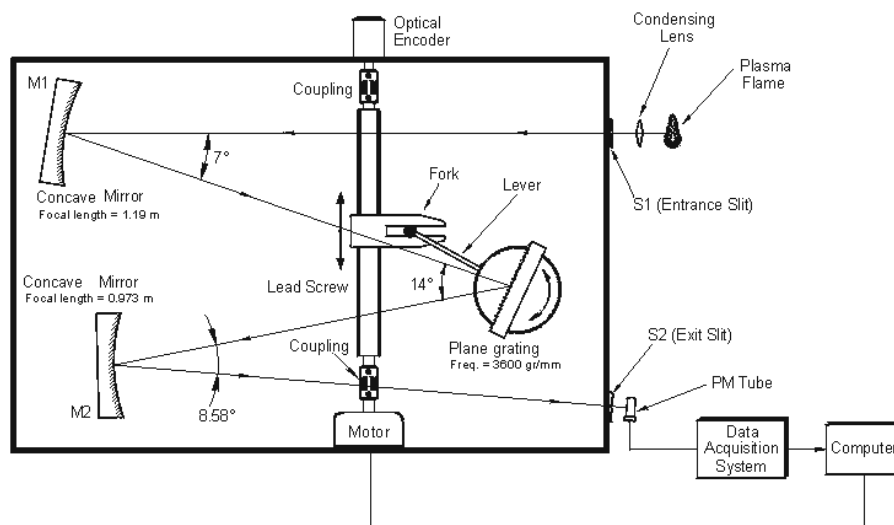


Fig. 1 Schematic of complete assembly of the scanning monochromator

indigenously designed and developed the following analytical instruments for the determination of various impurities:

1. Scanning Monochromator for determination of rare earth impurities like Ce, Gd, Sm, Dy, Er, Y and Yb in water samples
2. Polychromator for determination of trace impurities such as B, Cd, Cr, Be, Co, Mn, Mg, Cu, Ni, Si, Mo, Zr, Ca, Ga, Pb, Sn, Fe, Ti, Al and Zn in graphite/uranium matrix and also dissolved in water samples.

A brief description of analytical instrument, method of excitation, detection and observed determination limits of various elements are presented in this article.

### Scanning Monochromator [1]

The optical layout of a Czerny-Turner type of scanning monochromator is shown schematically in Fig. 1. The optical set-up of the monochromator consists of source of electromagnetic radiation, entrance slit, concave collimating mirror, plane diffraction grating, focusing mirror, exit slit, photo-multiplier tube (PMT), data acquisition system and personal computer. The entrance slit is kept at the focal point of concave spherical mirror to obtain a collimated beam of radiation. The beam of electro-magnetic radiation is incident at an angle to

the grating. The diffracted beams of electromagnetic radiation are dispersed at various directions by the grating and are focused by a concave spherical mirror on to the exit slit. The radiation of wavelength  $\lambda$  and bandwidth  $\Delta\lambda$  is isolated by passing through the exit slit of a narrow width (say 40 micron). The electromagnetic radiation is detected by a photo-multiplier tube fixed behind the exit slit.

We have used a plane diffraction grating of line frequency 3600 grooves/mm, a concave mirror of focal length 1.19 m and a focusing mirror of focal length 0.973 m in the monochromator. The reciprocal linear dispersion of the monochromator is 0.25 nm/mm and the resolution is 0.02 nm over the wavelength range of 200 nm to 450 nm. The various wavelengths at exit slit are obtained by the rotation of the grating driven by a stepper motor. A sine drive assembly is used for linearizing the wavelength scale.

The rare earth impurities are extracted from uranium and dissolved in water. Thus the sample for the analysis is in the form of a solution. The solution is nebulised in to a flame formed by an inductively coupled plasma (ICP) as a source of excitation. The plasma is generated in argon atmosphere by a 27.12 MHz RF generator of 1.0 KW forward power. The sample introduced into the plasma flame by the gas flow gets excited into neutral and ionic excited states

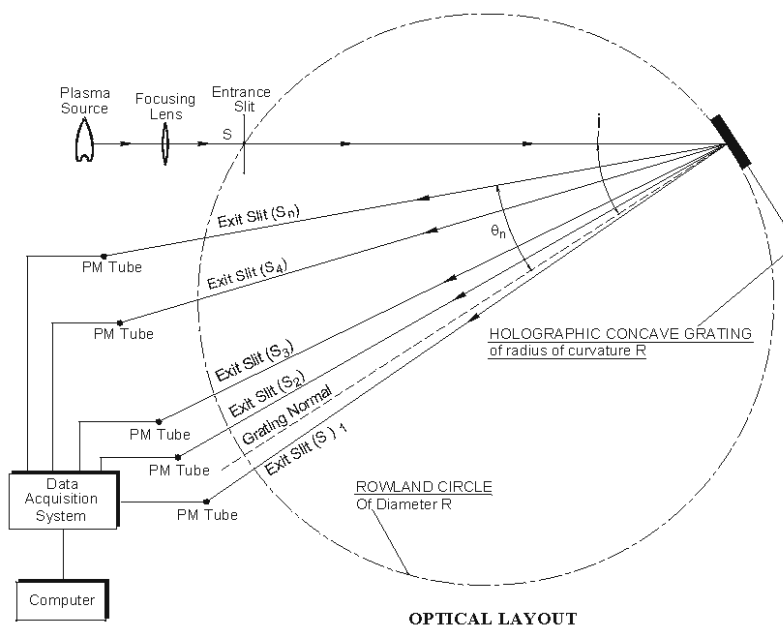


Fig. 2 Schematic optical layout of polychromator

and radiates in the form of a complex characteristic spectra of each element present in the sample. To detect the presence of a certain element, the most sensitive spectral line of the element is chosen and taken out of the exit slit of the monochromator. The radiation is detected by a PMT fixed at the exit slit. The output of the photo-multiplier tube is fed to a current amplifier coupled to a data acquisition system (DAS). The PMT current is converted into voltage which is then converted into frequency. The pulses generated in this manner are counted by an electronic counter. The intensity of the excited radiation is measured in terms of number of counts. Using a 1.0  $\mu\text{g/mL}$  standard solution, the peak position of the spectral line is located. Standards of various concentrations are used for calibration of the instrument. The calibration curve is prepared by plotting the counts versus concentration. This plot is then used to determine the concentration of unknown sample. Table 1 lists the detection limits obtained for various rare earth elements using the instrument. The detection limit given in  $\text{ng/mL}$  is a measure of the sensitivity of the technique in determining the concentration range of the particular element in the sample. This represents the lower detection limit of the element.

TABLE 1. Observed detection limits for various rare earth elements using the scanning monochromator.

Element	Wavelength (nm)	Detection limit (ng/ml)
Dy	353.602	22.6
Eu	420.505	3.3
Ce	399.924	37.0
Gd	355.047	23.0
Sm	360.949	37.8
Er	326.478	10.3
Yb	328.937	4.07
Y	371.03	2.2

#### Polychromator [2]

The optical layout of a polychromator is shown schematically in Fig. 2. The side view of the polychromator is shown in Fig.3. The polychromator consists of source of electromagnetic radiation, entrance slit, concave diffraction grating, exit slits  $S_1, S_2, S_3, \dots, S_{22}$ , photomultiplier tubes, data acquisition system and computer. When the entrance slit is illuminated by a spectral source, the



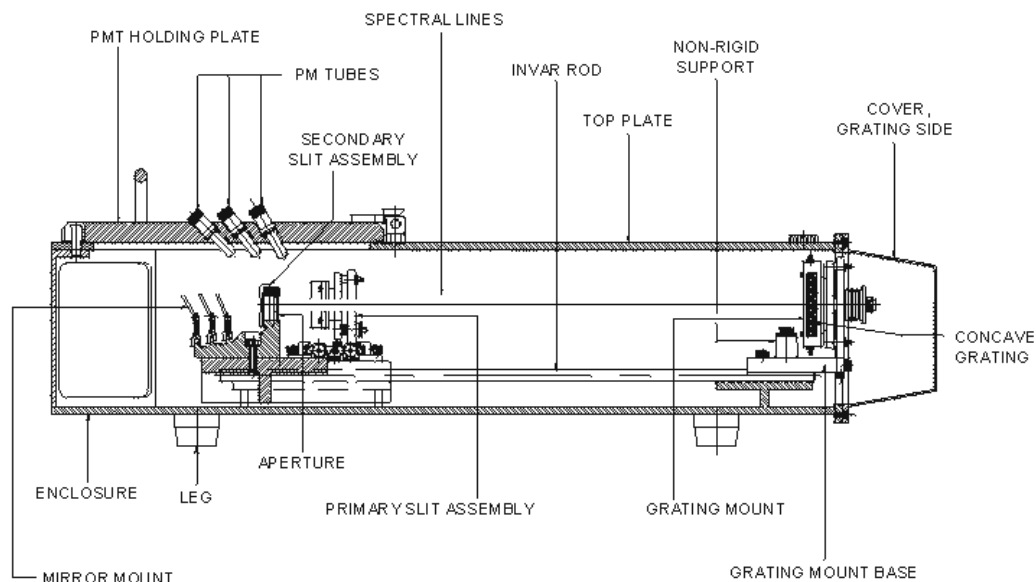


Fig. 3 Side view of polychromator

spectrum is focused sharply along the Rowland circle. The Rowland circle is defined as a circle tangential to the concave grating and of diameter  $R$ , where  $R$  is the radius of curvature of the concave grating.

The twenty exit slits are mounted along the Rowland circle precisely corresponding to the wavelengths used for determination of the twenty elements present in the sample. Two additional slits are also mounted along the Rowland circle. One of them corresponds to the wavelength of the uranium line for monitoring the intensity of the uranium flash (should it occur during arc burn) and the other is used for background correction. The reciprocal linear dispersion of the instrument is 0.39 nm/mm and the resolution is 0.04 nm. Radiation corresponding to the twenty wavelengths emerging out of the exit slits are detected by photomultiplier tubes placed behind each exit slit. The photomultiplier signal is recorded by an electronic system consisting of an integrator and a PC based data acquisition system. This instrument is capable of simultaneously analyzing 20 impurities such as B, Cd, Cr, Be, Co, Mn, Mg, Cu, Ni, Si, Mo, Zr, Ca, Ga, Pb, Sn, Fe, Ti, Al, and Zn at ppm/sub-ppm levels. Fig. 4 shows schematically an ICP torch assembly. The ICP source is an "electrical flame" generated by a high power (1 kW) radio

frequency (RFD) generator. The power from the RF generator at a frequency of 27.12 MHz is coupled to a load coil through which argon gas jet is made to flow. The RF power in the load coil is absorbed by argon gas converting it into argon plasma. The sample in the form of a liquid solution is introduced into the carrier argon gas. Minute aerosol particles of the sample are produced in the plasma due to the passage of the sample solution through a nebulising needle. The temperature of the plasma is about 6000K to 10000K, which is maintained by the inductive power transfer from the load coil. The atoms in the sample introduced into the plasma by the argon gas flow get excited into neutral and ionic excited states and radiate in the form of complex spectra characteristic of each element in the sample. To detect the presence of a certain element B (say) the sample is introduced into the flame. Standards of boron dissolved in deionised water with concentration in the range of 0.01  $\mu\text{g/mL}$  to 10.0  $\mu\text{g/mL}$  are prepared and injected in to the plasma flame. Intensity counts is measured for various concentrations of the standards and a calibration curve of concentration versus intensity is plotted for boron to find out its determination limit as shown in Fig. 5. Calibration curve is used for determining the concentration of boron element present in unknown sample under spectro-chemical analysis.

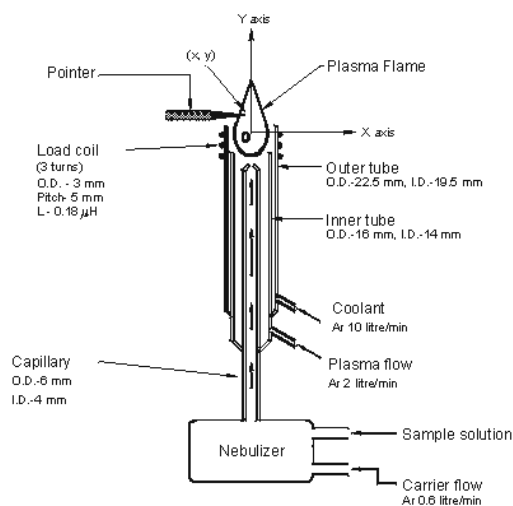


Fig. 4 Schematic diagram of I.C.P. torch assembly

Several standards containing mixture of 20 elements dissolved in deionised water with concentration in the range of 0.5  $\mu\text{g/mL}$  to 10.0  $\mu\text{g/mL}$  are also prepared for simultaneous multi-element analysis. The calibration plots (concentration versus intensity) for simultaneous analysis of mixture of twenty elements are also plotted and then used for the determination of unknown impurities. The typical determination limits observed for all the elements are 0.5  $\mu\text{g/mL}$  in twenty element simultaneous analysis using the inductively coupled plasma as a source of excitation. The instrument is found to be useful for simultaneous determination of twenty impurities dissolved in deionized water. This instrument has also been used for the simultaneous analysis of various elements like B, Cd, Cr and Be., in uranium matrix using DC arc as a source of excitation. With the DC arc as a source of excitation, the observed determination limits for the analysis of 14 elements in uranium matrix for B, Be, Cd, Co, Mn, Cr, Cu, Fe, Mg, Zn, Ti, Al, Ni and Pb are 2, 2, 2, 5, 5, 5, 10, 10, 10, 10, 10, 10 and 5  $\mu\text{g/g}$  respectively. With the DC arc as a source of excitation, the observed determination limits for the analysis of 18 elements in 'SPEX' graphite matrix for Cr, Zn, Cd, Be, B, Fe, U, Si, Ga, Pb, Al, Mn, Mg, Ca, Cu and Ni are 2  $\mu\text{g/g}$  whereas for Sn and Co they are 5 and 20  $\mu\text{g/g}$  respectively..

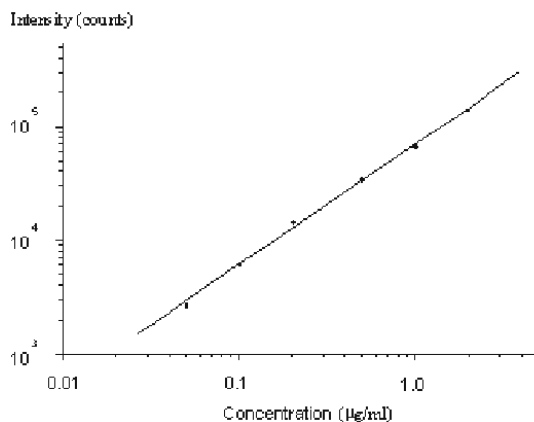


Fig. 5 Calibration plot showing the concentration versus intensity for the boron standards dissolved in water.

## Conclusion

The scanning monochromator designed and developed indigenously has been found to be useful for the determination of rare earth elements. The polychromator designed and developed indigenously has been found to be useful for the simultaneous analysis of 20 elements dissolved in water or present in graphite / uranium oxide powder. With the experience gained in the development and fabrication of analytical instruments, we are confident in taking up further developments in analytical instrumentation.

## Acknowledgement

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# Atomic Spectrometric Applications in Quality Control of Nuclear Power Reactor Fuels



**Shri B. Goapalan** obtained M.Sc. from Madras University (1966) and is from the tenth batch of BARC Training School. He joined the zirconium development group of Metallurgy Division, BARC in the year 1967 and actively contributed in planning, setting up and operation of quality control laboratory at Nuclear Fuel Complex, Hyderabad. Under the IAEA program he worked as a Research Associate at Ames Laboratory, ISU, Iowa, USA in the year 1981. Working with Dr. V.A. Fassel, the forerunner in the field of ICP-OES he had standardized a method for determination of impurities in uranium. Presently, he is the Senior Manager of Centralized Quality Control Laboratory, Nuclear Fuel Complex and is responsible for Process and Quality Control analysis including QA activities such as evaluation and clearance of process intermediates and products.

## Introduction

The thrust for the application of spectroscopic methods of analysis to nuclear materials dates back to early 1940s, when the need arose to analyze high purity uranium required for Manhattan Project. The method of 'Photographic atomic emission spectroscopy' was developed by Prof. Velmer A. Fassel and his group at the laboratory of Iowa State University, later came to be known as Ames Laboratory, USAEC [1]. Since then several countries started indigenous nuclear programs with a spurt in material development and characterization activities. Developments in the field of Analytical Spectroscopy provided complimentary and alternate techniques to Atomic Emission Spectroscopy. During the 60's, at the advent of direct readers, the photographic recording of spectra was replaced by electronic read-outs and the instruments became known as 'Spectrometers' instead of 'Spectroscopes'. Consequently a number of commercial spectrometers dedicated to analysis of nuclear materials were made available on custom fabrication basis by leading firms in the field. Today's state of the art spectrometers are all computer-controlled and incorporate several features like automatic sample introduction using

robotic arm, auto-programming of excitation conditions, remote control of instruments, data analysis, data communication through computer networks and analysis-based intelligent process control in the production plants.

## Nuclear Fuel, Reactor core and structural materials

Majority of nuclear power reactors in the World use uranium dioxide (both natural and enriched with respect to  $^{235}\text{U}$  isotope) as the fuel material. Uranium and plutonium oxides, carbides and nitrides have been used as fuel materials in fast breeder reactors. Thorium is used in the case of advanced power reactors as well as the blanket material in breeder reactors. All these materials have stringent specifications with respect to metallic and non-metallic impurities. The permissible levels have been fixed, based mainly on their neutron capture cross sections. For example, boron and cadmium have to be kept below 0.5 ppm and rare earths at still lower limits in uranium (Table 1).

Other than fuels, many materials used in nuclear reactor core have to be manufactured with purity levels much similar to the ones mentioned above. Zirconium alloys and stainless steel are used for fuel cladding, coolant channels and fixtures in

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**TABLE 1. Specifications of materials produced at NFC, in ppm unless indicated otherwise**

Element	ZrO <sub>2</sub>	Zr-sponge	Zr-2	Zr-4	Zr-Nb 2.5%	Natural UO <sub>2</sub> pellet	Enriched UO <sub>2</sub> pellet	ThO <sub>2</sub> pellet
Ag	-	-	-	-	-	1	25	-
Al	50	75	75	75	75	50	400	50
B	0.1	0.5	0.5	0.5	0.5	0.3	1	0.3
Be	-	-	-	-	-	-	-	1
C	-	250	270	270	125	200	100	100
Ca	50	30	30	30	25	50	250	200
Cd	0.3	0.5	0.5	0.5	0.5	0.2	1	0.2
Ce	-	-	-	-	-	-	-	4
Cl	-	1300	20	20	0.5	-	15	25
Co	15	20	20	20	20	-	75	1
Cr	100	200	500-1500	700-1300	200	25	400	25
Cu	50	50	50	50	50	20	400	50
Dy.	-	-	-	-	-	0.15	-	0.2
Er	-	-	-	-	-	-	-	0.2
Eu	-	-	-	-	-	-	-	0.08
F	-	-	-	-	-	10	25	10
Fe	150	1500	700-2000	1800-2400	650	100	400	100
Gd	-	-	-	-	-	0.1	1	0.2
H	-	25	25	25	5	1	-	1
Hf	100	100	200	200	50	-	-	-
Mg	50	600	20	20	20	50	200	50
Mn	50	50	50	50	50	10	200	10
Mo	50	50	50	50	50	4	400	20
N	-	65	65	65	65	-	100	75
Na	50	50	-	-	-	-	400	-
Nb	-	-	100	100	2.4 to 2.8%	-	-	-
Ni	20	70	300-800	70	70	30	400	30
O	-	1400	1000-1400	1000-1400	900-1300	-	-	-
P	-	100	-	-	10	-	-	50
Pb	20	100	130	130	130	-	400	20
Rare earths	15	15	-	-	-	-	-	-
S	-	-	-	-	-	-	-	50
Sb	-	-	-	-	-	-	-	2
Si	-	120	20	120	120	60	200	60
Sm	-	-	-	-	-	-	-	0.4
Sn	-	-	1.2%-1.7%	1.2%-1.7%	50	-	400	1
Ta	-	-	200	200	200	-	-	-
Th	-	-	-	-	-	-	10	-
Ti	50	50	50	50	50	-	-	-
U	3.5	3.5	3.5	3.5	3.5	-	-	100
V	-	50	50	50	50	-	400	5
W	-	50	50	50	100	-	100	-
Zn	-	100	-	-	-	-	400	-
Zr	-	-	-	-	-	-	-	20
Fe+Cr+Ni	-	-	0.18%-0.38%	0.28%-0.37%	-	-	-	-

Reference: NPCIL-PP-M-617, 620, 784, PP-E-1731, ASTM-B-349, ASTM-B-350

various types of reactors. Cadmium and hafnium are used in control rod assemblies. Reactor core components have to be of adequate strength, high temperature stability, low corrosion rate and low affinity for neutrons (Table 1).

### Fuel Manufacture

The Indian Nuclear Power Program is predominantly based on Pressured Heavy Water Reactors (PHWR). All these reactors use uranium dioxide in the form of sintered pellets as fuel and zirconium alloys (Zr-2/Zr-4) as the cladding material. The fuel channel is made up of a Calandria tube (Zr-2) and Coolant tube, also called as pressure tube, of Zr-2.5% Nb alloy. The twin Boiling Water Reactor units at Tarapur, Maharashtra use enriched uranium dioxide fuel manufactured from imported raw material, uranium hexafluoride.

Uranium mineral ( $U_3O_8$ ) mined from earth's crust is first concentrated and converted to Magnesium-di-uranate (MDU). At Nuclear Fuel Complex, Hyderabad, the MDU is converted to Ammonium-di-uranate (ADU) which is then calcined and reduced in hydrogen atmosphere to get uranium dioxide powder. The powder is palletized and sintered and clad with thin walled zirconium alloy tubes to form fuel pins. A number of fuel pins are assembled and welded together to get fuel bundles. The zirconium alloy materials required for cladding as well as for fabrication of core components are manufactured from zircon sand isolated from beach sands. Zircon is a silicate mineral and apart from zirconium, hafnium is present to the extent of 2%. Hafnium has a thermal neutron absorption cross section of 105 barns while zirconium 0.18 barns and hence from neutron economy point of view, hafnium has to be removed from zirconium. Because of very little differences in their atomic and ionic radii, these two elements occur together in nature and are difficult to separate. A series of chemical and metallurgical operations are involved in the production of hafnium free zirconium metal.

In all these process steps, impurity contents are required to be determined in various intermediates. For example, the complete removal of hafnium from zirconium in the solvent extraction purification step is to be monitored with Atomic Emission

Spectrometry or X-ray Fluorescence Spectrometry. Various other spectrometric techniques are employed during the entire process of manufacture of fuel bundles as described in the following sections. Besides the primary purpose of analysis of fuels, spectrometric methods have been gainfully employed for the analysis of raw materials and effluents.

### Atomic Emission Spectrometry

In Atomic Emission Spectrometry (AES), the sample is excited by thermal or electrical energy and the radiation emitted by the constituent atoms of the sample on their ions is measured and used for qualitative and quantitative analysis.

AES has several advantages like adequate sensitivity for ppm/sub ppm level impurity analysis, multi-element capability and small sample size (often milligrams) and rapidity. Though these are not absolute methods like classical chemical analysis, by careful standardization of analytical steps, reasonably accurate results (within 10-15% r.s.d) can be obtained. Boron determination at sub ppm levels and ppm level, determination of hafnium in zirconium matrix, determination of individual rare earth elements are all made possible, and that too simultaneously by the application of emission spectrometric methods.

Uranium gives rise to complex emission spectrum in the useful wavelength region of 240 to 330 nm and any attempt for direct excitation results in the enhancement of background spectrum. In order to improve the signal to noise (S/N) ratio for impurity elements, which are generally present in much lower levels, it is necessary either to separate out the matrix or suppress its effects in the spectrometric analysis. Early methods [2] adopted carrier distillation - DC Arc excitation procedure. In this method, the  $U_3O_8$  powder sample is mixed with carrier substance such as AgCl and charged into the crater of graphite electrode. During DC arc excitation in the spectrograph, the impurities in the electrode charge get distilled into the DC arc, in preference to refractory  $U_3O_8$ . Similarly, impurities in thorium oxide have also been determined using the DC arc method [3].



In tune with the development in the field, most of the laboratories have switched over to Inductively Coupled Plasma - Atomic Emission Spectrometric Techniques (ICP-AES) for the analysis of uranium, thorium, plutonium, etc. This is mainly because of the inherent advantages of ICP-AES method such as high dynamic range, high S/B ratio, sensitivity to refractory elements and direct solution analysis. The liquid sample introduction facility is especially suitable for nuclear fuel processing and manufacturing industries where many of the samples are received for analysis are in liquid form.

For the analysis of uranium samples, where the impurities to be determined are in trace levels, it is necessary to separate out the matrix even in the case of ICP-AES. It has been found that the presence of residual uranium more than 5 ppm level interferes with Gd (342.247 nm) line and the interference is appreciable at higher levels. A solvent extraction separation procedure using TBP, TOPO or combinations of both is adopted [4,5]. In the case of thorium, removal of matrix with TBP, Cyanex-923 has been successfully employed [6]. Solvent extraction using KSM-17 has been applied for separation of matrix in uranium, thorium and plutonium samples [7]. The matrix free aqueous solutions are directly nebulized in to the plasma. In this way, more than 20 elements including a few rare-earths elements in uranium samples can be analysed in a single setting with dedicated spectrometer. Normally a pneumatic nebulizer is conveniently employed for sample introduction into the plasma. A useful variation is the use of ultrasonic nebulizer, with which the detection limits of impurity elements, especially those of rare earths are improved, about ten fold [12]. Direct analysis of uranium sample is possible in the ICP-Mass Spectrometric method without the separation of matrix. Both the ICP-AES and ICP-MS procedures have been adopted as the standard methods by ASTM for the analysis of Uranium [8,9]. Encouraged by the advantages of plasma source of excitation, several allied techniques like DCP-AES, axial ICP-plasma and solid sample introduction in plasma source. have been applied for the analysis of impurities in nuclear materials.

It is worth mentioning here that emission techniques are used for the analysis of zirconium

oxide, sponge and zirconium alloys [10,11]. In the established DC arc method, zirconium oxide or the converted oxide from sponge and alloy is mixed and ground with BaF<sub>2</sub> buffer and Ga<sub>2</sub>O<sub>3</sub> internal standard in fixed ratios and a small charge of the mixture is loaded in graphite electrode. Excitation of sample in the DC arc and subsequent dispersion in quartz prism or grating spectrograph followed by photographic detection or electronic detection gives a good spectrum in UV region with fairly clean back ground. The optical densities are measured either manually or electronically to obtain the concentration of impurities.

#### **Atomic Absorption Method**

In Atomic Absorption Spectrometry (AAS), the sample solution is atomized with the help of flame or graphite furnace, thereby producing atomic vapour. A separate source of monochromatic light, such as hollow cathode lamps (HCL's) specific to the element to be analyzed for, is passed through the atomic vapour and the extent of absorption is measured at a characteristic wave length after dispersion.

A number of laboratories have used all variations of AAS technique namely flame, furnace, solid sample furnace, laser and ICP as an atomization source for the analysis of nuclear materials. AAS is generally used as a complimentary technique to atomic emission method. Determination of alkali elements is best done in the flame emission mode of atomic absorption spectrometry. Besides, AAS overcomes some practical difficulties like certain cases of spectral line interference, inadequate line sensitivity and background enhancement problems that are faced in the emission methods. Elements like Ag, Na, Si and Zn uranium are conveniently done using the AAS (Table 2). One of the promising techniques useful for the nuclear fuel process samples is the direct analysis of solids in graphite cuvette furnace AAS. Determination of as many as 17 nos. of impurity elements in uranium samples using AAS technique have been reported [19].

#### **Fluorimetry**

In fluorimetry the ultra violet or visible light energy is used to excite a molecular constituent of

**TABLE 2. Spectrometric analysis applied for the analysis of samples from nuclear fuel production plants, NFC**

Analytical Method	Samples Analysed	Analysed for
Atomic Emission Spectrography	Zr, U, Th & High purity materials	Trace level metallic impurities
Direct Reading (emission) Spectrometry	Zr oxide, Zr sponge, Zircaloy-ingots & components	Alloying Elements & Metallic impurities
Inductively coupled Plasma - Atomic Emission Spectrometry	U, Th, Zr base samples High purity materials & SS	Rare Earths & other impurities Trace impurities
Atomic Absorption Spectrometry (Flame and Furnace atomization)	U, Zr, Steel and other alloys  High purity materials	<ul style="list-style-type: none"> <li>• Ag, Na, Si and Zn in U</li> <li>• Alloying elements in Zr alloys</li> <li>• Trace impurities in alloys &amp; high purity materials</li> </ul>
X-Ray Fluorescence Spectrometry	U, Zr, Steel and other samples	U, Zr, Hf & major & minor constituents
Spectrophotometry	U, Zr, Th, Steel and other samples	Cl, N, Si, P and minor constituents

the sample and during the de-excitation process the molecule re-emits part of it as light energy in a longer wavelength. The intensity of the characteristic emission, called fluorescence, is proportional to the amount of constituent element in the sample.

In the nuclear fuel process industry trace amounts of uranium are measured in various materials like zirconium, zircaloy and effluents. In a typical method the sample is dissolved in nitric acid and uranium is extracted with organic solvent using  $\text{Al}(\text{NO}_3)_3$  as the salting out agent. Aliquots of organic phase are fused with flux material like  $\text{LiF}$ ,  $\text{Na}_2\text{CO}_3$  and fluorescence (excitation at 365 nm and emission at 555 nm) of uranium is measured. In the laser fluorimetric method the sample containing uranium is treated with potassium fluoride and tetra sodium pyrophosphate and excited by laser light of 337 nm and the fluorescence measured at 510 nm [13]. The later method has proved to be a very sensitive for determining uranium in ppb levels.

#### **X-Ray Fluorescence Spectrometry (XRFS)**

In WDXRFS (Wavelength dispersive), a beam of sufficiently short wave length X radiation is used to bombard a sample which in turn emits characteristic X-rays of longer wavelength.

Qualitative analysis involves measuring wavelength of the emitted lines whereas quantitative analysis comprises of measuring the intensity of the lines. In the EDXRFS (Energy dispersive) technique, the excitation of the sample is achieved either by the use of a radioisotope or an X-ray tube. Both the versions of XRFS techniques have been widely used [17] for the analysis of nuclear materials. Because of their simplicity and specificity XRFS methods are suitable for the analysis of heavy elements in the sample down to parts per ten thousand level.

In the uranium fuel process industry, the conversion of ore concentrates to nuclear pure uranium powder usually involves process steps like dissolution and solvent extraction and precipitation calcination. All these steps need close monitoring of uranium concentration and for this purpose XRFS methods are ideally suited. The samples are in solution form and hence homogeneous in nature. Uranium concentrations in the level 0.1 to 400 g/L are directly measured after suitable dilution wherever required. The techniques have also been applied for the determination of U and Pu content in mixed oxide fuel as well as for the determination of  $\text{Gd}_2\text{O}_3$  (a burnable poison in the reactor) added in the manufacture of certain types of reactor fuel. The

grain size of uranium dioxide pellet is affected by the concentration of sulphur present in it and in such cases, the application of XRFS procedure is recommended for determination of sulphur [18]. Traces of uranium in aqueous solutions could be pre-concentrated and analyzed by XRFS using thin film techniques [15].

Similarly, as mentioned before, the extraction purification process of hafnium free zirconium requires determination of these metals in various process intermediates. Solution sample-XRFS technique works well for carrying out routine analysis in both aqueous and organic solutions. Since in most of these samples zirconium is the matrix and hafnium concentrations vary between concentration range 0.1 to 3 g/L, the situation calls for matrix correction or suppression before measurement. It may be noted here that the hafnium,  $L_{\alpha}$  and  $L_{\beta}$  lines are overlapped by the second order reflection lines of matrix, zirconium  $K_{\alpha}$  and  $K_{\beta}$ . This problem has been overcome by employing Germanium (111) crystal (in WDXRFS) which cuts down the second order Zr lines [14] or by making use of Hf,  $L_{\beta}$  1,2 line with a proportional counter. Alloying constituents like Cr, Fe, Ni, Sn and Nb in various zirconium alloys have been determined by XRFS [16].

#### Miscellaneous Spectroscopic Techniques

Various other spectroscopic techniques like X-ray excited optical luminescence and atomic fluorescence, hyphenated techniques like GD-OES, Laser ablation-OES, spectrophotometry and hydride generator-AAS have also been applied for the analysis of impurities in nuclear materials. The main weakness in spectroscopic technique is the difficulties in determination of non-metals. Stringent specifications exist for the nuclear materials for their non-metallic impurity contents. For example, the maximum allowable limits are 0.5 ppm and 5 ppm for chlorine and hydrogen in Zr-Nb alloys, used for making pressure tubes for PHWR. Similarly, it is important to determine carbon, nitrogen and oxygen in these materials. Therefore, for the purpose of analysis of all these materials, the spectroscopic techniques have to be supplemented by other analytical methods.

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# Analytical Spectroscopy - Biological and Environmental Applications



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## Introduction

With increased awareness of the role of trace elements in functional biology a lot of efforts are being directed to improve the methodology of trace elemental assay in biological materials and in the environment that has impact on biocycle [1]. For trace metal assay, analytical spectroscopic methods have been the main work horses [2-5]. In recent past, newer techniques like ICP-MS, total reflection X-ray fluorescence (TXRF) are also contributing significantly in this area. ICP-MS also has been successfully interfaced to liquid, gas, and super critical fluid chromatographs for carrying out speciation work [6,7]. The present article deals with methodology for trace metal determination in samples of biological and environmental interests using Atomic Absorption Spectrometry (AAS), Inductively Coupled Plasma – Atomic Emission Spectrometry (ICP-AES), TXRF and ICP-MS methods developed in our laboratory [8-11]. Information on the trace elemental contents in biological and environmental samples has direct bearing on human health. The results obtained are discussed taking the population of Kalpakkam township and population around Periyar river in Kerala as real life samples.

The trace elements could be categorised into essential (As, Cr, Co, Cu, F, I, Fe, Mn, Mo, Ni, Se, Si, Sn, V and Zn) and toxic elements (Cd, Hg, Pb, Tl) [1]. While essential trace elements are key components of proteins (e.g. Fe on haemoglobin) and several metal enzymes (e.g. Se in glutathione peroxidase). The toxic elements exert their toxic effects mainly as enzyme inhibitors. Even essential trace elements, if they exceed certain minimum concentrations, start exerting toxic effects. Thus there is a definite range of concentration for every trace element, in our body, which represents a healthy state. Hence establishment of reliable reference values in body tissues and fluids with a narrow spread of ranges for several trace elements, particularly for the essential and toxic ones.

## Establishing Reference Values for Trace Elements in Blood of the kalpakkam Population

In several world populations, trace element related diseases have been reported in connection with the nutritional deficiencies. Based on the data collected on different populations Iyengar [1] and Caroli et. al. [12] have given the reference range of values for trace elements in human serum, whole blood and other fluids and tissues. As a part of obtaining such a data on Kalpakkam populations

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blood samples were collected in clean polythene vials, 5 µL of heparin added, and centrifuged to separate the plasma and red cells. Plasma was diluted ten times with water and analysed using ICP-MS. Red cells were digested using nitric acid and perchloric acid in a teflon bomb using microwave heating. The clear digest was diluted ten times and analysed by ICP-MS. For the determination of selenium, a hydride generation technique was used. The methods were standardised by using reference materials of serum supplied by Kaulson labs, USA. Polyatomic ion interferences resulting from the blood matrix (essentially from Na, K, Ca, S and Fe) were studied and corrected by use of synthetic matrix-matched blank solutions. Blood samples of both normal healthy subjects (to arrive at the reference values for our population) and those having high cholesterol were included in the study (to examine whether there is any correlation between lipid profile and trace element profile). Reference values obtained for our population for plasma and red cells are given in Table 1. Kalpakkam with its clean environment and the homogeneity of the population with similar dietary habits provides the necessary control group. From these values, it is found that the trace element levels in blood of Kalpakkam population is normal. No element is present at toxic levels. But the selenium levels are less indicating that there is some deficiency. As a follow up study, our dietary materials were analysed for Se and other trace elements using ICP-MS. Our selenium and zinc intake was found to be less as compared to RDA values whereas that of Mo (the pulses are rich in Mo) slightly higher (Table 2). But the blood levels of Zn and Mo were found to be normal indicating the possible high level of homeostasis for these elements in our body. But the blood level Se was found to be marginally less as compared to global average. The polished raw rice was not found to contain any Se, whereas, parboiled rice, wheat, ragi and pulses were found to contain some amount of Se. Fish, egg and milk were found to be rich sources. It has been found that non-vegetarians with parboiled rice/wheat as staple food consume approx. 40 µg/d of Se, while vegetarians with polished rice as staple food consume a meagre 20 µg/d. The recommended

dietary intake is 50 – 200 µg/d. But the deficiency of Se in our population is not that serious as in the Keshan disease regions of China [13]. Hence there is no room for undue anxiety. But as the role of Se in our health has been established as a constituent of very important antioxidant enzyme viz., glutathione peroxidase, it is prudent to include in our diet more of selenium containing foods to ward off Se deficiency. Some interesting correlations also were observed between trace element profile and coronary risk index calculated from lipid profile. The amount of Se, Fe and, K were found to be significantly less in the red cells of the “high risk” group, as compared to ‘no risk’ group. The amount of Na, K and Mg in plasma of the high risk group were found to be less than the no risk group indicating that these changed elemental levels could possibly be used as markers for coronary risk in addition to lipoprotein measurements [14-16].

**TABLE 1. Reference values for trace elements in blood plasma and cells of the Kalpakkam population**

Element	Reference values for Kalpakkam population	Reference values in literature on human blood [1,14]
Blood plasma (µg/L or as specified)		
Cd	<1	0.1
Co	<1	0.1 - 0.3
Cu*	0.8-1.1	0.8 - 1.1
I	50-75	60 - 70
Mn	<3	0.5 - 1.0
Mo	<2-10?	0.5
Ni	<3-5?	1 - 2
Pb	<5	< 1
Rb	200-280	-
Se	60-90	75 - 120
Zn*	0.7-1	0.8 - 1.1
Blood cells (mg/kg or as specified)		
Fe	750-940	-
Cu	0.6-0.9	-
Pb#	90-230	-
Rb	4-5.5	-
Se#	90-140	75-240
Zn	9-14	10-16

\*mg/L, #µg/Kg

**TABLE 2. Mean dietary intake of trace elements by the Kalpakkam population**

Element	Mean dietary intake (mg/day or as specified)				RDA or safe adequate Intake [17] (mg/day)
	HIG		LIG		
	Veg.	Non Veg.	Veg.	Non Veg.	
Cu	1.9	1.9	2.2	2.2	1.5-3
Zn	8.7	7	9.7	10.2	15
Rb	2.7	2.5	2.8	2.7	-
Mn	6.2	6.4	7.6	7.8	2-5
Sr	1.9	1.8	1.9	1.9	-
Fe	9.9	10.1	9.1	9.4	10-18
Mo*	340	330	380	390	75-250
Pb*	170	200	200	230	450
Se*	27	40	27	48	50-200

\* µg/day, HIG -High income group, LIG - Low income group.

## Applications in Environmental Research

### *Trace Metals in Sea Water*

Accurate and reliable analytical methods are required to characterise sea water with respect to the trace metals to understand the bio-geochemical cycle of these elements in the marine environment and for environmental monitoring. As the elements are present in the parts per billion/trillion levels, the analytes have to be separated from the interfering sea water matrix. Also, the practices of ultra trace analysis have to be scrupulously followed to minimise and control the analytical blanks to carry out measurements at such trace levels. We have used sodium dithiocarbamate to selectively complex the transition and other trace metals in sea water. Using this method, samples of candidate Standard Reference Material of sea water (C MARS, RRL, Trivanandapuram), received as inter laboratory comparison sample was analysed and reported. The details of the method are described below.

An aliquot of 100 ml was used for each experiment. The seawater (MARS-1) was taken in a clean teflon(FEP) separating funnel, and the pH adjusted to 6 . 1 ml of 1% sodium diethyl dithiocarbamate and 1 ml of ammonium acetate buffer was added. The extraction of the metal carbamates was done using 50 ml of chloroform (purified by washing thoroughly with dilute nitric

acid followed by high purity water). The organic phase was separated, evaporated to dryness and the residue containing the metals was dissolved in nitric acid and determined by ICP-MS. The blanks got were of the order of a few pico grams for the different elements. The results are tabulated in Table 3. To start with, the experimental conditions for optimum extraction was arrived at by spiking experiments carried out in synthetic sea water prepared in our lab using high purity water and specpure(purity 99.999%) chemicals viz., the chlorides of Na,K,Ca and Mg (JMC, UK) (Table 3). Standard Reference Materials of water (JAC-0032) and NIST 1643 d were used as a quality control check on our instrument calibration. The precision of our method has been found to be 5%(RSD) for Cu,Pb,Ni and Zn which are present at ppb levels in sea water and about 10% for Cd and Co which are present at several ppt levels.

### *Study of Toxic Element Pollution in Periar River, Kerala*

The river Periyar is an important major river catering to the agricultural and drinking water needs of the state of Kerala in India. In its last 15 km stretch, the river Periyar is the recipient of a wide variety of pollutants from the various industries such as zinc smelter, phosphatic fertilizer plant, caustic soda plant, rare earth processing plant and various

**TABLE 3. Analysis of Coastal sea water MARS-1 (concentration ng/ml)**

Element	(1)	(2)	(3)	(4)	(5)	(6)	Mean
Cd	0.078	0.085	0.085	0.095	0.085	0.06	0.081 ± 0.011
Cu	2.11	2.11	2.18	2.12	2.10	2.2	2.15 ± 0.04
Co	0.044	0.040	0.035	0.035	0.036	0.035	0.037 ± 0.003
Pb	1.3	1.12	1.21	1.1	1.33	1.26	1.22 ± 0.086
Ni	0.59	0.58	0.64	0.65	0.63	0.6	0.62 ± 0.026
Zn	8.6	9.0	8.7	9.3	9.7	9.2	

chemical industries located on its banks. Apart from this, agricultural run-off and urban run-off also contribute to the pollution of this river. With the collaboration of Environmental Radiological Laboratory, Udyogamandal, Cochin we undertook a systematic study of the toxic element pollution of waters and sediments of this major river. For elemental fractionation in sediments, sequential extraction gives information pertaining to their labile fractions that get released under various conditions such as change of pH, reducing and oxidizing conditions [18].

#### **Sampling and Standardization of Analytical Methods for the Analysis of Water and Sediments**

The study consisted of analysis of surface water and sediments from different locations (16 locations) covering the different regions of the river viz., background region, industrial region, upper back waters and coastal back waters. Water and sediment samples were collected before and after monsoon and analysed. The water samples were filtered with whatman 42 filter paper and acidified suitably. For cadmium determination, the acidity of the samples was kept at 0.1 N with hydrochloric acid; for Hg- 0.1 N with HCl with 20 mM cysteine hydrochloride; and for all other elements 0.1 N acidity with nitric acid. As the industries were located on both sides of the river the waters and sediments were sampled on both sides (denoted "right" or "left" with respect to the direction of flow of the river). A grab sampler was used to sample sediments. The water samples were immediately acidified and stored in clean polythene bottles. While the sediments samples were stored in clean polythene bags.

Elements such as Na, K, Ca, Mg and Fe were determined in water samples by AAS. The elements occurring at sub ppb and ppb levels such as Co, Cu, Zn, Ni, Pb, Rb, Sr, rare earth elements (La, Ce, Pr, Nd and Sm), U and Thorium were determined by using ICP-MS.

#### **Analysis of Sediments**

In the analysis of sediments, in order to avoid the variation of measured concentration of elements due to variation in particle size, generally sediments of particle size <63 µm are chosen and these were separated by sedimentation method [19]. The analysis of sediments was carried out after digestion of sediments with nitric and perchloric acid followed by leaching with hydrochloric acid and sequential extraction with a series of reagents using a protocol proposed by European Communities Bureau of Reference (BCR).

Sum of the concentration of an element in the above mentioned fractions can be considered as the total labile fraction for that element which could get released under favourable conditions and could eventually pose risks to aquatic life and to humans. Hence, analysis of these fractions assumes importance. The residual material remaining after sequential extraction was digested with nitric acid and perchloric acid and then leached with hydrochloric acid. The resulting solution was analysed to get more resistant residual components of the sediment matrix. In sediment samples Cu, Zn, Cd, Pb, Ni, Mn and Fe were determined by AAS. Elements such as Co, Ni, Rb, Sr, Zr, various rare earth elements (La, Ce, Pr, Nd, Sm), U and Th were determined by ICP-MS.

In the back waters region of the river, mixing of sea water occurs because of tidal influx. This resulted in high concentration of sodium chloride in the river water of this region. High salt concentration offers the problem of matrix effect in direct solution introduction mode of ICP-MS. Therefore, suitable pre-concentration methods are generally followed for the analysis of these samples. These samples could be conveniently measured with a sensitive cold vapour atomic absorption spectrometric technique (CV-AAS) developed in our laboratory earlier for analysis of sodium and uranium. Mercury contamination was expected as the chloralkali plant (uses mercury) is also discharging its effluents into this river. It is well known that methyl mercury species formed by methylation of inorganic mercury is more toxic than inorganic mercury species. Hence, speciation study of mercury was also undertaken. For speciation of mercury in water samples a method using high performance liquid chromatography coupled with ICP-MS (HPLC-ICP-MS) was standardized. In the case of mercury speciation in sediments, a solvent extraction method coupled with ICP-MS was developed and standardized. To get improved detection limits for mercury, vapour generation method coupled with ICP-MS was developed.

#### **Determination of Methyl Mercury by ICP-MS**

An IAEA certified reference material (IAEA Tuna fish-350) was used for method development and standardisation. 0.25 g of the material was washed with acetone and the various mercury species were brought into solution by shaking with 2 M hydrochloric acid for four hours in a mechanical shaker. From this solution, methyl mercury was selectively extracted by using toluene as solvent. As the introduction of organics into ICP-MS presents problems due to soot formation, the methyl mercury was back extracted into an aqueous solution of 20 mM cysteine which is a very efficient complexing agent for mercury. The aqueous phase containing the methyl mercury is analysed using a hydride generation- ICP-MS method. Our measurements were in very good agreement with the certified concentration values given by IAEA. The detection limit of the method was found to be 10ng/g.

#### **Determination of Cadmium by Cold vapour AAS(CV-AAS)**

Cold vapor AAS is an elegant technique in which the atomic vapour is just produced at room temperature is swept into the absorption cell with a transport efficiency close to 100%. Due to this superior sensitivities in the realm of ppb are attainable by this technique. Using this technique developed in our laboratory [20], the waters and sediments of the Periar river have been analysed. A quantitative measure of metal pollution in aquatic sediments is expressed in terms of 'index of geoaccumulation' which is calculated as  $I_{geo} = \log_2 (C_n/1.5 \times B_n)$ ,  $C_n$  is the measured concentration of the element and  $B_n$  is the geochemical background value.(i.e. average shale).  $I_{geo}$  value of 0-1 indicates nil pollution , 2-3 indicates moderate pollution and 4-6 indicates strong to very strong pollution [21].

Some of the important findings are as follows: The cadmium concentration in the Periyar river water is less than the environmental standard value of 2 ng/ml. In the water samples, only Zn showed higher concentration values than the critical concentration levels, whereas all other elements such as Co, Ni, Cu, U, Th and rare earth elements are below the critical concentration levels [22]. This study brought out the fact that the effluents from the industries present on the banks of the Periyar river have not polluted the river water significantly except for a moderate pollution of zinc. The sediments in the industrial area, however, are found to be considerably polluted with respect to Cd, Hg, Pb, and Zn (Table 6) The high geoaccumulation index ( $I_{geo}$ ) values obtained show considerable pollution with respect to these elements in the industrial region. The sequential extraction studies showed that considerable fraction of these elements are in the labile fractions. Mercury present (1-20 ppm) is essentially in the inorganic form and no methyl mercury could be detected in these sediment samples (<10 ng/g).

#### **Long Lived radionuclides in the Environment**

ICP-MS is gaining popularity as a quick method for the determination of long lived radionuclides in environmental samples by detecting the atoms themselves. The potential capabilities of ICP-MS for the detection of actinides were

**TABLE 6. Concentration of elements in the sediment samples of Periar**

Location	Region	Cd ppm	Cd Igeo	Zn ppm	Zn Igeo	Pb ppm	Pb Igeo	Hg ppm	Hg Igeo
Kalady	Background region	<3		306		105		0.12	
Alwaye	Industrial region	<3		404		60		0.36	
TCC outfall		3	2.7	663	0.3	108	-	19.6	5.8
Udyogmandal Right		37	6.4	3980	2.9	1580	3.7	5.8	4.0
Udyogmandal Left		5	3.5	424	-	126	-	11.6	5.0
Methnam right		30	6.0	958	0.9	126	-	1.1	1.6
Methnam left		5	3.5	418	-	90	-	2.6	2.9
Varapuzha right	Upper back waters	38	6.4	1702	1.7	120	-	2.2	2.6
Varapuzha left		7	4.0	439	-	78	-	2.1	2.5
Cheranaloore		32	6.2	979	0.9	84	-	4.1	3.5
Moolampally		23	5.7	951	0.8	66	-	4.9	3.8
Vaduthala		20	5.5	857	0.7	78	-	4.6	3.7
Ponnarimanga lam		15	5.1	873	0.7	78	-	3.2	3.2
Bolgatty	Coastal back waters	8	4.2	617	0.2	36	-	1.3	1.8
Opp. Maneka		5	3.5	409	-	30	-	0.78	1.1
Shipyards		<3		168	-	30	-	0.16	-

TCC – Trivancore and Cochin Chemicals

recognized and there is a growing literature on the subject [23]. Employing ETV-ICP-MS, single ion monitoring, R.D.Scott et. al. [24] showed that the limit of detection that could be achieved for actinides is  $2.5 \times 10^6$  atoms in environmental samples. Grain and Gallimore [25] have reported a detection limit of 100 ng/L (2 nCi/L) for  $^{99}\text{Tc}$  determination using In as an internal standard in an attempt to use this approach for determination of Tc in public water supply (limit 4 nCi/L).

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# Spectroscopic Techniques in Geochemical Exploration



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## Abstract

The most important analytical spectroscopic techniques used for generation of elemental and isotopic data are spectrophotometry, F-AAS, GF-AAS, XRF, INAA, ICP-AES, TIMS and ICP-MS. Some important applications of these techniques in mineral exploration studies are discussed, giving a brief outline of each technique. The relative advantages and disadvantages of the individual techniques over others are furnished. Analyses by spectroscopic methods mostly require preparation of the sample to suite the respective sample introduction systems. Use of both microwave dissolution and classical sample preparation methods are discussed. Some of the quality control schemes for obtaining precise and accurate geochemical data required in exploration studies using these techniques are also enumerated.

**Key words:** spectroscopic techniques, geochemistry, exploration, detection limits, microwave.

## Introduction

The key to industrial progress of any nation is the development of its mineral resources which play a vital role in the economy of that country. In order to exploit the vast mineral resources, it is necessary to undertake a systematic study and understand the geological processes that are recorded through space and time using an integrated approach involving geological, geophysical and geochemical investigations. Several natural processes and activities, such as creation of magma along mid-oceanic ridges, plate movements and subduction, orogenesis, weathering, erosion and sedimentation have each contributed their mite to the concentration of metals in the earth's crust [1]. Geochemical concepts are now virtually used in every exploration program. The objective of geochemical exploration is to delineate areas with the highest probability of mineralization in a cost-effective manner. The practical effectiveness of any geochemical method of exploration depends to a large extent on the availability of effective analytical procedures.

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The analysis of geological materials is one of the greatest challenges facing analytical chemists because of the extremely wide variety of sample types encountered and number of elements associated with each sample. In addition to these, the concentration of a given element can reach as high as 12 orders of magnitude when samples, such as natural water and ores are compared. Technological advances in instrumentation and analytical techniques, have brought a remarkable progress in mineral exploration studies especially, during the last five decades. Classical techniques such as gravimetry, titrimetry and other methods have been replaced by atomic, nuclear and mass spectroscopic techniques. Some of the most important instrumental analytical spectroscopic techniques commonly applied in the geochemical analyses are, spectrophotometry, flame atomic absorption spectrometry (F-AAS), graphite furnace atomic absorption spectrometry (GF-AAS), inductively coupled plasma atomic emission spectrometry (ICP-AES), X-ray fluorescence spectrometry (XRF), instrumental neutron activation analysis (INAA), thermal ionization mass spectrometry (TIMS) and inductively coupled plasma mass spectrometry (ICP-MS). A brief account of each of these techniques together with their usefulness to mineral exploration studies are given below:

### ***Spectrophotometry***

Some ions or ion complexes in solution absorb energy in the UV-visible region of the electromagnetic spectrum when light is made to pass through the colored solution. The absorbance of the colored solution at its characteristic wavelength is directly proportional to the concentration of the metal in question. Separation of elements by solvent extraction and estimation by spectrophotometry can often be combined by using organic solvents in which a compound of the desired element forms a strongly colored solution in one of the two solvents. These methods were widely used before AAS, XRF, ICP-AES became available. Several elements down to ppm levels can be estimated in a variety of rock samples. But on several occasions, these methods do not possess the required sensitivity and throughput rates needed for geochemical exploration studies.

### ***Flame-Atomic Absorption Spectrometry (F-AAS)***

Atomic absorption spectrometry developed in mid-1950s was the workhorse for trace element analysis in geochemical laboratories for over 3 decades. Introduction of this technique in the early 1960s revolutionized the geochemical exploration studies. Rapid, low-cost, sensitive measurement of more than 30 metals in a variety of sample media made the universal acceptance of F-AAS in geochemical laboratories [2]. Atomic absorption occurs when an outer electron of an analyte atom changes energy levels from neutral ground state to a higher energy level by absorbing radiant energy of a specific wavelength. The concentration of the analyte in an unknown sample is measured by comparing its atomic absorption signal with that of a standard of known analyte concentration. The advantages of F-AAS are that it is simple, reliable and requires minimal maintenance. For rapid analysis of a single element at a time in sample solutions, F-AAS is an excellent choice [3].

### ***Graphite Furnace Atomic Absorption Spectrometry (GF-AAS)***

The graphite tube furnace (pyrolytic-coated) was developed to achieve better sensitivity than that attainable by flame atomization. The resident time of individual atoms in the optical path using flame atomization is generally in the order of  $10^{-4}$ s compared to approximately 1-2 s for graphite furnace atomization [4]. Graphite furnace atomizer methods are typically 100 times more sensitive than flame methods for most elements in a wide range of samples. Sample solutions of 5-20  $\mu$ L are injected into the graphite furnace by auto-sampler. Three heating cycles usually follow, each with variable current and time settings. Initially, the solvent is evaporated during a slow heating cycle (drying stage), then the current is increased or ramped to the char cycle to burn off organic and other matrix components (ashing stage). Finally, in the atomization cycle which has temperatures of 2000-3000°C (atomization stage), the analyte is converted to ground state atoms that absorb incident radiation from the light beam passing through the graphite tube. The absorption signal produced in the atomization stage is a sharp peak the height (or area) of which is related to the amount of analyte present.

**TABLE 1. Analytical data obtained by Flame-AAS and GFAAS with Zeeman background correction on different sample sizes collected from an area in Rajasthan [3].**

Sample No.		Amount of sample dissolved	Zn	Pb	Fe	Mn	Cu	Co	Cd	Sb	Ag
1.	SOIL-A (+80 mesh)	50 g	5509	167	5.01%	608	219	17.09	1.20	0.60	0.50
2.	SOIL-A (+80 mesh)	30 g	5584	166	4.91%	623	212	15.85	1.20	0.68	0.52
3.	SOIL-A (+80 mesh)	20 g	5441	161	4.77%	584	201	14.64	1.11	0.65	0.45
4.	SOIL-A (+80 mesh)	10 g	5559	163	4.66%	592	201	16.09	1.10	0.68	0.48
5.	SOIL-A (+80 mesh)	5 g	5352	168	4.92%	594	206	14.65	1.10	0.60	0.50
6.	SOIL-A (+80 mesh)	2 g	5411	198	5.01%	608	202	15.08	1.18	0.63	0.47
7.	SOIL-B (+120 mesh)	20 g	4111	190	4.42%	578	187	16.58	1.19	1.00	0.45
8.	SOIL-B (+120 mesh)	10 g	4124	200	4.51%	595	190	15.51	1.10	0.96	0.42
9.	SOIL-B (+120 mesh)	5 g	4072	191	4.28%	587	190	15.50	1.15	1.01	0.43
10.	SOIL-B (+120 mesh)	2 g	4134	198	4.52%	579	197	16.10	1.22	1.03	0.40

Background interference is encountered in both flame and graphite furnace systems. Zeeman background correction has proved to be the most practicable background correction method and is extremely popular. GF-AAS is characterized by its very high sensitivity and is useful in exploration studies, especially for the determination of platinum, palladium, gold and its path-finder elements at ppb levels especially after pre-concentration stage either by solvent extraction or by fire-assay [3,5,6]. Hg, As, Sb and Se are very useful exploration path-finders for certain elements such as Au and Zn. But these elements have relatively low crustal abundances and cannot be estimated accurately by F-AAS. Hg may be separated and concentrated as a cold monoatomic vapor and determined by cold vapor atomic absorption spectrometry [7]. Table 1 presents

analytical data obtained by F-AAS and GF-AAS in a basemetal exploration program.

#### ***X-ray Fluorescence Spectrometry (XRF)***

XRF is the best general purpose instrumental analytical technique available at present for the analysis of solid geological samples. This technique can be used for the determination of all the major elements as well as many important trace elements (e.g. Rb, Sr, Y, Nb, and Zr) in geological samples at concentrations down to a few ppm and sub-ppm levels. With the exception of INAA, XRF is one of the few analytical techniques in which determinations are normally made on solid samples (usually prepared either as pressed powder pellets or fused glass discs). When properly applied, this

**TABLE 2. Determination of precious metal concentrations (ppm) by different techniques in sulfide-bearing Shankar chromitites and adjacent gabbro samples from Nuashai area, Orissa [12]**

Sample type	Pt			Pd			Au			Ag		
	F-AAS	INAA	ICP-MS	F-AAS	INAA	ICP-MS	F-AAS	INAA	ICP-MS	F-AAS	INAA	ICP-MS
Sanker	1.6-9.6	-	0.2-1.4	5.5-11.8	-	3.0-8.8	1.3	0.002-0.1	0.1-0.3	4.0	5.8-6.0	2.4-6.7
Iodechro mitite Gabbro	1.5-1.56	-	0.1-0.4	5.52	-	0.7-4.1	-	0.004	0.05-0.2	-	0.39	0.2-6.5

technique can provide highly precise and accurate data relatively quickly. In XRF analysis, the sample is excited by a beam of primary X-rays and the intensities of the emitted characteristic secondary X-ray fluorescence radiation are measured as a measure of concentration of a particular element. This method has been effectively utilized in the rapid and accurate determination of several elements like Mo, Sn, W, Bi, Ta, As, Se, Cd, Sb and Tl even at trace concentration levels [8]. An unusual application and one difficult to achieve with any other technique other than the present-day laser ablation-ICP-MS is the analysis of slabs of whole rock to provide rapid and reasonably accurate major and trace element data. Portable XRF is also effectively used for in-situ determination of gold concentrations in gold exploration studies [9].

#### ***Instrumental Neutron Activation Analysis (INAA)***

INAA has played an extremely important role in geochemistry, especially in the analysis of meteorites and lunar samples. The main advantages of the technique are the ability to analyse very small samples for many elements of low concentration range (ppb) and its non-destructive nature. This technique is based on measuring gamma radiation induced in the sample by irradiation with neutrons. The primary source of neutrons for irradiation is usually a reactor. The method is highly selective and extremely sensitive for a wide range of elements [10]. INAA provides a cost-effective rapid means of analysis and has been effectively used in gold exploration studies (Table 2). For elements like PGE a chemical separation prior to irradiation is necessary to obtain better sensitivities and to eliminate interferences. Hoffman et. al. [11]

described a nickel sulfide fire assay pre-concentration procedure which effectively collects all the PGE and gold from large sample sizes (~50 g) and separates PGE from other matrix. It is necessary to use large sample sizes in exploration studies to overcome “nugget effects” for PGE and gold. The REE, Hf, Ta, Cs, W, Th, U and some PGE which are difficult to determine by other techniques such as AAS, XRF, etc., are commonly determined by INAA. Its weaknesses are that turnaround time is usually 10-12 days and that it cannot provide useful information on basemetals such as Cu and Pb which can be analysed more quickly and accurately by other techniques such as F-AAS and ICP-AES. However, it is a potential exploration tool when used in combination with other techniques like XRF, F-AAS and ICP-AES for the determination of Au, As, Sb and W, and a range of lithogeochemical indicators such as Cr, Na and K.

#### ***Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)***

The application of optical emission spectrometry in the analysis of geological materials experienced a major upheaval in the late 1970s. The technique is based on the principle that during reversion to the ground state, an excited atom or ion releases absorbed energy as light (photons) at characteristic wavelengths; the intensity of the emitted light is determined as a measure of concentration of that particular analyte. Samples in the form of solutions are nebulized into ICP. The spectrometer may be a scanning type (sequential) or may incorporate an array of fixed detectors (simultaneous) or a combination of both. Spectral interferences exist but are not unduly troublesome and can usually be avoided by suitable choice of



emission lines. ICP-AES is one of the most powerful and cost-effective multi-element analytical techniques available to the analytical geochemist capable of determining over 70 elements in the periodic table with detection limits in ppb and sub-ppb levels. This technique is particularly good for REE and boron. For the determination of precious metals, extensive preconcentration techniques such as Pb or NiS fire-assay have to be employed before Au, Pt and Pd are determined by ICP-AES.

#### ***Thermal Ionization Mass Spectrometry (TIMS)***

Prospecting studies for rare and precious metals and diamonds using isotopic ratio correlation approaches have brought the mass spectrometry into the mineral exploration industry in recent years [13]. In TIMS, measurements are made by evaporating a small aliquot of an analyte solution on to a filament made of W, Ta or Re-wire. After evaporating to dryness, the filament is mounted in the mass spectrometer and heated. The sample is progressively volatilised and partially ionized and the ions so formed are collected by electrostatic plates and transmitted through a magnetic sector mass analyzer system. Usually the voltage is varied in a fixed magnetic field and each specific  $m/z$  from light to heavy ( $^7\text{Li}$  to  $^{238}\text{U}$ ) is successively brought to focus on the detector (Faraday cup or electron multiplier). Multi-collector instruments are capable of providing extremely precise isotopic ratio data. Although these techniques are used for age dating studies, they also find their utility in mineral exploration studies. Pb-isotope ratios determined by TIMS were used to discriminate between economic magnetic ironstones and “barren” ironstones of similar mineralogy in gold exploration studies [13].

#### ***Inductively Coupled Plasma Mass Spectrometry (ICP-MS)***

One of the most significant advances in analytical spectroscopy for elemental analysis in recent years has been the use of an inductively coupled plasma ion source in conjunction with a quadrupole mass spectrometer (ICP-MS) where samples are introduced into the ICP in the form of solution. Positively charged ions produced in the plasma are extracted into a quadrupole mass spectrometer through a differentially pumped

system and analysed. Extremely low detection limits (ppt and sub-ppt), range high sample throughput, small sample quantities required for analysis, versatility and isotopic capability are some of the important features which have made ICP-MS the most powerful technique for analysis of geological materials [14]. This has revolutionized trace element geochemistry and has been applied successfully in several exploration programs for precious metals [15-17]. Tables 2,3,4 and 5 present data obtained by ICP-MS in gold and other precious metal exploration studies. This technique is also used effectively for the determination of Pb-isotope ratios in gold exploration studies [13]. Technical advances during the last two decades in ICP-mass spectrometry have brought in two more instruments namely, magnetic sector-ICP-MS and time-of-flight-ICP-MS. The magnetic sector-ICP-MS has taken the detection limits for several elements to ppt-ppq levels with precisions for isotope ratios comparable to those obtainable by TIMS with extremely larger throughputs [19]. It is expected that these two techniques will also provide the necessary impetus required in exploration studies.

#### ***Comparison of Different Spectroscopic Techniques***

Most of the above described analytical techniques are multi-element techniques except spectrophotometry and AAS (both flame and graphite furnace) which can detect only one element at a time. However, F-AAS is the most commonly used technique in the mineral exploration industry because of its simplicity and low operating cost. Although GF-AAS offers superior detection limits for many elements, the technique is basically low productive. XRF is considered the best technique for estimation of major elements and is considered to be capable of sensitive determination of certain geochemically important trace elements, such as Rb, Sr, Zr and Th. Another method which is widely used in mineral exploration industry mainly in developed countries is INAA. However, in India its application is restricted as there is only one irradiation facility at BARC, Mumbai. Moreover, INAA is also a time consuming method, not independent as it requires nuclear reactor near-by and longer cooling times for certain trace elements. But ICP-AES and ICP-MS are extremely high productive and are best suited to

**TABLE 3. Concentrations of gold obtained by ICP-MS in different international gold reference materials and an in-house standard [15]**

Sample No.	Rock type	Au	
		ICP-MS value [14]	Certified value
GAu 11	Stream sediment	12.0 ± 2 ppb	11.40 ppb
GAu 12	Stream sediment	25.0 ± 3 ppb	21.50 ppb
GAu 12	Soil	61.0 ± 5 ppb	50.00 ppb
GAu 12	Soil	0.12 ± 0.02 ppm	0.10 ppm
CH-3	Gold bearing sulfide ore	1.38 ± 0.14 ppm	1.40 ppm
MA-2b	Gold ore	2.36 ± 0.22 ppm	2.39 ppm
CCU-2b	Copper concentrate	5.60 ± 0.5 ppm	5.89 ppm
Aj-ore	Banded iron formation	7.89 ± 0.32 ppm	9.31 ppm

**TABLE 4. Concentrations (µg/g) of Pt, Pd, Au and Ag obtained by ICP-MS in various precious metal ore reference samples [18]**

Precious metal ore	Pt		Pd		Au		Ag	
	ICP-MS value [17]	Certified value	ICP-MS value [17]	Certified value	ICP-MS value [17]	Certified value	ICP-MS value [17]	Certified value
SARM-7	3.72±0.21	3.74	1.47±0.10	1.53	0.32±0.02	0.31	0.43±0.03	0.42
PTC-1	2.71±0.19	2.52	11.11±0.22	12.7	0.63±0.03	0.65	5.84±0.25	5.8
PTM-1	5.87±0.23	5.8	8.17±0.31	8.1	1.84±0.04	1.8	64.18±1.29	66
UMT-1	0.12±0.01	0.129	0.11±0.01	0.106	0.05±0.01	0.0482	0.83±0.06	-
GTS-1	0.04±0.01	-	1.82±0.07	-	0.29±0.01	0.346	0.85±0.04	-

**TABLE 5. Concentrations of gold (ppb) in natural water samples from wells adjoining abandoned mines in lateritic terrain in Wyanad - Nilambur Gold Field, Kerala, in comparasion with anomalous concentrations [12].**

Sample location	Gold concentration range (ppb) [15]
Ground water samples (ten) from Wynad-Nilambur Gold Field, Kerala	0.050 - 0.220
Background concentration of gold in natural water	<0.001 - 0.005
Anomalous concentrations of gold in natural waters from mineralized area	0.01 - 2.8

**TABLE 6. Comparison of the detection limits offered by selected instrumental analytical techniques for a few elements of importance in exploration studies.**

Element	F-AAS (ppm)	GF-AAS (ppb)	XRF (ppm)	INAA (ppm)	ICP-AES (ppb)	ICP-MS (ppt)
As	3	0.2	10	1	25	0.5
Cr	0.06	0.01	10	1.5	1.1	0.4
Co	0.05	0.02	9	0.14	6.3	0.1
Cu	0.03	0.02	6	-	0.6	0.2
Au	0.10	0.10	-	0.006	-	0.1
Ag	0.02	0.005	-	2	6.8	0.2
Pt	1	0.2	-	2	77	0.3
Pd	0.2	-	-	10	-	0.3

mineral exploration applications. Precious metals are extremely difficult to determine accurately at background levels. But procedures involving solvent extraction and AAS or ICP-AES are able to offer detection limits down to ppb levels. In the fire-assay procedures, the precious metals are extracted into a small button which is separated from the slag and determined by F-AAS, GF-AAS, ICP-AES or ICP-MS. If one considers the power of detection along with other characteristics, such as limited interference effects, ease of analysis sample throughput and element coverage, ICP-MS certainly is the best analytical technique among all with its detection limits considerably better than those of all other analytical techniques (Table 6).

#### **Sample Preparation Schemes**

Analysis by spectroscopic methods practically always necessitates a simple or more complex preparation of the sample to suite to their respective sample introduction systems. These steps are generally most critical part of the chemical analysis because they are responsible for the most important errors. This is particularly true for the solid samples which have to be generally brought into solution in order to satisfy the needs of the sample introduction systems of the main spectroscopic techniques usually utilized in geochemical laboratories (except XRF and INAA). Conventional sample decomposition is by acid digestion using a single mineral acid or a mixture of different acids. Another important digestion procedure is by the use of fusion

methods with different kinds of fluxes. Microwave digestion systems in recent years have helped to a large extent to speed up the sample dissolution procedures besides reducing the contamination effects (Table 3). Further developments are taking place in the sample dissolution techniques which include automation and robotics technology.

#### **Need for Data Quality in Exploration Studies**

Exploration geochemists need targets for analytical precision which depends upon the particular geochemical contrast that is being investigated. Interpretation of geochemical data is based on the information derived from chemical analysis of samples processed in several stages. Hence, it is essential that greater emphasis needs to be given to the reliability of geochemical data which in turn have a bearing on interpretations [20].

#### **Quality Control Measures**

In general, all spectroscopic techniques suffer from various interference effects (spectroscopic interferences, matrix effects, etc.) specific to the type of analytical technique in use. Although these interference effects cannot be totally removed, they can certainly be minimised. Also, the necessity for quality assurance of analytical measurements requires development and introduction of procedures to continuously check the quality of analytical measurements [21,22]. Use of certified reference materials (CRMs) for calibration purposes is one of the necessary tools for quality control as

these CRMs help in minimizing interference effects and their use provides traceability to the analytical data to the national and international measurement system.

#### Future Directions

A combination of atomic, nuclear and mass spectroscopic techniques consisting of F-AAS, GF-AAS, XRF, INAA, ICP-AES, TIMS and ICP-MS will be the major analytical instrumentation for accurate determination of elements including REE and PGE at different concentration levels. With isotope ratio data giving vital clues in exploration studies, different mass spectrometric techniques like quadrupole-ICP-MS, magnetic sector-ICP-MS and TIMS are bound to play a big role in these studies. Future developments in sample decomposition methodology need to focus on throughput, precision and accuracy and cost-effectiveness. Use of certified reference materials for the calibration of instrumental methods and maintaining the quality of geochemical data enable to make unambiguous interpretations.

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# Determination of Inorganic Arsenic Species in Water Samples by High Performance Liquid Chromatography - Inductively Coupled Plasma Mass Spectrometry

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## Introduction

Arsenic, As, chemically a non-metal or metalloid belongs to Group VA of the Periodic Table. It has got only one stable isotope of mass 75. Its principal valency states are +3,+5 but also exhibits -3 as in  $\text{AsH}_3$ .

All arsenic compounds which are soluble in acid or water are poisonous. Maximum permitted value by World Health Organization (WHO) is  $50 \mu\text{g L}^{-1}$ . USEPA has recently lowered permissible limit of arsenic concentration in drinking water from  $50 \mu\text{g L}^{-1}$  to a  $10 \mu\text{g L}^{-1}$ , in the light of the recent epidemiological evidence to support the carcinogenic nature of the ingested arsenic and its connection with liver, lung and kidney diseases and other dermal effects [1].

Recently the contamination in ground waters used for drinking, cooking as well as for agricultural purposes has attracted worldwide attention. In nearly 20 countries, incidents of arsenic contamination of ground waters have been reported. Major groundwater contamination problems have been reported from Bangladesh and West Bengal [India], where, in many districts waters drawn from different tube wells are reported to have higher levels of arsenic than permissible limits.

The toxicological effects of arsenic depend on the chemical form in which the element is ingested, the dose and the duration of exposure. Inorganic arsenic species are more toxic than the organic forms, with As (III) being more toxic than As(V). In water, arsenate is more likely to be prevalent in

aerobic surface waters and arsenite in anaerobic groundwater.

This article briefly describes suitable analytical techniques for the determination of arsenic, separation and pre-concentration, approaches to remediation of arsenic from potable waters and speciation analysis of arsenic.

## Methods of Detection and Determination

Isolation of arsenic as arsine is important in the ultratrace level determinations in samples such as river, lake and sea water where the arsenic concentrations are in the low micrograms per litre levels.

## Stability and Sampling of Arsenic (Species) in Water

There is considerable conflicting information regarding the stability of inorganic arsenic species in water [2-5]. Ground water samples contain fairly large quantities of iron (in the form of very fine ferric oxyhydroxide particles) which tend to settle down as precipitate on long standing or stick to the walls of the sampling container. This particulate matter adsorbs arsenic and hence unacidified samples tend to show very low arsenic values. The usual procedure of filtering and then acidifying to pH=1 for sample storage also would show lower values. Hence to assess realistic body burden levels, the water samples should be acidified and then filtered, so that the arsenic attached to the fine particulate matter is also released into the sample.

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### Analytical Techniques for the Determination of Arsenic in Water Samples

The ease of formation of molybdoarsenic acid on reaction with molybdenum in acidic media has been widely used in developing very sensitive techniques such as heteropoly molybdenum blue method. The trapping of arsine into silver-diethyldithiocarbamate was another sensitive methods practiced earlier. Neutron activation analysis (NAA), provides very good sensitivity due to the high activation cross section of 4.3 barns for  $^{75}\text{As}$ ; the convenient half life of  $^{76}\text{As}$  (26.5 hrs) enabling direct gamma ray intensity measurements for INAA in samples containing low Na, Br and K. Most accurate determinations of arsenic are made by radiochemical NAA (RNAA). But the irradiation of water samples is prohibited in many reactor environments; hence pre-sample treatment like separation and pre-concentration of arsenic on some suitable media (ferric hydroxide/bismuth sulfide), have to be carried out. NAA can be mostly used for the validation of other spectrochemical methods but not as a routine method for large number of water samples.

### Co-precipitation and gathering of Arsenic

$\text{Fe}(\text{OH})_3$  has been used for co-precipitation of arsenic in aqueous media. The co-precipitation is nearly quantitative up to  $\text{pH} = 8.5$ . Other co-precipitating hydrous oxides, in increasing order of collecting efficiency are  $\text{Al} > \text{Ti} > \text{Fe}(\text{III})\text{In} > \text{Zr} > \text{Ce}(\text{IV})$ .  $\text{As}(\text{III})$  is poorly co-precipitated in comparison to  $\text{As}(\text{V})$ , to about 50%.  $\text{KMnO}_4$  has been used to destroy organic molecules binding arsenic and also to covert all  $\text{As}(\text{III})$  to  $\text{As}(\text{V})$  but when neutron activation analysis is going to be the determination technique it is better to oxidize by adding with Fenton's reagent, Hydrogen peroxide + Ferrous ions (in the form of Ferrous ammonium sulphate), to the aqueous sample (typically 500 mL to 1000 mL). The resulting fresh precipitate of ferric oxy-hydroxide effectively gathers all the arsenic (V). Arsenic in very low concentrations ( $0.5 \mu\text{g/L}$ ) in river and sea waters can be isolated by this procedure.

### Hydride generation as means of Isolation of Arsenic

$\text{As}(\text{III})$  and  $\text{As}(\text{V})$  differ in their efficiency of conversion to arsine ( $\text{AsH}_3$ ) with the former being more efficient and near complete. Hence all the arsenic is converted into  $\text{As}(\text{III})$  in a pre-reduction step using  $\text{KI} + \text{Ascorbic acid}$ . L-Cysteine is an efficient and rapid reductant, especially for determinations using GFAAS. The arsine can be generated either in a batch mode or continuously using a Hydride generator, with sodium borohydride as the reductant at appropriate acidity. The arsine can be trapped on the graphite furnace at an elevated temperature or preferably on furnaces coated with noble metals or alloys such as  $\text{Pd/Au/Pt}$  prior to the atomization step [6]. Hydride generation- ICPMS offers the ultimate detection limits for total arsenic determination at sub  $\text{ng/mL}$  levels, eliminating the usual interference of  $\text{ArCl}$  (mass 75) which occurs while using direct solution nebulization in normal ICP-MS systems. Transition elements like Ni, Cu; noble metals like Pd and Pt and  $\text{H}_2\text{S}$  hinder the evolution of arsenic and result in systematic low recoveries. Hence these species have to be removed prior to the arsine evolution step.

### Speciation Analysis of Arsenic in Water Samples

The chemical form in which a particular element is present determines its bio-availability and hence its nutritional value or toxicity. The toxicity of arsenic compounds decreases in the following order: arsenite is more toxic than arsenate, than monomethylarsonic acid (MMA), than dimethylarsinic acid (DMA), than arsenic metal, than arsenobetaine. The methylation and bio-accumulation take place in some aquatic animal species like mussels, with arsenobetaine being the most abundant end product of the methylation sequence. However, the determination of inorganic arsenic species  $\text{As}(\text{III})$  and  $\text{As}(\text{V})$  are to be considered more important in view of (1) their established toxicity through consumption of arsenic tainted water and (2) the efficacy of arsenic removal technologies critically dependent on the predominant chemical form in the particular water source.

Ion exchange [7] and ion-pairing reverse phase chromatography [8] coupled with ICPMS or HGAAS/AFS are the frequently used approaches for

the determination of arsenic species. Phosphate / carbonate and other buffers have been used mostly in the separation of the arsenic species. Both long and short (guard) columns have been used for the studies [9]. Addition of acids / buffers to a sample is known to affect the integrity of the sample [10]. In addition, these buffers are reported to clog and erode the nickel sampling cones in ICPMS [11].

We have investigated two procedures for the separation of As(III) and As (V) using anion-exchange chromatography (AEC) and reverse phase ion-pair chromatography (RPIPC) in combination with ICPMS, without adding any buffers in the mobile phase. The separation was carried out either on a 25 cm long anion-exchange or a reverse phase column at room temperature and the species were well resolved and eluted within 5-6 min, enabling the determination of the inorganic arsenic species. The methods were used to determine the arsenic species in municipal (Manjira river) water and in a few groundwater samples drawn from shallow tube wells of 50 - 100 ft depth, at different locations in the city of Hyderabad, India. In addition, we used this method to evaluate a procedure suitable for the remediation of arsenic in drinking water.

A VG Plasmaquad PQ3 ICP-MS instrument (VG Elemental, Winsford, Cheshire, England) with a double pass Scott-type spray chamber cooled to 4°C using a Neslab recirculating chiller, a Meinhard concentric nebuliser and a Fassel type torch, was used to detect and determine the arsenic species. The time resolved mode of analysis was used for data acquisition. The operating parameters of the ICP-MS are given in Table 1.

**TABLE 1. ICPMS operating parameters**

RF Power, W	1380
Cool gas flow rate, l min <sup>-1</sup> .	13.5
Intermediate gas flow rate, l min <sup>-1</sup> .	0.81
Nebuliser gas flow rate, l min <sup>-1</sup> *	0.55-0.70
Spray chamber temperature, °C	4
Time resolved analysis, m/z	75, 77
Dwell time per m/z, ms	250

\*Optimized daily for both the eluents

## IC-ICPMS Approaches for Arsenic Speciation Analysis in Water Samples

In the present work, Anion Exchange Chromatography (AEC) and Reverse Phase Ion-Pair Chromatography (RPIPC) were used to study the separation of the inorganic arsenic species and its application in the analysis of ground water.

### Anion-Exchange Chromatography

The inorganic arsenic species As(III) and As(V) occur as neutral or negatively charged compounds depending on the pH. For the retention of arsenite (pKa = 9.2), on anion exchangers it is necessary to work in a basic environment, else As (III) will elute within the void volume. Zbinden et.al. [12] have reported the use of AS9 (HC) column for the speciation of arsenic in food products, where they have used gradient elution using a mixture of NaHCO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub> and NaOH as the mobile phase and obtained ppt level detection limits. However, the same gradient method was not found suitable for the AS11 column. Various other combinations of these reagents were tried for both gradient and isocratic elution, but isocratic elution with NaOH alone could provide the desired separation. Therefore, an isocratic elution with only NaOH as the mobile phase was used. The concentration of the mobile phase was optimized to get a good baseline separation of the two species.

### Reverse Phase Ion -Pair Chromatography

A polymer based Ion Pac NS1 (Dionex) reverse-phase column along with the Ion Pac NG1 guard column was used. Usually acetonitrile (ACN), iso-propanol or methanol is used as the organic solvents in the mobile phase. The use of organic solvents in ICPMS might require the use of oxygen to burn off the carbon deposits if any. Hence, the initial studies with acetonitrile were done using conductivity detection. A mobile phase combination of 20% ACN and 2 mM of TBAH was found to produce well separated peaks for As(III) and As(V) and the elution was completed within 7 minutes.

Such a large concentration of ACN, if used in the analysis by IC-ICPMS, might result in plasma instability and deposit carbon on the sampling cone requiring the use of oxygen to burn off the carbon.

Hence an alternate organic solvent that would provide similar or faster elution times but at lower concentrations was sought. Based on the consideration of both the solvent polarity parameter,  $P'$  and the dielectric constant,  $\epsilon$  of the solvent, a derived function ( $P' + 0.25\epsilon$ ), could be used to identify solvent strengths in RPIPC. Lower the value of the function, stronger would be the solvent as eluent. Iso-propyl alcohol (IPA) was chosen based on the above criterion. By varying the amounts of IPA and TBAH in the mobile phase, it was found that by using only 8% IPA and 1mM TBAH, a separation similar to the one obtained using 20% ACN and 2 mM TBAH could be achieved. Therefore a mobile phase combination of 1mM TBAH and 8% IPA was used for the isocratic separation of arsenic species by the coupled IC-ICPMS technique.

Thus 1 mM TBAH and 8% IPA solution (pH ~6.2) gave good separation; hence no buffers were needed. A 100  $\mu$ L injection loop was used for sample injection. The operating conditions for the chromatographic system are summarized in Table 2. The two species, As (III) and As(V) were eluted within 7 minutes. It was also observed that this mobile phase combination did not produce any visible carbon deposit on the sampling cone, and the instrument could be operated for several hours without any apparent loss of efficiency of separation or stability of the plasma.

The operating conditions of the two IC systems are given in Table 2.

#### Characteristics of the Two Methods

The elution profiles obtained using the AEC and RPIPC approaches are given in Fig 1. Initially a

**TABLE 2. Operating conditions for the chromatographic system**

HPLC/IC System	Dinex Model DX-300
<i>Anion-exchange chromatography</i>	
Column	Dionex Ion Pac AS11 (250 x 4.0 mm i.d., 10 $\mu$ m), Dionex Ion Pac AG11 guard column (50 x 4 mm i.d.)
Mobile phase	16 mM sodium hydroxide and 1% iso-propyl alcohol, isocratic mode
Inject volume	25 $\mu$ L
Flow rate	0.6 mL min <sup>-1</sup>
Temperature	25°C
pH	~11
<i>Reverse Phase Ion-Pair Chromatography</i>	
Column	Dionex Ion Pac NS1 (250 x 4.0 mm i.d., 10 $\mu$ m), Dionex Ion Pac NG1 guard column (50 x 4 mm i.d.)
Mobile phase	1 mM tetrabutylammonium hydroxide and 8% iso-propyl alcohol, isocratic mode
Injection volume	100 $\mu$ L
Flow rate	1 mL min <sup>-1</sup>
Temperature	25°C
pH	~6.2

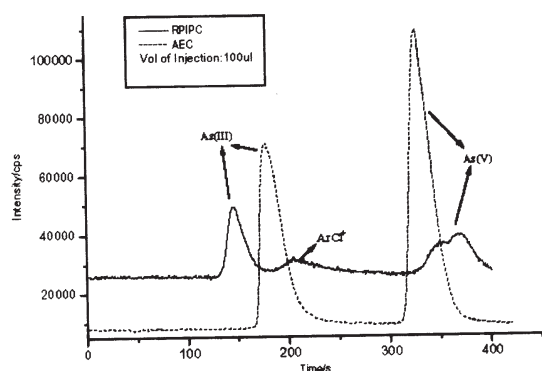


Fig. 1 Elution profile of a  $20 \mu\text{g L}^{-1}$  mixed standard solution, analysed by both the methods.

100  $\mu\text{L}$  loop was used for injection in both the methods. The retention time of As(III) was more in the AS11 column, due to the higher operating pH. The AEC approach gave larger peak heights and better profiles for both As(III) and As(V) compared to the RPIPC separation.

The detection limits for the two methods are given in Table 3. The detection limits obtained by RPIPC method are an order of magnitude less compared to the AEC method. The sensitivities reported in the present work were found to be adequate for the investigation of arsenic species in natural water samples. Fig. 2 shows the typical elution profiles of the mixed standard solutions containing 1, 3 and 5  $\mu\text{g L}^{-1}$  of each As(III) and As(V) species obtained by AEC method.

### Application of the Method

#### Analysis of River and Groundwater Samples

Samples of municipal potable water (Manjira river) supplied to the city and ground water samples from shallow tube wells of 50-100 ft. depth were collected in clean polyethylene bottles, at different locations within a radius of 30 - 40km in the city of Hyderabad. The samples were not acidified but were analyzed on the same day.

The contents of Ca, Mg, Al and Fe were determined and found that Ca and Mg were present

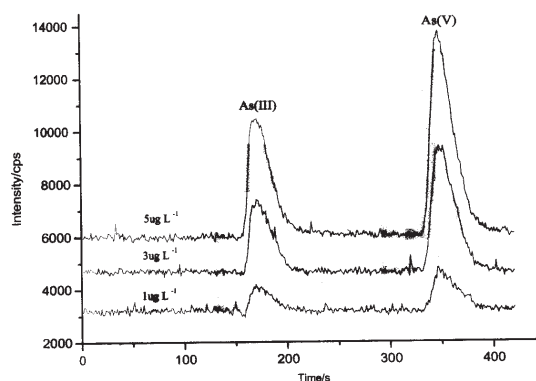


Fig.2 Elution profile showing the mixed standard of As(III) and As(V), analysed by AEC method. Refer table 2 for chromatographic conditions.

**TABLE 3. Limits of detection (LOD) obtained for both As(III) and As(V) by AEC and RPIPC methods**

	LOD <sup>a</sup> ( $\mu\text{g L}^{-1}$ )	
	As(III)	As(V)
AEC <sup>b</sup>	0.29 (0.7)	0.11 (4.0)
RPIPC <sup>c</sup>	1.0 (2.0)	1.5 (5.0)

<sup>a</sup>Calculated as three times the background standard deviation.

<sup>b</sup>Volume of Injection = 25  $\mu\text{L}$

<sup>c</sup>Volume of Injection = 100  $\mu\text{L}$

The numbers given in the bracket corresponds to the % RSD (n=5).

at 4 and 10  $\text{mg L}^{-1}$  levels. Hence, the water was passed through a strong cation exchange resin in  $\text{H}^+$  form (Dowex-50). Both Ca and Mg were considerably reduced by two orders of magnitude after this ion exchange treatment. The treated water, was analysed for As(V), and it was estimated to be close to  $4 \mu\text{g L}^{-1}$ . Almost 100% recovery was obtained with the ion exchange treated municipal water relative to the standards prepared using high purity water. The absence of As(III) in the municipal (river) is significant.

The ground water samples contain higher levels of Ca, Mg and Al compared to river waters. The RPIPC method was found suitable for the direct

analysis of the ground water samples for the determination of arsenic species. Elution was carried out at a lower pH (~ 6.2), and at this pH, the spiked groundwater samples for both the species gave better than 95% recovery relative to the aqueous standards. The results show the presence of only As(III) and little As(V) in the groundwater samples. The estimated As(III) concentrations in the ground water samples ranged from 2-3  $\mu\text{g L}^{-1}$  levels. It is seen that the AEC method, despite having a better sensitivity than the RPIPC method, is unsuitable for the direct analysis of the inorganic arsenic species. It requires an additional ion-exchange treatment step in the determination of inorganic arsenic species to reduce the levels of these elements to less than 100  $\mu\text{g L}^{-1}$  levels.

The present method was applied to study the stability of the species in potable municipal water after passing the filtered water (using a 0.45  $\mu\text{m}$  filter) through a standard filter consisting of a column of silver impregnated charcoal followed by UV- irradiation. The water thus purified was collected in clean PFA (perfluoro alkoxy) containers and spiked with 10  $\mu\text{g L}^{-1}$  of each species. One of the containers was kept at 5°C and the other at ambient temperature (ca.22°C). No appreciable change in the concentration of the two species at both the temperatures was observed. Probably any bacteria if present, could have been destroyed by the UV-irradiation. Thus, bacterial contamination also needs to be considered as one of the factors influencing the inter-species conversion.

#### Remediation of Arsenic in Groundwater Samples

CCCM is involved in the development of a procedure for the remediation of arsenic in drinking water, which involves the oxidation of As(III) to As(V) followed by co-precipitation of As(V) with ferric hydroxide. The efficacy of the various oxidising agents such as  $\text{H}_2\text{O}_2$ ,  $\text{KMnO}_4$ ,  $\text{Cl}_2$  for converting As(III) to As(V) was tested and it was found that treatment with hydrogen peroxide along with ferrous ammonium sulphate (Fenton's

reagent), provided the most efficient conversion of As(III) to As(V). After oxidation, filtration through sand could reduce the arsenic from initial levels of 0.5 - 1.0  $\text{mg L}^{-1}$  to less than 10  $\mu\text{g L}^{-1}$  levels. The treated water showed no signal above the background for both As(III) and As(V). These studies were carried out using the RPIPC approach [13].

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# Trace Elemental Analysis by Total Reflection X-ray Fluorescence Spectrometry



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## Introduction

X-ray fluorescence (XRF) method is a non-destructive method for the elemental analysis. The method has broad dynamic range and can be used for the analysis of wide range of concentration for all elements beyond beryllium. XRF methods are being routinely used for quality control and development of process parameters in steel, cement, petroleum, chemical and nuclear industry etc. XRF is an instrumental method of qualitative and quantitative analysis for chemical elements based on the measurement of wavelengths and intensities of their spectral lines emitted. Characteristic X-ray spectra are emitted when a specimen is irradiated with a sufficiently short wavelength X-radiation.

Intensities of these X-rays are proportional to the concentration of the analyte.

The XRF spectrometers are of two types, wavelength dispersive (WD) and energy dispersive (ED). The essential difference between the two is in the components used for the separation and detection of the characteristic lines. In the WD system, the primary X-ray beam from the X-ray tube excites the characteristic line spectrum of its elements. The primary beam consists of the continuum and the spectral lines of the target. Radiation emitted from the sample is collimated and then impinged on an analysing crystal. The crystal diffracts the radiation at different angles, according to Bragg's law. This angular dispersion of the radiation permits the

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sequential or simultaneous detection of X-rays emitted by elements in the sample. In the ED system, excitation is either by gamma rays from radioactive sources or by X-rays from an X-ray tube. Dispersion is made by solid-state detectors and multichannel analyser. Si(Li) is the most commonly used detector for X-rays. The quantitative analysis of the fluorescence spectrum with an ED detector allows the identification and quantification of the elements present in the sample.

The detection limits in XRF are determined by peak-to-background ratio. The high background because of scattering from the sample and support material often inhibits the good detection limits in X-ray spectrometry. Further, due to severe matrix effects the technique is not suited for different matrices, as this requires a fresh calibration and removal of matrix effects. These factors are taken care in Total reflection X-ray Fluorescence (TXRF) spectrometry. TXRF method is based on the conventional EDXRF analysis technique. TXRF makes use of the fact that X-rays falling at smooth flat surface at a glancing angle less than the critical angle of the material are totally reflected. This reduces the background and increases the analyte line intensity as the sample is excited by incident and totally reflected beams thereby improving the detection limits of the elements considerably. In addition, since the sample is taken in very small amount (few  $\mu\text{g}$ ) in the form of thin film, matrix effects are negligible.

TXRF spectrometry is comparatively new and specialised analytical technique for the identification and quantification at trace and sub-trace level of elemental concentration. The technique is finding wide-ranging applications in different areas like analysis of surface and near surface layers of semiconductors, development of nuclear and advanced materials, environmental studies, mineralogical investigations, chemical oceanography, medicine and high purity chemicals etc.

### Instrumentation

TXRF is a variant of EDXRF. TXRF spectrometers are designed and operated on the basis of classical dispersion law and Fresnell's equation according to which the total reflection is valid for a

perfectly flat and smooth surface. TXRF analysis is based on three parameters critical angle  $\phi_c$ , reflectivity and penetration depth.

The detection limit  $D_L$  is related to analyte peak area and background as follows:

$$D_L = \frac{\text{concentration}}{\text{peak area}} \times 3 \times \sqrt{\text{background}} \quad (1)$$

Reflectivity differences at different glancing angles for a particular wavelength are used to cut off the undesired radiation. The cut-off of Bremstrahlung facilitates the operation of X-ray tube at full potential. The schematic of TXRF instruments is shown in Fig. 1. The X-ray beam from the X-ray tube after passing through a filter is still polychromatic. Thereafter, it is passed through a slit and is reflected from the first reflector at a glancing angle less than the critical angle of the desired radiation. Totally reflected radiation from this reflector is monochromatic and is used for analysis. This monochromatic beam in form of a paper strip passes on a flat reflecting surface holding the sample at an angle less than the critical angle. The characteristic X-rays thus emitted enter a Si(Li) detector and their intensities are measured. The detector axis is perpendicular to the sample support surface in contrast to EDXRF set up where it makes an angle of about 45 degrees. For trace elemental analysis of residues, the measurements are required at a fixed position whereas for thin layer or surface profiling a change in angle is also required from 0 to 2 degree in steps of 0.01.

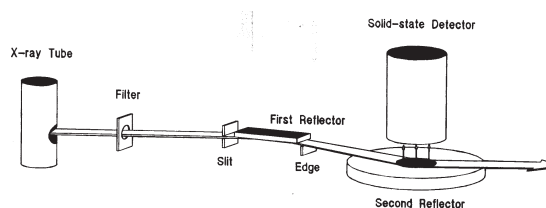


Fig. 1 Instrumental set-up for TXRF

### Analytical Strategy

TXRF is a microanalytical method [1-2]. Normally samples are analysed as received but in a few cases, pre-treatment may be required. Sample

should be converted to solution, suspension, fine powder or thin film for the analysis. The analyte should be separated from the major matrix for the analysis of ultra traces. For sample treatment, clean room working conditions are necessary. TXRF is capable of analysing multielements in one go; spectrum is displayed on the monitor as it progresses. Quantification can be carried out after adding internal standard of an element, which is not present in the sample and determining the relative sensitivities of the elements to be analysed. For the surface and thin layer analysis, elemental intensities have to be measured with respect to glancing angles. From these angle dependent elemental intensity profiles, the elements present in different layers are analysed [1].

In TXRF, a small specimen of few micrograms is taken for the analysis. In few cases homogenisation of the sample and removal of any bulk matrix may be required as a pre-analysis step. Sample preparations are easier for the liquids compared to solids. Solids can be dissolved in suitable solvent and an aliquot taken for the analysis. Different materials may require different treatment. Small amount (5 to 100 µL) of solution is placed on a sample carrier. Total mass of the solution should be about 1 to 200 µg. The samples are pipetted out on a clean sample support. This solution volume is dried to form a smooth bright spot residue of about 1 to 5 mm diameter. Solid bulk sample can be taken in specimen form by method of ablation or even by rubbing the sample on sample support. Wafers not profiled can directly be applied as flat disks. Total wafer can be analysed by a displacement device. Sample support should be hydrophobic and have certain properties like easy machinability to a perfectly smooth and flat surface, should be immune to aggressive chemical and mechanical stresses, free from its own fluorescence lines and contaminations etc. Plexiglas, glassy carbon, boron nitride and quartz glass are some of the materials used as sample carriers.

For quantification of the multielements in a sample, the instrument is calibrated using multielement standards (MES) containing all the elements to be analysed but having no interfering characteristic X-ray lines. If there are interferences of the elements then two or more MES may be

prepared. The TXRF spectra of these MES are recorded in similar manner and in same instrumental condition as for the actual samples. Intensities of characteristic X-ray lines of the elements present are determined with the computer program. These integrated intensities are divided by the concentration of the respective elements present. This gives the absolute sensitivity for each element. The absolute sensitivities of analytes when divided by absolute sensitivity of a particular element give the relative sensitivities of the analytes. The quantification is made by the following relation:

$$C_x = \frac{N_x / S_x}{N_{is} / S_{is}} C_{is} \quad (2)$$

where N is net intensity, S the relative sensitivity and C the concentration of either analyte (x) or internal standard (is). The reliability of determinations can be judged by precision, which is below 5% and accuracy slightly poorer.

Fig. 2 shows the detection limits obtained by means of isolated element peaks measured on matrix free standard solutions. These are better than 10 pg for more than 60 elements for a counting time of 1000 s using a twin excitation source equipped with Mo- and W-anode. The W-anode can be used for excitation with the W-L $\alpha$  line in order to better detect elements of low atomic number. The detectability of elements with atomic numbers below 12 is increasingly affected by a poor fluorescence yield, poor peak resolution and other

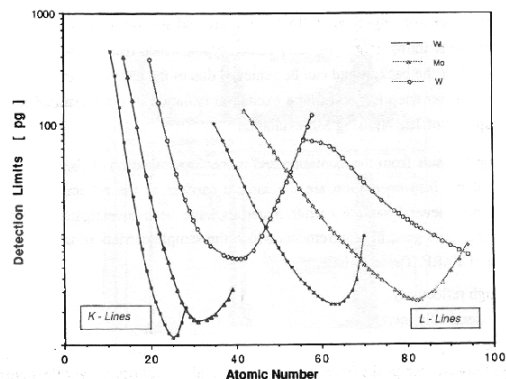


Fig. 2 Detection limits for Mo- and W-excitation (Mo=Mo K $\alpha$ , WL=W L $\alpha$ , W= 20 keV W Continuum)

Element	TXRF	INAA	ET-AAS	ICP-MS
Ni				
Mg F				
Cr Y				
K Zn Ge				
Pt Ta Mo Zn				
Cl				
Pd Sn Nd				
Rb Ba				
Co Se				
Sb Gd				
As Cd Rh Sr La				
Ag Na W Al				
Hg U				
V Cu Ga				
Sm				
Au Hf				
Ir Lu				
Mn Eu				
In				
Dy				
Al				
Si				
P				
Cl				
S				
Ag In Sn				
Pd Cd Sb Sn Pb				
Mo K Hf Ta				
W Ba Co La				
Pt Au Hg Pb Bi				
Rb Sr Y				
Ni Ti Cu Se As				
V Co Zn Ga Ge				
Cr Mn Fe				
Al				
Cr Mn				
Co Cu Fe Mo				
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Pd				
Rb				
Gd				
Mn				
Nd				
Pt				
Au				
Dy				
Ga				
Pb				
Eu				
Bi				
Ca				
La				
Hf				
Rf				
Fe				
Co				
Ho				
In				
Lu				
Pr				

## Applications

## Industrial Applications

- (a) **Quality Control:** TXRF has been used for the quality control of semiconductors, wafers, ultra pure acids, bases, and solvents, high purity metals e.g. Al, Fe or Si. Minerals, synthetic oils, crude oils, lubricating oils, motor oils etc. [1-9] have been analysed by TXRF.
- (b) **Nuclear Industry:** It has been used to determine the low concentration of Nb in irradiated steel samples e.g. core components of a nuclear power plant and trace elements in materials required for construction of future fusion power plants, determination of chemical composition of spent nuclear fuel, U and Th concentration in monazite processing etc. [6,8, 10-11].
- (c) In addition, it has been used for the analysis of inorganic materials, pigments, textile fibres etc.

Thin layer materials with a layer thickness in the range of nanometers are used as high-tech materials in integrated circuit (IC) technology and glass industry. The need for ultra-clean surfaces is a major driving force in the processing of semiconductors. Metallic contaminants at the surface of silicon wafer seriously hinder the performance of IC. Impurities can be present on surface of a wafer as a particulate, thin film or bulk type. In order to eliminate unwanted contaminants, it is necessary to identify and quantify them at different stages of manufacturing and processing. Trace element analysis of these layers is the real breakthrough in the application of TXRF [1-2, 12-13]. High sensitivity detection levels of  $5 \times 10^9 - 1 \times 10^{10}$  atoms/cm<sup>2</sup> are achieved for several impurities. In the case of granular residues, intensity of the X-ray line above the critical angle will remain almost constant as the sample is completely excited by the incident beam. At critical angle, it will almost become double of the previous value, since incident beam as well as reflecting beam excites the sample. In the case of thin films, the intensity will increase



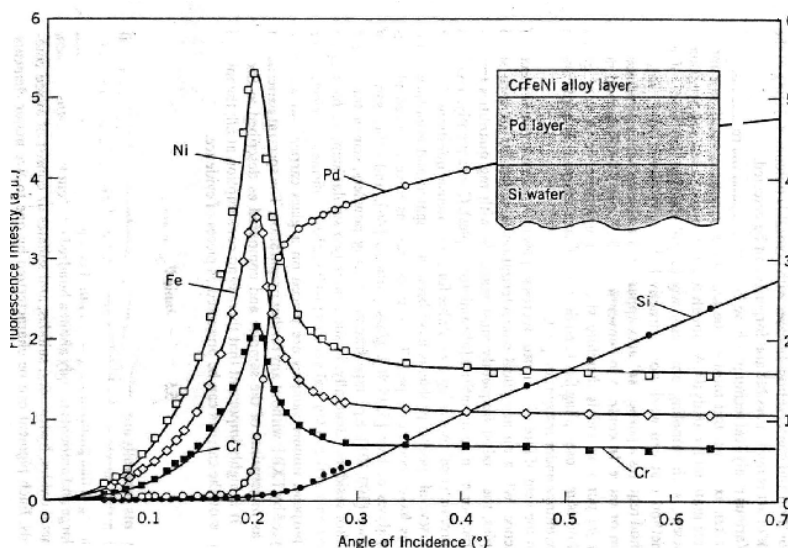


Fig. 3 Qualitative picture of type of elemental analysis results on the basis of variation in X-ray intensities in TXRF spectra

with decrease in glancing angle reaching maximum at the critical angle after which it decreases with the decrease of glancing angle and becomes zero finally. For the bulk type of sample, it will be maximum at angles above critical angle, then decreases drastically to almost zero at the critical angle and remain so until the grazing angle reaches zero. For the quantitative estimation of the impurities in different layers theoretical models of the plots are made for different composition. These plots are compared with the experimental plots. The composition corresponding to the best-fit plot is result of the analysis. In Fig. 3 fluorescent intensities of five elements Si, Pd, Cr, Fe and Ni are given which shows that there is a Pd layer on Si wafer and Cr, Fe and Ni are present in surface layers [1].

#### Ultrapure Acids

TXRF has been used for purity check up of ultrapure acids. Strong peaks were observed for S (73 ppb), Fe (9.4 ppb) and Pb (4.5 ppb) before purification in TXRF spectrum of ultrapure hydrofluoric acid. These peaks were drastically reduced after sub-boiling distillation [3].

The results of intercomparison experiments with ICP-MS from a sample of concentrated nitric acid are shown in Table 2. The results of most of the

elements are in good agreement with the ICP-MS results. For elements such as Ti, Mn and Fe there are differences, which can be explained by molecular ion interferences in the MS spectra. This comparison ensures the reliability of TXRF analysis.

#### Environmental Application

TXRF has been used for the analysis of rainwater, tap water, river water, seawater and wastewater, sea sediments etc. Another recent environmental application of TXRF is its use for characterisation of aerosol particles [14]. Recently, studies have been made to assess the applicability of TXRF for trace element analysis of ice-cores [7]. These analyses give information about past environmental pollution.

#### Elemental Analysis of Ice-cores

As mentioned earlier, TXRF has been utilized for trace element analysis of ice samples collected from Colle Gnifeti glacier (Switzerland) 4550 m asl in Alps. Such ice cores are one of the best archives of past environmental pollution. Their dating and subsequent analysis gives information about past atmospheric temperature (from isotopic ratios e.g.  $^2\text{H}/^1\text{H}$  or  $^{18}\text{O}/^{16}\text{O}$ ), radiative forcing (from the concentration of trapped greenhouse gases e.g.  $\text{CH}_4$ ,



**TABLE 2. Intercomparison of ICP-MS and TXRF analysis results of concentrated HNO<sub>3</sub> sample**

Element (ng/ml)	ICP-MS HNO <sub>3</sub> Mean Std. Dev. n=3	TXRF	
		HNO <sub>3</sub> direct Mean Std. Dev. n=6	HNO <sub>3</sub> preconc. Mean Std. Dev. n=3
S	-	322.64 ± 9.38	33.4 ± 9.18
K	-	3.92 ± 0.21	3.09 ± 0.07
Ca	-	3.91 ± 0.34	4.34 ± 0.06
Ti	0.9 ± 0.2	0.57 ± 0.12	0.37 ± 0.02
V	-	< 0.08	0.04 ± 0.01
Cr	0.95 ± 0.01	0.87 ± 0.04	1.00 ± 0.01
Mn	0.26 ± 0.01	0.42 ± 0.02	0.39 ± 0.01
Fe	28.60 ± 0.30	34.25 ± 0.36	34.96 ± 0.28
Co	0.27 ± 0.01	0.34 ± 0.05	0.29 ± 0.04
Ni	2.50 ± 0.06	2.02 ± 0.06	2.07 ± 0.01
Cu	0.70 ± 0.04	0.85 ± 0.03	0.96 ± 0.01
Zn	3.00 ± 0.05	4.40 ± 0.14	4.41 ± 0.03
Ga	0.04 ± 0.01	< 0.05	< 0.01
Sr	0.04 ± 0.01	0.05 ± 0.01	0.04 ± 0.01
Zr	-	0.30 ± 0.09	0.13 ± 0.01
Mo	-	-	0.15 ± 0.01
Ag	< 0.01	< 0.01	< 0.05
Cd	0.05 ± 0.01	< 0.15	0.06 ± 0.02
Ba	0.90 ± 0.02	1.04 ± 0.13	0.96 ± 0.04
Tl	< 0.02	< 0.05	< 0.02
Pb	1.06 ± 0.01	1.16 ± 0.04	1.10 ± 0.01
Bi	0.07 ± 0.01	0.05 ± 0.02	0.06 ± 0.01

CO<sub>2</sub> and N<sub>2</sub>O), volcanic eruptions (from SO<sub>4</sub><sup>-2</sup>, NO<sub>3</sub><sup>-3</sup>, and metallic impurities), storms (from dust, sea salt, Al, Si, Ca etc), nuclear weapon testing (radioactivity and fission products) etc. Pollutions of anthropogenic and natural origin can also be differentiated. To decipher these ice cores a large number of ice samples are required to be analysed for a wide range of elements present in very small concentration (ppt or ppb level). TXRF was used for the analysis of ice samples for the first time. Preconcentration and TXRF analysis methods of ice

samples were standardised using 1 ml of ice samples. Elements Si, P, S, K, Ca, V, Cr, Mn, Fe, Ni, Cu, Zn, Ga, Se, Rb, Sr, Zr, Nb and Mo were analysed using W tube and Quartz/Plexiglas sample supports in multi element standards and ice samples with different precision and accuracy depending on the sensitivities of elements and their concentration. Some elements in these ice samples were earlier analysed by ICP-MS, an intercomparison of both measurements was made [7]. An intercomparison plot of ICP-MS and TXRF results reported for Ca

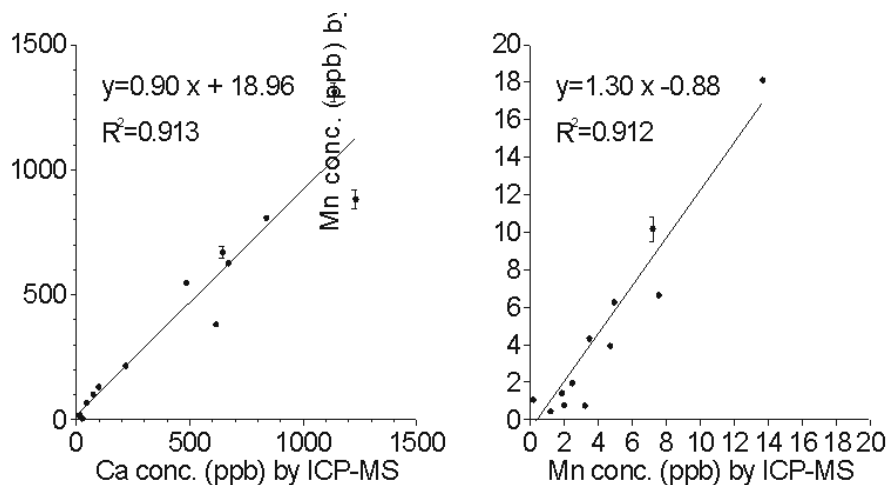


Fig. 4 Intercomparison of TXRF and ICP-MS results for Ca and Mn in ice samples

and Mn are shown in Fig. 4. Most of the elements compare within 15% with ICP-MS results and with a precision of  $1\sigma < 5\%$ . TXRF method can analyse solutions as well as suspensions alike in ice samples.

### Medical Applications

Either depletion or accumulation of trace elements affects biological functions of human beings. Because of this trace element determination in medical field has found and extensive interest. It has been used for the analysis of whole blood, blood serum, organ tissue, hair and dental plaque etc [1].

### Analysis of Human Lung Tissue

As an example of application in medical field, Klockenkaemper and von Bohlen [5,15] have investigated the microtome sections of lung tissues of a foundry worker and painter. TXRF analysis of lung tissue of the painter consists mainly components of paint and varnishes e.g. Ti and Pb whereas the lung tissue of foundry worker contains excessive amount of iron.

### Determination of Uranium in Human Urine

Uranium has been classified as a toxic chemical. It affects the kidneys with nephritis being the primarily chemically induced effect in animals and humans. Uranium in water and urine is most commonly measured by means of solid fluorimetry using either laser excitation or ultraviolet light after

the fusion of the sample with a pellet of carbonate and sodium fluoride. The sample preparation involved in this technique is rather tedious, while the detection of uranium is impeded by the interference of other metals. A TXRF method for uranium analysis in urine after preconcentration has proven to be relatively fast, offering detection limits that allow for monitoring uranium intake above normal levels. The urine samples were analysed by measuring the TXRF spectra of 4- $\mu$ L aliquots of a urine sample digested and preconcentrated. Direct measurement allows only the determination of elements having concentrations in the ppm range. After preconcentration, all alkaline earth elements are removed, leading to a clearly detectable uranium peak in TXRF spectrum [16].

### Trends in TXRF Analysis

TXRF is being assessed for its application in many new areas with improvements in instrumentation and sample preparation methodology etc. as described below:

1. Analysis of low Z elements has been always a challenging job in XRF because of very low excitation efficiency with most of the exciting anodes, low fluorescence yield, high background due to scattering by low Z elements etc [8]. TXRF is very much suitable for these elements. Improvements are being made to analyse low Z elements in various

matrices. Synchrotron radiation source produces a tuneable, polarised X-ray beam of order of 3-5 times intensity of conventional X-ray tubes. It is very much helpful for the analysis of lower Z elements with detection limits up to fg level. However, wider usage will require easier access to Synchrotron Light sources, which are very few in the world.

2. For the lateral and vertical resolution for micro distribution analysis by TXRF.
3. Combination of XRD, X-ray absorption and X-ray emission techniques with TXRF may give very good information about crystal structure and chemical state [2-4].
4. TXRF and X-ray reflectometry (XRR) can be combined to work in tandem for layer analysis.
5. For the characterisation of near surface layers.
6. Elements to be analysed can be deposited on glassy carbon carriers by electrochemical/chemical reaction and can be analysed. Alternatively, solids can be decomposed electrochemically and diffused to electrolyte, which can be analysed by TXRF.
7. Wavelength dispersive total reflection X-ray fluorescence (WD-TXRF) and Vapour phase deposit total reflection X-ray Fluorescence (VPD-TXRF) are other areas attracting interest of the scientists.

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## Literature Update : Atomic Absorption and Emission Spectrometry



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The analytical atomic spectrometry is under going fast changes with time. It appears that the advent of powerful detectors and more flexible hybrid techniques, the limits of detection and areas of application are expected to make a substantial progress in the near future. In what follows a literature update of work in AAS and AES, in these areas, is given.

### Atomic Absorption Spectrometry

#### Sample Introduction

One of the critical areas possible is the sample introduction technique as the present technology using standard nebulization technique is constrained

by the poor efficiency of nebulization (5-10%). The sample introduction can be achieved by Flow Injection, Online-pre-concentration, Nebulization, by Chemical Vapor Generation, by Solid sampling or by Electrothermal Vaporization.

#### Flow Injection (FI)

Flow injection belongs to a family of methods based on simple injection in to a flowing stream, which carries the analyte through a chemical modulator in to a detector [1]. It exploits chemical reaction to transform analytes into species that can be selectively modified by detector Several reviews of flow injection (FI) atomic spectrometry [2-4]

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have highlighted the advantage of using FI techniques for on line sample pre-treatment. For the determination of alkaline earth metals in soils by flame AAS [5], samples were introduced via a single line FI manifold to minimize the errors due to the high dissolved solid content, and for the determination of Cr in lubricating oils [6], on line emulsification with the aid of ultrasound produced a fluid that could be introduced directly into the atomizer for determination by ETA-AAS. Dissolution or leaching procedures have been implemented in a FI or continuous flow mode. Arsenic was determined in soils by on-line microwave assisted leaching from injected slurry followed by HG-AAS [7]. When applied to the analysis of tap and sea water [8], the Cr(III) retained on the column was eluted with 0.5mol/L HCl and determined by FAAS. Preconcentration in a flame by trapping on a refractory oxide was used in the determination of Te in water [9]. The analyte was collected on an alumina-coated slotted silica tube for 2-5 min and then atomized by a step change in the acetylene flow rate. The sensitivity was over two orders of magnitude better than that of conventional nebulisation.

#### *Preconcentration*

Many of the published accounts of research in FAAS online area do not make clear how the optimization was carried out. Often the figure of merit is a vague compromise between sensitivity and throughput, although in most of the cases the driving force for the method development is to obtain an improved LOD. Literature includes the determination of Cu in sea water [10], Ni in magnesium oxide [11], Cu in mussels and in low alloy steels [12], Cd, Cu & Pb in waters, citrus leaves, pine needles and in spinach leaves [13], Ca & Mg in thorium matrix [14].

In FAAS off-line methods, several metals viz. Cd, Cr, Cu, Fe, Ni and Zn [15] were preconcentrated by retention on carboxymethylcellulose from fuel ethanol samples. The eluent was 1 mol per litre HCl and the enrichment factor was 20. The Cd, Cr, Cu, Fe, Ni, Zn, Mn and Pb were retained from water samples as the pyrocatechol violet complexes on activated carbon [16]. In determination of Fe by FAAS [17], preconcentration by co-floatation with

Pb hexamethylenedithiocarbamate gave an LOD of 0.3 µg/L.

In case of ETA-AAS online, a polymethacrylate resin retained Au and a characteristic mass of 20 pg was determined. The Co content of natural waters was determined by a pre-concentration procedure in which the analyte was retained on the interior walls of a knotted tubular reactor that had been pre-coated with a chelating agent [18]. Four chelating agents APDC, 8-hydroxyquinoline, 1-phenyl-3-methyl-4-benzoypyrazol-5-one and 2-nitroso-1-naphthol-4-sulfonic acid were evaluated and 1-phenyl-3-methyl-4-benzoypyrazol-5-one selected as the best. An enhancement factor of 28 and an LOD of 8 ng/l were obtained for Co. The interference from Al was overcome by the addition of fluoride while Cu and Fe were masked by thiourea. Bi and Pb were determined [19] in acid solutions of Fe and Al alloys preconcentration as the complex with dithiophosphoric acid o,o-diethyl ester on activated carbon. The analyte complexes were eluted with ethanol into an autosampler cup, is prevented using 10 µL of xylene prior to each uranium sample loading. The possible interference from Fe(III) was overcome by reduction to Fe(II).with ascorbate. The on-line preconcentration gives many fold enhancement, suggesting that the extraction procedure have better efficient. Pre-atomization losses of B in uranium matrix in ETA-AAS as B<sub>2</sub>O<sub>3</sub> was overcome by addition of Ti and ascorbic acid [20]. A number of elements in uranium matrix were determined directly without prior chemical separation of the matrix. The atomization processes involved in the ETA-AAS for the direct determination of nanogram amounts of Ag, Be, Ca, Cd, Cr, Co, Cu, Fe, Li, Mn, Na, Ni, Sn and Zn in presence of U,Pu matrix containing 4%Pu and 25%Pu, U in 100% Pu, Be, Cu, Zn in Al-U matrix, Co,Cr,Mn in high purity Ga, Al leaching from Al vessels in tamarind & tomato have been reported from our laboratory.

In case of ETA-AAS, multiple injections of sample solution into a hot tube, to give a total volume of 90 µL, allowed the determination [21] of V in milk with an LOD of 0.6 µg/L. Sample was dried and ashed between injections. BaF<sub>2</sub> modifier stabilized V up to 2000°C. For the determination of As and Sb in



steel, the analytes were reduced to trivalent states with ascorbic acid and KI solution, complexed with the ammonium salt of dithiophosphoric acid o,o-diethyl ester and retained on activated carbon [22], Fe(III) was reduced to Fe(II) and was not retained. The analytes were eluted with a small volume of HNO<sub>3</sub> solution to give enrichment factors of between 5 and 10. Several speciation procedures, based on selective solid-phase reaction chemistry, have been developed. A number of liquid-liquid extraction procedures have been devised. Pb was determined in blood, homogenized by sonication [23], after extraction of the APDC complex into IMBK. A 20 µL subsample was atomized from a W-coil for an LOD of 0.6 µg/L. In comparison with the results obtained for the analysis of 20 samples by graphite furnace AAS, the W-coil results were 8% low. The LOD for Mn was 0.02 µg/L, and trace metals in sea water by ETA-AAS recently published [24]. A modified digestion procedure was reported [25] for analyzing Ag in environmental samples.

Using indirect methods, a number of procedures have been devised in which pre-concentration has been combined with the determination of an element that can be related to the analyte. Pesticides in water were determined by ETA-AAS by determining Cu [26]. To determine P in foodstuffs [27], the bismuth phosphomolybdate complex was extracted into IMBK and the Bi determined by FAAS. The LOD achieved was 8 µg/L.

Chemical vapor generation method is mainly concerned with the determination of multiple hydride forming elements. The number of elements which may be determined by hydride generation is growing, with generation of volatile species of Ag, Au, Cu and Zn. A multiple micro flame quartz tube atomizer has been evaluated [28] for the determination of Se. In presence of As as intereferent it was found that, in comparison, with the commonly used extremely heated quartz tube, the new device had improved resistance to atomization interferences with no loss in sensitivity. The generation of the hydrides of Ag, Au, Cu and Zn from aqueous solution on reaction with sodium tetrahydroborate (III) has been reported [29] by Sturgeon et.al. The elements were detected by AAS with a quartz tube atomizer; losses during transport

were minimized by using a short length of Teflon tube.

Use of direct solid sampling with AAS is well established. Detection limits for solid sampling ETA-AAS, can rival those obtained by ICP-MS. A number of approaches to solid sampling are commercially available and therefore widely used. An approach to the evaluation of data quality in direct solid sampling for ETA-AAS was described by Luckert et.al. [30]. Calibration was performed close to the limits of decision, detection and quantitation in order to estimate the lower limits of these parameters. The values are 2-20 times lower than those obtained by decomposition methods. Slurry sampling has become a widely accepted form of solids analysis.

### **Instrumentation**

In a comprehensive article [31] covering instrumentation, atomization mechanism, interferences and modifiers, Jackson predicted that the future of ETA-AAS might be simple, inexpensive instruments, such as those based on W-coil atomizers. Low RSD values in the determination of µg/L levels of analyte, fast analysis times and reduced method development times are also given as evidence to the continuing improvements in the technique. The non-uniformity over the entire absorption volume leads to analytical error when atomization conditions differ for samples and standards, unfortunately, this is usually the case. Matrix modifiers are conventionally used to minimize differences in standard and sample atomization conditions. L'vov endorsed the application of spatial resolution and cited the approach as a significant step towards absolute analysis in ETA-AAS [32]. Measurement of absorbances integrated in terms of both wavelength and time is seen as a parallel requirement for standardless analysis. Continuum source and boosted output hollow cathode lamps are compared for this task, and L'vov concludes that the simpler approach, technologically, is the use of line sources.

### **Atom Cells for AAS**

For the technique of flame atomic-ionisation spectroscopy, used an atomic absorption instrument comprising a graphite tube atomizer with

controllable electric heating, a propane-butane-air flame atomizer and a pumped nitrogen laser were used. Au was measured in  $\text{AgNO}_3$  with a programmed heating cycle and the response of Au was said to be independent of the matrix. A Ta coil atomizer for AAS was used with Ar as the shielding gas and 3  $\mu\text{L}$  aliquots of sample solution were atomized, giving characteristic concentrations for Cd, Cu and Zn of 2, 30 and 7 ng/mL, respectively, and good results for standard materials.

#### *Sources for AAS*

##### *Multi-element and continuum source*

True et.al. [33] developed a multi-element graphite furnace CSAAS system comprising a Xe short arc source, a Thermo-Jarrell-Ash atomizer and control unit, a high resolution echelle polychromator and a CCD detector. Up to eight elements were measured over broader than usual wavelength ranges and good analytical results in the measurement of trace elements in drinking water were claimed.

##### *Line sources for AAS*

Varian [34] publicized new 'solid cathode' HCLs for AAS in which the cathodes are made from alloys of four or six metals viz. Ag-Cd-Pb-Zn or Co-Cr-Cu-Fe-Mn-Ni. During construction, the lamps are heated in vacuo to remove adsorbed gases and to deposit some cathode material on to the base of the inner lamp wall. High emission and long lifetime are claimed and a particular advantage is that multi-element cathodes facilitate and speed up the multi-element operation of a fast sequential spectrometer.

#### *Basic Studies*

##### *Flames*

The number of fundamental studies of flames has been reduced significantly off late. A study of interferences in the flame during analysis of Li [35] and the role of oscillator strength in atomic absorption spectroscopy is discussed [36], where universal method for the determination of atomic lifetimes and hence absolute oscillator strengths of atomic resonance lines for almost any element in the periodic table was given. Elimination of

interferences was achieved using the method of standard additions and elevated flame temperatures

#### *Furnace*

The elucidation of atomization processes, interferences and modifiers mechanisms in furnaces continues to be an active area of research. A review [37] of investigations of surface structure and chemical species formation is discussed, the results of these fundamental studies as probes for surface interactions and for the development of new furnace designs were considered. The deterioration of the graphite tube atomizer due to U matrix, the effect of uranium/plutonium on the determination of a number of analytes, the effect on analyte absorbance due to U/Pu was correlated with the change of partial pressure of oxygen released from U & Pu matrix, and for Be, was ascribed to the formation of stable Pu-Be compounds ( $\text{PuBe}_{13}$ ). Microgram amounts of Al, Mn and Yb oxides were slowly heated in both isothermal and non-isothermal furnaces. The signals obtained in both types of furnace were identical which was interpreted by the authors to provide support for the gaseous carbide reduction mechanism. The mechanism of the carbothermal reduction of FeO, CoO, NiO and  $\text{Cu}_2\text{O}$  was the subject of a paper by L'vov [38]. Katskov et.al. [39-41] has published interesting and apparently controversial results of their studies into nitrate vaporization in ETA-AAS. L'vov, however, disputed this mechanism, claiming that mistakes in theoretical calculations and experimental interpretation led to erroneous conclusions [42].

#### *Atomic Emission Spectrometry*

##### *Sample Introduction*

This technique is employed for determination of Fe in soil extracts and analysis of Fe, Cr, V and W by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) in tool steel samples [43-45]. A solid sampling technique [46] was developed for the Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) determination of ultra trace amounts of lanthanides chemically separated from U/Pu fuel materials. The near total introduction of sample vapour into the plasma allows determination of Dy, and Eu at the 0.4 ng level and Gd, Sm at 1 and 2 ng levels respectively

with a precision of 10% RSD. An Electrothermal Vaporization-Inductively Coupled Plasma Atomic Emission Spectrometry (ETV-ICP-AES) is the hyphenated analytical concept followed for simultaneous determination of about sixteen trace metallics including the four critically important rare earths (Dy, Eu, Gd and Sm) in  $\text{ThO}_2$  and  $\text{U}_3\text{O}_8$  at sub-nanogram concentrations without prior chemical separation of the major matrix. Such an approach is unique in analytical spectroscopy of nuclear fuel materials [47]. The two common exit points in an ETV-for ICP-AES were compared by Kantor [48]. In one version the vapour streams upwards through the transverse hole of the longitudinally heated tube (UPS), while with the other version the vapour streams towards one of the ends of the tube (ENS). When pure Argon is used as the internal gas, the ENS is less effective than UPS for medium and low volatile elements because of the possible condensation of the vapour on the coolest part of graphite tube, close to the outer end.

#### *Preconcentration*

Zn was retained from river water samples as the complex with 2-(5-bromo 2 pyridylazol)5-diethyl amino phenol [49] followed by elution with 30%  $\text{HNO}_3$ . Compared with pneumatic nebulisation, an enhancement of 42 fold was obtained. The Limit of detection (LOD) for a 10 ml sample volume was 90 ng/L. Cd, Cu and Pb were preconcentrated on sulfhydryl cotton from pH 5.5 solution flowing at 2 ml/min. The eluent was 2 mole/L HCl and LOD were 0.5, 0.7 and 3  $\mu\text{g/L}$ . The interference of Al on the determination of Zn was overcome by the selective retention of Zn as the thiocyanato complex on polyurethane form. The procedure was applied to the analysis of Al alloys containing Zn in the range 50-300 mg/kg. An automated, solid phase extraction procedure for the determination of transition metals and rare earths elements has been devised [50]. Heavy metals such as Cd, were collected [51] by a pretreated asphaltite ash ion exchanger, from industrial wastewaters. Hf and Zr were retained [52] by N-benzoyl N-phenyl hydroxylamine immobilised in an inert polymer support from rock digests. A liquid-liquid extraction procedure was devised [53] for the determination of Th, U in apatite minerals with introduction of organic solvent (diisobutyl ketone) in the plasma.

#### *Nebuliser*

Nebuliser for ICP-OES [54] have been compared on the basis of noise power spectra and wash out times for solutions containing salts ( $\text{NaCl}$ ,  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{NaBH}_4$ ) in concentrations up to 10%. The influence of spray chamber design on both steady state and transient acid interferences in ICP-AES has been studied [55]. The best S/B for low energy lines was achieved at a spray chamber of  $80^\circ\text{C}$  while for the high-energy lines the best temperature was  $120^\circ\text{C}$ . A large-bore, direct injection, high efficiency nebuliser has been developed [56] for ICP-AES and ICP-MS which was less prone to blockage than a conventional direct injection, high efficiency nebuliser. Ultrasonic nebuliser (USW), while attractive because of higher sensitivity and lower LOD, produce a high solvent load that is usually deleterious to plasma operation. Edible oils were analyzed for the P content by ICP-OES [57] by the formation of an emulsion in  $\text{H}_2\text{O}$  with a surfactant ethoxy nonylphenol.

#### *Instrumentation*

A 22 channel Paschen range mounted Spectrometer with an ICP source and individual PM detector has been constructed in house and described by Shukla et al [58]. A scanning echelle spectrometer having wavelength stabilisation with detection and background correction using a specially designed back illuminated CCD was described by Becker-Ross et al [59].

An ICP emission spectrometer was developed with an axially viewed ICP source [60] incorporated by a 5-turned induction coil and a torch, outer quartz tube of which was 50 mm longer than that used in conventional ICP/AES (Inductively Coupled Plasma Atomic Emission Spectrometry). The spectro-analytical characteristics of the spectrum obtained between 200 and 500 nm was revealed to be similar compared with a vertically viewed ICP source. The detection limit of Pb(II) at 220.35 nm was 11 ppb which was 5 times lower than that obtained with a vertically viewed ICP source. Inductively coupled plasma (ICP)-echelle optical system coupled with a charge-injection device (CID) detector [61] was evaluated for precision and noise. The ways to reduce the flicker noise and fluctuations are discussed review with 58 references, on the state

of art and development trends of ICPs as radiation and ion sources has been given by Broekaert [62]. Sample introduction, the use of CCD detectors, the future of tunable plasma sources in analytical spectroscopy and the potential of hyphenated techniques are also discussed. A semi-empirical equation to describe the electron number density in the analytical zone of the ICP as a function of rf power, height above the load coil and water flow rate has been described by Nakamura et al [63]. Spectral interference in the determination of trace elements in environmental materials by ICP-AES and the effect of charge transfer reactions on analyte excitation and ionisation have been addressed [64].

### Studies

The development of a method for the estimation of burn up of nuclear fuels by the determination of  $^{236}\text{U}$  by high-resolution inductively coupled plasma spectrometry has been demonstrated [65]. In the extraction of uranium [66] by 100% TBP in 6M  $\text{HNO}_3$  recoveries for 15 impurity elements Al, Ca, Cd, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ti, Zn, Zr are reported. Comprehensive studies have been carried out on the extraction behaviour of thorium, (U-Pu) matrix vis-à-vis 17-20 trace elements using a novel extractant viz: cyanex-923. The near total extraction of thorium/ (U-Pu) and quantitative separation has been established using ICP-AES [67-68]. Similarly chemical extraction of Ag from uranium using cyanex 471X and its subsequent determination by ICP-AES has been reported by Argekar et.al [69]. The carrier distillation technique used for selective volatilization of trace metals in  $\text{U}_3\text{O}_8$  with d.c. arc excitation is adopted for the release of analytes from the solid sample into the ICP source by inductive heating of the sample [70-71]

Tellurium in simulated nuclear spent fuels (SIMFUEL) has been determined [72] by hydride generation-inductively coupled plasma atomic emission spectrometry (HG-ICP-AES). Similar work is reported for determining the metallic elements in SIMFUEL containing the platinum group elements [73]. Analytical conditions of ICP-AES for the direct determination of molybdenum [74] in the uranium matrices without separation process have been investigated. Analysis of noble metals in the environment, Th and U in geological samples, determination of major-to-ultra

trace elements in green tea leaves and green tea infusions, concentration of toxic metals and radionuclides in breast milk samples, Si and other impurities in zirc alloy samples [75-79] are other areas wherein ICP finds wide usage. An inductively coupled plasma-optical emission spectrometric (ICP-OES) method has been reported for the determination of trace levels of thorium (5-50 ppm) in various grades of zirc alloy [80]. Results show excellent recovery of thorium in synthetic standards and the method is precise within 5% RSD at 10 ppm level

### Conclusions

Literature update gives an idea of the recent developments in two promising analytical spectroscopic techniques viz. ETA-AAS and ICP-AES with regard to new methodologies and sample introduction.

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