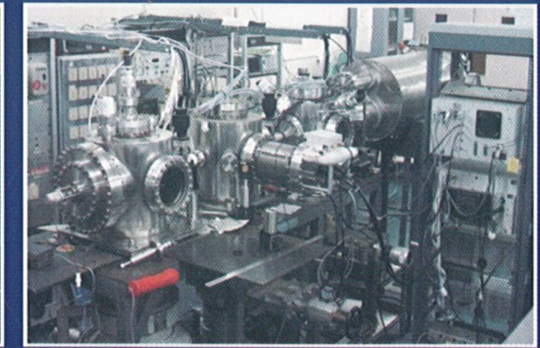
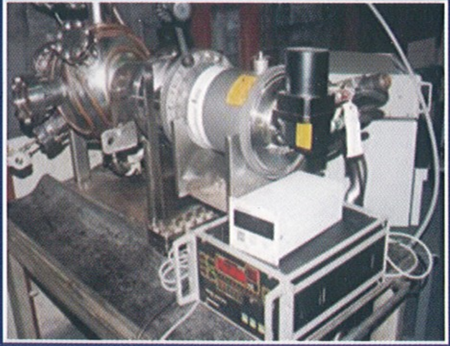
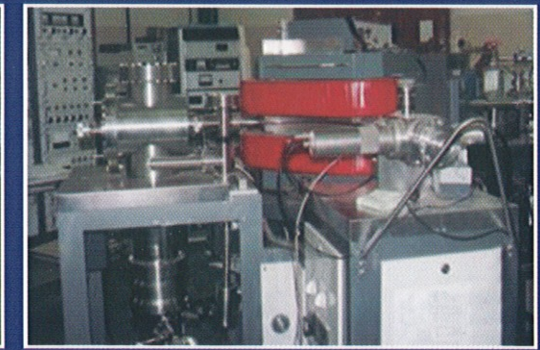
APPLICATIONS OF MASS SPECTROMETRY IN NUCLEAR FUEL CYCLE

Theme Meetings on
Mass Spectrometry in Nuclear Fuel Cycle
(MSINFC-2005)
&
Isotopic Ratio and Concentration Measurements by TIMS & ICP-MS
(MSINFC-2006)

December 21 –23, 2005 & August 2 - 4, 2006

Convention Centre, Anupuram

PROCEEDINGS

Edited by

P.R. Vasudeva Rao
M. Sai Baba
Vidya Sundararajan
R. Balasubramanian

Organised by
IGCAR, Kalpakkam
&
Indian Society for Mass Spectrometry

Sponsored by
Board of Research in Nuclear Sciences
Department of Atomic Energy
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Foreword

Mass spectrometry is a versatile analytical technique owing to its high sensitivity, high selectivity, high precision and high accuracy and it finds applications in all branches of science. Closing of the Nuclear Fuel Cycle is one of the priorities of the Department of Atomic Energy. Mass spectrometry plays a vital role in each step of the fuel cycle covering a spectrum spanning from the characterization of the ore, fuel fabrication, post-irradiation measurements, reprocessing and waste management.

I am happy to note that two theme meetings on the topics "Applications of Mass spectrometry in Nuclear Fuel Cycle" and "Isotopic Ratio and Concentration Measurements using TIMS and ICP-MS" have been conducted at IGCAR and the proceedings are being published as a book. I congratulate, Dr. P.R. Vasudeva Rao, Dr. M. Sai Baba and the team for conducting the theme meetings effectively and for consolidating the presentations in a book form.

I am confident that this book will be useful to researchers and student community who would like to pursue R&D careers in this important area of high significance to nuclear energy and many other sectors of national significance and priority.

Baldev Raj

(Baldev Raj)

Editorial

Mass spectrometry finds extensive applications at various stages of nuclear fuel cycle. Mass spectrometry based methods play a very important role in nuclear material accounting. It is an indispensable tool in enrichment studies. Mass spectrometry has been extensively used for R & D of the fuel cycle, be it for understanding the fuel behaviour at high temperatures or fuel-clad interactions. Expertise exists in our department in the development, upgradation and modernization of mass spectrometers.

Mass spectrometry being an expensive and complex technique, a synergetic approach and sharing of experience between various users in the department will go a long way in achieving the full potential of this technique. In addition, indigenous development of mass spectrometers, which can meet all the users' requirements, is an important goal of our department. Two theme meetings one on a broader topic "Applications of Mass Spectrometry in Nuclear Fuel Cycle" and another more focused on "Isotopic Ratio and Concentration Measurements by using TIMS and ICP-MS" were organised at IGCAR. These two meetings have enabled a comprehensive discussion on the status of the application of mass spectrometry in various aspects of nuclear fuel cycle.

In the theme meetings, apart from three plenary talks, thirty seven theme talks were delivered and a concluding panel discussion on the "Indigenous development, inter-comparison experiments and potential areas of application of mass spectrometry" was conducted. Full manuscripts of selected papers covering the major theme areas of the meetings, and the abstracts of the rest of the papers are included in this book. We are thankful to all the speakers for their valuable contributions as well as for sending their papers for bringing out this book. We thank Dr. Baldev Raj, Distinguished Scientist and Director, IGCAR, for his support, encouragement and guidance. We thank Dr. V. Venugopal, Director, RC&I Group, BARC for chairing the panel discussion and for the encouragement and support for organising the theme meetings. We are also thankful to Dr. C.K. Mathews, Dr. H.C. Jain and Dr. K. Gopalan who have been the pioneers in the development of applications of mass spectrometry in India, for participating and giving enlightening lectures in the meeting. We thank BRNS for the financial support and ISMAS for co-sponsoring the event.

M. Saibaba

P. R. Vasudeva Rao

M. Sai Baba

Vidya Sundararajan

R. Balasubramanian

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Thermal Ionization Mass Spectrometry: An Overview

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1. Introduction

In any mass spectrometer analyte elements or molecules must be ionized first before they can be mass analyzed. Thermal ionization mass spectrometers (TIMS) are based on ionization of elements and their molecules into positive or negative ions, as they evaporate from a hot metal surface, usually a narrow flat filament. TIMS have played a key role in the isotopic analysis of elements that are particularly important in nuclear technology and geo-cosmochronology. Applications in nuclear technology include various measurements in different steps of the nuclear fuel cycle *[1,2]*. Geo-cosmochronogical applications depend on enrichment of isotopic abundance due to accumulation of decay products of naturally occurring radioactive isotopes *[3]*. A very recent application of TIMS is to measure the relatively small variations in isotopic composition of elements like, Mg, Ca, Fe, Cu, Zn, Cd and Mo due to mass dependent fractionation of isotopes during natural (physical, chemical and biological) processes *[4]*. Such measurements are very useful in understanding metabolic pathways and in clinical diagnosis. Increasingly sophisticated and demanding measurements needed in the above areas have driven the technical advances in TIMS especially in the last four decades. As a result, TIMS now represents a very mature technology providing high sensitivity, high precision of isotopic ratio analysis and excellent selectivity.

Modern TIMS have evolved from the original design of Dempster in 1918, and consist of six basic functional elements - 1. Sample introduction, 2. Ion production and collimation, 3. Mass separation, 4. Ion detection, 5. Vacuum system and 6. Instrument control/data handling. Although conceptual refinements in each of these elements have evolved in academic institutions, the engineering sophistication necessary to fabricate and integrate them into a complete instrument is beyond individual small groups. Development and production of state of the art TIMS are now in the domain of a few commercial firms. In this overview, significant advances in each of these units are briefly described without going into great theoretical and design details. The list of references is not exhaustive but sufficiently representative on TIMS specific topics covered in this article.

2. Sample Introduction

Sample introduction consists in coating the sample as a thin uniform layer on a suitable filament (tantalum, rhenium or tungsten) in a filament holder, and attaching it to the front end of an ion source. In older TIMS it was possible to introduce only one filament assembly into the ion source housing at a time. This required breaking vacuum to remove the previously analyzed sample assembly, attach a new one and then reevacuate the ion source housing, if not the entire mass spectrometer analyzer tube, to required low pressure, typically 10^{-7} torr. This meant a considerable loss of time. A substantial saving in time for evacuation has now been realized by introducing at a time a batch of samples into the source housing and evacuating it just once to analyze all of them. This is accomplished by mounting many filament assemblies on the periphery of a circular magazine (barrel) and then pivot it inside a larger source housing in such a way to bring each sample in front of the ion source one after the other and in any sequence. An incidental advantage of this multiple sample magazine is that while one sample is being analyzed, the next sample in the selected sequence can be preheated to condition it.

3. Ion Production and Collimation

3.1 Ion production

Ion production on a hot filament is described by the Saha-Langmuir equation *[5]*. This equation gives the degree of ionization (the ratio of positive ions, n^+ to neutral atoms, n^0 leaving the surface) as

$$(n^{+}/n^{0}) = (g^{+}/g^{0})\ exp\ [e\ (W - IP)/kT)]$$

where (g^{+}/g^{0}) is the ratio of statistical weights for ion and neutral atoms (equal to ½ for alkali elements), W, work function of the metal filament, IP, first ionization potential of the evaporating element, T, absolute temperature, e, electronic charge and k, Boltzman constant. The efficiency of ionization depends exponentially on the difference between work function and ionization potential. If IP is less than W, efficiency is almost 100%. The Saha –Langmuir equation applies to the ideal case of re-emission as ions of neutral atoms striking a hot filament. In the practical case of evaporation of a discrete layer of sample on a filament, ion emission will differ significantly from that given by the equation for many reasons *[6]*. As samples are normally coated as a chemical compound (chloride, nitrate or oxide), both molecules and atoms may be emitted during evaporation. Molecules may be dissociated before or after ionization. There is also the possibility of chemical reaction of the sample with the metal surface to form alloys. Presence of impurity species in sample layer could also complicate the emission process by either suppressing or enhancing it.

Evaporation and ionization of sample from a single filament requires that the operating temperature of the filament is a good compromise between steady evaporation and good ionization efficiency. If evaporation is excessive at the temperature required for good ionization, sample may be exhausted before the ionization temperature is reached. This limitation of a single filament can be avoided by separating the evaporation and ionization temperatures using double/triple filament assemblies *[7]*. In such multifilament configurations, temperature of the filament coated with the sample can be adjusted for steady and sufficient evaporation of neutral species on to a nearby filament whose temperature can be independently adjusted for good ionization efficiency. This arrangement is closer to the ideal case represented by the Saha-Langmuir equation.

In view of its simplicity and ease of use of single filaments, many recipes have been developed to enhance the ionization efficiency of specific elements/molecules on single filaments. *[8,9,10]*. Some elements like Nd ionize much more efficiently as oxides than as metal ions. Measurement of oxide ions will require correction for oxygen isotopes to retrieve the corresponding elemental isotope ratios. A common technique for improved ionization is to oxidize the filament surface (Ta and W) before coating the sample on it. It also helps if the sample is loaded on a discrete layer of Ta_2O_5 deposited on the filament. Very dramatic enhancement in ionization efficiency for Pb has been achieved by loading the sample in a mixture of silica gel + orthophosphoric acid on a Re filament *[8]*. But for this recipe, application of Pb isotopes in earth sciences would have been severely limited. It is not clear how these empirically developed recipes work. It is believed that these activator layers store the sample in its bulk to reduce evaporation rate while at the same time provide a relatively large area and work function. For example a monolayer of oxygen on tungsten increases the effective work function by 1.9 eV.

Negative ion production on a hot metal surface is given by a modified form *[11]* of the Saha-Langmuir equation given above for positive ions as

$$(n^{-}/n^{0}) = (g^{-}/g^{0})\ \mathrm{exp[e(EA-W)/kT]}$$

where EA is the electron affinity of the analyte element or molecule, and other parameters the same as defined above. Efficiency of negative ion formation is high for elements/molecules with high electron affinity evaporating from a filament of low work function. Lanthanum and barium salts are usually applied to the filament surface to reduce the effective work function. Both negative atomic ions and oxide ions are formed. Transition group metals Mo, Tc, W, Re, Os, Ir and Pt are best measured as negative ions. The application of the parent daughter Re-Os system to geochronolgical studies has become routinely possible through negative ion mode of analysis *[12]*. Heumann *[13]* has given a good description of filament materials and ionization processes as relevant to TIMS.

3.2 Mass fractionation

An unfavourable feature of thermal ionization is mass fractionation which inevitably takes place during evaporation of the sample. Lighter isotopes are preferentially evaporated from the filament resulting in a lighter isotopic composition of the emitted ion beam relative to that of the solid sample. While this fractionation is mass dependent, its exact dependence on mass is very complicated *[14]* because of the interplay of different processes on a hot filament. The evaporated upper layer of the sample may not be rapidly equilibrated with the bulk of the sample. Sample may change its chemical state with time or temperature, and hence evaporate in different form during the course of a measurement. As the sample quantity is finite, this fractionation will continuously deplete it in lighter isotopes.

Three empirical relationships have been developed to correct for fractionation to achieve increased precision in isotopic analysis of especially elements used in geo-cosmochronolgy. These are *[15]*

$$^{ij}R_C = {}^{ij}R_O\,[1 + \alpha\,(m_i - m_j)] \qquad \text{Linear law}$$

$$^{ij}R_C = {}^{ij}R_O\,[1 + \beta]^{(m_i - m_j)} \qquad \text{Power law}$$

$$^{ij}R_C = {}^{ij}R_O\,[m_i/m_j]^{\gamma m_i} \qquad \text{Exponential law}$$

where $^{ij}R_o$ is the observed fractionated ratio of two isotopes with masses m_i and m_j respectively, $^{ij}R_c$, the corrected (not necessarily true) ratio in the sample, and α, β and γ are the fractionation factor per unit mass in the three cases, respectively. If at least one ratio in an element is constant and known (or assumed), it can then be used as an internal standard to correct other isotope ratios for mass fractionation in the ion source using one of the above three relations *[16]*. For example, ^{87}Sr abundance in a rock or mineral sample varies due to radioactive decay over geologic time of ^{87}Rb contained in them. As the three other Sr isotopes are not affected by any radioactive decay process, mass fractionation observed in ^{88}Sr/^{86}Sr can be used to correct it in observed ^{87}Sr/^{86}Sr ratio. If an element does not have any fixed isotope ratio, a mixture of two artificially enriched isotopes (double spike) is added to the unknown sample to monitor mass fractionation, and apply a suitable correction to the desired isotope ratio(s). As three of the four isotopes of Pb are radiogenic, a ^{207}Pb-^{204}Pb double spike has been used for high precision measurement of the three radiogenic isotopes relative to the single nonradiogenic ^{204}Pb isotope. Although none of the empirical relations is an exact representation of the actual fractionation process, the exponential law has been found to be closest to it [15] especially for light elements like Ca.

3.3 Ion collimation

Ions emitted from the filament must be quantitatively extracted, accelerated to a homogeneous energy and focused into a fine beam with a very small divergence before mass separation. This acceleration and focusing is done by a stack of electrode plates with different sizes of slits in them. An exploded view of a typical lens stack is shown in Fig. 1*[3]*.

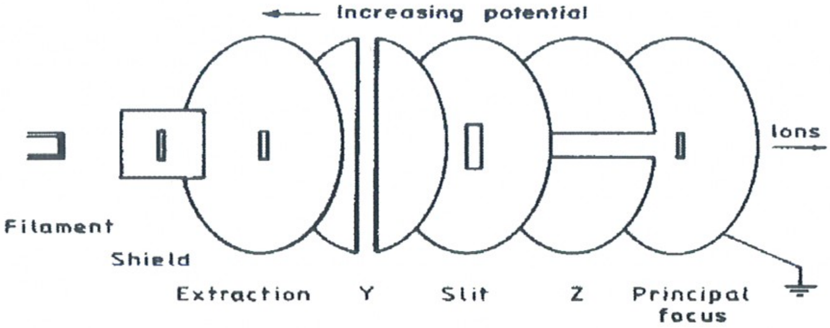

Fig. 1 Exploded view of a collimator stack showing a typical sequence of focussing plates. The ion beam emerges along the x axis.

A highly stable DC voltage of about +8000 volts is applied on the filament, and successively lower voltages on the other plates with the last plate containing the final source slit at ground potential. Ions emitted in different directions from the front face filament are extracted through a relatively large slit in the filament shield by a lateral 'draw out' electric field between the shield and extraction plates. As the extracted beam traverses between the plates, it is both accelerated to the full potential and focused into fine beam on the source slit by adjusting the voltages on the various plates. Two of the plates are split into two halves in two orthogonal directions. A relatively small differential voltage between the split half plates riding on their mean voltage is used to align the beam in two directions onto the final slit. In so called 'immersion lens' ions accelerate progressively between each pair of plates, whereas in so called 'einzel lens' a suitable combination of acceleration and deceleration between plates is used to focus the beam. The design of this electrostatic lens has not changed much over the years. In a well designed lens with the filament precisely aligned in front of it, loss of beam on edges of slits is minimal. So the main lens stack needs to be cleaned of any progressive sample deposits on slit edges only periodically. This cleaning is now easy, as the entire stack can be removed as a unit and cleaned in suitable clean solvents.

As ions emitted from the filament have a very small energy spread (~0.2 eV), a beam accelerated to about 8000 V is extremely homogeneous in energy, better than 100 ppm. Lens stack for negative ions is the same except the filament is kept at a high negative potential. Electron emission from the filament due to it low work function may produce some complication. It is assumed that no mass fractionation is induced by the lens stack. Use of a small permanent magnet in the lens stack in one commercial design may be responsible for a non-ideal mass fractionation reported by some workers.

4. Mass Separation

The mass dispersion and direction focusing actions of a homogeneous magnetic field on an ion beam of uniform energy was first used by Dempster in 1918. He used a semicircular field. With the development of focusing theory for sector magnetic fields in the 1930s, sector magnets with deflection angle of either 60° or 90° became the choice for TIMS because of their compact size, lower power consumption and convenience of locating the source and detector outside the magnetic field region. Theory of direction focusing in sector magnetic fields is given in many publications *[17,18]*. The following description is intended to help visualize the magnetic field action in a practical TIMS.

Fig.2 shows the top and side views of trajectories of ions emerging from a point in the source slit in a 90° sector magnetic field.

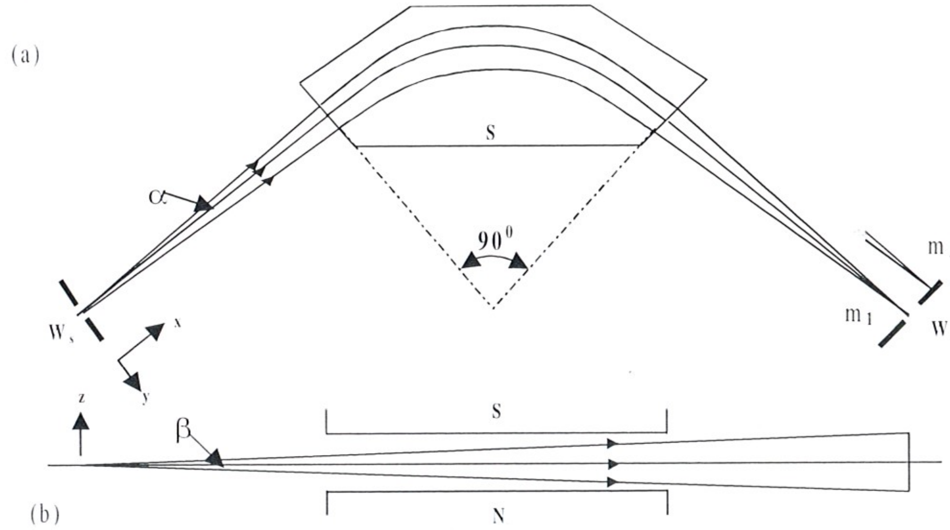

Fig. 2 (a) Top view of a 90° sector magnet showing mass separation and focussing in the x-y plane for normal beam entrance. (b) Front side view showing no focussing in the z direction.

Let us consider the emergent beam ion beam to consist of only two isotopes of mass m_1 and m_2 ($m_2 > m_1$). In the top view, the x–y plane (the plane of the paper) corresponds to the middle plane between the pole pieces with the central axial beam along the x-axis and divergent with a small angle, α in the y direction. The side view shows a small divergence (β) of the beam in the z direction. The m_1 component in the axial beam normally incident on the magnetic field will describe an arc of a circle of radius, r within the magnetic field and emerge tangentially to this arc from the other boundary of the field. The extreme paraxial rays of this mass will also describe an arc of radius r, but the outer beam will describe a slightly longer arc and the inner beam a slightly smaller arc relative to that of the axial beam. So their trajectories will converge on that of the axial beam some distance away from the magnet known as the focal length for direction focusing in the x–y plane or y direction. This focusing is not perfect due to a small aberration, $\sim r\,\alpha^2$. This means that the width of the refocused beam will not be equal to the width, W_s of the beam emerging from the source slit but slightly larger by $r\alpha^2$. The heavier m_2 component of the beam will describe an arc of radius larger than r, and hence will be focused at a point spatially separated as shown in the top view from the m_1 component by $r\,(m_2 - m_1)/m_1$. This is known as the mass dispersion of the magnet at this mass range. If the magnetic field is varied to scan the mass resolved beams across a slit (called the collector slit) with a width W_c slightly larger than $W_s + r\alpha^2$, each beam will be fully transmitted through this slit for a small range of the magnetic field resulting in a trapezoidal signal with a flat top *[6]*. This flat top is very critical for high precision beam measurements despite small fluctuations in acceleration voltage or magnetic field. If the leading edge of the m_2 signal just coincides with the trailing edge of the m_1 signal, the two will be resolved. W_s, W_c and radius, r of deflection in the magnetic filed are selected for a mass resolution of about one in 300.

With normal incidence of the beam shown in Fig.2, there is no magnetic force on ions diverging in the z direction i.e., from the middle plane of the magnet. The beam therefore continues to diverge in this direction, as shown in the side view (lower panel) in Fig.2. The upper and lower parts of the diverging beam may hit the inside wall of the flight tube and hence be lost. Besides this loss of transmission, ions striking the flight tube may give rise to spurious reflections at the collector. It was known even by 1940 that for oblique incidence of ions on a magnetic field the curvature of the fringing field would generate a force on ions diverging from the median x–y plane toward this plane. In 1951 Cross *[19]* showed that for an oblique angle of incidence and exit at 26.5° the fringing field induced force will focus the ions in the z direction at exactly the radial focal point. Such a focusing in two perpendicular directions is known as stigmatic focusing. As shown in Fig.3 *[6]*, the beam diverging from the middle plane will be deflected by fringing field at the entrance to travel parallel to the middle plane between the pole pieces.

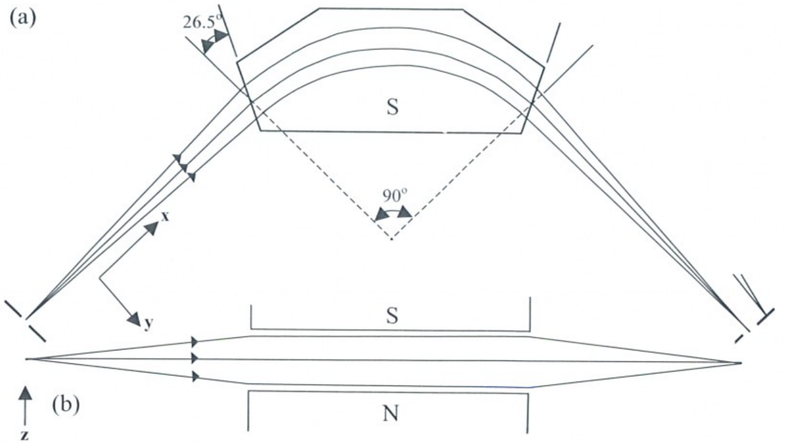

Fig. 3 (a) Top view of a 90° sector magnet showing mass separation and focusing in the x-y plane for oblique (26.5°) beam entrance. (b) Front side view showing focussing in the z direction also.

The fringing field at the exit point will converge this beam back to the median plane exactly where beams diverging in the x–y plane will converge. This will obviously lead to maximum possible transmission of ions along their entire flight path.

An incidental but very important advantage of this geometry is an almost two fold increase of mass dispersion for a given radius over the conventional normal incidence geometry. For this reason this arrangement is also known as extended geometry ion optics. It is surprising that stigmatic focusing magnets were incorporated in TIMS only in the 1970s by commercial firms. The pressing reason for incorporation of this geometry was that the larger dispersion facilitated an easy accommodation of multiple ion detectors along the focal plane for simultaneous collection of isotopic ion currents. The focal plane both in normal and oblique incidence geometry is highly oblique (~30°) to the main axial beam *[6]*. This means that collectors must be moved along this inclined plane and that spacing between collectors for unit mass difference will be very uneven. In one commercial design, the focal plane is rotated nearly perpendicular to the main beam axis by giving a slightly curved shape to the pole boundaries. It is claimed that this configuration is better suited for dynamic multicollection (more details are given in 5.2).

5. Ion Collection and Detection

5.1 Faraday cup detector

The standard ion detector in TIMS is a Faraday cup (in the form of a narrow metal box open at one end) located just behind the collector slit and connected to a DC amplifier with negative feedback through a high ohmic resistor R, as shown in Fig. 4 *[6]*.

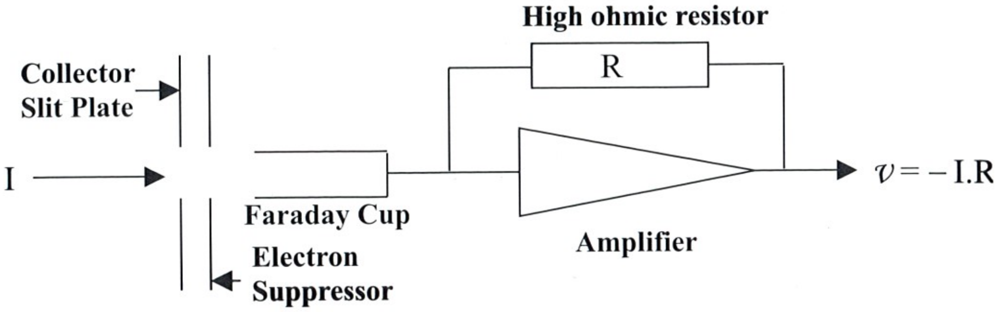

Fig. 4 Schematic of a Faraday cup + amplifier ion current detector behind the collector slit and electron suppressor plates. R is a high ohmic feedback resistor.

The ion current, I, collected by the Faraday cup will induce an equal charge neutralizing electron current flowing through the feedback resistor to produce an output voltage signal $v = IR$ (sign not shown). This output voltage is measured with a high precision digital voltmeter for further processing. With only one detector mass resolved ion beams have to be measured one after the other by varying or switching the magnetic field. In order that the output voltage precisely and accurately represents the incoming ion current, the detector system must meet very stringent specifications. (1) Faraday cup should prevent the escape from it of any back-reflected ions and secondary electrons or sputtered negative ions from the impact of energetic ions. The latter is achieved by a suitable negative voltage on an electrode (called the electron suppressor plate) in front of the Faraday cup. Escape of reflected ions is prevented by using a deep Faraday cup. In very recent improved and long life Faraday cups back reflection of ions is avoided by embedding them inside a layer of porous carbon at the bottom of the cup. (2) The insulator resistance at the input to the amplifier must be much higher than the high ohmic resistor (typically 10^{11} ohms) to ensure that the charge compensating electron current flows mainly through this resistor. (3) The amplifier response must be highly linear over the range of ion currents to be measured. Modern solid-state (MOSFET) amplifiers are quite linear and stable, and have low input current. But any dependence of the value of feedback resistor on the voltage across it (known as its voltage coefficient) can cause significant nonlinear response. Modern high ohmic resistors are free of this effect, but they still show a large temperature dependence – in the range of 200 ppm/°C. It is therefore now a standard practice in TIMS to maintain this resistor in an evacuated and temperature stabilized (± 0.01°C) housing.

The smallest ion current that can be measured using the above detector is limited by electrical noise generated in the input circuit of the amplifier. Johnson noise generated in the feedback resistor is the dominant source of input noise, and is given by *[6]*

$$v = 7.4 \times 10^{-12}\ (T.R.f)^{0.5}\ \text{volts}$$

where T is absolute temperature, R, value of feedback resistor in ohms, and f, bandwidth of amplifier. For typical values (300 K ,10^{11} ohms and 10 Hz, respectively) of these parameters, v is 130 microvolts. This corresponds to a current through R of ~ 1.3×10^{-15} A. This noise current sets 10^{-13}A as the smallest ion current that can be measured with reasonably high signal to noise ratio using a Faraday cup+amplifier combination.

Sequential collection of mass resolved ion beams in a single ion detector degrades the theoretically obtainable precision with a given ion current for two reasons in practice. First each ion beam is measured for only a small fraction of the time for each cycle of the sequence depending on the number of beams to be measured and the time (typically 2 seconds) for the magnet to settle after each switching. As the statistical precision from collection of N ions is $1/\sqrt{N}$, each beam must be measured repeatedly to accumulate sufficiently large number for the required precision even for the lowest abundant isotope of interest. This means not only a long analysis time (a few hours) but also a larger change in mass fractionation for small samples, in particular. Secondly, the drift of beam intensity between each cycle (typically a few tens of seconds) introduces an error from time interpolation, which could be significant for large and nonlinear drift of beam intensity with time. These two reasons have limited the best precision in single collector TIMS to not better than 50 ppm in favourable cases like Sr and Nd. Simultaneous collection of all isotopic currents of interest in as many ion detectors (known as static multi-collection) drastically reduces analysis time for a given ion statistical precision by optimal utilization of the available ion currents, and completely eliminates any error from short term fluctuations and long term drift of ion beams. This led to the development of multiple detector systems in TIMS.

5.2 Multiple collection of ion beams

Simultaneous collection of two ion beams was implemented as early as the 1940s *[20]* for high precision hydrogen, carbon, nitrogen, oxygen and sulphur isotope ratio analysis. But multicollection in TIMS had to wait until the early 1980s because of stringent design and engineering considerations. The physical (spatial) separation between two isotopes with unit mass difference in the high mass range must be large enough for mechanical accommodation of two collectors in the focal plane. This became easy with the introduction of large dispersion stigmatic focusing magnets. The position of collectors must be individually adjustable to micrometer precision to collect isotopes of different elements. As the high megohm feedback resistors will not be equal to each other at parts per million level, there must be a provision to calibrate the relative gains of amplifiers. This is usually done by feeding a very constant current sequentially into each amplifier and comparing the corresponding output voltages. Temperature dependence of these resistors requires that they are kept in an evacuated and temperature stabilized housing.

With simultaneous collection of two ion beams it would appear to be possible to measure their ratios to any degree of precision provided the necessary number of ions can be collected for each beam. For example, two ion currents, each of about 5×10^{-11} A, would result in the collection of 10^{12} ions in about 10 hours, resulting in an excellent ion statistical precision in their ratio of about one ppm. It should be noted that the accuracy of this ratio will depend on the collection efficiency of the two Faraday cups, and that the precision of the ion current ratio will not in general apply to the corresponding isotope ratio in the sample because of unknown mass fractionation in the ion source. In practice the precision of ion current ratio measurement in static multicollection will be limited by the uncertainty in calibrating the relative gains of the amplifiers. With the present state of the art, the uncertainty of electronic calibration of each amplifier is about 5 ppm, which propagates into an uncertainty of 7 ppm in ratio calculation. This means that the ultimate reproducibility of static ion current ratio measurement is about 7 ppm at best. If a higher level of precision commensurate with the number of ions collected is needed, ion currents must be so measured that gain factors get cancelled out in ratio calculations. Two approaches are possible for such a cancellation of amplifier gains, namely dynamic multi-ion collection (conventionally known as dynamic multicollection *[6]* and dynamic multi-ion detection (known as virtual amplifier system in a commercial design) *[21]*.

5.3 Dynamic multi-ion collection (dynamic multi-collection)

The principle of dynamic multi-collection is shown schematically in Fig.5 for the simple case of dynamic double collection.

Of the three incoming ion beams, I_a, I_b, and I_c, I_a and I_b are first measured simultaneously in detectors 1 and 2, respectively. The magnetic field is then switched so that I_b is now measured in detector 1 and I_c in detector 2. It is obvious that the mass difference between I_b and I_a and between I_b and I_c should be the same for this is to be possible. The output voltages during the two sequences are given by

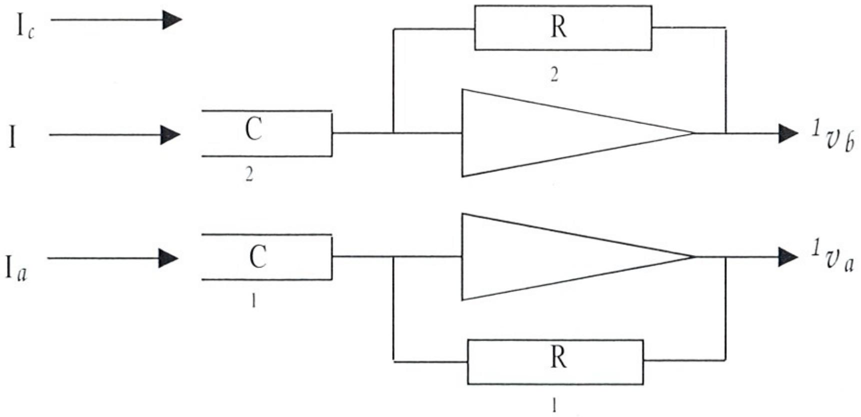

Fig. 5 Schematic of a dynamic dual ion-collector system to cancel both amplifier gain and Faraday cup efficiency factors.

$$^1V_a = I_a \cdot R_1 \cdot C_1, \qquad ^1V_b = I_b \cdot R_2 \cdot C_2$$

$$^2V_b = I_b \cdot R_1 \cdot C_1, \qquad ^2V_c = I_c \cdot R_2 \cdot C_2$$

where R_1 and R_2 are the feedback resistors in the two channels, and C_1 and C_2 the cup efficiencies assumed to be close but not exactly equal. Note that the cup efficiency factor is not explicitly included in the output in Fig.4, as it was assumed to be exactly unity. These two sets of apparent voltages can be combined to give

$$(I_b/I_a) = [(^1V_b/^1V_a)\,(^2V_b/^2V_c)\,(I_c/I_a)]^{0.5}$$

The gain and cup efficiency factors of both channels get cancelled, and (I_b/I_c) ratio is now given by the apparent output voltages and (I_c/I_a) ratio. This procedure is useful when only one isotope varies and the other two isotopes are invariable between samples. A well known example is the measurement of $^{87}Sr/^{86}Sr$ ratio against a constant and known (or assumed) value of 8.37521 for $^{88}Sr/^{86}Sr$ ratio, known as internal standard. If the current ratio (I_c/I_a) is now replaced by the isotopic ratio 8.37521, the current ratio (I_b/I_a) will directly give the isotopic ratio $^{87}Sr/^{86}Sr$ after correction for mass fractionation in the source according to power law given earlier. The accuracy of this ratio will depend on the accuracy of the power law correction for mass fractionation. This ratio will differ slightly if linear or exponential law is used instead for correction.

5.4 Dynamic multi-ion detection

In this, ion beams are not switched between different collectors but the electrical connections between collectors and amplifiers are switched, as shown schematically in Fig.6 for a two detector system.

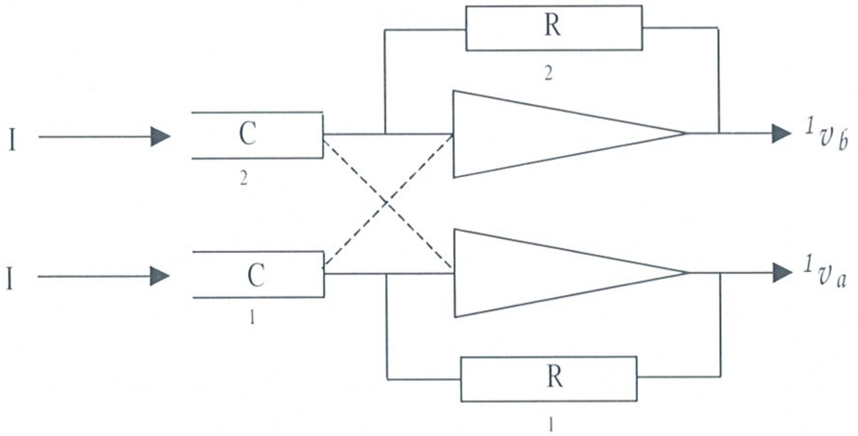

Fig. 6 Schematic of a dynamic dual ion-detector system to cancel amplifier gain factors only.

I_a and I_b are first measured in cups 1 and 2 connected to amplifiers1 and 2, respectively. Next the collector connections to the amplifiers are interchanged as shown by the dotted lines for the second measurement sequence. The output voltages during the two sequences will be given by

$$^1V_a = I_a.R_1.C_1,\ ^1V_b = I_b.R_2.C_2$$

$$^2V_a = I_a.R_2.C_1,\ ^2V_b = I_b.R_1.C_2$$

These equations can be combined to give

$$(I_b/I_a) = (C_1/C_2)[(^1V_b/^1V_a)(^2V_b/^2V_a)]^{0.5}$$

Gain factors of the amplifiers are cancelled out, but not cup efficiencies. The ratio of the two beams is now given by the measured apparent output voltages without being tied up to any other ratio, unlike in the previous case. However, a second fixed or standard ratio is required for mass fractionation correction. The accuracy of this ratio will be determined by the accuracy with which the cup efficiency factors can be measured. Measurement of the cup efficiencies to a few ppm is very difficult in practice. However, cup efficiencies change only very slowly unlike amplifier gains, so reproducibility in the short term (a few months) will be satisfactory. A matrix of four relays will be required for interchange of connections for two detectors, and as many as 81 relays for a nine amplifier system.

The concept of switching amplifiers between collectors is fairly straightforward, but its implementation was considered problematic because of possible transients due to make and break in the sensitive collector and amplifier connections, cross talk between relays and possible leakage paths between relays and to ground. One commercial manufacturer has successfully overcome these problems using a matrix of solid-state relays between the collector and amplifier banks. It is called the 'Virtual Amplifier' design *[21]*. Using such a system and with careful correction for mass fractionation in the ion source, a long term external precision of ppm (2 sigma) has now been realized *[22]* for some elements. Such extraordinarily high precision may not be needed in nuclear technology, but has been necessary to address a few studies in earth and planetary sciences. For example, it has recently been established that the $^{142}Nd/^{144}Nd$ ratios in primitive meteorites and terrestrial rocks are not equal as believed so far, but differ by about 20 ppm. This small difference has profound implications for the chemical differentiation of the embryonic earth *[23]*.

5.5 Individual ion detection

It was noted earlier that amplifier noise limits the smallest current that can be measured with a Faraday cup+amplifier combination to about 10^{-13} A. Currents smaller than this are best measured by directly counting the ions individually, as they arrive at the collector. A current of 10^{-14} A corresponds to a stream of $\sim 5 \times 10^6$ ions per second. The charge on a single ion is too small (1.6×10^{-19} Coulomb) to produce a large enough voltage pulse to directly drive an electronic counter. A secondary electron multiplier (SEM) consisting of discrete number dynodes is therefore used to multiply each ion into many secondary electrons. An ion hitting the first dynode will release a few secondary electrons which are then successively multiplied by the chain of dynodes by a factor of about 10^5-10^7 *[6]*. This big electron pulse will produce a large enough voltage pulse to activate a high-speed electronic counter. It would appear that an electronic counter with a capacity of 5×10^6 counts per second is adequate to count each ion in the above stream. But as arrival times of ions at the SEM are not uniform but random subject to Poisson statistics *[6]*, pulse resolving time or dead time of the counter should be much smaller than 200 nanoseconds so as not to miss any closely spaced ion arrivals. The practical limit for ion counting is now about 5×10^6 ions per second. SEMs are practically noiseless devices, as they produce less than a few stray or fake counts per minute. This means SEMs can detect very low ion currents of about 10^{-17}A. SEMs are available with discrete or continuous dynodes known as channeltrons. They can be used to detect both positive and negative ions.

Another option, though more elaborate and expensive, for conversion of single ions into a large number of electrons for counting is known as the Daly detector *[24]*. Ions entering the collector slit are accelerated to a polished aluminium knob kept at a negative potential of about 30 kV. The secondary electrons emitted from this electrode are accelerated to hit a metallized grounded scintillator in front of the electrode to produce a number of photons. These photons leave the vacuum enclosure through a glass window to be detected by a standard photomultiplier as discrete pulses. Daly detector has more often been used not for discrete ion counting but as a Faraday cup with built-in amplification. It cannot be used to detect negative ions. Daly detectors are not favoured now because of the availability of much cheaper SEMs with excellent gain, stability, linearity and low noise. The relatively large size of early SEMs allowed only one of them to be used in TIMS along the main axial beam. Compact channeltrons and miniature discrete dynode SEMs now facilitate simultaneous multiple ion counting in special applications. Commercial TIMS are now available with as many as 9 Faraday cups and 8 SEMs positioned along the focal plane. An SEM alone may not be adequate to measure a very weak ion current, because of what is known as abundance sensitivity.

5.6 Abundance sensitivity

Abundance sensitivity refers to the contribution of the tail at the low mass side of a very intense beam one mass unit away. Usually it is measured at mass 237 in the presence of an intense $^{238}U^+$ beam. It arises from a slight loss of energy and direction by ions in the intense beam due to their collisions with residual gas molecules and scattering on edges of beam defining apertures in the flight path. Even with ultrahigh vacuum to reduce such collisions, abundance sensitivity will be about 1-5 ppm *[25]*. This will preclude the clean measurement of very weak isotopes in the presence of heavier and far more abundant isotopes. Examples are the extremely low ratios of $^{230}Th/^{232}Th$, $^{233}U/^{238}U$ and $^{236}U/^{238}U$ in the range 10^{-6}-10^{-7}. $^{230}Th/^{232}Th$ ratios have geochronological significance *[25]*.

Tandem magnetic analyzers were first used to improve abundance sensitivity, but were bulky, power intensive and costly. These were replaced with simpler cylindrical electrostatic analyzers to reject ions of wrong energy and direction from entering the detector *[21]*. In recent designs some kind of a retardation potential lens system is placed after the final exit slit so that only ions above certain energy are transmitted to the detector. One such retardation lens is known as Retarding Potential Quadrupole (RPQ) filter *[21]*. This consists of special beam shaping quadrupole lenses to reject ions of false direction and energy. Critically tuned RPQ filters improve abundance sensitivity to better than 10 ppb. A schematic of a complete ion optical system incorporating all the elements described above is shown in Fig.7 *[6]*.

The central radius of the 90°-sector magnet is 230 mm. It is a stigmatic focusing magnet with its pole boundary rotated by 26.5° relative to the normal direction. The object focal length, 460 mm length, is exactly twice the radius, but the image focal length is longer - about three times the radius. This is an asymmetric stigmatic focusing system. Four paraxial Faraday cups are shown along an inclined focal plane. The axial beam is detected a little beyond the exit slit. It can be directed into a Faraday cup offset to one side or into

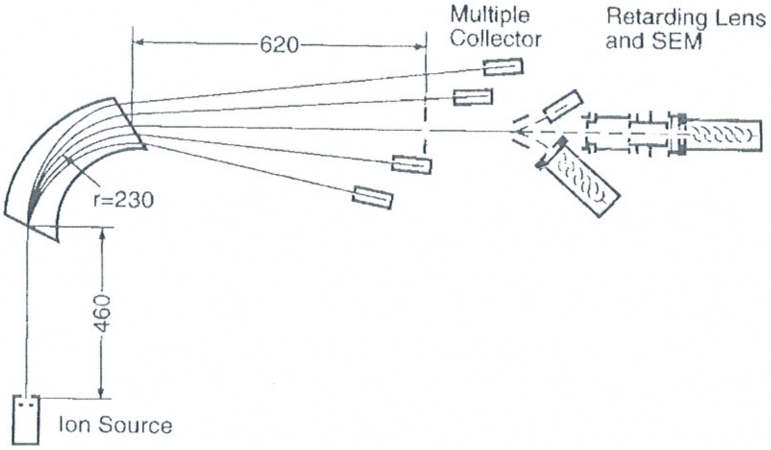

Fig. 7 Schematic of a representative ion optic system showing all its elements

the SEM offset to the other side by a suitable voltage on the deflection plates shown. In the absence of any such deflection voltage the axial beam will go through the RPQ lens onto the online SEM.

6. Vacuum System

Advances in vacuum systems for TIMS have drawn on developments in general in vacuum technology driven by many other demands over the years. Many metals and alloys were used to fabricate vacuum enclosure and inner parts of TIMS until the 1960s. Non-magnetic stainless steel carefully selected for low trapped or dissolved gas content is now the preferred construction material. Glass-to-metal seals for vacuum feedthroughs are now replaced with rugged ceramic-to-metal seals with low leakage paths to reduce the risk of high voltage flash-over in the source side. Neoprene elastomer O-rings were replaced with viton O-rings for demountable joints because of their low degassing characteristics. In modern T-IMS most vacuum joints use standard size conflat flanges with copper gaskets with gold wire sealing in special locations. Elastomer seals are now restricted to frequently opened ports –such as the one to introduce sample magazine.

(Diffusion+ rotary oil pump) combination was the only choice for evacuation of TIMS until the 1950s. Mercury rather than oil was selected as the working fluid in diffusion pumps for applications requiring clean vacuum free of organic or mineral oil contamination. Vacion pumps were first used on the analyzer side in the 1960s for cleaner and higher vacuum. This was combined with a beam or online valve between the source and analyzer enclosures so that the high vacuum in the latter can be maintained when the former is vented to atmospheric pressure for sample changing. Although a vacion+titanium sublimation pump combination has successfully been used to evacuate source housing after initial pumping down to rotary pump pressure, it took a very long time to reach working vacuum ($< 10^{-6}$ torr). It could not handle large gas loads from samples during their initial warm-up. The standard option for source pumping is now a turbomolecular pump+ rotary pump combination, because turbomolecular pumps have high pumping speeds, reach working vacuum in a short time and have become reliable. It is also common to provide a liquid nitrogen cooled surface above the source housing for additional pumping speed especially for condensable gases and vapours. With the only opening between the source and analyzer being the very narrow source slit, a substantially high differential pressure can be maintained between the two sides – analyzer being at low 10^{-9} torr range while source side at a low 10^{-7} range.

7. Instrument Control/Data Handling

If TIMS made use of the developments in vacuum technology, it thrived on the rapid developments in automatic control of and data storage and reduction in many analytical instruments including other type of mass spectrometers based on computerization. Until the 1960s control, operation and data acquisition in TIMS were entirely manual, laborious and time consuming. The first step was offline processing of digitized ion currents in a central large computer, which released the operator from the tedium of analog recording of data on a chart recorder and subsequent data reduction. Every other aspect of TIMS operation was still manual. The development of programmable magnet power, ion source control and filament current supplies spurred by the availability of inexpensive desk top computers in the 1980 and 1990s led to a gradual automation of the entire machine without operator intervention. A typical modern control and data system for TIMS is a Pentium based PC with >10 M bytes of memory, a 1-2 Gbyte hard disc and a compatible graphic printer *[6]*. Loaded with highly sophisticated modular software developed by professionals in the academic world, this data system performs all operations fully automatically. It carries out filament warm-up to operating level, ion source focusing, precise peak centering, peak height adjustments, collector selection and spacing for each analysis, peak switching according to any desired sequence and data acquisition. It facilitates data quality (statistical) checks and even diagnostics for trouble shooting. All samples on a sample magazine can be pre-programmed for analysis in any sequence one after the other night and day. The latest trend is remote monitoring and control of the machine over the internet from wherever the operator happens to be. Indispensable though they are now, these sophisticated data systems render the basic TIMS somewhat opaque to most users.

8. Conclusions

With the foregoing conceptual and technical advances in each of its functional elements, modern TIMS facilitate acquisition of the highest quality of isotopic information from extremely small and rare samples, and are easy to operate even by novices. TIMS now represents a very mature technology with very little scope for further dramatic improvements. The primacy of TIMS is being threatened by the fast evolving multicollector plasma mass spectrometer (MC-ICP-MS) in terms of much higher ionization efficiency, range of elements, sampling of solid samples with high spatial resolution using laser ablation and online coupling to chromatographic devices. As of now TIMS and MC-ICP-MS are regarded as complementary techniques that individually offer particular analytical strengths.

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Current Status of ICP-MS: An Overview

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1. Introduction

The rapid and continuous development of human activities has increased the need for chemical characterization (both elemental and isotopic) of different materials in many fields to enable important decisions to be made daily in different fields such as, science, industry, environment, health, economy and legal affairs. Many times detection and accurate estimation of almost all the elements/isotopes in the periodic table at μg/ml (ppm), ng/ml (ppb), pg/ml (ppt) or fg/ml (ppq) levels in a wide variety of materials in these fields are required (Balaram *et al*, 2006, Satyanarayanan *et al*, 2006). Most often, the sample volumes are relatively small and the analytical demands are very high requiring extremely high sensitive instrumental analytical techniques. Inorganic mass spectrometry is one of the most important analytical techniques for chemical characterization. Technical advances over the past 50 years, have enabled different types of mass spectrometers to meet most of the requirements in various branches of science (Balaram, 2002). Currently a range of mass spectrometric techniques are available for inorganic analytical applications. Some of the most important mass spectrometric techniques are, spark source mass spectrometry (SSMS), glow discharge mass spectrometry (GDMS), laser ionization mass spectrometry (LIMS), secondary ion mass spectrometry (SIMS), thermal ionization mass spectrometry (TIMS), accelerator mass spectrometry (AMS), resonance ionization mass spectrometry (RIMS) and inductively coupled plasma mass spectrometry (ICP-MS). These techniques are employed in inorganic analysis for the precise estimation of both elemental and isotopic concentrations in a variety of materials for different applications in many fields of science and technology.

2. History and Development of ICP-MS

Gray (1975) was the first to demonstrate the potential of the plasma source mass spectrometry in 1975. The major innovation in the design of ICP-MS is the interface between the ICP and the quadrupole mass spectrometer. Babat was the first to demonstrate the first successful operation of ICPs at atmospheric pressure in 1942. Latter on it was used as a source for atomic emission spectroscopy before it was demonstrated to be an ideal source for mass spectrometry. The principle of ICP-MS can be understood with reference to the schematic diagram given in Fig. 1. Samples in the form of a solution are introduced through the peristaltic pump at a rate of about 1 ml/min into the central region of the plasma at atmospheric pressure with the help of a nebulizer and a water-cooled spray-chamber system. The sample is heated to a temperature of approximately 9000 K in the plasma, resulting in a series of processes involving desolvation, vaporization, dissociation, atomization and ionization (Fig. 2) in the 'analytical zone' of the ICP. At this temperature, chemical interference effects are insignificant, and essentially all atoms are ionized to a very large extent.

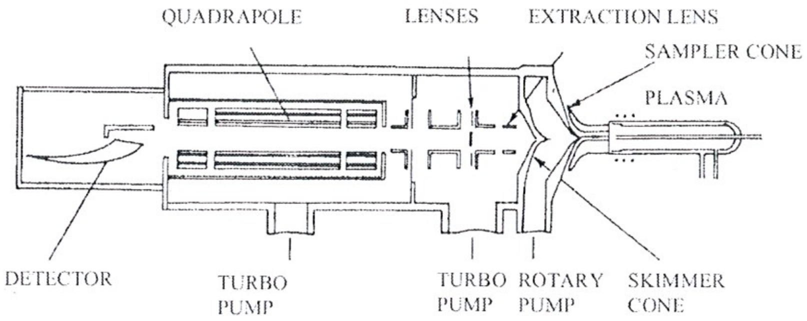

Fig. 1 Schematic diagram of the chain of events leading to the formation of ions in the argan plasma

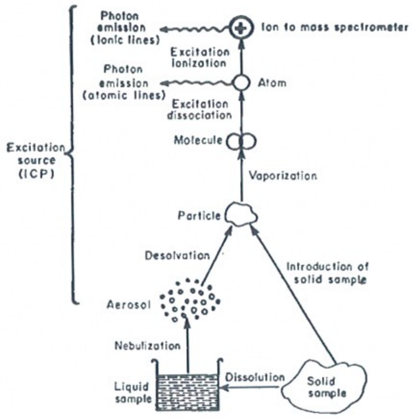

Fig. 2 Flow chart showing the chain of events leading from sample to the formation of ions

Majority of the elements in the periodic table are expected to ionize to the extent of about 90% in ICP. The efficiency of ionization in the argon plasma, as calculated by the Saha equation, shows that the formation of singly charged ions is very efficient in argon plasma and over 54 elements are expected to be ionized with an efficiency of 90% or more (Houk, 1986). Alternatively, solid samples can be analyzed by laser ablation, where the ablated particulate matter is swept by argon gas into the ICP source. A fraction of the positively charged ions produced in the plasma is transported through a narrow aperture of the sampler cone. Here the plasma beam expands at supersonic speeds because of vacuum conditions (1 mbar) and is sampled by the skimmer cone. The ion beam and the plasma gas pass into a further high vacuum region (1×10^{-4} mbar) and pass through a system of electrostatic lenses, which extract the positively charged ions and focus them in a form suitable for transmission through the quadrupole mass spectrometer, which is kept in a very high vacuum region (2×10^{-6} mbar). Mass analysis is accomplished by applying AC and DC voltages to opposite pairs of quadrupole rods such that ions with desired charge-to-mass ratios oscillate in the plane parallel to the rods and are transmitted to a detector. Ions with other mass-to-charge ratios collide with the rods are pumped out through the vacuum system. For multi-element analysis, the applied voltages may be changed continuously to obtain the mass spectrum for the selected masses of interest. Entire periodic table can be scanned ten times in one second. Alternatively, for greater sensitivity, the peak transmission energies of desired masses may be monitored sequentially (peak hopping). A mass spectrum is normally obtained by many such repeat scans (say 100) which may take around 60 sec. This process of mass scanning is very rapid, and the instrument can obtain a spectrum for the entire mass range of ^{7}Li to ^{238}U in about 1 min. One such spectrum is shown in Fig. 3 for a 100 ng/ml multi-element solution, the position of the peak in the spectrum reveals the nature of the element (isotope) in the sample and the height of the peak its concentration. Since the number of registered ions from a given isotope, of course depends directly on the concentration of the relevant isotope (element)

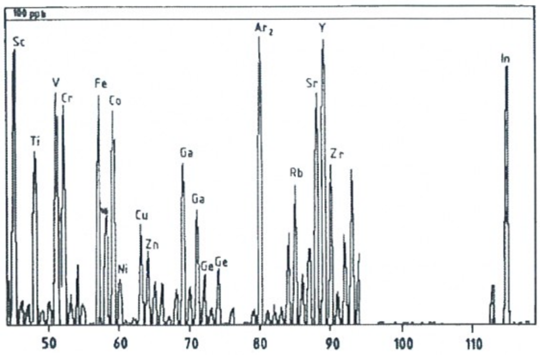

Fig. 3 ICP-MS spectra of a 100 ng/ml multi element solution

in the sample, quantification is straight forward. Design of the ion-optics makes the ions from the sample to take a curved trajectory around a central photon stop eventually to be counted by an off-axis detector. This arrangement suppresses photon noise as the detector is also sensitive to photon radiation from ICP and produces a low background signal of < 1 count per second as against a count rate of about 30 million counts for a 50 ng/ml solution of a mono-isotopic element like rhodium by the current generation ICP-MS instruments. Detection limits, mainly influenced by the relative abundance of the isotope selected for analysis for most elements are currently in the range 0.001 to 0.1 ng/ml. These detection limits are obtainable under multi-element operating conditions. The quardrupole mass analyzers which yield essentially better than unit mass resolution over a mass range up to 300 amu. The analyzer can scan very rapidly the entire useful mass range (0-240 amu) or a selected mass window of interest.

The interferences in ICP-mass spectrometry are classified broadly into two categories: spectral or isobaric and non-spectral or matrix induced. Mass spectral overlaps arise from (i) the plasma gas and entrained air (e.g. Ar^+, $ArAr^+$, ArO^+, ArN^+, $ArOH^+$ (ii) acids used in sample preparation (e.g. $ArCl^+$, ClO^+, NOH^+, SH^+) and (iii) concomitant matrix elements (e.g. $^{56}Fe^+$ on Cr^+ ; TiO^+ on ^{62}Ni, ^{63}Cu, ^{64}Zn, ^{65}Cu and ^{66}Zn). Fortunately all elements in the periodic table (excepting In) have at least one isotope free from isobaric overlap by other elements, though it may be of lower abundance and so involve a compromise in sensitivity. The most important limitation of this technique is non-tolerance to high total dissolved solids in the sample solution. More than 0.2% of total dissolved solids cause clogging of the sampler and skimmer cones. For all practical purposes running of <0.1% solutions is recommended for obtaining reasonable long-term stability (Balaram, 1995; Balaram and Gnaneswara Rao, 2003). A few of these problems are minimized by the use of internal standardization and matrix matching standards (Balaram, 1996). Due to simple sample introduction in the ICP source at atmospheric pressure, coupling techniques such as ultrasonic nebulization (UN), flow injection (FI), high pressure liquid chromatography (HPLC), hydride generation (HG), electro-thermal vaporization (ETV) and laser ablation (LA) to ICP-MS are easy to realize. The dominant use of the ICP-MS has been in measuring elemental concentrations. However, quadrupole ICP-MS has been proved to be a good choice for the isotopic ratio analysis of few elements, such as B, Os, Re, Pb and U (Rao *et al.,* 2004; Suryanarayana *et al.,* 1998).

2.1 Laser Ablation (LA) Sample Introduction

Gray (1985) demonstrated the applicability of the introduction of solids directly into the plasma by laser ablation and subsequent detection and determination of ions by mass spectrometry (Fig 4). He used a ruby laser and demonstrated the applicability of this technique to geological materials for both trace element determination and measurement of isotopic ratios. This unique combination has already achieved several breakthroughs in geochemical, environmental and marine fields. LA extends the capability of ICP-MS to enable the direct multi-element analysis of solid samples from *percent* to *ppb* levels. Sample decomposition

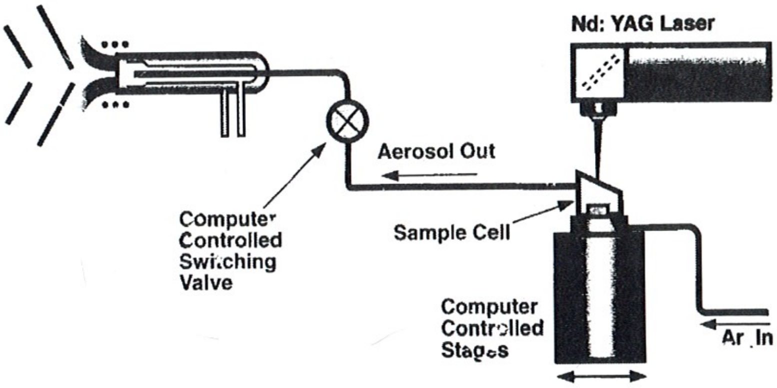

Fig. 4 Laser Ablation Sample Introduction

and associated problems such as incomplete dissolution, contamination, analyte losses due to volatilization, etc., are avoided. The technique can be used for *in-situ* microanalysis as well as bulk analysis. As the sample vapour is introduced into a dry plasma, the interference effects associated with water and acids are eliminated/minimized. We can get spatial information about the distribution of an element in solid materials which will be lost if the sample is dissolved. Only a small portion of the surface needs to be used in the analysis and the sample can be stored for repeated use. The samples are analysed at atmospheric pressure which facilitates fast change over of samples and hence high throughputs are possible.

LA-ICP-MS has been applied virtually to all kinds of samples for characterization of trace element composition. The technique allows routine analysis of wide range of solid materials. It has been very widely applied in isotope geochemical studies especially in conjunction with multi collector magnetic sector ICP-MS instruments. It is of particular importance to nuclear, semiconductor, mineralogical and ceramic industries.

2.2 Cool – Plasma Technology

Cool-plasma is a technique in which the power applied to the load coil of the ICP is reduced (~620 W for cool plasma against ~ 1350 W for normal mode) resulting in the reduction of interfering background species. A few elements like Fe are interfered by the polyatomic species from the plasma gas, by matrix elements and combination of both. Nevertheless these elements are important in analytical chemistry. The most important interfered elements are ^{56}Fe (interfered by $^{40}Ar^{16}O^{+}$), ^{40}Ca (interfered by ^{40}Ar) and ^{39}K(interfered by $^{38}Ar^{1}H$ and ^{40}Ar). The cold plasma has been proved to be suitable for the determination of certain problematic elements in ICP-MS, especially Li, Na, Mg, K, Ca and Fe (Wollenweber *et al.,* 1999). This technique is primarily useful for for the estimation of trace element impurities in high-pure materials, such as de-ionized water and mineral acids.

2.2.1 Collision/reaction cell technology

The latest development for the reduction of argon based interferences in ICP-MS is the collision/reaction cell or hexapole technologies. Today's ICP-MS systems are several times more sensitive than the first commercial systems, and background levels have decreased by more than a factor of 100. The "cool plasma" technique has become popular for eliminating certain argon based interferences, especially for the determination of Fe, Ca and K. But "cool plasma" technique suffers from a drawback in its requirement for each sample to be run twice, once under "normal" conditions for bulk of the elements and once under "cool plasma" conditions for the interfered elements. The collision/reaction cell technology can be used to remove these interferences by eliminating the source of the problem, i.e. the formation of the molecular species. The collision/reaction cell will normally be inserted between the ion-lens and the mass analyzer of a conventional ICP-MS. It is believed that polyatomic ions existing in the linear quadrupole, encounter a number of collisions with the collision gas atoms in the collision/reaction chamber. These polyatomic ions are not sufficiently stable to survive even a few of such collisions. The ideal collision/reaction gas will react with polyatomic isobaric interferences, or neighboring m/z interferences, but not with the analyte ions. The reaction gas can also be chosen to react exclusively with the interfering polyatomic ion to produce a polyatomic species at a new m/z that has no interference on the analyte ion. If a neutral atom or molecule is produced, that will be pumped away. Generally ammonia, helium, hydrogen, xenon and methane gases are used to eliminate atomic and polyatomic spectral interferences arising from plasma and atmospheric gases. For example, in the determination of arsenic in chloride matrix, hydrogen is the preferred reaction gas because it reacts faster with $^{40}Ar^{35}Cl^{+}$ than $^{75}As^{+}$. The following reaction scheme will explain how the interference of $^{40}Ar^{35}Cl^{+}$ on $^{75}As^{+}$ is eliminated.

$$ArCl^{+} + H_2 \text{ ----> } ArH_2^{+} + HCl$$

$$ArH_2^{+} + H_2 \text{ --------> } H_3^{+} + Ar$$

Using this technology, it is possible to selectively attenuate many of the polyatomic ions (such as ArO^{+}, ArC^{+}, ArCl^{+}, etc.) in quadrupole ICP-MS analysis for the interference-free estimation of elements like Al, K, Ca, V, Cr, Mn, Fe, As and Se.

2.3 Collision / Reaction Interface (CRI) Technology

In the collision/reaction interface (CRI) technology which was interduced very recently a reactive gas like hydrogen is injected directly into the plasma through the orifice of the cones. This innovative approach causes collisions, electron-ion reactions and ion-molecular interactions which in turn lead to reduction/elimination of interferences before the analytes are extracted into the ion optics. Both cones have channels to allow CRI gas to be injected into the plasma and promote collisions as well as reactions. This feature is found to be extremely valuable in the estimation of elements such as As, Se, Fe, Cr, Al, V, etc., which are prone to interference effects under normal circumstances.

ICP-quadrupole mass spectrometry is one of the most sensitive analytical techniques applied for the determination of trace and ultra-trace concentrations in environmental, high purity materials, biological, geological, nuclear, metallurgical, archeological, marine samples and technical products (Balaram, 1995, 1996, 2005; Balaram *et al.*, 2000; Balaram, 2005, 2006).

2.4 Sector Field or High Resolution-ICP-MS (HR-ICP-MS)

The most severe spectral interferences observed in ICP-MS are caused by polyatomic (molecular) ions originating from combination of certain elements from the plasma gas, atmospheric gases, water, reagents and the sample solution. Argon, oxygen, nitrogen and hydrogen are thus the dominant constituents in combination with additional elements from the matrix. Elements such as Ba and Ce with a high oxide bond strength will cause interference effects by the formation of corresponding oxide ions with an oxide ion ratio ranging 0.1 to 1.5% with respect to elemental peak (Jarvis *et al.*, 1991; Balaram, 1995). Apart from this, elements with a relatively low second ionization energy, such as Ba can partly occur as doubly-charged ions. The degree of production of doubly-charged ions is normally below 1%. These interference can not be reliably corrected mathematically, because of rate of formation depends on the plasma and ion optic conditions. Finally, there are isobaric overlaps, such as ^{106}Pd and ^{106}Cd or ^{108}Pd and ^{108}Cd. Because of the constant nature of isotopic ratios, isobaric interferences can be predicted and corrected within certain limits by mathematical equations provided the other isobar is free of interference. These problems are mostly as a result of low mass resolution of the conventional quadrupole ICP-MS instruments. They provide only a limited resolution (unit mass resolution) and cannot resolve and eliminate the spectral interferences caused by atomic or molecular ions having the same nominal mass of interest. The result is an erroneously large positive signal at the mass affected. Problems such as those descried above have led to look for alternatives for quardupole mass filters. The most effective solution to these problems is the use of a double focusing mass analyzer, an electric sector used in conjunction with a magnetic sector instead of a quadrupole mass filter to obtain a significant increase in mass resolution. This type of instrument is known as Sector Field or High Resolution-ICP-MS (HR-ICP-MS).

2.4.1 Overview of HR-ICP-MS

A schematic diagram of a HR-ICP-MS (Thermo Elemental, UK) is shown in Fig. 5. This is a double-focusing system consisting of an ICP source, a sampling interface, an electrostatic analyzer (ESA),

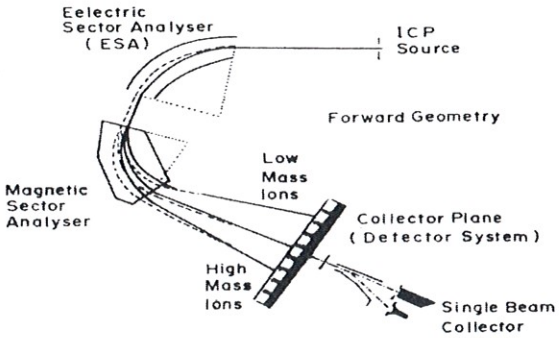

Fig. 5 Schematic diagram of Sector Field ICP=MS

a magnetic sector analyzer (MSA) and a detector system. The sample solution is fed to the plasma through a nebulizer-spray-chamber system, which is water-cooled to reduce solvent loading to the plasma. The ICP source will ionize most elements including elements like hafnium that are difficult to be ionized with thermal sources. Cooling of the nebulizer-spray-chamber system will minimize polyatomic ion formation (e.g ArO^+, MO^+, etc.). Ions are extracted from the ion-sampling interface and injected into the field of ESA, which is an energy-focusing device. The ESA in combination with MSA focuses ions with different energies on to the same point on the detector system. The spectrometer has the capability of adjustable resolution by changing the width of the source slit and the collector slit under computer control. This combination produces excellent flat-peak shapes at low resolution and in addition ensure good focusing across the entire mass range and full focal plane of multi-collector array (Bradshaw *et al.,* 1989; Belshaw *et al.,* 1998). A large mass dispersion enables greater resolving power with less signal reduction. Under-resolving spectra will lead to an incomplete removal of interference. Over-resolving spectra will lead to an unnecessary loss of signal sensitivity. A resolving power (RP) of 10000 is the industry standard high-resolution specification for inorganic mass spectrometers. However, an adjustable slit mechanism allows to obtain resolution settings well in excess of 10000 RP. This is required to resolve common interferences like $^{40}Ar_2$ on ^{80}Se, $^{40}Ar^{35}Cl$ on ^{75}As and $^{40}Ar^{16}O$ on ^{56}Fe (Fig. 6). The instrumental detection limits are improved by about three orders of magnitude compared to conventional quadrupole-ICP-MS. This is mainly because magnetic sector mass spectrometers have an inherently low background signal (<0.5 count/sec), these devices exhibit a very high signal-to-noise ratio, giving detection limits in the parts per trillion (ppt) to parts per quadrillion (ppq) concentration range (Yamasaki *et al.,* 1994). The combination of ICP ion source with a magnetic sector field mass spectrometer fitted with a multi-collector detector system, has given a new perspective, especially to isotope abundance measurements.

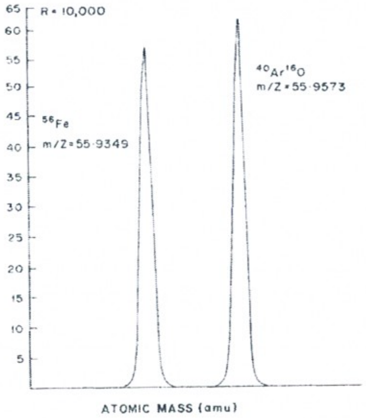

Fig. 6 High resolution mass dispersion for ^{56}Fe and $^{40}Ar^{16}O$

Since its development in 1989, HR-ICP-MS has been virtually applied to all kinds of samples for the characterization of elemental as well as isotopic compositions. With widespread popularity currently HR-ICP-MS is enjoying, there is a possibility that this technique, particularly the multi-collector systems (MC-ICP-MS) slowly replace TIMS in high precision research areas, such as planetary, earth, ocean and environmental sciences.

2.5 Development of Time of Flight Mass Spectrometer (ICP-TOF-MS)

A less attractive feature of quadrupole ICP-MS is the moderate signal stability over reasonably short time, typically 1-5% RSD. The origin of instability has several sources, such as flicker in plasma, changes in nebulization efficiency and variations in the plasma tail where the ions are sampled. The signal stability can be increased significantly by measuring intensity ratios to an internal standard provided that sequential measurements of analyte and internal standard are performed within a short time span. The speed limitation of quadrupole based ICP-MS instrumentation is responsible for a number of weaknesses of the technique including limited precision at high speed scanning and for a large number of elements, low sample throughput for full mass range analysis and limited capability in handling samples with transient peaks with less than 0.1 second duration for multi element analysis. HR-ICP-MS instruments normally do not allow this kind of scanning speeds except for a short mass range and are also very expensive. Another important limitation of scanning mass spectrometers is that the total time for a measurement is directly proportional to the number of isotopes measured. (Emteborg *et al.,* 1999)

There are considerable advantages in the use of a faster mass spectrometer coupled to ICP, for example, time-of-flight mass spectrometer (TOF-MS) as outlined by Hieftje and his co-workers (1997). In time-of-flight analyzers, ions of different m/z values are separated due to difference in their flight times, in a field-free space (drift tube), after acceleration through a fixed potential. This analyzer offers high speed analysis and ultra-high mass range and is becoming very popular in organic mass spectrometry for bio-molecules. It has high transmission efficiency, low sample consumption and superior detection limits since no scanning losses are present. In this case, the plasma can be placed either orthogonal or axial to the time-of-flight mass spectrometer. Coupling of ICP source to a TOF-MS is a recent development to remove some of the limitations of quadrupole and magnetic sector spectrometers.

2.5.1 Working Principle of ICP-TOF-MS

Ions are guided from the atmospheric pressure ICP into a three stage differential pumping system using a conventional sampler-skimmer arrangement with a third differential pumping aperture. In the final pumping stage, ion optics guide the ion beam into a repeller region where all ions are electrostatically accelerated to a uniform kinetic energy into a field-free flight tube (Fig. 7). The ion beam is reflected back at the end of its flight to the drift region and reaches the detector after travelling an equal distance in the reverse direction. This leads to velocity focusing and an increase in overall flight-path and both these factors help in significantly increasing the resolution. Since all the ions are accelerated to a uniform kinetic energy, ions of different masses (m/z) will have different velocity in the flight tube following the equation:

$$KE = 1/2\ mv^2$$

where K = kinetic energy, m = mass of the ion and v = velocity of the ion

The mass is related to the time taken to reach the ion detector. The relationship between mass and time is

$$t = k \times m$$

where t is the time taken to reach the detector, k is a constant and m is mass. The true advantage of time-of-flight mass spectrometer is its high speed mass scanning capability.

Since each m/z species has a slightly different velocity, each isotope value will arrive at the detector at a different time. The amount of time for an ion to reach the detector is then converted to a m/z value for all masses and a mass spectrum will be generated. Once the heaviest ion (uranium) in the spectrum has arrived

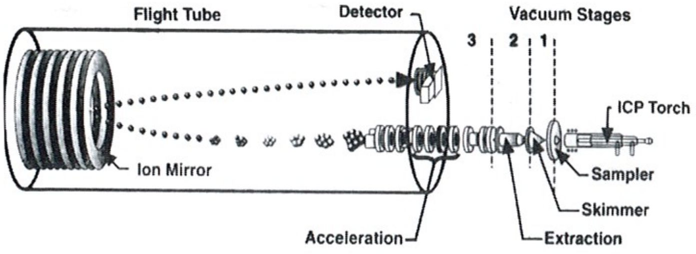

Fig. 7 Schematic diagram of Axial ICP-TOF-MS

at a detector before the smallest mass ion (hydrogen), acceleration of another ion bundle takes place. Acceleration and detection of full mass spectra can take place at a rate as fast as 30 KHz or 30,000 times every second. The continuous production of ions in the ICP requires modulation since a new bundle of ions can only be allowed to enter the flight tube when the heaviest ion reaches the detector. The measurement over the whole mass range is essentially simultaneous and more than 30,000 full mass spectra per second can be acquired. The repetition rate of a TOF-MS instrument is determined by the flight time of the slowest (heaviest) ion. These systems offer possibility of observing individual time slices of entire mass spectrum. For each individual scan, analyte ion intensities are measured simultaneously as compared to the fast but sequential scans obtained from a quadrupole mass spectrometer. This means that isotope ratios can potentially be determined with greater precision than quadrupole systems. The main advantage of ICP-TOF-MS is thus speed, leading to a much higher sample throughput compared to quadrupole and magnetic sector systems. One mass spectra obtained by ICP-TOF-MS is shown in Fig. 8.

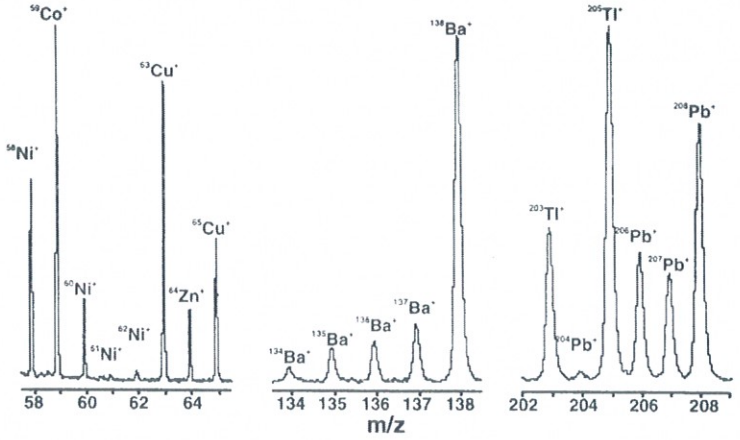

Fig. 8 ICP-TOF-MS spectra

The recent introduction of ICP-TOF-MS in the chemical laboratories opened a number of practical advantages, such as phenomenal data acquisition speed, simultaneous plasma sampling, reduced mass bias, a superior sample throughput, improved accuracy and detection limits, which led to several applications in a wide variety of fields. (Emteborg *et al.,* 1999).

3. Conclusions

Over the past 30 years, the inorganic mass spectrometer instrumentation has also been revolutionized by the use of computers, multi-collector systems, micro-electronics, improvements in efficiency of ion production and vacuum technology, and other advances in ion optical design. Mass spectrometry has progressively adopted technological advances developed in other scientific areas especially in chemical technology to improve the sensitivity and precision with which element and isotopic abundances can be measured. The most recent development in the evolution of mass spectrometry is the advent of quadrupole ICP-MS and subsequent development of HR-ICP-MS and ICP-TOF-MS instruments. These instruments have the advantage of being able to analyze samples in liquid or solid form for most of the elements in the periodic table including Rare Earth Elements and Platinum Group Elements in a variety of samples. The other developments such as cool plasma, collision/reaction cell, collision reaction interface technologies in all forms of ICP-MS instrumentation, their hyphenation to other sample introduction techniques like laser ablation, flow-injection, ultrasonic nebulization, hydride generation, electro-thermal vaporization, HPLC, etc., would increase the utility value of these instruments in several branches of science and industry.

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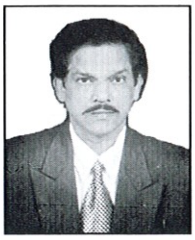

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Mass Spectrometric Studies on Materials of Relevance to Nuclear Fuel Cycle

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1. Introduction

Mass spectrometry plays an important role at various stages of nuclear fuel cycle. Mass spectrometric data from the post-irradiation analysis provides valuable information such as fuel burn-up, isotopic composition of the fissile atoms and fission gas release percentage. Fuel burn-up is one of the parameters that needs to be experimentally measured for validating the reactor physics codes. Spent fuel solutions from the reprocessing plants also need to be analysed for obtaining concentration and isotopic composition data of U and Pu, for the purpose of nuclear material accounting. Thermal Ionisation Mass Spectrometry (TIMS) is an effective tool for measuring the precise and accurate isotopic abundances of solid samples. In favourable cases, elemental concentration could be determined, by employing Isotopic Dilution method [1-5]. The mass spectrometry group at Chemistry Group, Indira Gandhi Centre for Atomic Research, has been employing this method for the determination of isotopic ratios and elemental concentrations of samples related to post irradiation examination of both fast and thermal reactor fuel solutions. A quadrupole based mass spectrometer was also employed for fission gas release studies pertinent to FBTR fuel pins. Some examples are given here to describe the application of mass spectrometry for studies on irradiated fuels.

Most of our initial studies were centered on standardising methods for carrying out isotopic ratio and concentration measurements with spent fuel solutions [6-8]. Uranium separated from dissolved irradiated thoria solutions was mass spectrometrically characterised to prepare ^{233}U spike. Subsequently, spent fuel solutions from thermal and fast reactor were analysed for the isotopic compositions as well as concentrations of uranium and plutonium to deduce burnup [9-11]. Spent fuel solutions from the reprocessing plants were also analysed for obtaining isotopic composition data. Isotopic ratio and concentration measurement of boron in heavy water was carried out to meet the analytical requirements of Madras Atomic Power Station in the initial stages of its commissioning. Extensive analytical support was also given to the boron (^{10}B) enrichment program of the Fast Reactor Technology Group of our Centre, by carrying out isotopic ratio measurements on boron [12]. Exploratory studies were carried out for the determination of isotopic composition of the constituents of stainless steel with a view to develop neutron fluence monitors [13-14]. Dissolved irradiated thoria solutions were analysed for the isotopic concentration of uranium [15]. A summary of these measurements is given in Table 1.

2. The Instrument

A VG Micromass 30 BK mass spectrometer was employed in these studies. It is a 90° sector single focusing magnetic analyser with a radius of curvature of 30.5 cm with a Daly Scintillation detector/Faraday cup for ion detection [Fig. 1]. The data acquisition is done using a PC [16] and/or a recorder. Six filaments can be housed in the sample holder. Originally, the mass spectrometer was operable either in Thermal Ionisation mode or with a Knudsen effusion source. The mass spectrometer has been substantially modified in house subsequently [17,18] and the instrument was bifurcated, to operate both the mass spectrometers simultaneously and independently. A turbo molecular pump has replaced the ion pump/titanium sublimation pump combination, which was originally used for achieving source vacuum. The concentration range of the solutions studied was generally in the range of μg/g or μg/ml. Precision of the isotopic ratio measurements has been around 1 to 2% RSD for minor isotopes and better than 1% for the major isotopes.

TABLE 1: Details of some of the Thermal Ionisation Mass Spectrometric studies carried out in our laboratory for various applications.

Sample	Element	Application	Tracer	Reference
Determination of concentration				
Nd_2O_3	Nd	Standardisation of the analytical method	^{150}Nd	6-7
Heavy water	B	[a]	^{10}B	[b]
Irradiated Thoria solution	U	Calibration of ^{233}U to be used as spike	^{238}U	8
Spent fuel solution from MAPS	Nd	Determination of burn up	^{142}Nd	10
Spent fuel solution from FBTR	U	Determination of burn up	^{233}U	9,20,25
	Pu		^{242}Pu	
	Nd		^{150}Nd	
Irradiated Thoria solution	U	Reprocessing	^{238}U	15
Determination of isotopic composition				
Boric acid	B	^{10}B enrichment		12
Spent fuel solution from KARP reprocessing plant	U	Nuclear Material accounting		[b]
	Pu			
Stainless steel	Fe, Cr, B	Neutron Fluence measurement		13,14

[a] Analysis carried out for MAPS during the first commissioning of MAPS [b] unpublished work

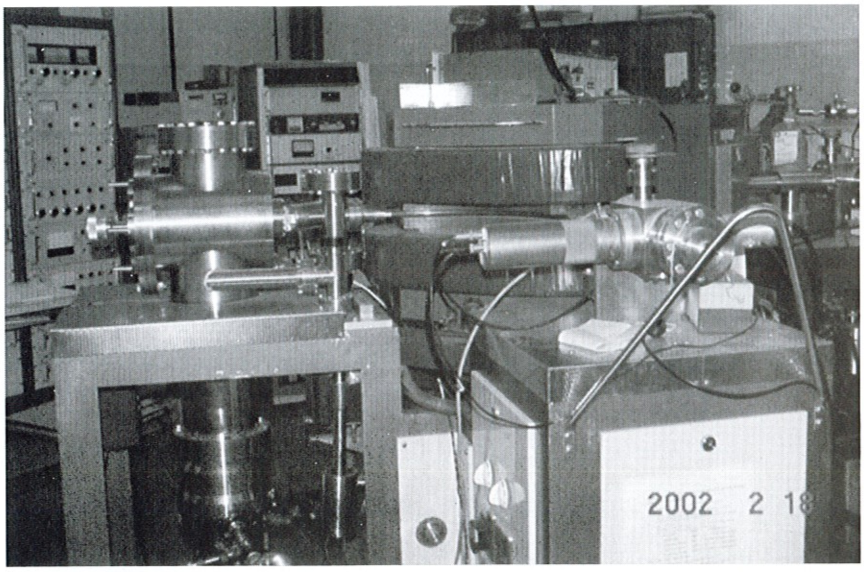

Fig. 1 VG Micro Mass Thermal ionization mass spectrometer employed in the studies.

3. Determination of Burn-up

Fast breeder test reactor at Kalpakkam utilises a uranium-plutonium mixed carbide with a high plutonium content as the fuel (Pu/U+Pu=~0.7). The reactor is being operated successfully with the carbide fuel and has already crossed a burn-up of 155 GWd/t. Employing thermal ionisation mass spectrometry, we have characterised the irradiated fuel solutions discharged at 25, 50 and 100 GWd/t [9, 20, 25, 26]. The aim was to determine the isotopic compositions as well as the concentrations of the actinide elements U and Pu, and of the fission product element Nd and to deduce subsequently the burn-up of the fuel-pellet dissolved.

3.1 Sample preparation

One of the important pre-requisites for reliable mass spectrometric measurements of irradiated fuel solutions is the availability of pure fractions of the elements of interest (U, Pu and fission product monitor Nd in the present case) so as to avoid isobaric interferences. We have standardised the methods of chemical separation of the irradiated mixed carbide fuel solution [11] and subjected the same for mass spectrometric analysis. A two-stage ion exchange procedure has been standardised which yielded well-separated uranium, plutonium and neodymium fractions from the fuel solutions [7]. The separation procedure available in literature [19] has been modified for achieving improved separation efficiency. γ-spectrometry was also employed to ascertain the consistency of elution pattern of rare earth fractions while separating neodymium from other rare-earths [20]. In the case of the dissolver solution of fuel irradiated to 100 GWd/t, neodymium was separated by HPLC method [26]. For obtaining concentration by isotope dilution method (IDMS), appropriate tracers were added to the fuel solutions prior to chemical separation. ^{233}U, ^{242}Pu and ^{150}Nd were employed as tracers for the IDMS measurements with U, Pu and Nd respectively.

3.2 Results of Burn-up measurements

The burn-up data calculated based on reactor codes is compared with those obtained in the present study in Table 2. The burn-up of the fuel discharged at 25 GWd/t was also measured employing HPLC based method standardized in our laboratory [23] and the data is compared in the same table. While the agreement amongst the experimentally obtained burn-up data is good, the calculated data differs marginally from the experimental data. A better agreement was seen in the case of 50 GWd/t (2.45%) and 100 GWd/t (3.8%). The dissolver solution of the fuel discharged at 25 GWd/t corresponds to a pellet at the end portion of the fuel pin and hence the difference in the experimental and calculated values.

TABLE 2: Summary of burn-up data on FBTR mixed carbide fuel. Burn-up data for MAPS fuel is also given in the table for comparison.

Method	Burn-up		Some details about the method	Ref.
	at% Fission	MWd/t		
Mixed carbide fuel of FBTR				
Calculation	2.81	25,000	Reactor physics code	
Mass spectrometry	2.000	17,798	^{148}Nd as fission product monitor	9,11
HPLC based method	1.998	17,778	La as fission product monitor	21
	2.082	18,525	Nd as fission product monitor	21
Calculation	5.62	50,000	Reactor physics code	
Mass Spectrometry	5.49	48,850	^{148}Nd as fission product monitor	20
	10.82	96,280	^{148}Nd as fission product monitor	26
Uranium oxide fuel of MAPS				
Calculation	1.096	9159		
Mass spectrometry	0.900	7520	^{148}Nd as fission product monitor	10
HPLC based method	0.914	7620	Nd as fission product monitor	21
HPLC based method	0.942	7854	La as fission product monitor	21

Mass spectrometric method of burn-up determination has the advantage of obtaining isotopic abundances of the actinides and fission products. The variation of relative abundance of isotopes of uranium, plutonium and neodymium as a function of burn-up is shown in Fig. 2 & 3. Amongst the uranium isotopes a very slight decrease in the relative abundance of ^{235}U with burn-up was seen. In the case of plutonium, the relative abundance of ^{239}Pu has decreased and that of ^{240}Pu has increased with burn-up. These observations are in accord with the relative cross sections for the fast neutron fission. The isotopic composition of fission product neodymium generally remained same within error limits at all the three burn-ups. Difference between

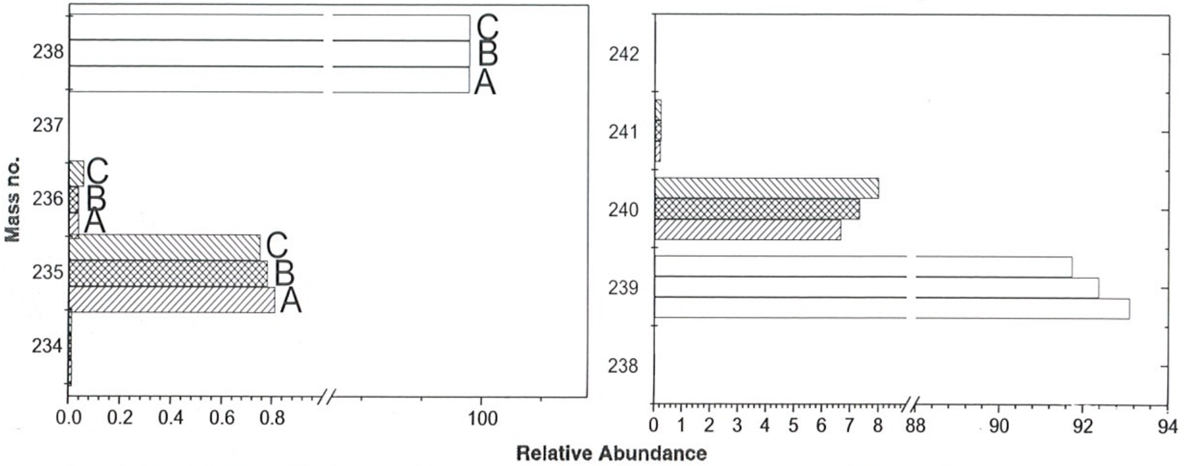

Fig. 2 Comparison of isotopic abundance of U and Pu as a function of burn-up for FBTR fuel.
A. 25,000 MWd/t, B: 50,000 MWd/t, C: 100,000 MWd/t.

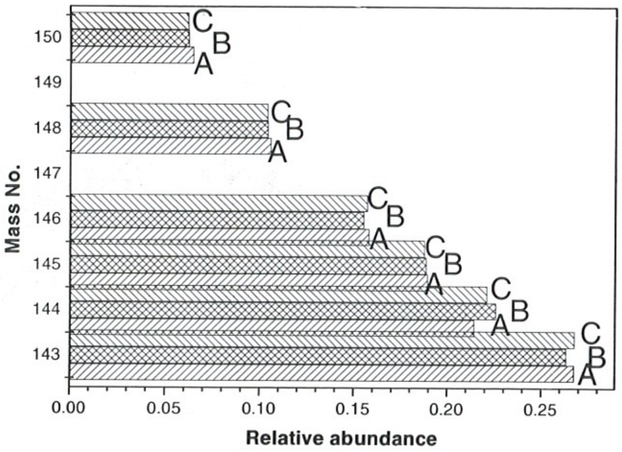

Fig. 3 Comparison of isotopic abundance of Nd as a function of burn-up for FBTR fuel.
A: 25,000 MWd/t B: 50,000 MWd/t, C: 100,000 MWd/t.

relative abundances obtained experimentally and the reported fission yields due to ^{235}U, ^{238}U and ^{239}Pu [22] are compared in Fig. 4. The deviation was almost negligible in the case of ^{239}Pu indicating that the fissions are predominantly due to ^{239}Pu.

U/(U+Pu) ratios, calculated from the experimentally determined concentration of U and Pu in the dissolved solution of 25, 50 and 100 GWd/t and those calculated using KRIGEN code [23] are compared in the Fig. 5. The calculated data while agreeing with the experimental data within 5% shows higher rate of Pu depletion with burn-up. The deviation has increased from ~0.6% at 25 GWd/t to ~1.2% at 100 GWd/t.

4. Fission Gas release measurements

Fission gas release studies on the irradiated fuel pins of thermal and fast reactor is one of the important aspects of post irradiation examination. For a new fuel, the knowledge of percentage release of fission gases is essential for making certain decisions such as continuation of irradiation to higher burn-up or raising the reactor power to higher linear ratings. This is more so for a fuel like mixed carbide fuel where retention of fission gases in fuel pellets could lead to fuel swelling and clad stress.

Mass spectrometry was employed to characterise the irradiated mixed carbide fuel of FBTR for fission gas measurements from the fuel pin [24]. The fission gas samples (krypton, xenon and helium fill-gas) were extracted by employing the specially fabricated device for puncturing the fuel pins and collecting the gas

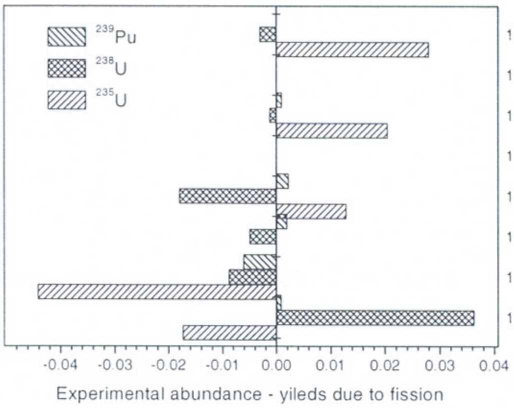

Fig. 4 Experimental abundance – reported fission yields for ^{235}U, ^{238}U and ^{239}Pu. A minimum difference is seen in the case of ^{239}Pu indicating that the fissions are predominantly due to ^{239}Pu

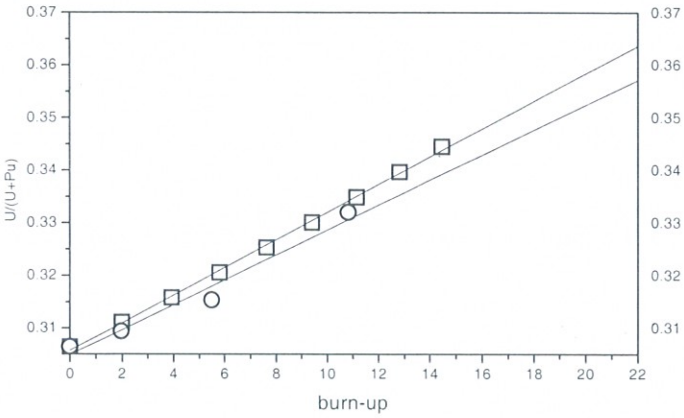

Fig. 5 U/Pu ratio as a function of burn-up for FBTR fuel. The data obtained experimentally and calculated employing KRIGEN code are compared.

samples inside hot cells. The gas collected inside the sample flask was inlet to the mass spectrometer through a micro leak valve, opened to a pre-determined position at which pressure calibrations were done. EXTREL make quadrupole mass spectrometer (which forms a part of the high temperature mass spectrometric facility) was employed for the fission gas analysis.

The isotopic abundance of the fission gases Xe and Kr obtained from a fuel pin discharged after 50 GWd/t is shown in Fig. 6. The isotopic composition of the naturally occurring xenon and krypton are also shown in the same figure for comparison. The average % of fission gas release as a function of burn-up is shown in Fig. 7. If one takes into consideration the helium produced due to α-decay and assumes it to be 100%, the extent of fission gas release increases by a factor of 1.94. Release of krypton from the fuel matrix is higher compared to that of xenon and the total (Xe+Kr) release is nearly equal to that of Xe. The ratio of Xe to Kr in the released fission gas was found to be 5.18±0.14 at 25 GWd/t and 6.70±2.54 at 50 GWd/t when compared to the ratio of the relative yields of xenon and krypton for fast fissions (~10). This is taken as an indication that krypton is loosely bound to the fuel matrix than that of xenon[25].

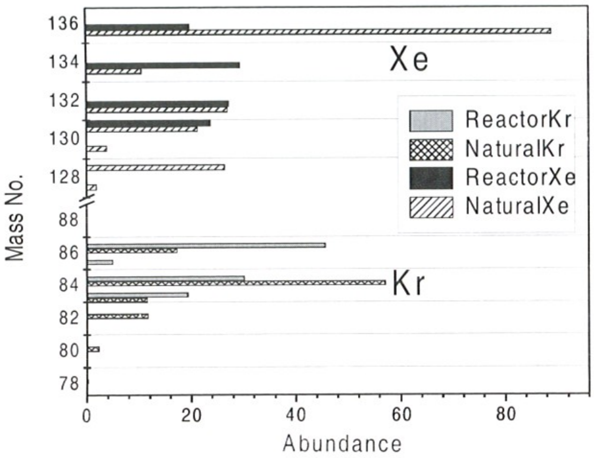

Fig. 6 The isotopic abundance of the fission gases Xe and Kr obtained from a fuel pin discharged after 50,000 MWd/t

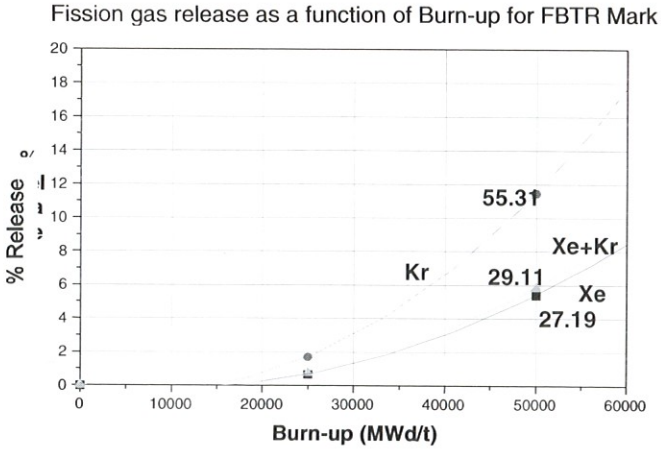

Fig. 7 The average % of fission gas release as a function of burn-up

Acknowledgements

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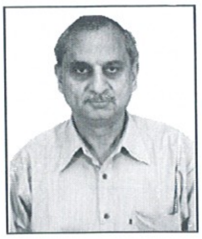

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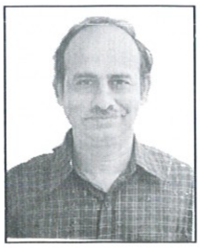

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Measurement of Thermochemical Properties of Nuclear Materials

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1. Introduction

Irradiation of a reactor fuel results in a chemistry of great complexity, because of the generation of a large number of new elements during fission. This is especially so in the case of fast reactor fuels that would be irradiated to high levels of burn-up resulting in the formation of significant amounts of fission products. High temperatures, steep temperature gradients prevailing in the fuel pins and the occurrence of many competing chemical interactions between fuel and fission products, amongst the fission products themselves, between the fission products and the clad, and finally between the fuel and coolant in the event of a clad failure make the chemistry of the fast reactor fuel a challenging subject of study. To understand various aspects pertinent to these chemical interactions, it is necessary to have basic thermodynamic data generated for both condensed and vapour phases of many substances. Thermo-chemical information is also necessary to understand and establish new methods of reprocessing like pyro-chemical reprocessing etc. High temperature mass spectrometry offers a convenient means of obtaining such information.

At Chemistry Group, extensive studies were conducted on binary systems M-Te (M = Fe, Cr, Ni, Mo, Mn) which are of great relevance in understanding the fission product tellurium induced chemical attack of the clad employing Knudsen effusion mass spectrometer. Apart from measurement of vapor pressures and deriving thermodynamic properties, basic aspects of vaporization chemistry are investigated in detail as well, which include:

(i) Determination of homogeneity ranges of non-stoichiometric compounds
(ii) Determination of thermodynamic data across the homogeneity range of non-stoichiometric compounds
(iii) Effects of condensed phase transitions in congruently vaporising systems
(iv) Univariant two-phase vaporization equilibria in a ternary system

These studies have yielded information on vaporization behavior, composition ranges of existence of the non stoichiometric phases and important thermodynamic properties. Application of mass spectrometry to derive thermodynamic information mainly to understand fuel-clad interaction [1-14] are summarised in this paper.

2. The method

The Knudsen effusion mass spectrometric method (or very often referred to as high temperature mass spectrometric method) is a very effective tool for the study of reactions in both gas phase as well as the condensed phase [15]. A mass spectrometer with a Knudsen effusion vapour source, offers a unique opportunity to study both gas phase and gas-solid (or gas-liquid) equilibria. In this method, vapour in equilibrium with one or more condensed phases (either solid or liquid) is sampled, without disturbing the equilibrium conditions, ionised in an ion source (generally an electron impact ion source), mass analysed and detected by using either an electron multiplier and/or a Faraday cup. An electron impact ion source, where electron energy can be varied, enables one to measure the ion intensities of various ions as a function of electron impact energy and derive appearance energies. Gas phase processes like fragmentation, dissociation etc., can be studied with ease. As equilibrium vapour is sampled from the Knudsen effusion cell, it also enables one to study the equilibrium properties (like vapour pressure etc) and arrive at the thermodynamic properties (like enthalpy, entropy etc).

3. The Instrument

A Knudsen effusion mass spectrometric facility (Figure 1) was set up for the first time in the country in 1982. A VG Micromass mass spectrometer (MM 30BK) was employed for vaporization studies. It consists of a Knudsen cell furnace assembly which permits effusion of equilibrium vapour, an electron impact ionization source where the gaseous species are ionized, a 90° sector, single focusing magnetic analyzer (with a radius of curvature of 305 mm) for mass analysis of the positive ions, and a secondary electron multiplier/Faraday cup for ion detection. Alumina Knudsen cells (platinum liner was used in some of the studies) were used in the present study. The Knudsen cell had the dimensions: i.d., 7.5 mm; o.d., 10.0 mm; height, 10.0 mm; and orifice (knife edged) diameter, 0.5 mm. It was placed inside a molybdenum cup having a removable but tightly fitting lid made of tungsten with a 3 mm diameter hole collinear with the Knudsen-cell orifice. This assembly was heated by means of electron bombardment from two encircling tungsten filaments. Temperatures were measured by a chromel-to-alumel thermocouple, inserted through the base of the molybdenum cup and calibrated against the melting temperature of silver. With excellent temperature control, permitted by 'thermocouple control mode' of heating, the temperature measurement was accurate within ± 3 K.

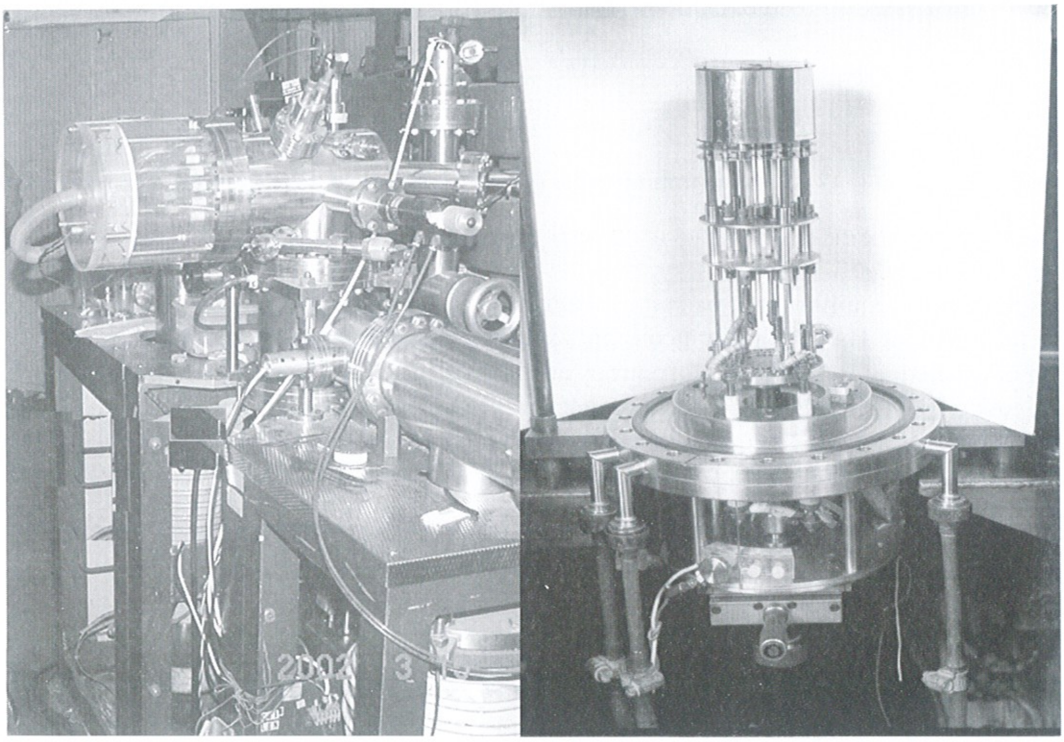

Fig. 1 Knudsen Effusion Mass Spectrometer (VG MM 30BK) and the Electron bombardment furnace used for heating the samples

4. Methodology of determination of various properties using mass spectrometer

Different steps involved in any mass spectrometric measurement are:

(a) Identification of ionic species present in the mass spectrum

(b) Assigning them to respective neutral species

(c) Converting the measured ion intensities to partial pressures

(d) Determination of thermodynamic quantities

Partial pressure is related to ion intensity by the relation: $p = k I^+ T / (s\sigma h)$, where k, is instrument calibration constant, h, the isotopic abundance, s, the multiplier response and σ the ionisation cross-section.

A number of methods have been employed for determining k, the instrumental constant. Some of them are:

(a) Measurement of the ion intensities of a reference material whose vapour pressure is known

(b) Quantitative evaporation of the sample while monitoring the ion intensities

(c) Employing a reliably known equilibrium constant involving some of the species present in the equilibrium vapour

4.1. Determination of Thermodynamic Data

Host of thermodynamic data can be derived from the temperature dependence of partial pressures. One resorts to second-law method or third-law method or both to derive the thermodynamic data [16].

Second-law method: Standard molar Gibbs free energy change (ΔG^o_m) for any general reaction at any given temperature T is given by the relations [16] :

$$\Delta_r G^o_T = -RT \ln K$$

and

$$\Delta_r G^o_T = \Delta_r H^o_T - T\Delta_r S^o_T$$

where K is the equilibrium constant. Combining the two expressions and rearranging gives rise to

$$\ln K = -\Delta_r H^o_T/RT + \Delta_r S^o_T/R.$$

Measurement of equilibrium constant as a function of temperature can thus yield the enthalpy and entropy of the reaction. The equilibrium constant as a function of temperature is fitted to a straight line by the method of least-squares. Enthalpy and entropy are derived from the slope and intercept of such equation. The enthalpies derived using such method, are generally referred to as second-law enthalpies and corresponds to the mean temperature of the investigation. If the heat capacity data of all the constituents of the reaction are available, the enthalpy and entropy can be converted to a reference temperature (generally 298.15 K) by using the relations:

$$\Delta_r H^o_{298.15} = \Delta_r H^o_T - \{ \sum_{products} (H^o_T - H^o_{298.15}) - \sum_{reactants} (H^o_T - H^o_{298.15})\}$$

and

$$\Delta_r S^o_{298.15} = \Delta_r S^o_T - \{ \sum_{products} (S^o_T - S^o_{298.15}) - \sum_{reactants} (S^o_T - S^o_{298.15})\}$$

Third-law method: Enthalpy of reaction can also be written as,

$$\Delta_r H^o_T = -RT \ln K + T\Delta_r S^o_T$$

and

$$\Delta_r H^o_{298.15} = -RT \ln K - T\{ \sum_{products} fef - \sum_{reactants} fef \},$$

where *fef* is the Gibbs free energy function $= -(G^o_T - H^o_{298.15}/T)$.

fef can be calculated from the heat capacity data and absolute entropy at 298.15 K ($S^o_{298.15}$) by using the relation:

$$fef = (H^o_T - H^o_{298.15})/T - (S^o_T - S^o_{298.15}) - S^o_{298.15}$$

where $(H^o_T - H^o_{298.15})$ and $(S^o_T - S^o_{298.15})$ are enthalpy and entropy increments. Enthalpy and entropy increments can be calculated from the heat capacity data. For gaseous species these functions can be calculated from molecular parameters and can be experimentally determined by spectroscopic methods. Many of the compilations of thermodynamic data like JANAF [17] tables should be referred to obtain the enthalpy and entropy increments and Gibbs free energy functions. These are the methods suggested for estimating these functions when experimental data is either partially available or not available at all [17, 18].

Details of identifying the neutral species in the equilibrium vapour, obtaining the temperature dependence of their partial pressures and deriving thermodynamic data by employing Knudsen effusion mass spectrometry can be found in reference 15 and references quoted there in. More details about the instrument, studies on metal-tellurium systems are given elsewhere [19, 20, 21].

4.2. Temperature dependence of partial pressures over Metal-Tellurium systems

The species identified in the equilibrium vapour over different metal telluride systems are given in Table 1. Temperature dependence of partial pressures of $Te_2(g)$ and Te(g) over Metal-Metal Telluride systems studied at Chemistry Group are listed in Table 2 [1-4, 6-8]. The temperature dependence of partial pressures of $Te_2(g)$ and Te(g) over the Metal + Metal rich telluride phases are shown in Figures 2 and 3.

Table 1: Details of the species present in the equilibrium vapour over the Metal-Metal tellurides

System	Phase	Species present in the vapour phase
Fe-Te	$Fe+FeTe_{1-x}$	Te(g) and $Te_2(g)$
	$FeTe_{1-x}+FeTe_{2-y}$	$Te_2(g)$ and $Te_3(g)$
Ni-Te	$Ni+Ni_3Te_2$	Te(g) and $Te_2(g)$
Cr-Te	$Cr+ CrTe_{1-x}$	Te(g) and $Te_2(g)$
Mo-Te	$Mo+ Mo_3Te_4$	Te(g) and $Te_2(g)$
	$Mo_3Te_4 + MoTe_2$	Te(g) and $Te_2(g)$
Mn-Te	$Mn + MnTe_{1-x}$	Mn(g) and Te(g)
	$MnTe_{1-x} + MnTe_{2-y}$	$Te_2(g)$

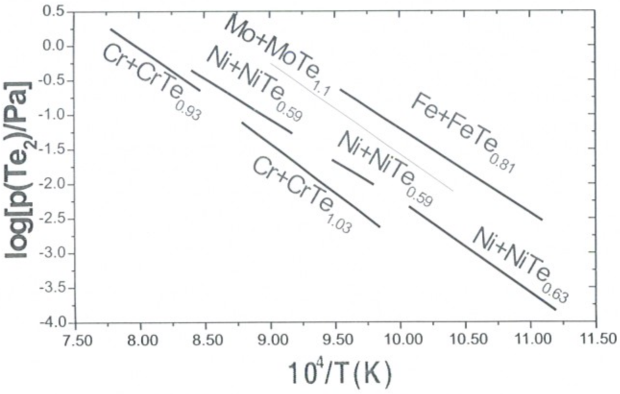

Fig. 2 Partial pressures of $Te_2(g)$ over Metal-Metal Telluride systems studied

Table 2: Temperature dependence of partial pressures of Te (g) and Te$_2$ (g) over Metal-Metal Telluride systems

Species	Phase field	Temperature range (K)	log[p/Pa] = - A/T(K)+B		p/Pa, at 1000 K
			A	B	
Te	Fe+FeTe$_{1-x}$	901-1048	12 227 ± 400	11.03 ± 0.41	6.35×10^{-2}
	Ni+Ni$_3$Te$_2$[a]	893-993	13 350 ± 425	11.11 ± 0.45	5.75×10^{-3}
	Ni+Ni$_3$Te$_2$[b]	1020-1055	11 189 ± 510	8.95 ± 0.49	5.77×10^{-3}
	Ni+Ni$_3$Te$_2$[b]	1090-1190	11 930 ± 400	9.67 ± 0.35	5.50×10^{-3}
	Cr+CrTe$_{1-x}$	1015-1138	14 360 ± 452	11.51 ± 0.42	1.41×10^{-3}
	Cr+CrTe$_{1-x}$[c]	1180-1285	13 091 ± 533	10.44 ± 0.43	2.23×10^{-3}
	Mo+Mo$_3$Te$_4$	960-1110	13 238 ± 116	11.67 ± 0.11	2.70×10^{-2}
	Mn+MnTe	1120-1250	16 099 ± 285	10.53 ± 0.24	2.70×10^{-6}
	Mo$_3$Te$_4$+MoTe$_2$	820-950	14 120 ± 196	13.01 ± 0.22	7.76×10^{-2}
Te$_2$	Fe+FeTe$_{1-x}$	885-1048	10 759 ± 284	11.12 ± 0.29	2.30
	Ni+Ni$_3$Te$_2$[a]	893-993	12 563 ± 223	10.95 ± 0.24	2.44×10^{-2}
	Ni+Ni$_3$Te$_2$[b]	1020-1055	10 883 ± 461	9.31 ± 0.44	2.67×10^{-2}
	Ni+Ni$_3$Te$_2$[b]	1090-1190	11 187 ± 344	9.65 ± 0.30	2.90×10^{-2}
	Cr+CrTe$_{1-x}$	1015-1138	14 894 ± 408	12.00 ± 0.38	1.28×10^{-3}
	Cr+ CrTe $_{1-x}$[c]	1180-1285	13 015 ± 533	10.36 ± 0.43	4.62×10^{-3}
	Mo+Mo$_3$Te$_4$	960-1110	13 631 ± 97	13.00 ± 0.10	2.34×10^{-1}
	FeTe$_{1-x}$+FeTe$_{2-y}$	659-759	11 341 ± 97	13.92 ± 0.14	3.67×10^{-1}[d]
	Mo$_3$Te$_4$+MoTe$_2$	820-950	14 979 ± 210	15.72 ± 0.24	5.51

[a] Ni-rich Ni$_3$Te$_2$ Phase.

[b] High temperature modification of Ni$_3$Te$_2$ phase.

[c] High temperature modification of CrTe$_{1-x}$ phase.

[d] at temperature 790 K.

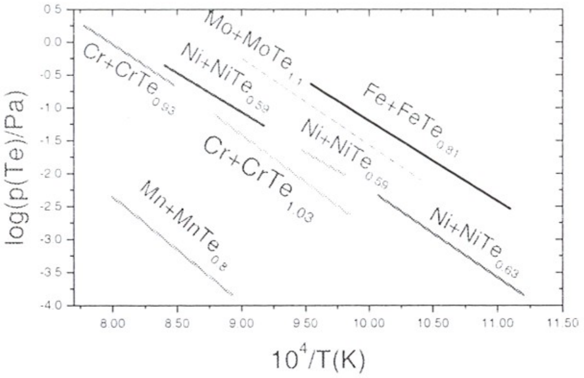

Fig. 3 Partial pressures of Te(g) over Metal-Metal Telluride systems studied

5. Determination of binary phase diagram information

For a sample belonging to a two-component system and vaporising incongruently (vapour phase composition different from that of the condensed phase composition), the pressure-composition-temperature relations of different phases present can be derived. In these experiments, weighed quantities of samples with known initial composition are taken. The ion intensities of the species vaporising are monitored as a function of time and temperature. The weight loss due to vaporisation is obtained by weighing the sample at the end of the experiment. The phase diagram information is obtained by the application of Gibbs phase rule to pressure-composition data. Gibbs phase rule dictates that, for a two component system and at constant temperature, the partial pressure should remain constant when two condensed phases (and vapour phase) are present. When only one condensed phase (and vapour phase) is present then the vapour pressure either increases or decreases depending upon the composition change. This property can be effectively utilised to delineate the phase boundaries. The details of the procedure for converting the ion intensities measured as a function of time to partial pressure as a function of composition and deriving phase diagram information is described in detail elsewhere [15,19-21].

5.1. Determination of homogeneity ranges of non-stoichiometric compounds

Many of the transition metal tellurides exhibit non-stoichiometry. Making use of the property of preferential evaporation of one of the components from these metal tellurides, homogeneity ranges of many of these phases were determined [2, 4, 5, 7, 8, 10]. An example of the studies on Mn-Te system to find out the homogeneity range of the non-stoichiometric phase $MnTe_{1-x}(s)$ is shown in Fig. 4. Equilibrium vapour of the two-phase mixture of Mn(s) and $MnTe_{1-x}(s)$ consisted of Mn(g) and Te(g), with the $p_{Mn}/p_{Te} \sim 10^3$. On continuous vaporisation of the sample isothermally, the condensed phase becomes relatively richer in tellurium. The ion intensities (which are proportional to partial pressures) remain constant so long as the condensed phase is a two phase mixture and vary across the homogeneity range of the non-stoichiometric phase. In the case of $MnTe_{1-x}(s)$, thermodynamic activity of Mn decreases and that of Te increases which is shown in the Fig.4.

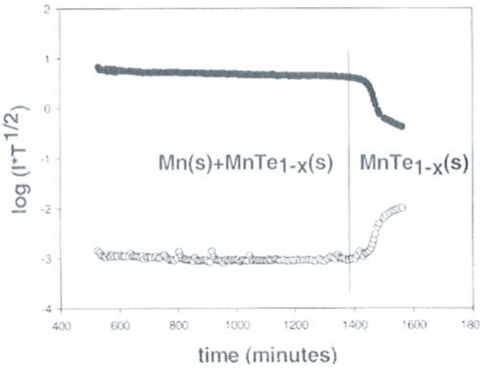

Fig. 4 Determination of the phase boundary of non stoichiometric $MnTe_{1-x}$ phase

The homogeneity ranges of number of non-stoichiometric transition metal telluride phases ($FeTe_{1-x}$, $CrTe_{1-x}$, Mo_3Te_4, $MnTe_{1-x}$) were determined employing Knudsen effusion mass spectrometry and are given in the Table 3.

Table 3: Homogeneity ranges of some of the non-stoichiometric metal telluride phases determined

System	Phase	T(K)	Homogeneity range	
			M-rich	Te-rich
Fe-Te	$FeTe_{1-x}$	868	$FeTe_{0.81}$	$FeTe_{0.94}$
Cr-Te	$CrTe_{1-x1}$	1075	$CrTe_{1.03}$	
Cr-Te	$CrTe_{1-x2}$	1235	$CrTe_{0.93}$	
Mo-Te	Mo_3Te_4	950-975	$MoTe_{1.1}$	$MoTe_{1.3}$
Mn-Te	$MnTe_{1-x}$	1205-1280	$MnTe_{0.8}$	

5.2. Determination of thermodynamic data across the homogeneity range of non-stoichiometric compounds

Besides homogeneity ranges of non-stoichiometric phases, the vaporisation experiments also yielded partial molar thermodynamic quantities across the composition ranges of their existence. The results obtained for the non-stoichiometric phase $MnTe_{2-y}(s)$ are shown in the Fig. 5. The partial molar Gibbs free energies and the integral molar Gibbs free energy of formation of the $MnTe_2$ phase as a function of n(Te)/n(Mn) at T = 650 K are shown in Fig. 5. While the tellurium activity was obtained from the measured partial pressures of $Te_2(g)$, that of manganese was derived by employing Gibbs-Duhem integration method [10]. Thermodynamic data across the homogeneity ranges of the non-stoichiometric telluride compounds determined in such a fashion are given in Table 4.

Table 4: Gibbs energy of formation (kJ/mol) of non-stoichiometric telluride phases determined

System	Phase	T(K)	M-rich		Te-rich	
			Formula	$\Delta_f G^\circ_m$	Formula	$\Delta_f G^\circ_m$
Fe-Te	$FeTe_{1-x}$	298.15	$FeTe_{0.81}$	−21.1	$FeTe_{0.94}$	−29.7
Cr-Te	$CrTe_{1-x1}$	298.15	$CrTe_{1.03}$	−70.3		
Cr-Te	$CrTe_{1-x2}$	1232.5	$CrTe_{0.93}$	−55.7		
Mo-Te	Mo_3Te_4	298.15	$MoTe_{1.1}$	−65.1	$MoTe_{1.3}$	−67.0
Mn-Te	$MnTe_{1-x}$	298.15	$MnTe_{0.8}$	−90.0		
	$MnTe_{2-y}$	650	$MnTe_{1.87}$	−128.8	$MnTe_{2.03}$	−129.0

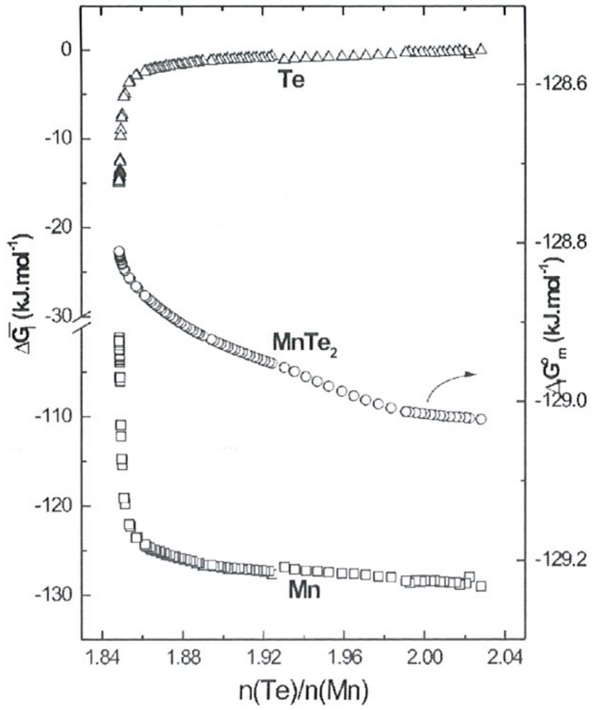

Fig. 5 Partial and Integral thermodynamic quantities across the homogeneity range of the non stoichiometric metal telluride phase, $MnTe_2$ in Mn-Te system.

6. Effects of condensed phase transitions in congruently vaporizing systems

Phase transition of a congruently vaporising condensed phase in a binary system, may be accompanied by a change in the composition. Such variations in the congruently vaporising compositions are reflected in the vaporisation behaviour. $MnTe_{1-x}$ phase (in Mn-Te system) is an example of a congruently vaporising phase which undergoes phase transition from $\alpha \leftrightarrow \beta$ at 1228 K. Variation of ion intensities recorded when the temperature of sample was changed across the phase transition temperature is shown in Fig. 6. Immediately after the temperature change, p(Mn) showed a decrease while p(Te) and $p(Te_2)$ showed an increase. Such an anomalous increase is due to the fact that the congruently vaporizing composition (CVC) of α-MnTe is Mn-rich relative to that of β-MnTe and hence when the temperature is decreased, the condensed phase loses excess tellurium to attain the CVC of the low temperature α-phase. The intermediate stable region where vaporization is incongruent corresponds to three-phase equilibrium involving α, β and vapour. When excess tellurium is lost by effusion from Knudsen cell, the partial pressures returned to those corresponding to CVC of α-MnTe [9, 22].

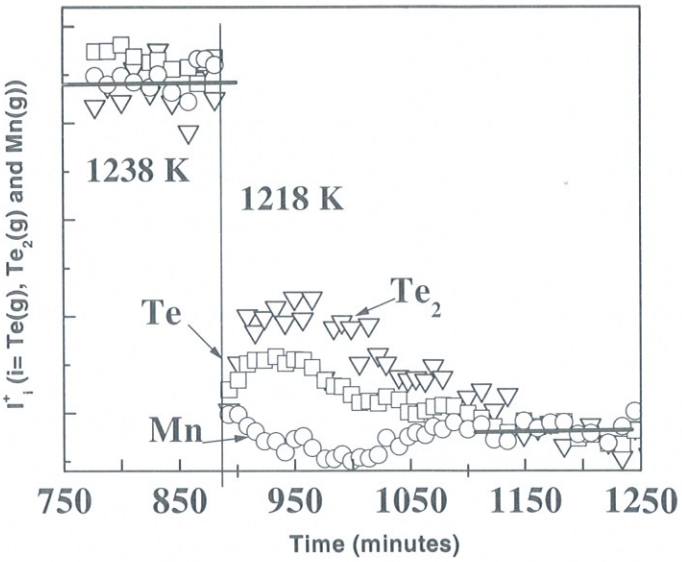

Fig. 6 ion intensities of Mn(g), Te(g) and Te_2(g) over $MnTe_{1-x}$ phase when the sample is subjected to change from 1238 K to 1218 K

7. Univariant two-phase vaporization equilibria in the ternary Mn-Te-O system

A ternary phase diagram of the Mn-Te-O system at 950 K has been established in the composition range in and around the $MnO-TeO_2$ pseudo binary line for the first time (shown in the Fig. 7). Various preparation

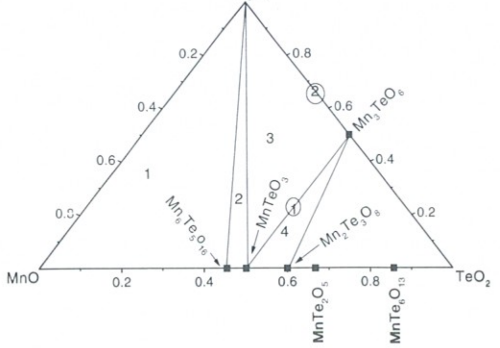

Fig. 7 Ternary phase diagram of Mn-Te-O in the composition range lying on and around $MnO-TeO_2$ binary line.

methods were employed to confirm the coexistence of different ternary phases [13]. Thermodynamic data of the ternary phases $Mn_6Te_5O_{16}(s)$, $MnTeO_3(s)$, $Mn_2Te_3O_8(s)$ and $Mn_3TeO_6(s)$ were determined for the first time [14]. During the course of our detailed investigation on Mn-Te-O system, we identified a univariant two-phase mixture consisting of the phases $MnTeO_3$ and Mn_3TeO_6. The transition from three-phase ($MnTeO_3(s)+Mn_2Te_3O_8(s)+Mn_3TeO_6(s)$) to two-phase mixture ($MnTeO_3(s)+Mn_3TeO_6(s)$) was accompanied by anomalous turn around in the partial pressure of $Te_2(g)$. At 950 K while the partial pressures of $TeO_2(g)$ and $TeO(g)$ decreased monotonically and settled at a lower value, that of $Te_2(g)$ initially decreased and after a turn around increased and settled at a pressures higher than that corresponding to the three phase mixture. The details are shown in Fig. 8.

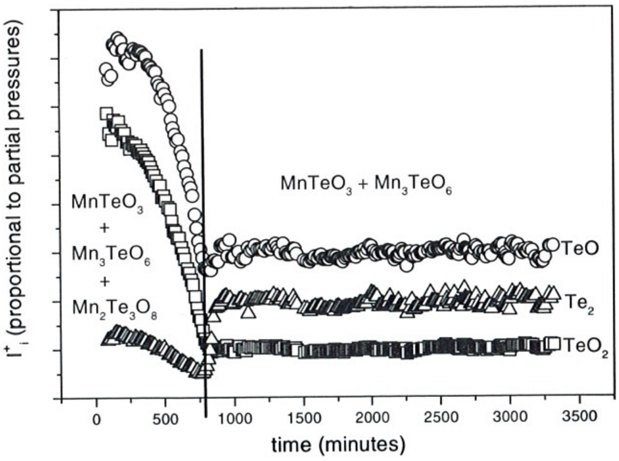

Fig. 8. Variation of ion intensity (proportional to partial pressure) as a function of composition. While partial pressures of TeO(g) and $TeO_2(g)$ decreased when the sample underwent phase transition that of $Te_2(g)$ initially decreases and subsequently increases and settles at a higher value.

The univariant nature of vaporization of the two-phase mixture ($MnTeO_3 + Mn_3TeO_6$), was verified by calculating the Te-to-O ratio in the effusate ($R_{effusate}$). The variation of $R_{effusate}$ as a function of time during two vaporisation experiments is shown in Fig. 9. $R_{effusate}$ value, which was initially around 0.5 increased to

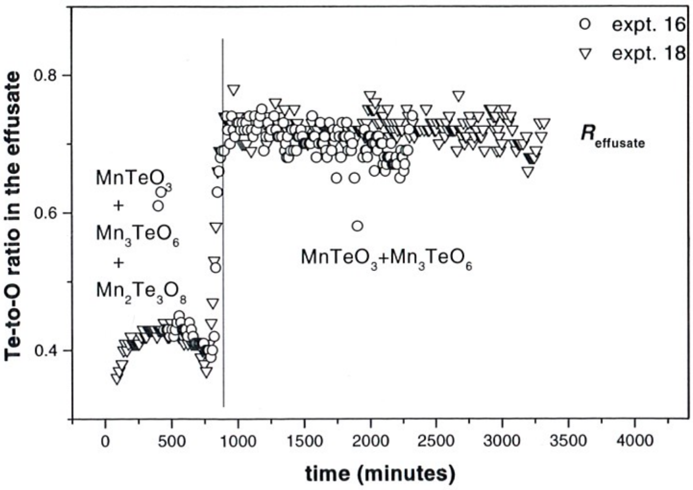

Fig. 9 Variation of Te-to-O ratio in the effusate ($R_{effusate}$) as a function of time during two vaporisation experiments

0.7 before remaining constant for the rest of the duration of each experiment. We believe that the kind of univariant, quasi congruent vaporization behaviour, observed by us in this ternary system is rather uncommon, with the pertinent ternary phases $MnTeO_3$ and Mn_3TeO_6 lying on two different tie lines joining the binary oxides of Mn and Te[23].

Acknowledgements

What is presented here is the work of the entire mass spectrometric group. It is a pleasure to acknowledge the contributions of the members of the group, Shri. R. Balasubramanian, Smt. S. Nalini, Shri D. Darwin Albert Raj and Dr. R. Viswanathan.

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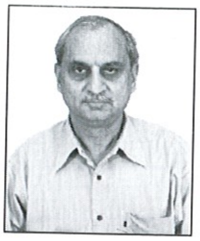

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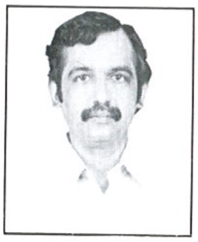

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Thermodynamic Properties of Fission Product Carbides

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1. Introduction

The FBTR fuel is a two-phase mixture of (U,Pu)C and $(U,Pu)_2C_3$ with an overall Pu/(U+Pu) ratio of 0.7 for Mark I fuel and 0.55 for Mark II fuel. The sesqui-carbide phase (6-12 wt% for Mark I fuel) is expected to be richer in Pu than the mono-carbide phase; in the case of the Mark I fuel, in fact the M_2C_3 has a Pu/(U+Pu) ratio of nearly one. This fuel is subjected to fast neutrons, high-temperatures and thermal gradient and has reached a burn-up well beyond 150 GWd/t. The chemical state of the carbide fuel at such high burn-up which in turn depends on the carbon potential of the fuel needs to be determined[1]. The carbon potential of the fuel depends on a number of factors like sesquicarbide content, plutonium content and oxygen impurity. The chemical state of the fuel influences the chemical state of fission products. The thermodynamics of the carbides of the fission products like rare earths, barium, strontium, molybdenum and zirconium plays a significant role in the determination of the chemical state of the fuel. As rare earths (constitute about 30% of the total fission yield), exhibit different type of carbides like monocarbide, sesquicarbide and dicarbides and since they can be substituted for plutonium in various studies, an experimental programme to determine the thermodynamic properties of rare earth dicarbides was initiated in our laboratory.

2. Thermodynamic Properties of Rare Earth Dicarbides

Even though a large amount of information is available on the chemistry of rare earth elements in aqueous and organic solutions, much less is known with respect to their basic binary compounds especially the carbides. A survey in the literature revealed that only limited thermodynamic data of rare earth dicarbides are available and there is considerable discrepancy in the reported thermodynamic data, owing to their high reactivity and susceptibility to hydrolysis, which make them difficult to work with. Though a number of standard techniques like effusion techniques, EMF methods and calorimetric methods have been utilised in the determination of thermodynamic data almost all of the methods suffer the disadvantages like handling of the reactive carbide, long equilibration times which results in the reaction of sample with the container and requirement of high temperatures for determination of the data (EMF methods are done at low temperatures). None of the methods are particularly useful for determining the thermodynamic properties of the dicarbides between 1200 - 1700 K that happens to be the operating temperature range of the nuclear reactor. A new method, termed as the *Dynamic effusion mass spectrometric method*, has been developed in our laboratory to determine the thermodynamic properties of dicarbides.

3. Dynamic Effusion Mass Spectrometric Method

The *Dynamic effusion MS method* which was developed for the determination of equilibrium pressures of CO(g) in the carbide-oxide-graphite equilibria, is described. As this method involves the continuous measurement of effusion pressures under dynamic conditions by using a mass spectrometer, this method is termed as the *Dynamic effusion MS method.* This method has broad applicability and does not suffer from many of the disadvantages of the other vapour pressure measurement techniques described in the earlier section. It makes use of the fast reaction between the oxide and the carbide(or carbon) at high temperatures[2]. The salient features of this method are in its simplicity of equipment, very small equilibration times and in that the dicarbide phase whose properties are to be determined, is generated *in situ* by the carbothermic reduction of the corresponding oxide. A highly compacted pellet of the sample containing an intimate mixture of the oxide, carbide and/or graphite is heated to high temperatures. The rate of release of CO(g) through the pores of the pellet is measured as a function of time. This can be related to the equilibrium pressure of CO(g) for the given phase field, at that temperature. The principle and the theory of the method have been discussed in detail in an earlier publication[3].

The carbothermic reduction of the oxide proceeds according to the following equation

$$\langle REO_{1.5}\rangle + 3.5 \langle C\rangle \langle LnC_2\rangle + 1.5\ (CO)\ \{RE=La,Nd,Sm,Dy,Gd\} \tag{1}$$

$$\langle CeO_2\rangle + 4 \langle C\rangle \langle CeC_2\rangle + 2\ (CO) \tag{2}$$

The effusion pressures of CO(g) is measured by means of a quadrupole mass spectrometer from which the equilibrium CO pressure over the dicarbide-oxide-graphite phase field can be computed. From the equilibrium pressure the Gibbs energy of formation and enthalpy of formation of the dicarbide have been determined.

3.1 Experimental procedure

Samples were prepared from mixtures of $REO_{1.5}(s)/CeO_2(s)$ and C(s) (purity >99.999 %). The oxide was blended with graphite slightly in excess of the stoichiometric amounts. The sample was then pelletised at 25 MPa to give pellets with the dimensions 6 mm in diameter, 1 mm in thickness and weighing about 90 - 100 mg. The pellets were degassed at around 473 K for 12 hours in vacuum before the experiment. The pellets were heated rapidly at about 100 K min^{-1} to the experimental temperatures by means of an induction generator in a high vacuum chamber (Fig. 1) and maintained there for short time periods (approx. 10 minutes). During this time the CO(g) effusing out of the pellet through the wide mouthed, open tantalum crucible was recorded as a function of time by using the quadrupole mass spectrometer (SPECTRAMASS, DAQ/DXM 200 or SRS RGA 200). After recording the decay of CO(g) for about 5 minutes the furnace power was lowered to zero and after about five minutes, the same pellet was heated to the next higher temperature and the experiment was continued. The steps as mentioned above were repeated until the effusion pressures crossed the limiting operating pressure of the QMS (approx. 10^{-7} bar). Temperatures were measured with an optical pyrometer, which was sighted onto a blackbody hole on the side of the crucible.

At the end of each experiment, the sample was analysed for the phases present by X-ray diffraction (Debye-Scherrer) employing Cu-K_α radiation. Care was taken to avoid the reaction of lanthanum carbide

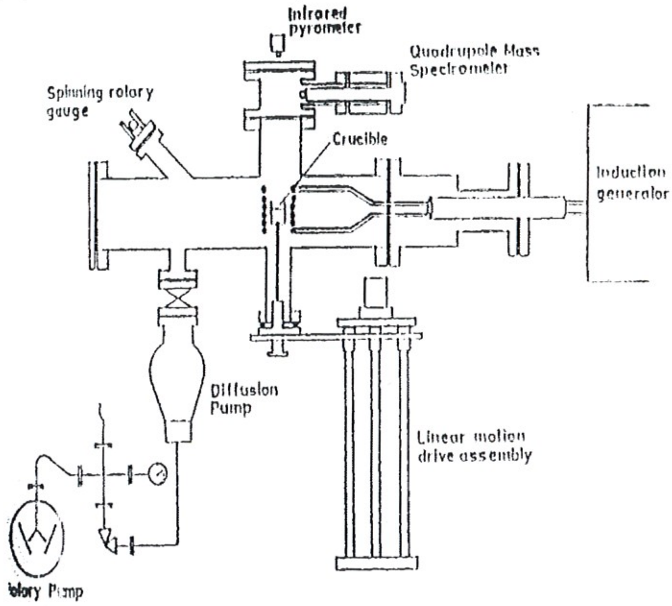

Fig. 1 Schematic of the experimental set-up

with air/moisture during the XRD measurements by coating the sample with xylene. The reacted pellets were also examined by means of an optical microscope in order to establish the formation of a different phase.

3.2. Method of calculation

The equilibrium CO(g) pressure in the pellet was computed by measuring the CO(g) pressure in the high vacuum chamber as a function of time by using a quadrupole mass spectrometer as described below. The CO(g) released by the carbothermic reduction of the oxide accumulates in the pores of the pellet that gets sintered during the process. The effusion of the gas through the pores of the pellet causes the CO(g) pressure in the chamber, to increase to a maximum value very quickly and then to fall. This process can be described in terms of the rate of production of CO(g) in the pellet, its release to the vacuum chamber and its ultimate removal from the vacuum chamber by the pumping action. When the rate of production of the gas inside the pellet is higher than its release from the pellet, there is an increase of pressure in the pellet. Since the rate of pumping out is very high in comparison to the rate of release to the chamber, the chamber pressure will indicate the pressure inside in the pellet.

The pressure, p_{eff}, of CO(g) in the chamber (after subtracting the background pressure) at 298 K, as a function of time 't' as recorded by the QMS, was plotted against the time, t. The CO(g) pressure increased to a maximum value initially and then decreased exponentially. The decay portion of the curve was fitted to an exponential function of the form:

$$p_{eff} = p_o \,.\, e^{-kt} \tag{3}$$

p_o and k are the constants derived from the least-square fitting of this data. k is termed as the decay factor which denotes the rate of effusion of CO(g) from the pellet and is a constant for a given sample at that temperature. p_o is the maximum CO(g) pressure. From the values of p_o and k for a particular temperature, the equilibrium CO(g) pressure, p_{CO}, for that temperature was calculated according to the equation :

$$p_{CO} = p_o T k^{-1} C \tag{4}$$

The derivation of the above mentioned equation is reported in our previous paper[1]. T is the temperature of the pellet and C is a constant. For our system the nominal value of C is approximately equal to unity.

3.3. Validation of the method

The *Dynamic effusion MS method* has been validated by determining the equilibrium CO pressures over a well-studied unambiguous system like, Al_2O_3-C-Al_4C_3. The experimental data on the measurement of equilibrium CO pressures are given in Table 1.

TABLE 1: Equilibrium CO(g) pressures over the Al_2O_3 – C – Al_4C_3 system

T(K)	Max.Chamber Pressure (p_o) torr	Decay factor (k)	Equilibrium Pressure (P_o) (atm)	P_{th}	$C = P_o/P_{th}$
1423	6.55E-7*	0.36198	3.39E-6	3.40E-6	0.9953
1528	1.22E-6	0.06806	3.49E-5	3.50E-5	0.9992
1548	2.15E-6	0.08493	5.15E-5	5.27E-5	0.9764
1553	3.93E-6	0.13799	5.82E-5	5.85E-5	0.9941
1598	8.78E-6	0.12749	1.45E-4	1.40E-4	1.0336
1608	2.01E-6	0.02416	1.76E-4	1.69E-4	1.0420
1613	9.86E-6	0.10885	1.84E-4	1.85E-4	0.9880
1673	7.19E-6	0.02711	5.84E-4	5.45E-4	1.0703
1713	1.51E-5	0.03179	1.07E-3	1.07E-3	1.0005
1718	1.45E-5	0.02896	1.13E-3	1.16E-3	0.9747

* Read as 6.55×10^{-7}

The first three columns of the table list the sample temperature, the maximum pressure in the chamber, and the decay factor, *k*, respectively. The measured pressure, calculated by using equation 4 and by taking $C = 1$, is compared with the theoretical pressure, P_{th}, computed from the available thermodynamic data[4] of Al_2O_3 and Al_4C_3. The last column of the table, C, gives the ratio of the measured pressure and the theoretical pressure. It can be seen that this value is 1.008 ± 0.047, which is very close to 1. [5].

3.4 Absence of oxycarbide

One of the problems of preparing the carbide by carbothermic reduction is the possibility of formation of an oxycarbide. The schematic of the reaction pathway is given in Fig. 2.

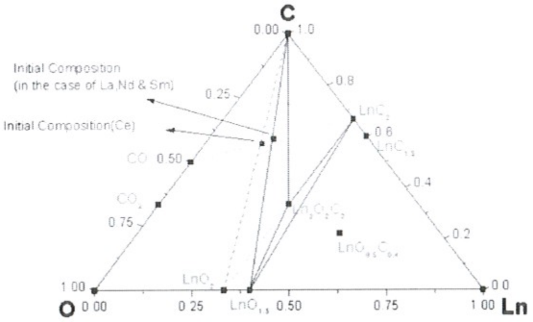

Fig. 2 Reaction pathway

It is obvious from the figure that the oxycarbides intercepts the reaction pathway only in the case of reduction of $LaO_{1.5}$, CeO_2 and $NdO_{1.5}$ as the known oxycarbide in each case has been $RE_2O_2C_2$[RE=La,Ce,Nd] while oxycarbide of the type $REO_{0.5}C_{0.4}$ [RE=Sm,Dy] are only known to exist. The absence of formation of the oxycarbide has been disproved in all our experiments due to the following reasons. Firstly, as the crystal structures of the oxycarbide and the dicarbide are different the characteristic XRD diffraction lines in each case are significantly different from the other. Secondly, the reaction equilibration time is extremely small thereby minimising the probability of interaction between the oxide and dicarbide. Thirdly, it has been observed that most oxycarbides are likely to be stable at much higher temperatures than our reaction temperature regime.

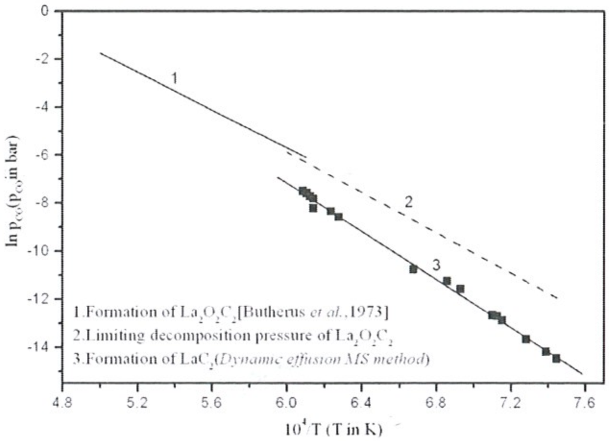

Fig. 3 A plot of ln p_{CO} against Temperature for the $LaO_{1.5} - C - LaC_2$

An attempt was made to prove the absence of formation of oxycarbides by using the mass spectrometric technique in the present study. From the Gibbs energies of formation of the oxycarbides that are available in the literature, the equilibrium CO(g) pressures over the oxycarbide-oxide-graphite phase field has been calculated. The limiting pressures for the decomposition of the oxycarbide, $RE_2O_2C_2$[RE=La,Ce,Nd], to the corresponding dicarbide (REC_2) have been calculated based on the results from the *Dynamic effusion MS method* and from the corresponding Gibbs energies of formation reported in literature[6] and have been plotted in the case of $LaO_{1.5}$-C-LaC_2 system in Fig. 3. The lower p_{CO} pressures obtained in the present study in comparison to the calculated limiting pressures is taken as further confirmation of absence of the oxycarbide phase.

3.5. Confirmation of the phases

The XRD pattern of the sample at the end of the measurement indicated the presence of the three-phase mixture $REO_{1.5}$(s), REC_2(s) and C(s). The same was observed in one of the samples which was quenched after seeing a temperature of about 1300 K, the minimum of the temperature range of the present measurements. An independent high temperature XRD by heating the oxide-graphite mixture from 1373 to 1773 K was carried out in the case of each of the rare earths in order to ensure the presence of requisite phases at the time of measurement of equilibrium CO(g) pressures.

4. Derivation of thermodynamic data

4.1. CO pressures and Gibbs energies of formation of the dicarbide

The equilibrium CO(g) pressures over the various RE-C-O [RE:La,Ce,Nd,Sm and Dy] have been plotted in Fig. 4[7-11].

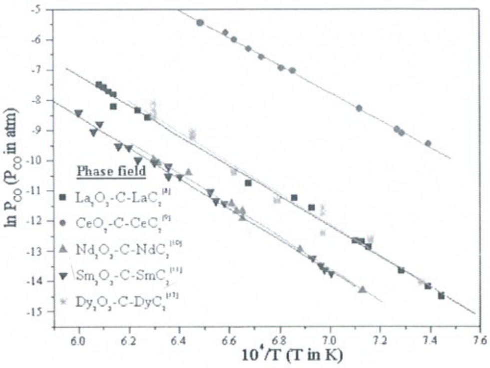

Fig. 4 Plots of ln p_{CO} against temperature for various $REO_{1.5}$ – C – REC_2 phase fields

TABLE 2: List of equilibrium CO(g) pressure equations for the various $REO_{1.5}$ – C – REC_2 phase fields along with the temperature range

S.No.	Condensed phases	Vapour pressures(in bar) ln p_{CO} = B–A/T	Temperature range T (in K)
1.	La_2O_3 (s) – C (s) – LaC_2 (s) [7]	22.9 – (50130/T)	1350 – 1650
2.	CeO_2 (s) – C (s) – CeC_2 (s) [8]	23.6 – (45609/T)	1350 – 1550
3.	Nd_2O_3 (s) – C (s) – NdC_2 (s) [9]	23.5 – (53013/T)	1400 – 1600
4.	Sm_2O_3 (s) – C (s) – SmC_2 (s) [10]	22.6 – (52000/T)	1425 – 1675
5.	Dy_2O_3 (s) – C (s) – DyC_2 (s) [11]	23.8 – (51282/T)	1350 – 1600

Table 2. lists the dependence of ln p_{CO} with reciprocal temperature for the various RE-C-O system along with the temperature regions in which the equations are valid.

The Gibbs energies of the reaction(1) in the case of each of the RE-C-O systems were derived from the corresponding equilibrium CO(g) pressures. By incorporating the appropriate Gibbs energy data of the other constituents (oxide,graphite,CO) from literature[4], the Gibbs energy of formation of the rare earth carbide at the experimental temperature range could be calculated (Fig. 5).

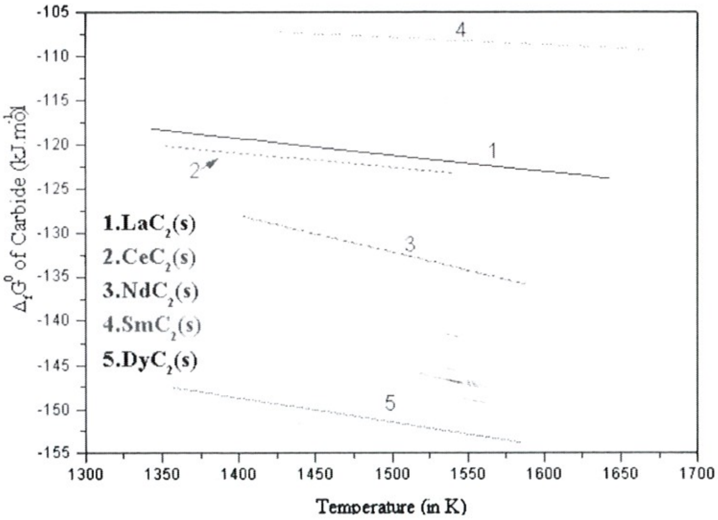

Fig. 5 Plots of $\Delta_fG^\circ_{298}$ against temperature for the various rare earth carbides

4.2. Enthalpies of formation of the dicarbide

The second-law enthalpies of the respective reactions (equation (1) and (2)) at the mid-temperature of measurement was obtained from the slope of the ln p_{CO} versus 1/T curve. The enthalpy of reaction (equation (1) and (2)) at the mid-temperature of measurement was converted to the enthalpy of the reaction at 298 K by including the corresponding enthalpy increments of $REO_{1.5}$(s), C(s) and CO (g) from the literature [4]. Enthalpy increments of REC_2(s) were estimated as suggested in the following equation (5)

$$\{(H^\circ_T - H^\circ_{298})_{REC_2\,(s)} = (H^\circ_T - H^\circ_{298})_{CaC_2(s)} - (H^\circ_T - H^\circ_{298})_{Ca(s)} + (H^\circ_T - H^\circ_{298})_{RE\,(s)} \qquad (5)$$

$$((G^\circ_T - H^\circ_{298})/T)_{REC_2\,(s)} = ((G^\circ_T - H^\circ_{298})/T)_{CaC_2(s)} - ((G^\circ_T - H^\circ_{298})/T)_{RE\,(s)} \qquad (6)$$

From the corresponding functions of isomorphous CaC_2[3] in the absence of experimentally determined thermal functions. Similarly, the third-law enthalpy of reactions was derived from each of the equilibrium CO pressure data at each temperature, by using the Gibbs energy functions of $REO_{1.5}$(s), C(s), CO(g) from the literature[4] and that of REC_2(s) estimated from the Gibbs energy functions of CaC_2 as described in equation (6) mentioned above. The thermodynamic functions of REC_2(s) were also calculated by using the corresponding thermal functions of $UC_{1.94}$[4] and $ThC_{1.94}$[4] (as per equation 5 and 6) and used for deriving the enthalpy of reaction using the second-law and third-law methods.

The enthalpies of formation of REC_2(s) at 298 K were derived from the corresponding enthalpies of appropriate reaction (derived using the second-law and third-law methods) and by taking the values for the enthalpies of formation of $REO_{1.5}$(s), C(s) and CO(g) at 298 K, from the literature [4]. A tabulation of the enthalpy of the reaction and the enthalpy of formation of individual rare earth by second and third law methods are indicated in Table 3.

TABLE 3: Comparison of the enthalpies of formation of various rare earth dicarbides derived using the *Dynamic effusion MS method*

Dicarbide	$\Delta_f H^\circ_{298}$ (kJ , mol^{-1})						
	based on the thermal functions of the dicarbide derived from the corresponding functions of						
	CaC_2 (s)		$UC_{1.94}$ (s)		$ThC_{1.94}$ (s)		Selected value#
	2nd law	3rd law	2nd law	3rd law	2nd law	3rd law	
LaC_2 (s)(7)	– 90.6 ± 8.4	– 80.1 ± 3.6	– 75.4 ± 8.4	– 57.8 ± 3.6	– 95.4 ± 8.4	– 59.5 ± 3.6	– 58.6 ± 10.1
CeC_2 (s)(8)	– 95.5 ± 9.0	– 96.8 ± 1.4	– 80.1 ± 9.0	– 118.8 ± 1.4	– 100.1 ± 9.0	– 121.4 ± 1.4	– 120.1 ± 11.0
NdC_2 (s)(9)	– 70.1 ± 8.6	– 67.3 ± 1.0	– 51.5 ± 8.6	– 90.1 ± 1.0	– 74.7 ± 8.6	– 91.6 ± 1.0	– 90.8 ± 6.0
SmC_2 (s)(10)	– 72.0 ± 7.0	– 75.0 ± 3.0	– 56.0 ± 7.0	– 84.0 ± 3.0	– 76.0 ± 7.0	– 86.0 ± 30	– 85.0 ± 8.0
DyC_2 (s)(11)	– 100 ± 18	– 107 ± 5	– 83 ± 18	– 130 ± 5	– 105 ± 18	– 132 ± 5	– 131 ± 19

#- Overall error in the measurement

5. Conclusions

A new method termed as the *Dynamic effusion mass spectrometric method* has been developed in order to determine the thermodynamic properties of highly reactive rare earth dicarbides. These properties were compared with the properties of the fuel in order to arrive at the chemical state of rare earth fission products in irradiated fuel.

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Applications of Mass spectrometry in Reprocessing Plants and for Nuclear Material Accounting

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1. Introduction

In a reprocessing plant, special nuclear materials namely plutonium and uranium are separated from the irradiated fuel dissolved solution containing host of fission products by process called PUREX. Proper accounting of these nuclear materials is essential due to the strategic importance, propensity for criticality and other health and safety aspects associated with it. Hence, a well defined nuclear material accounting procedure is followed either under international safeguards or under state system. For the purpose of nuclear material accounting, it is essential to determine precisely and accurately the amount of plutonium and uranium present in input, products and waste discards of the reprocessing plant. Among these key measurement points, input assumes greater importance as it is the first point in the fuel cycle plutonium produced in the reactors is physically measured and compared with the data predicted by the reactor physics. Thermal ionization mass spectrometer (TIMS) plays an important role in the determination of plutonium and uranium present in the input solution and isotope dilution mass spectrometry (IDMS) is the only accepted measurement technique for this purpose because of its high precision, better sensitivity and tolerance of non-quantative separation . Isotope composition of plutonium and uranium at the input and products are also required to be carried out to know the fissile content and also to supplement the data on specific activity of the plutonium for the radiometric method followed in process and plant control analysis. TIMS is best suited instrument for the precise and accurate isotope ratio measurements of plutonium and uranium in solution. The paper presents our experiences in the use of thermal ionization mass spectrometer in the two power reactor reprocessing plants, viz., PREFRE, Tarapur and KARP, Kalpakkam.

2. Nuclear material accounting

Fuel reprocessing plants are termed as bulk handling facilities for the purpose of nuclear material accounting. In these facilities special nuclear materials like plutonium and uranium are separated from spent fuels by PUREX process. Handling of such special fissionable materials is associated with conventional safety as well as security aspects which demand an efficient and sensitive nuclear material accounting and surveillance practices. The Material Unaccounted For (MUF) statement derived from material balance equation is internationally accepted as an index of assurance with respect to physical presence of nuclear material. Material balance equation is given as,

$$\text{MUF or ID} = (\text{BI} + \text{I}) - (\text{P} + \text{WD} + \text{EI})$$

where ID is inventory difference BI and EI are Beginning Inventory & Ending Inventory, I, P & WD are input, product and waste discard of the plant.

One of the factors contributing to MUF is the error associated with the measurement which is indicated by LEMUF (Limit of Error for MUF). Hence, measurement errors should be as low as achievable to determine the true magnitude of MUF. It is achieved by following highly precise and accurate measurement techniques for the input and product of the plant where bulk of the material processed is accounted. Irradiated fuel dissolved solution is accounted for the plutonium and uranium content at the input point and isotope dilution mass spectrometry is the only universally accepted technique for the purpose of guaranteeing high precision accuracy and sensitivity. High amount of fission products associated with plutonium necessitates a high sensitive method. Thermal ionization mass spectrometers are best suited for precise isotope ratio measurement[1] of plutonium and uranium which yields a valuable information on their fissile content as all the isotopes are not fissionable.

It is required to determine the total quantity of nuclear material present in a tank for the purpose of nuclear material accounting. Generally, an analytical method gives concentration of U or Pu in wt/lit, which needs to be multiplied by volume or weight of the solution in the tank to obtain quantity of U or Pu. The volume or weight of solution present in the tank is measured remotely by differential pressure method. TIMS also plays a key role in calibrating the tank for obtaining the volume of the solution and an independent method also developed to determine the total quantity of plutonium without having to know the volume of the solution as described later in the chapter

3. Instruments used in reprocessing plants

Application of mass spectrometry in reprocessing in India was started for the first time in 1974 at PREFRE, Tarapur using an indigenously developed TIMS by TPPED, BARC. It was a single collector instrument using electron multiplier in magnetic scan mode. The instrument was successfully used in several processing campaigns including two safeguards campaigns. Subsequently a commercial TIMS having multi collector system capable of giving ultra high precision in the isotope ratio measurement of U and Pu was installed in 1984 for the same application and since then extensively being used. For the next power reactor reprocessing plant at Kalpakkam, again an indigenously developed TIMS from TPPED / MSESS BARC was installed in 1999.

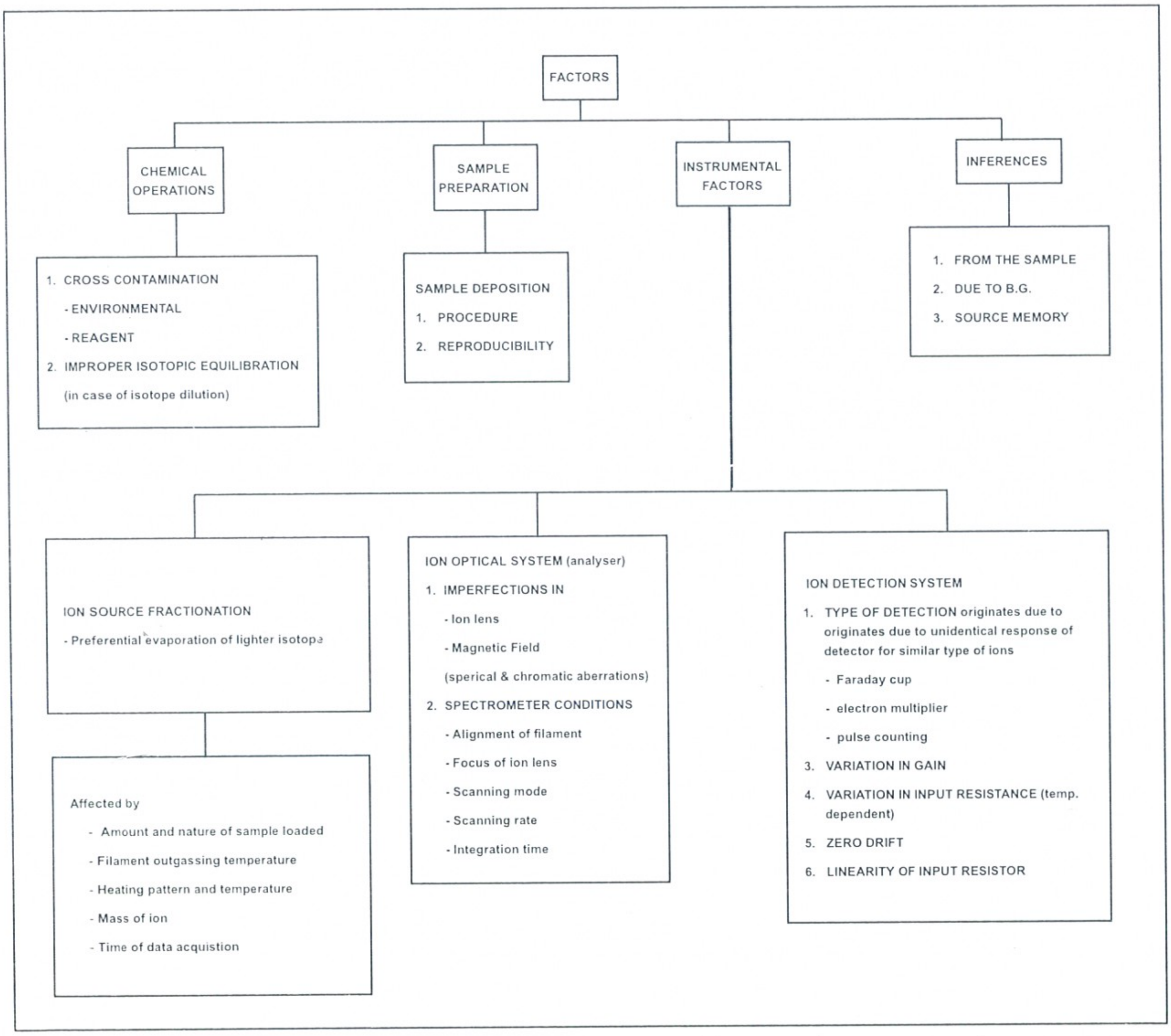

Fig. 1 Factors governing accuracy and precision of isotope ratio measurement

4. Problems faced in precise isotope ratio measurement

The reliability of isotope ratio analysis using thermal ionization mass spectrometer is mainly limited[2] by the following parameters, (i) Chemical operation prior to mass analysis, (ii) sample preparation and deposition, (iii) instrumental factors and (iv) interferences. Fig. 1 gives further details of these parameters.

4.1 Mass discrimination in source

Among the contributing factors, mass discrimination at source due to fractionation[3–5] is an important one to be looked into. Fractionation is the process by which lighter isotope is preferentially vaporized and ionized thereby leading to variable systematic error. Fraction curve, a plot of isotope ratio with time is shown in Fig. 2. There are various factors which influence the reproducibility of fractionation curve namely, (i) amount and nature of sample deposited, (ii) filament degassing temperature, (iii) heating pattern, (iv) mass difference of the isotopes and (v) duration of data collection.

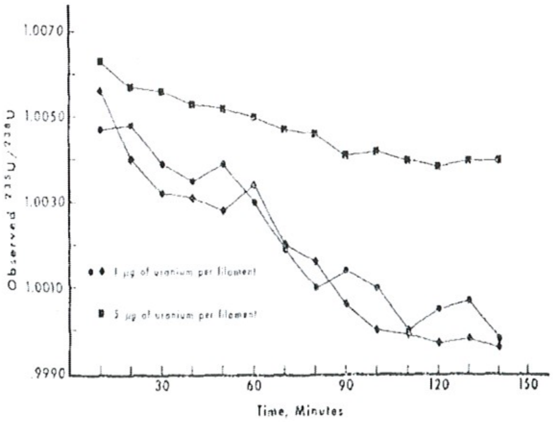

Fig. 2 Uranium isotopic fractionation curves: 1 μg and 5 μg of uranium on filament[3]

4.2 Correction methods for mass discrimination

4.2.1 Use of external isotope standard

Isotope standard of similar composition is analyzed under a set of parameters. All these factors are critically controlled and maintained constant for standard as well as sample so that a correction called mass discrimination factor (MDF) can be applied to get precise results.

Mass discrimination factor or K factor $\{(B) = 1/dM\ \{\ (\text{Observed ratio/True ratio})\ \} - 1)$

where dM = mass difference ($dM = M_1 - M_2$, $M_1 > M_2$ and the ratio measured is M_2/M_1

Corrected isotope ratio $(M_2/M_1) =$ Ratio measured $[1 + dMB)$

4.2.2 Internal normalization

In this method, the correction factor described is determined from the sample isotope ratio measurement itself. For this purpose, the sample should have two isotopes of known ratio which is also measured along with isotope ratio of sample to obtain the correction factor. Typical example of this technique is the $^{87}Sr/^{86}Sr$ ratio measurement. For normalization ratio of $^{88}Sr/^{86}Sr$ is also measured in every scan

Correction factor $(F) = 1/2 * [(R_{88/86}\ \text{measured}/R_{88/86}\ \text{true}) - 1]$

Corrected $R_{87/86} = R_{87/86}$ measured $* (1 + F)$

In the case of plutonium concentration using double spike technique, $R_{242/244}$ and $R_{235/233}$ are used for normalization for plutonium and uranium respectively. It is detailed during concentration measurement discussions.

4.2.3 Total evaporation technique

Total evaporation and ion current integration provides another method[6-8] to overcome error due to fractionation. In this method, the sample is vaporized totally an ion currents produced by all isotopes are integrated using a multi-collector system. The reproducibility of several measurements of isotope ratio of uranium and plutonium are reported to be improved by a factor of 2 to 4 and the accuracy was comparable to the conventional method. Since the entire sample has to be evaporated totally, very small amount of sample needs to be deposited. There are difficulties in adopting the method in case of formation of more than one species of ions (e.g. metal and oxide ions) and also the instrument should be tuned for collection of ions from the beginning.

4.3 Errors at the collector

Mass discrimination occuring at the detector depends on the type of detector used. For example, in the case of electron multiplier, the error is unidirectional. Mass discrimination factor method using external standard also corrects this type of error.

The problem in the use of multi collector is the variation in the gain of different amplifiers causing error in the isotope ratio measurement. The error is determined electronically and correction to each ratio is applied. Before data collection, amplifiers are detached from detectors and a constant voltage is measured through each amplifier and ratios of amplifiers gains are calculated and the same is corrected for each isotope ratio measured. The amplifiers have certain background signal due to noise that is determined by using long integration time and each isotope signal is corrected for the background of respective amplifier.

During the measurement of abundance of minor isotope, adjacent to major isotope, it is required to apply abundance sensitivity correction to get the correct isotope ratio.

5. Concentration measurement by Isotope Dilution Mass Spectrometry (IDMS)

Since the ion intensity depends upon the various parameters of the instrument, out put signal cannot be related to the amount of sample taken for analysis. Hence, isotope dilution method is followed where the sample is spiked with a tracer that is normally not present in the sample and from the change in the isotope ratio of major isotope to spiked isotope before and after spiking, concentration is calculated. The greatest advantage of the technique is that no quantitative separation is needed. ^{242}Pu and ^{233}U are normally employed as spikes for the determination of plutonium and uranium respectively.

5.1 Isotopic equilibration

It is an important step in isotope dilution technique. It is essential to ensure that the sample and spike are chemically similar so that they behave identically during evaporation and ionization at source. Isotope equilibration is also important if any separation procedure is followed to remove any interfering ions. Different procedures for isotope equilibration of plutonium include (i) treatment with concentrated nitric acid (ii) mixture of nitric acid, phosphoric acid and HF, (iii) redox treatment with peroxide and (iv) redox treatment with ferrous sulfamate and sodium nitrite. Evaluation of these procedures conducted conclusively proves that redox method using ferrous and nitrite is superior. For uranium one of the acid treatments indicated is adequate and the same is followed.

5.2 Spikes for plutonium

For several years ^{242}Pu was used as spike for plutonium. Non availability of ^{242}Pu spike in pure form was a major problem in continuing this technique. Use of plutonium of different isotope composition as alternate spike was first reported by FCD, BARC and the same was demonstrated in an field experiment[9] conducted at PREFRE, Tarapur. This is possible due to the commercial availability of very high precision mass spectrometers so the slight change in the isotope ratio could be measured reliably. A comparison of different spike isotopes of plutonium [M = 239, 240, 242 & 244] made at FCD also shows the superiority of ^{239}Pu spike. Low burn-up plutonium from research reactor is used as spike for plutonium of power reactors and vice versa. Since 1985, PREFRE is using this spike.

5.3 Large Size Dry spike method (LSD)

Normally irradiated fuel dissolved solutions are diluted suitability so that microgram amount of plutonium spike is used. In the LSD method mixture of plutonium and uranium in milligram quantities are added to undiluted dissolver solution. This is possible due to the use of ^{239}Pu spike. This will avoid dilution error and reduce the error due to contamination. An inter comparison study[10] of this method was conducted between PREFRE, Tarapur and SAL, IAEA which showed an agreement of better than 0.1%

5.4 Double spike technique

Double spike technique using ^{242}Pu and ^{244}Pu is employed to correct for error due to fractionation. Since the 244/242 ratio of the spike is known, the same is compared with the measured value in each scan and the correction factor is applied for 242/239 ratio. During a safeguarded campaign, the advantage of the technique was demonstrated[11] at PREFRE, Tarapur.

5.5 Resin bead technique

It is a method of preparing extremely small size of Pu & U sample from input tank solution free of fission products on ion exchange resins for transportation to SAL laboratory from the reprocessing plants for verification purpose. The resin bead is directly loaded on the rhenium filament for mass spectrometric analysis. Better ion intensity is reported.

6. Tracer technique for nuclear material accounting in input solution

Tracer techniques for the input accountability of plutonium and uranium in reprocessing plants by MAGTRAP and LEADTRAP was developed by RCD, BARC and the same was demonstrated[12,13] in PREFRE, Tarapur. The tracer technique is used to determine the total quantity of plutonium or uranium in the input solution without knowing the volume of solution. A triple spike isotope dilution technique is used for this purpose which involves the addition of known quantity of a mixture containing ^{233}U, ^{242}Pu and ^{26}Mg to the dissolver solution. After spiking, isotope equilibration and separation, mass spectrometric analysis is carried out for 233/238, 239/242 and 26/24 isotope ratios for uranium, plutonium and magnesium respectively. By using combined spike, it is not necessary to know the aliquot volumes of the sample aliquot and spike for determining the total quantity of plutonium or uranium. This is called MAGTRAP method. In the case of LEADTRAP, lead tracer is used instead of magnesium.

7. Performances of different mass spectrometers used/in use

PREFRE, Tarapur is using this technique for the past 30 years. During the first 10 years the plant used MS2790 developed by TPD, BARC. In spite of the fact that it was an old generation instrument with single SEM collector and analysis by magnetic scanning and recording on a strip chart recorder, the instrument was successfully used for several campaigns of research reactor fuel processing as well as two campaign of safeguarded power reactor fuel processing. During the safeguarded campaign, all the input samples were also analyzed by SAL and the results were within declared capability of the facility (plant). Due to aging of the instrument, it was replaced by a commercial instrument MAT 261 from Finnigan MAT and carried out several campaigns of power reactor fuels from RAPS, MAPS and KAPS. The campaign of RAPS was under safeguards and nearly 30 input samples were also analyzed by SAL and excellent agreements[14] in isotope ratio as well as concentration measurements between the laboratories were realized. Summary of inter lab comparison on isotope ratio measurement is shown in Table 1. KARP, Kalpakkam uses a multi collector TIMS developed by MSESS, BARC. Instrument is being used for isotope ratio measurement of plutonium and uranium products of the plant. Due to problems in the external precision and sensitivity, it is yet to be used for concentration measurement by IDMS. Efforts are being made to solve these problems. Action has been initiated to introduce this technique in PP, Trombay also.

Table 1: Summary of isotope ration measurement by PREFRE and SAL

Isotope ratio	No of batches	Inter lab difference in % (PREFRE / SAL)	RSD (%) of difference
240/239	30	– 0.02	0.08
241/239	30	0.20	0.45
242/239	30	0.22	0.43

8. Conclusion

Thermal ionization mass spectrometers are used in both power reactor reprocessing plants. Good expertise is available in using this technique for reprocessing applications. It is observed that better precision and accuracy is achieved in plutonium concentration measurement compared to uranium. This may be due to effective isotope equilibration step followed for plutonium.

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Upgradation and Modernisation of the Mass Spectrometers

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Substantial investments are made at the time of purchase of an analytical instrument of the complexity of the mass spectrometer. The scientist puts in diligent work and specifies a 'state-of-the-art' instrument, within the allocated budget. Suppliers of international standing are contacted and finally, a well considered choice is made. A perfect job has been completed at that point of time. However, the journey into the future is a bit uncertain. Technological advances cause earlier versions to fall out of favour and force them to fend for themselves as spares and services taper off to a point of non-existence. This is when the maintenance engineer can rise beyond mere component-tinkering and elevate himself to a development engineer. The word 'maintenance' should not be restrictive to the sense of 'maintain status quo' but should widen to mean 'maintain currency'. When the sense of 'maintaining currency' is adopted, the Upgradation and modernization are the inevitable positive outcomes of trying to hold on to legacy instruments and not let go of them, at least not when they are just beginning to age.

Being inherently modular in nature, mass spectrometers that are also constructed in a modular grain, lend themselves to easy upgradation and modernization. This is more applicable to the sector magnet analyzer based mass spectrometers, rather than the QMS variety because the former is an assemblage of more conventional power supplies, while the latter employs specialized power supplies. Upgradation by way of retrofitting, not only enhances the life of the instrument, but also holds the promise of enhancing the performance. Another spin off is that the indigenous content in the instrument tends to keep increasing as the upgradation proceeds.

The dual mass spectrometers at the Chemistry Group have 'metamorphosised' themselves through various technological changes and remained largely current and meeting the demands of the Group. Taking the mass spectrometer on the upgradation route becomes realizable only when the maintenance engineer develops a holistic view of the instrument and understands the interplay between the modules in realizing the overall performance. With this comprehension of the context, obsolete modules can be replaced with contemporary designs and the mass spectrometer can march on its evolutionary path.

The data acquisition system has been found to have the shortest technological life cycle and three generations of these have turned over in our mass spectrometers. A proprietory HP 'calculator' with a specialized interface suiting it, was a leap ahead, when the mass spectrometer was acquired in 1979. The PC with a family of standard plug-in cards arrived on the technological scene just at the time when the HP Calculator was going out of vogue and cut off from its life support supplies. The comprehension of the intimate interplay between the instrument and the proprietory interface, paved the way for altering the instrument side to adapt to the standard PC interfaces. This brought great flexibility and versatility to the instrument apart from making the data system easily maintainable. This stage prevailed for over 15 years.

The advent of the later Pentiums saw the disappearance of the industry standard ISA bus slots, as the PCs began to lean more towards information technology domains rather than industrial automation. At this juncture, industry standard micro-controller systems with their rich 'Euro crate interfaces' took over and the mass spectrometer continued its evolutionary path and acquired enhanced computational power and enhanced variety and multiplicity of interfaces, to bring more instrument parameters under control, as exemplified by the following cases: With a slave system of a vast array of interface boards, a lot many functions can be automated in vintage instruments.

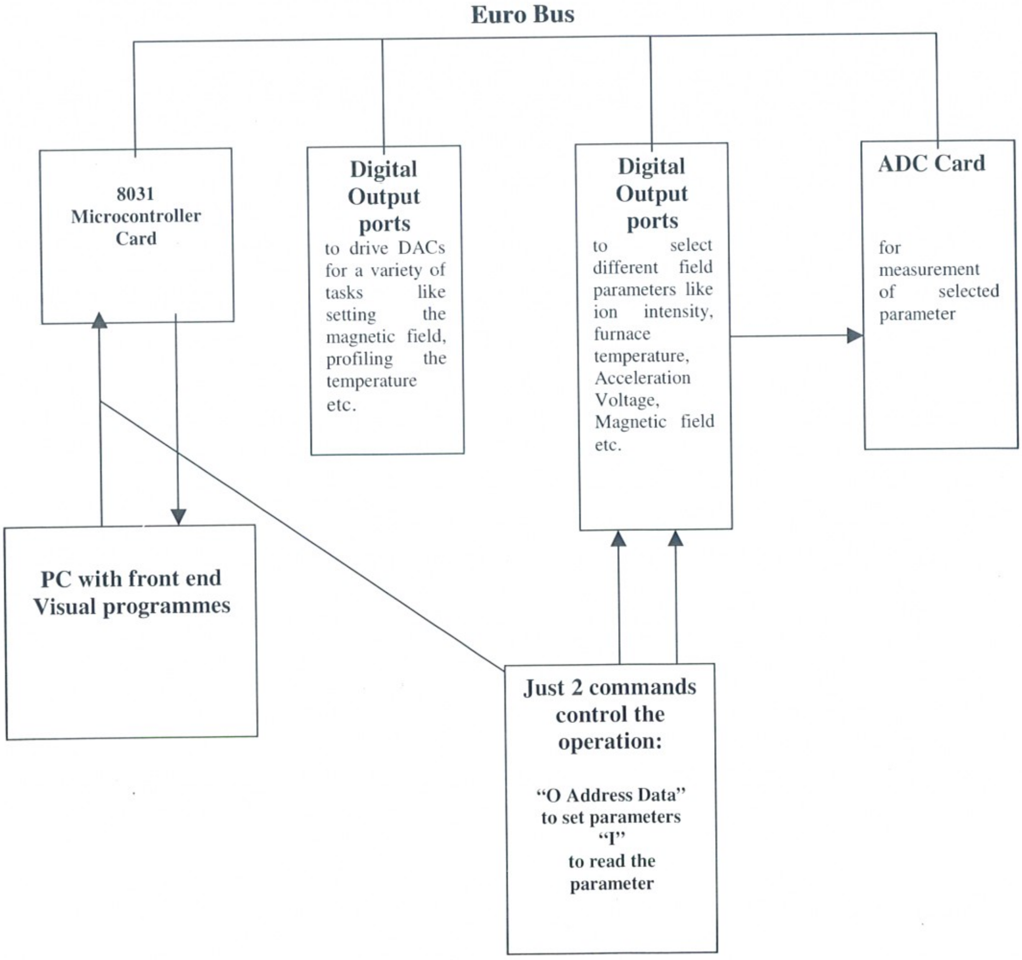
The intensity measurement chain comes with a lot of automation in recent versions of the mass spectrometer, whereas vintage instruments basically had a manual control over the measurement parameters.

Through digital output ports, it is possible to program the gain of the ion signal measuring amplifier. With the settings of all standard runs stored in a file, it is possible to set all the instrument parameters very close to the best settings. It will only remain to make fine adjustments prior to collecting the measurements.

With the above hardware configuration there is such a variety and number of interface cards available that many automation schemes can be achieved. A sample of the actions achievable is given below:

- Selection from a range of measurement variables-ion intensity, Acceleration voltage and magnetic field. This helps to monitor stability.
- Automatic gain selection for the ion signal amplifier.
- Profile the furnace temperature
- Vary the electron energy through opto-isolators, for measurement of appearance potential.
- Set the magnetic field for peak jumping.
- Manipulate the focus voltages to perform auto focussing.
- Ion shutter actuation.

Through interfaces and optical isolators, it is possible to inject controls into high voltage segments of the mass spectrometer. This concept was tested in principle and a final implementation will soon be done. The ion source of the mass spectrometer is floated at the potential of the accelerating potential. The ion source



in our K-Cell mass spectrometer employs electron impact ionization as the means of producing ions from the sample vapour. The electron energy circuit is floated at high potential and the variation of this potential through the opto isolated interface enables the determination of the appearance potential in an automated manner. DAC interfaces allows the gradual raising of temperature in the K-Cell furnace. This obviates the necessity of an operator stationed for this routine action.

The harnessing of visual programming languages like VB and VC++ have brought in friendly graphical user interfaces (GUI) and the vintage instrument easily transforms into an easily configurable system.

Within instrument modules, replacing custom designed SCR controls, with commercially available general purpose ones, brought maintainability to the system. Of course, this requires the maintenance engineer to comprehend the points of control. Considering that the sector magnet mass spectrometer is predominantly a large collection of myriad power supplies, indigenous sub-systems easily blend into the scenario.

Thus, a complete comprehension can take the mass spectrometer on an evolutionary path, going from strength to strength, until a death knell is sounded by the need to revolutionise the requirement to a different philosophy.

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Ion Sources and Sample Preparation Methods for TIMS

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1. Introduction

One of the key aspects to be considered for any mass spectrometric application is the choice of a suitable ion source. For isotopic applications, different modes of ionization such as electron impact, thermal ionization, spark source, glow discharge, secondary ionization, field desorption, and more recently plasma sources are generally employed. Among these techniques, thermal ionization mass spectrometry (TIMS) has been widely exploited for the isotopic analysis of solid elements, particularly for measuring low abundant isotopes present in few hundreds of nanograms of an element. Reliable isotopic composition measurements lay emphasis on sensitivity, selectivity, high precision and accuracy and a thermal ionization (TI) source is endowed with all these features. A thermal ion source essentially consists of a filament assembly (with a single, double or triple filament configuration) for ion formation and a plate-system for the acceleration and shaping of the ion beam. The general outline of the operation of a thermal ionization source, various geometrical arrangements and related developments are discussed in this paper.

A good sample preparation technique ensures reliability of a mass spectrometric analysis. Best possible sensitivity and precision are achieved by careful control of chemistry at this stage. The development of novel sample loading/deposition procedures and studies on the ion source chemistry of polyatomic species in a thermal ion source have thrown open many analytical options for isotope scientists. Several laboratories have succeeded in their efforts to evolve sample preparation techniques aimed at improving the ease of use, sensitivity and economy. Special designs such as "thermal cavity" ion sources aimed at improving ionization efficiency have also been discussed in this paper.

The information given in this article is not necessarily the review of various aspects of ion source and sample preparation but attempts to give adequate background and brief account of active research going on in various laboratories in this area of mass spectrometry.

2. Thermal ionization source - principle of operation

When neutral atoms or molecules are heated on a hot metallic surface of work function, 'W' (eV) and temperature, T(K) there is a probability that ions will also evaporate in addition to neutral particles. Ionization efficiency (the ratio of the number of positive ions formed to the total number evaporated) is given by *Langmuir - Saha* equation,

$$n^{+}/n^{0} \propto \exp((W - I)/kT)$$

n^{+} = no. of ions;	n^{0} = no. of neutrals
e = Electronic Charge	W = Work function (in eV) of metal surface on which analyte is deposited.
T = Temperature in Kelvin.	I = First ionization potential (in eV) of the analyte
k = Boltzmann constant.	

The above relation suggests that high ratio of positive ions to neutral species is realisable by using a filament surface of high work function and element of low ionization potential (IP < 7 eV). In the case of elements with high IP, increase in temperature would help in increasing the ionization efficiency. The above description is for the formation of positive ion, generally referred to as positive thermal ionization mode (PTI). For the analysis of metals with high electron affinity (A) and certain non-metals (halogens), negative thermal ionization (NTI) mode is employed. In that case, (W - I) term in the above equation, is replaced by

(A-W). Species with electron affinity greater than 1.9 eV are known to yield high ionization efficiency for negative ions.

2.1 Advantages of thermal ionization source

The main advantages of thermal ionization sources are (i) high ionization efficiency requiring sample size as low as a few nanograms. (ii) low ion energy spread (~0.1 to 0.2 eV) or practically mono-energetic ion production making a single focusing sector field mass spectrometer adequate. (iii) elemental selectivity (iv) relatively less mass discrimination and (v) absence of /negligible background or memory effects.

2.2 Choice of filament material

Work function and melting point are the two main criteria to choose a filament material for loading the sample. The other features of a good filament material are good weldability and low vapour pressure. Of the pure metals, platinum was the first widely used filament material, the reason being its highest work function (5.32 eV) and its availability in ribbon form. But its relatively low melting point (1772° C) led to the use of other materials such as tungsten, tantalum and rhenium. Rhenium is widely used in many applications, because of the attractive compromise it provides between work function and melting point (5.1 eV and 3180° C respectively). A typical rhenium filament source employs high purity rhenium (99.995%, zone refined) with width of 0.030" and thickness of 0.0012."

2.3 Filament configuration

Before loading the sample, filaments are welded onto the metal posts sealed in glass or ceramic beads in different configurations. Various configurations developed over these years mainly aim at achieving better sensitivity and better focusing conditions. Single filament configuration is generally used for species with low volatility. In this configuration, vaporization and ionization take place at the same surface. However for species that are highly volatile but difficult to ionize, (in which case sample evaporates before the ionization temperature is reached) multifilament sources come in handy. In this arrangement, the volatile sample evaporates from one or two filaments (sample filament/s) at a relatively low temperature (thus prolonging the sample utility) and ionization takes place in another filament at a higher temperature giving rise to good ionization efficiency. In a triple filament source, two sample filaments are welded sideways symmetrically with respect to the ionization filament positioned at centre [1]. In a V-shaped filament, the sample is placed in a shallow groove. Neutrals evaporating from the hot groove have more chance to have contact with the walls of the filament before leaving the immediate region of the filament surface, resulting in higher ionization efficiency [2]. A novel filament configuration aimed at reducing background contribution in the isotopic analysis of iron has been reported by Dixon *et al.*[3] The platinum posts in ceramic insulators with filament made in a dimple shape, have helped to obtain cleaner spectrum for iron and this improved the sensitivity too.

Cavity sources: Use of cavity-type sources has been reported to improve sample utilization efficiency significantly. In this source, a metal tube (or crucible) is used instead of a filament for evaporation and ionization of the sample. However, high ionization temperature is achieved by the bombardment of high energy electrons from the heated filament surrounding the crucible (Fig. 1). As the sample is evaporated

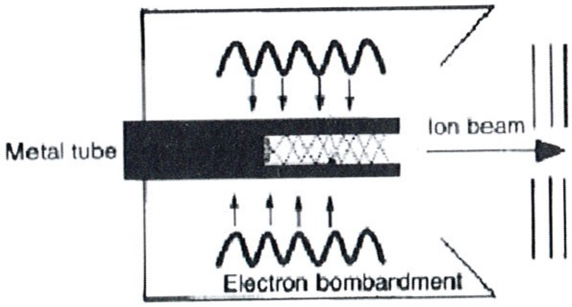

Fig. 1 Thermal cavity ion source - A schematic view

inside the crucible, the neutral gas atoms interact with each other and with the inner wall of the cavity as well to produce ions. Compared to the conventional filament sources, high degree of such interactions is achieved due to high temperature, greater surface area and limited volume in the cavity. A prototype cavity source employing quadrupole mass spectrometer has been reported by a research group from Los Alamos Laboratory [4]. In this work, the sample is introduced in either solid or solution form. Interestingly for U and Pu solutions (1 μg load), ionization efficiency of 7-8% (which is not obtained on the surface sources) has been observed. High efficiency, low complexity and simple sample loading are claimed to be the advantages of this new source. Similarly, ORNL in collaboration with IAEA have conducted preliminary ionization efficiency experiments on uranium and plutonium samples for environmental applications using cavity sources.

2.4 Improvement in sample handling

Towards upgrading the sample handling capabilities, manufacturers of TIMS have come up with design of sample turrets which can hold as many as 20 filament carriers (with provisions of easy fixing and aligning) and this has enabled continuous analysis possible without breaking the vacuum. Added benefit of automation to such facility is the unattended operation for routine analysis.

3. Sample preparation

Samples for TIMS analysis should be available in the purest possible chemical form in order to ensure good ion emission. The thermal energy provided by the hot filament should not be lost by way of evaporating or forming ions of contaminant species [5]. That is, the contaminant takes away the energy required for ionization of analyte. Therefore, it is important to isolate the target element from complex matrix, challenging though, and load the pure fraction on to the filament. For radioactive species such as uranium and plutonium, the smallest possible sample is required in view of the associated hazards. Procedures for complete dissolution, followed by preconcentration techniques like solvent extraction and / or chromatographic techniques are well documented for individual elements [6]. Methods used for sample preparation pertaining to different matrices have been summarized by Bacon [7].

3.1 Loading techniques

Choice of proper loading technique is one of the prerequisites for obtaining a stable and intense ion beam and the nature of chemical form of the species for analysis varies for different elements. Normally, a dilute solution (containing a few hundreds of nanogram down to a few picograms) in nitrate form is used for metallic species. For elements like boron (having IP of 8.3 eV), the sample is converted into easily volatile alkali metal borates for directly loading onto the filament. In the case of sulphur, an insoluble metal sulphide (As_2S_3) is used for loading. Especially for high IP (more than 7 eV) elements, chemical additives for enhancing the ion emission are used.

There are three other sample loading techniques viz., (i) electro deposition (ii) resin bead and (iii) silica gel technique widely used for different applications. While the first two are often used for radioactive samples, the third one is suitable for high IP (more than 7 eV) elements like Pb, Fe, Cr, Cd and Zn also (See Table 1).The geochemical researchers have made extensive investigations on loading techniques for lead.

TABLE 1: Loading conditions for certain high IP elements

Loading technique	Element/Fil.Temp. in ° C
silica gel/phosphoric acid	Tl/700; Cu/950, Cd/1150; Zn/1500 Pb/1180
silica gel/boric acid	Cr/1200; Fe/1260

In the case of negative thermal ionization technique (NTI), addition of chemicals such as lanthanum nitrate, barium hydroxide helps to reduce work function which in turn helps to increase the ion current. The evolution of this technique has greatly contributed towards meeting analytical challenges such as sensitivity, isobaric interferences etc. encountered in PTI techniques for certain elements especially in the field of geo- and nutritional sciences. NTI technique has been beneficially employed in Re/Os dating method, whose applicability was hindered, up to now by analytical difficulties arising from the extremely low osmium concentration in mineral matrix and the lack of sensitive and precise isotope ratio measurements. Introduction of oxygen or Freon into the ion source during analysis (with osmium load of (100 pg-1ng)) has improved the precision and sensitivity unmatched by SIMS, RIMS and ICP-MS techniques [8].

3.1.1 Electro deposition

Electrodeposition as loading techniques has been reported way back in 1982 [9]. For high sensitivity objectives, electro deposition techniques are suggested as possible alternatives especially for actinides and other fission product isotopes. For instance, a research group at Idaho National Labs has recently reported such a technique for electro deposition of technetium, an element of radiological safety concern [10].

In the case of U and Pu, the element is electroplated on a single rhenium filament, followed by overcoating a thin layer of platinum on the filament. The mechanism reported by Deng Zhongguo *et al* [11] is as follows: the sample atoms thermally diffuse through a platinum layer before they can evaporate as neutral atoms or as ions. Since thermal diffusion is generally a much slower process than direct evaporation and a platinum layer limits the prompt escape of neutral atoms, the filament can be operated at higher temperature, yielding higher ionization efficiency without rapid loss of the sample. The ion current observed for the 100 ng uranium or 50 ng plutonium is 2×10^{-14} A, lasting for about 40 to 60 min.

3.1.2 Resin bead technique

In nuclear technology, the concerns for environmental effects of radiation and mandate to adhere to the safeguard regulations have driven the scientists to develop new sampling cum-loading technique using resin-beads. The resin bead provides the matrix for chemical separation, physical transportation and thermal ionization. This technique has been used for inter laboratory experiments involving nanogram quantities of uranium and plutonium [12]. The use of this technique minimizes the steps involved in sampling operations associated with radioactive samples. Additionally, the "point load" emission of resin bead and the reductive action of carbon from the resin enhance the ion yield [13]. In Safeguards Analytical Lab of IAEA at Seibersdorf, this technique is presently being employed to conduct analyses of low amounts of uranium and plutonium in high active waste samples which had to be diluted to an extent at which the conventional analytical procedures are very hard to perform [14].

For environmental monitoring of enriched uranium samples (soil, water etc.) the purified fractions of uranium were absorbed in resin bead and then transferred on the filament to concentrate the solution in the centre of the filament for better ion emission characteristics [15]. Recently, in NIST, a comparative study has been undertaken to explore the detection limit for plutonium isotopic measurements using direct loading, electro deposition and resin bead techniques. The study concludes that resin bead method provides the better sensitivity (μBq orders of ^{239}Pu) compared to the other two methods [16].

3.1.3 Silica Gel Technique

In this technique, the element of interest is loaded on to the silica gel/phosphoric acid or boric mixture and then resistively heated on a Re or Ta filament to form a "bead". The advantage is that silica gel layers store the sample in the bulk of the layer and reduce the evaporation rate, while at the same time increasing the work function [17]. The recent work by Kani and Nohda [18] claims that colloidal silicic acid instead of silica gel contributes greatly to obtain stable and intense ion beam. Recently, Delmore's group from Idaho National Lab, have performed extensive experimental and computational work to explain the thermal ion formation by silica gel procedure. For instance, material loaded for lead analysis by this technique has been identified as molten glass emitter and shown with an ion source imaging instrument that lead ions originate from the surface of the molten glass [19].

4. Further scope

To quote from a report on the meeting of international TIMS users, "Improvement in the characteristics of thermal ion emitters has been a neglected area of research, but given the generally low (usually < 10 % and often < 1%) ionization efficiencies for many elements, this could prove to be a fruitful area of research and development," especially where the precision is limited by the number of ions counted during a measurement [20].

Summary

Thermal ion source offers itself as the most suitable one for isotopic applications involving inorganic solids. Novel ion source and filament designs together with improved loading techniques add to the strength of the technique in terms of ionization efficiency and sensitivity.

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Mass Analysers for TIMS

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1. Introduction

Mass spectrometers are usually classified based on the type of mass analysers used. They are an important component of any mass spectrometer. Most of the thermal ionisation mass spectrometers employ magnetic and quadrupole mass analysers either separately or in series. This article describes the principles, advantages and few applications of magnetic and quadrupole mass analyser based TIMS with the objective of providing background information on mass analysers for a practicing TIMS analyst.

2. Magnetic analysers

Generally, an ion optics system required for precise isotopic ratio work must fulfill two minimum conditions: 1. it should have a large lateral mass dispersion so that one or more detectors can be placed on the focal plane of the system 2. its ion transmission should be high, stable and independent of mass. There are other aspects like high resolving power, energy focusing that also need to be considered, but dispersion and transmission are of primary importance. A magnetic analyser as ion optical system has remained a right choice meeting such requirements. Magnetic analysers are the oldest and still occupy the centrestage for high precision TIMS studies.

When an ion with charge e and velocity v moves across a magnetic field B in a perpendicular direction, a force, F, is induced on it whose direction is perpendicular to both the velocity and the magnetic field

$$F = evB \tag{1}$$

Since the magnetic field is applied perpendicular to the motion of the ions, the magnitude of velocity will not be affected by the field and hence the ion experiences a force whose magnitude is constant but direction is always at right angles to the velocity of ion and hence the ion traverses a circular path. The kinetic energy acquired by ions after leaving the ion source is equal to the potential energy, eV (charge x acceleration voltage) available in the electric field between the accelerator plates.

$$\frac{1}{2}\mathrm{m}\mathrm{v}^2 = \mathrm{eV} \tag{2}$$

As the ions move in a circular path with a radius of curvature r, the force in the radial direction F, becomes equal to the centripetal force, mv^2/r. Considering all these, one can derive the equation for mass analysis for a magnetic analyser.

$$\frac{m}{e} = \frac{B^2 r^2}{2\mathrm{V}} \tag{3}$$

For the best separation of masses, one must provide an ion beam as homogeneous in energy as possible. The applied magnetic field acts both as an optical lens and as a prism for the ions. The lens action is seen from the radially diverging ions in front of the magnet getting refocused after having left the magnetic field. They are focused at a particular radial image distance as shown in Fig. 1. Owing to the mass dependence of the radius of movement of the ions, the magnetic sector focuses ions of different mass to different locations on the focal plane of the system. Like any other optical system the lateral enlargement factor, G, is given by the ratio of image width to object width. The lateral dispersion of masses for symmetrical arrangement (object and image distances from the effective face of the magnetic field are equal) is given by $D = r_m\ (\Delta m/m)$. Where $\Delta m/m$ is the relative mass difference between adjacent beams and r_m is mean radius of mass, m. Both D and G depend only on geometrical factors like deflection angle, slit distances etc.

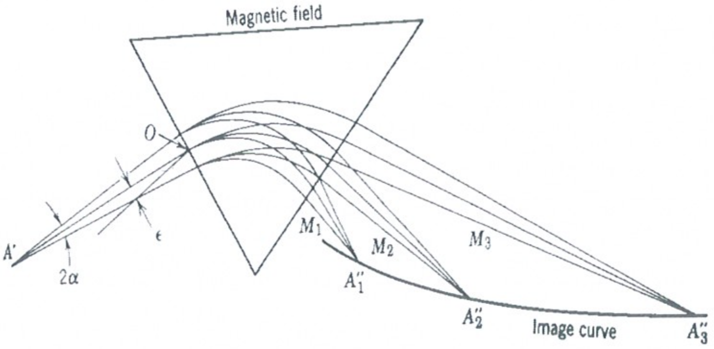

Fig. 1 Direction focusing and mass separation in sector magnetic field.

2.1 Historical perspective

Magnetic analyser with thermal ionisation source was first designed by Dempster in 1918 [1] using semicircular deflection. For several years after magnetic field focusing theory has made feasible the use of sector fields, these direction-focusing instruments continued to employ exclusively the Dempster's semicircular deflection configuration. It was Nier who first described a sector instrument with 60^0 deflection [2]. This configuration became soon popular as it required a smaller magnet than does the 180^0 implying lower costs and power requirements but with the same focusing and dispersing properties. Also it enabled ion source and detector to be removed far from the influence of the magnetic field. This was the predecessor for many of the modern sector instruments incorporating 60^0 or 90^0 analyser. Using the 60^0 sector instrument, Nier measured ^{207}Pb/^{206}Pb and ^{238}U/^{235}U ratios (139 ± 1) for geochronological studies. This work set a land mark which demonstrated the age of Precambrian and provided accurate isotopic data to calculate the age of earth.

2.2 Different geometries

The single focusing magnetic analyser, discussed so far, is basically direction focusing in nature. Since the ion beam emanating from a thermal ionisation source has a small energy spread (~0.2 eV), conventional single stage sector focusing mass spectrometer with normal entry of ion beams is adequate for many of the applications. For analysis requiring higher resolution it is necessary to focus the ions with respect to both direction and velocity, as the ions leaving the ion source have both angular and energy aberrations. This is achieved by double focusing where in addition, an electrostatic field (E) is used for velocity focusing. After emerging from the electrostatic field, ions of different velocity groups are brought to the entrance slit which are subsequently dispersed by magnetic field (B). In the forward geometry configuration (EB), the electrostatic field precedes magnetic field and in reverse geometry (BE), it is the other way around. Two most commonly used configurations are (i) Nier-Johnson geometry (forward geometry) where focusing occurs at a single point and (ii) Mattach-Herzog geometry (reverse geometry) where focusing occurs in a plane and hence simultaneous detection is possible.

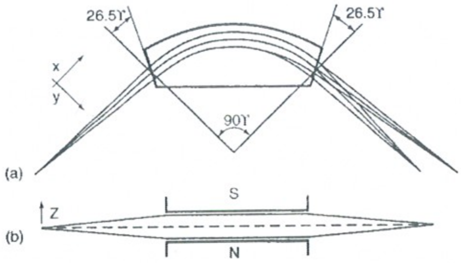

Fig. 2 (a) Radial and (b) axial focusing of a magnetic sector mass spectrometer with oblique beam entrance and exit.

Both single and double focusing discussed above correspond to ion beam entry perpendicular or normal to the magnetic field, meaning "Normal geometry". With this arrangement only radial focusing is achieved and no axial focusing occurs for beams traveling out of the middle plane in magnetic field. There is no magnetic force that could deflect them back to middle plane. By making the entrance angle of the ion beam oblique (extended geometry) to magnetic field, one can additionally achieve axial focusing as focusing happens in Z direction also. As a result of this, dispersion is doubled for the same radius of curvature as that used for normal geometry. This helps in higher transmission efficiency without sacrificing the resolution. As can be seen from Fig. 2, the diverging ion beam enters the analyser and out of plane particles move parallel to the poles within the magnetic field. The axial focal distance and radial focal distance become equal and this is also known as 'stigmatic focusing'. This feature significantly reduces the size of the magnet. Virtually all modern mass spectrometers offer extended geometry analysers.

2.3 Abundance Sensitivity

Another important figure of merit apart from resolution and sensitivity for a TIMS application, is the abundance sensitivity which is defined as ratio of peak ion current at mass M to the background current at adjacent mass. The magnitude of abundance sensitivity is a measure of the instrument's ability to measure a faint isotope adjacent to a more abundant one. Even at low pressures, a certain amount of peak diffuseness occurs due to

1. scattering of ion beam by residual gases
2. energy spread in the ion beam
3. electrostatic repulsion within ion beam
4. scattering of mass components far from central beam by solid parts of instrument (e.g.) solid wall of analyser tubes.

These result in peak tailing as shown in Fig. 3. It is usually mass dependent, decreasing with increasing mass. Generally the faint isotope present on the lower mass side of abundant isotope suffers more because gas phase collisions result in loss of ion energy and the magnet acting like prism disperses the ions with lower energy to lower mass.

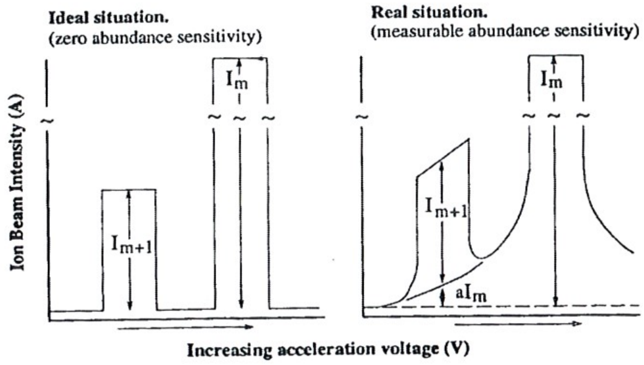

Fig. 3 Peak shapes in ideal and real situations.

Conventional single focusing mass spectrometers with a radius of curvature of 30 cm have an abundance sensitivity typically around 10^5-10^6 in the 238 mass range. The abundance sensititvity usually limits the dynamic range of the isotope ratio measurements especially for the measurement of minor isotopes. High resolving power is not the solution to improve abundance sensitivity, for the tails will remain. Use of advanced instrumentation like multiple stage tandem anlysers or extended geometry configuration has helped in improving this factor by two to three orders of magnitude. Traditionally multistage analysers are used in series separated by a defining slit. This slit is placed at the collector position of the first analyser. The first analyser acts as an isotope separator. The ions are further accelerated and then pass through the second analyser before reaching the collector. Those ions from the strong ion beam which are scattered in the first analyser and would thus cause peak tails are resolved into separate peaks in the second analyser. Some examples of improved abundance sensitivity using multi stage analysers can be found in references [3-5]. The incorporation of Retarding Potential Quadrupole (RPQ) [6] or wide aperture retarding potential (WARP) filters [7] also have greatly improved the abundance sensitivity in current generation instruments.

The main advantage of magnetic analysers lies in its high precision and accuracy, providing flat-topped peaks, higher resolution, stable ion beam and higher abundance sensitivity especially with improved instrumentation. The high precision measurements possible with TIMS using magnetic analyser enabled its widespread usage to various applications in nuclear technology, geology, earth sciences etc., But such a high precision comes at a cost both in terms of instrumentation and in analysis time. Therefore one needs to justify using this method for a specific application for its uniqueness or the value of its information.

3. Quadrupole analysers

In many instances, the problems related to samples, their chemical treatment and other factors limit the precision rather than the mass spectrometer. Therefore, in search of a cost efficient solution, a compact TIMS with quadrupole mass analyser (THQ) was developed by Heumann and coworkers at the University of Regensburg [8]. In quadrupole analysers, mass separation is achieved solely with electric fields. It is a path-stability mass spectrometer where the quality determining the stability of ion path is the specific charge. This non magnetic mass spectrometers employ a combination of direct-current (dc) and a radio frequency (rf) field as a mass filter. These analysers are dynamic in nature as opposed to magnetic analysers which are static in nature. The ion trajectories are influenced by a set of time dependent forces which render their trajectories somewhat more difficult to predict.

3.1 Principle

An ideal quadrupole analyser consists of four long hyperbolic cylinders in a square array as shown in Fig 4 with specific inner space dimensions. Because of difficulty in manufacture, most quadruple mass filters employ circular rods instead of hyperbolic rods. These are mounted precisely at the corners of a square at a distance $2r_0$ from each other. Opposing pair of rods are electrically connected with dc and 'rf' voltages. Best approximation using circular rods are obtained when the radius of the rods are $r = 1.1487r_0$ where r_0 is the radius from the centre of the four rods to the inside edge of the rods. In a quadrupole mass filter, the electric

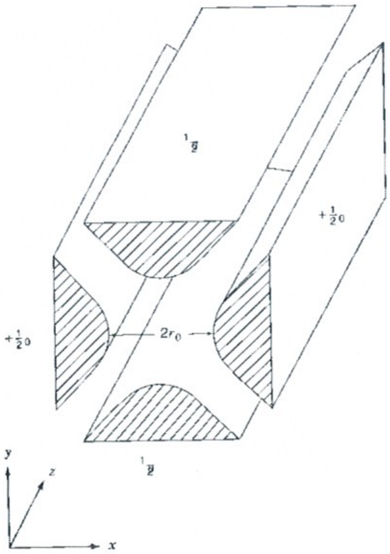

Fig. 4 Quadrupole rods

field exist along x and y directions and there is no field in the z direction (i.e.) along the direction of ion transit. The equation of motion of a charged particle in a quadrupole field in the final form after some mathematical treatments is given by Mathieu equation [9] and this describes the ion trajectories.

$$\frac{d^2u}{d\zeta^2} + (a - 2q\cos 2\zeta)\,u = 0 \tag{4}$$

where u represents the coordinates of axes, a , q and ζ are dimensionless parameters given respectively by $a = 8e\,U/m\,\Omega^2$; $q = 4eV/m\Omega^2\,r^0_2$; and $\zeta = \Omega t/2$; t is the time and Ω is the angular frequency. As can be seen, a is related to dc and q to 'rf' voltages. One can derive stable bounded solutions for the Mathieu equation in the x and y directions and are shown in Fig. 5. The overall stability diagram for the quadrupole mass filter is constructed by superimposing the stable regions for ion trajectories in x and y directions and this is shown in Fig. 6. Ions can be transmitted by the quadrupole mass filter only if they are stable in both x and y directions simultaneously. (i.e.) their a and q values must lie in the region of overlap. Such regions are labelled A, B, C, D in the figure. Of these, the regions B, C, D involve rather large values of the applied potential as well as trajectories which although theoretically stable may exceed the physical boundaries of the quadrupole device. In other words, one has to construct very large quadrupole rods. For any given set of dc and rf voltages only ions of a specific m/e value avoid collisions with rods and successfully traverse the quadrupole along the z axis to reach the detector; all other ions collide with the quadrupole surfaces. Hence, the region nearest origin depicted by A is practically operable. Its expanded portion in the positive quadrant is shown in Fig. 7. An operating line is selected by establishing a constant a/q or U/V ratio. The line segment which intersects the stability diagram corresponds to those values which belong to ions whose trajectories are stable. At the apex of the diagram the resolution is infinity but sensititvity is zero. At lower positions the resolution is low but a range of masses can pass through. In the region of higher resolution, peaks are triangular in shape and in low resolution regions they are trapezoidal. The mass scanning is achieved by varying either the 'rf' or dc voltages, while keeping their ratio constant.

3.2 Advantages of Thermal Ionisation - Quadrupole Combination (THQ)

The THQ combines the traditional quadrupole advantages of rapid peak switching, rapid mass scanning and fast switching between positive and negative ionisation with those of thermal ion source. Therefore it is possible to analyse metals as well as nonmetals with this instrument by IDMS. The fact that no beam defining slits are required contribute to enhance the sensitivity considerably. Its compactness makes it relatively easy to transport, an important advantage for process plants. THQ has already proven its applicability in the analysis of different materials. Some examples and details on the applications of THQ can be found else where [10-12].

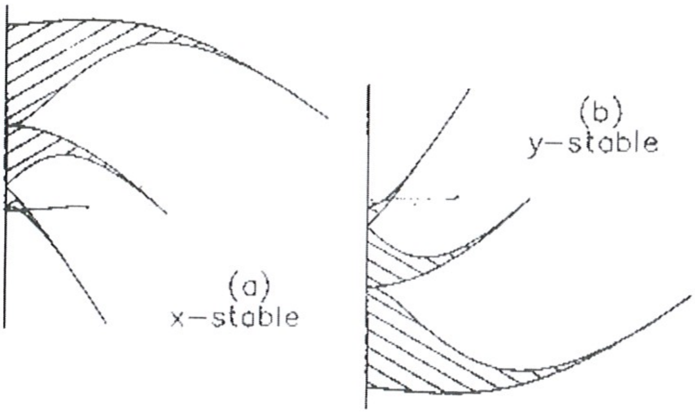

Fig. 5 Stable regions in quadrupole (a) in *x*-direction and (b) in *y*-direction

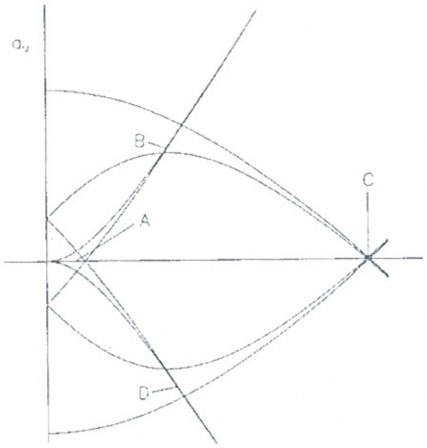

Fig. 6 Stability diagram (as per Mathieu equation) simultaneously in x and y directions.

Heumann *et al.* [8, 13] have analysed isotopic ratios of boron and halogens with both THQ and magnetic sector instruments. The relative external standard deviation of·0.2 to 0.6 % was obtained for THQ, while sector instrument gave deviations of 0.1 to 0.2 %. The elements B, C, N, Se, Te, Cl, Br, I were analysed as anions using THQ demonstrating the ease with which THQ can anlyse the negative ions. Mckown *et al.* [10] converted their EI-QMS to THQ to serve as the basis of a mobile laboratory to provide on-site isotopic analysis of U and Pu.

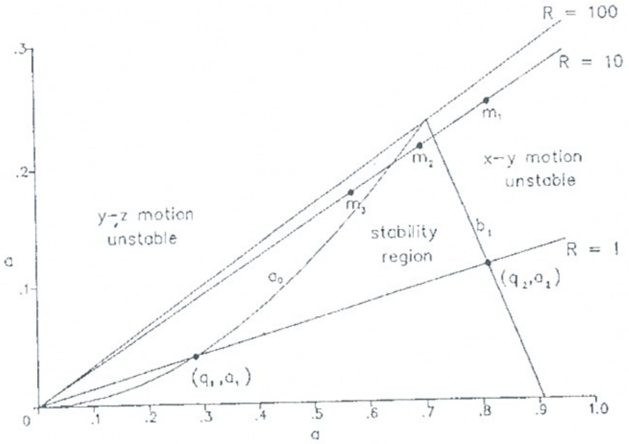

Fig. 7 Expanded portion of the stability diagram near the origin.

A comparison of results obtained for the same sample using magnetic sector and THQ reveal [8, 13] that although results with THQ are slightly less precise in some cases, they are as accurate as those obtained using magnetic mass spectrometers. Hence wherever it is desired to obtain isotope ratios with relatively less emphasis on precision, THQ is very good and cost efficient alternate to magnetic sector instruments.

3.3 Other Combinations

Recently even thermal cavity ion sources with Time of Flight analyser configurations have also been developed [14]. But their ability is restricted to a limited area of research.

4. Summary

Magnetic sector based TIMS since provides flat topped peaks coupled with good resolution is the best option wherever high precision measurements are involved. Hence in nuclear technology and geology these instruments find widespread usage. Wherever it is desired to obtain isotope ratios with relatively less emphasis on precision, THQ is a suitable and cost efficient alternate to magnetic sector instruments. Its compactness makes it relatively easy to transport, an important advantage for process industries for checking the isotope ratio of intermediate products.

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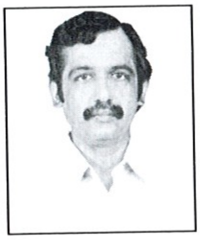

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Detectors for Mass Spectrometry

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1. Introduction

Ion production, mass separation, ion detection and a very high vacuum system to support the entire process can be considered as the four pillars of mass spectrometry. The interesting feature in this is that the structure of mass spectrometry can not stand with any one of the four pillars failing. From the time J.J. Thompson first used the photo plate as the detector, the field of ion detection has seen many changes based on need and technology evolution.

Ion detection forms the third stage of a mass spectrometric analysis. Though different principles and instrumentation may be involved in different detectors, most of them give the final output as an ion current, which will be either equal or proportional to the number of ions arriving at the detector. Different kinds of detectors are used/ required based on considerations such as sensitivity, response time, life time of the detector etc. The qualities of a good detector may be listed as: better multiplication efficiency, precise and accurate measure of the number of ions received, low noise level, low time constant, long life without degradation, low cost, easy maintainability, resistance to exposure to air and possibility of rejuvenation. A brief account of the ion detectors used in mass spectrometry is summarised below.

2. The Photographic Plate

Though obsolete and almost vanished from usage, a mass spectrometrist cannot afford to forget the photo plate as an ion detector for the simple reason that it is the first kind of ion detector used in the first mass spectrometer by the father of mass spectrometry. A photographic plate contains a thin coating of an energy sensitive compound, usually a silver salt (AgBr), spread evenly in gelatin as the medium on a glass substrate. The mechanism of image development on a photo plate can be explained in a simplified form as below:

The energy received from the incident particle, ion in this case, releases electrons from the surroundings to neutralise the Ag^+ ions from the silver salt to get a latent image of silver. While developing the photo plate, the latent image formed is developed into a black image by chemical amplification and the unused energy sensitive material is removed while fixing. Therefore the regions where ions arrived, appear as black lines and the rest of the regions appear as the transparent support plate. The darkness of the line is a measure of the number of ions incident in that area and their relative positions indicate the mass of the ions. The intensity of the ions can be read with the help of a densitometer.

The photo plate is a multiple ion collector. Therefore all the masses involved can be simultaneously collected and this avoids the need for mass scanning and more importantly the uncertainties connected with fluctuation in ion production. For this reason, in fact photo plates assumed renewed usage during the initial development of spark source mass spectrometry, since the spark ion source is known for its inherent instability in ion production. However, the arrival of ICPMS and other difficulties associated with this detector made it to vanish from mass spectrometric studies.

The main drawbacks of the photo plate can be listed as its low sensitivity and the fact that online results of the analysis is not possible apart from the problems associated with its handling. A line in a photographic plate becomes readable only when $\sim 10^4$ ions are incident upon it, which means that in the case of low abundant masses, either they can not be measured or one has to continue the measurement for a long time. In the former case, an important aspect of mass spectrometry is lost and in the latter case it puts undue burden on the analyst, which in some cases may not be possible. Since the results of an analysis will be known only after the analyst develops and reads the images, it will take a long time before the analysis results are known. Further, a single plate may be used to record the spectra of many samples, which will further increase the overall analysis time.

The handling problems associated with photo plates do not require a detailed explanation. The plates should be handled very carefully without exposing to light. Every time while loading and removing the plates, one has to break vacuum in the mass spectrometer and since this results in collector side vacuum getting affected, it can have a huge effect on the quality of the mass spectrum. Developing and reading the mass spectra also become an art on its own account and naturally the photo plate lost out in the race when other options with attractive and useful evalved with time.

3. The Faraday Detector

The Faraday cup (or some times referred to as the Faraday cage for obvious reasons) is another simple and accurate ion detector. In its simple form, it can be a simple metal cup like receiver or even can be a small metal strip. The ions incident on this receiver get neutralised by taking one electron per incident ion of unit charge (or by the release of an electron to it, if it is a negative ion). This flow of electrons causes a small electric current flow, which when amplified and measured gives an exact measure of the number of ions incident on the detector.

The case is not that simple and straight forward when ions, that are highly accelerated (which is very often the case in mass spectrometric studies) arrive at the Faraday cup. Since the accelerated ion carries energy in the kV level, it can cause secondary electron emission from the metal surface. In order to maintain the equation as one electron per incident ion of unit charge, the secondary electrons emitted should be recaptured within the detector. For this purpose the construction of the detector is slightly modified and these modified detectors are sometimes called Faraday cages. Schematically it can be represented as shown in the following Fig.1.

The plate on which the ions arrive is kept in a glancing angle so that the emitted secondary electrons cannot find their way out of the cage. A very small number of them which can in principle escape out, are also prevented from doing so by applying a small negative voltage on a repeller plate (shown as line before the detector), kept just above the ion entry port. This small negative potential can essentially keep all emitted secondary electrons with in the collector, but will not affect the incoming positive ion in any significant way since the ion beam is highly energetic.

In the present day scenario, the important role played by Faraday detector is perhaps its role in multiple collection devices. Multiple ion collection has revolutionised the achievable precision and accuracy of mass spectrometric measurements. This is due to the fact that, the inherent fluctuations in ion production (however small they may be) can only be corrected to the possible extent, in other methods, whereas it is almost eliminated in the multi collection technique. Relative standard deviations as low as 0.01% or lower are routinely quoted on measurements made with such collector systems.

Due to its simple construction, compact size and highly reliable output, Faraday cups are the most preferred multiple collector assembly. The poor sensitivity and long time constants, generally considered to be the weak point of this detector are more than compensated by its advantages. However, one has to be careful about using them in that since very low current signals are involved, small sensitivity difference that can be caused by temperature variation and moisture can affect performance. Therefore, uniform sensitivity of all the cups should be ensured. This is usually done, by keeping all the detectors in a thermo stated container, preferably under vacuum.

Another difficulty in the use of Faraday cup is during the measurement of low abundant ions. In that case, the number of ions arriving at the detector will be low and the resultant ion current will also be low. Beyond a few pico amperes, the detector becomes insensitive. (On the other hand, at very large ion current levels also – in the order of 1×10^{-8} A- due to space charge effects, the performance of the Faraday cup will be affected). However, in recent times very sensitive ammeters, such as the Keithley meters, have been used to measure the current output from Faraday collectors, which has resulted in significant increase in sensitivity.

4. Multiplying Type Detectors

Sensitivity of ion detection can be improved with multiplying type of detectors. The Secondary Electron Multiplier (SEM), Channel Electron Multiplier (Channeltron), Daly Scintillation detector, Micro Channel Plates (MCP) fall under this category. However, they vary among them in sensitivity limits (multiplying efficiency), life time of the detector, sensitivity towards exposure to air and response time. Depending upon application, these detectors find wide application in mass spectrometers.

4.1 The Secondary Electron Multiplier (SEM)

Fig.1 The Faraday Cage

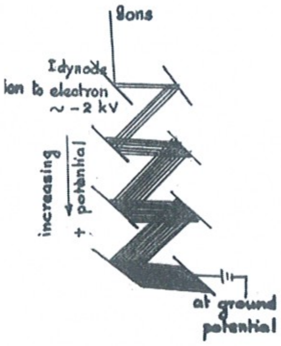

Fig. 2 Multiplication of electrons in an SEM

The principle of secondary electron emission is made use of in this detector [Fig.2]. To make this process more efficient, surfaces with high secondary electron emission (low work function) and many stages of multiplication are employed. Usually an array of dynodes made from 2% Cu-Be alloy or 2% Ag-Mg alloy known for their low work function, arranged in a Venetian blind type structure is employed. Approximately 20 stages of multiplication are commonly employed. The first dynode converts an ion into certain proportionate number of electrons and subsequent dynodes multiply electrons at each stage. In order to facilitate electron multiplication and direct them properly, the dynodes are set to receive increasingly positive (less negative) potential. The first ion-electron conversion dynode will be kept at the highest negative potential (typically around –2 to –3 kV). Therefore the positive ion, which already comes with a sufficiently large positive potential, is further accelerated when it strikes the first dynode. Each subsequent dynode will have a less negative voltage on it (by a suitable array of resistors attached to them), which will be seen as a more positive potential by the emitted electrons. This helps to direct them towards the next stage as also to multiply further. The last dynode will be kept at ground potential, and therefore the electrons arriving on it produce an electron current, which is proportional to the number of ions arriving at the detector. Multiplication efficiencies in the order of 10^5 to 10^6 are very common, and efficiencies as high as 10^7 have also been reported.

The SEM suffers mainly from two disadvantages. Since secondary electron emission is a function of the velocity (among other factors such as the work function, incident angle, physical condition of the surface etc.),with which the ions strike the conversion dynode, they have a tendency to release more secondary electrons when lighter masses (that are supplied with the same energy as the heavier masses at the time of leaving the ion source, and hence travel with higher velocity) arrive. This will result in the over estimation of the lighter mass relative to the heavier mass and this effect is known as the mass discrimination effect (MDF).

The second disadvantage of the SEM comes from the fact that they loose efficiency over time and are often sensitive to exposure to air. Efficiency reduction is attributed to many factors such as deposition of hydrocarbon molecules on the surface of the dynodes, constant deposition of analyte molecules on the conversion dynode (which with time may no more be a Cu-Be or Ag-Mg surface) and due to exposure to air. There are reports in the literature, which deal with the rejuvenation of SEM by heating in O_2, in atmospheric pressure at 300°C. Not much success has been reported in this direction. Moreover, with the advancement of channel electron multipliers and multipliers that resist exposure to air, SEM has often been replaced by this kind of advanced detectors.

The problem of mass discrimination associated with electron multipliers can be solved in many ways. (i) A standard sample of known composition can be analysed and from the deviation from the expected value a correction factor per amu can be arrived at. This factor may be tested from time to time. (ii) If a measurement can be done simultaneously with the SEM and a Faraday detector (which does not suffer from MDF), the correction factor can be calculated. (iii) The pulse counting devices if employed as an ion detector, MDF error can be avoided (iv) In the non-availability of the above options, the square root of the ratio of the inverse of the mass numbers can be applied as a rough correction.

4.2 The Pulse Counting Detector

Instead of measuring the ion current as an analogue out put, the number of pulses generated by the arrival of each ion can be counted by a suitable pulse counting device. Such detectors can be more sensitive as also free from MDF. Usually such pulse counting devices are used in combination with SEM. A discriminator is used to select only those pulses whose height is more than the set discriminator level and this helps to eliminate stray or background pulses. Since the difference in velocity of the ions result only in the pulse height and not in their number and each pulse higher than the set discriminator level is counted as one pulse, error associated with differential velocity is eliminated.

Since pulse counting can be done to very low levels of count rates (a few counts/sec), the sensitivity of pulse counting devices are usually better by an order (or even more) than multipliers. However, at very high count rates, there can be coincident counts and this may result in the under estimation of ion intensities. Present day technology allows even count rates as high as a few million pulses/sec. However, generally the current (analogue) signal is used at high ion arrival rates. At fairly low ion arrival rates, measurements will be done both by the current mode and pulse counting mode and conversion factor between the current signal to pulse signal will be obtained. At low ion arrival rates only pulse counting is employed. When all the signals are converted to equivalent count rates, the measured signals will be free from MDF.

4.3 Channel Electron multiplier (Channeltron)

The channeltron is an improvement over the SEM, overcoming some of its defects. It is usually made in the shape of a trumphet. It has a continuous electron-multiplying surface as against discrete dynode plates in the SEM. The differential voltage required for electron multiplication and guiding them to the other end of the detector, (to give the ion current signal) is provided by the dynode material itself, due to its high resistance. Therefore, electrons make semicircular paths inside the chaneltron tube, striking the surface at several locations and getting multiplied at each striking point. The large ion entry point and the chance of ions/ electrons to strike a different surface point keep the sensitivity of the channeltron high for longer durations. Moreover, many channeltrons can be repeatedly exposed to air without degradation of performance. Channeltrons can be sensitive to photons. Therefore, they are some times mounted off-line from the ion path to avoid light from the ion source. In such cases, a conversion dynode is used with fairly high applied voltage to convert ions to electrons and these electrons are fed to the detector for multiplication. This arrangement helps to increase sensitivity, reduce noise and improve life time of the detector.

4.4 Daly Detector

The advantages of using a separate conversion dynode and electron multiplying surface seen earlier in the case of the chaneltrons is improved both in terms of construction and energetics in a Daly scintillation detector system. The Daly detector [Fig.3] was introduced much before channeltrons. This has three essential components; a cathode, a scintillator and an electron multiplier. The cathode is usually made of Al or with an aluminised surface and is maintained at a high negative potential. Ions, which arrive already with sufficiently large energies are further, accelerated by the applied voltage on the cathode and emit secondary electrons. These secondary electrons are directed on a scintillator material usually kept inside the vacuum system. The resultant photons are sensed by a photo multiplier tube usually kept outside the system (but the photo multiplier tube will be under vacuum) to give a multiplied ion current as the final output. Multiplication efficiencies as high as 10^7 are possible with such detectors. Material deposition on the cathode surface, though a reality does not affect performance since energies involved are very high. The scintillator and photo multiplier tube however see only electrons and photons and therefore their performance characteristics are not much affected with time. Therefore, Daly detectors have much longer life.

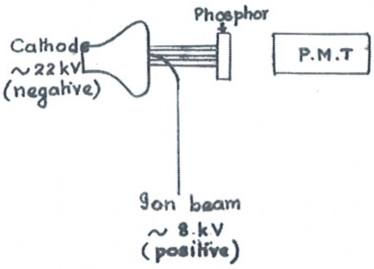

Fig. 3 Schematic Diagram of the Daly Detector

4.5 Micro Channel Plate (MCP)

Low time constant is a desirable quality for all detectors used in mass spectrometric analysis; but this is a must and should be very low for detectors used with time of flight analysers. This is because the time of arrival between different masses may be extremely small (in the nanosecond or lower ranges) as the mass of the ion increases and the signal due to the arrival of one mass should be over before another mass arrives. To meet this important requirement micro channel plate (MCP) detectors are used. These detectors are usually available as small discs of ~ 1 – 2 mm thick. They contain millions of micro channels and each channel acts as a mini multiplier. Multiplication efficiency in the order of 10^7 is possible with very low time constants.

5. Guard rings

Even though a guard ring is not a detector in itself, it has a role to play in the right type of ion detection and hence needs a mention here. Guard rings are very useful in avoiding stray signals from metastable ions being received at the detector. A metastable ion is an undesirable species. Since they lose their identity (mass, charge and energy) before they reach the detector, they will travel with less energy and arrive at unintended points. If a guard ring maintained at source potential is kept just before the detector, the genuine ions will be unaffected by this potential where as the metastable ions which have less energy will be deflected away from the detector.

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Operating Experience with Indigenous Thermal Ionization Mass Spectrometer at Kalpakkam Reprocessing Plant

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1. Introduction

Kalpakkam Reprocessing plant (KARP) processes the spent fuel from Madras Atomic Power Station (MAPS) by using the PUREX process, solvent extraction process for the recovery of Uranium and Plutonium. Characterization of special materials of the plant is an essential step for the effective nuclear material management programme of the plant. Mass spectrometric measurements such as isotopic composition and concentration measurements are absolutely essential for the characterization of special nuclear materials by way of determining the concentration of materials of interest i.e. uranium and plutonium and other valuable factors like specific activity, burn-up etc. Thermal ionization mass spectrometry (TIMS) has proven itself to be a versatile method for the isotopic content and concentration for inorganic solids.

Keeping this in view an Indigenous thermal ionization mass spectrometer with multicollector configuration with extended geometry (TIMS-3) [Fig.1] was fabricated by TP & PED, BARC and has been working at Kalpakkam reprocessing plant (KARP) successfully since the year 2000. Accountability laboratory of KARP has been engaged in carrying out analyses which are required or the purpose of nuclear material accounting (NUMAC) including isotopic studies required for the input and output inventory of the plant using this indigenous thermal ionization mass spectrometer. The data obtained using the instrument including the concentration of uranium and plutonium in the input and product streams of the plant and their isotopic composition determination play a pivotal role in the nuclear material management purposes and the data obtained are found to be in good agreement with similar analyses carried out at FCD, BARC using an imported instrument.

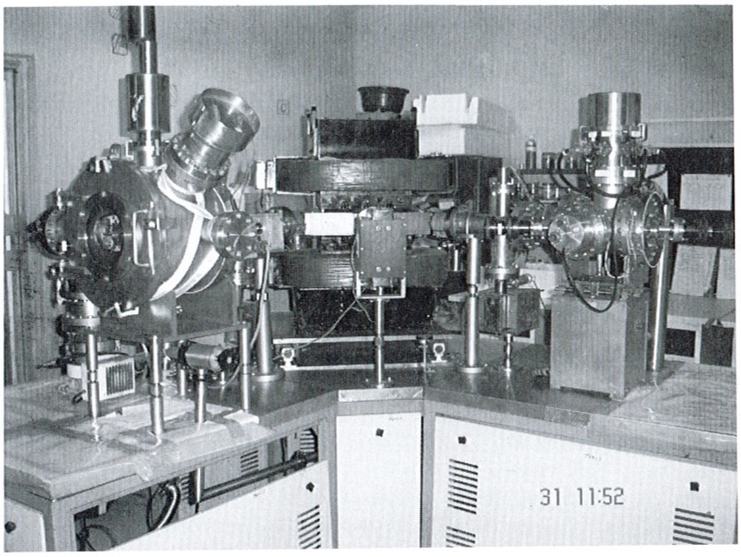

Fig. 1 Indigenous Thermal Ionization Mass Spectrometer at KARP (TIMS-3)

2. Salient features of TIMS-3

TIMS-3 uses a thermal ionization source with 16-assembly turret and has a multicollection system, with five rugged faraday cups. It uses a triple filament assembly [Fig. 2] with rhenium as the filament material.

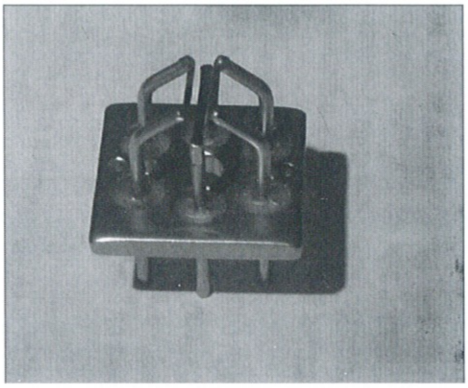

Fig. 2 Triple filament bead used in Indigenous TIMS-3

It uses a sector magnetic analyzer with extended geometry, the angle of entry and exit being 26.5 degrees. It has a resolving power of 450 at 10% valley and has a mass range of 3-280 amu at 5 KV. For achieving the required high vacuum for the analytical determinations, six pumps including two rotary pumps, one turbo molecular pump and three Ion-getter pumps are being used. The salient features of the instrument are given in Table 1. The instrument has special facilities like filament heating and ratio measurements through an interface, which has the attributes of advanced software. The supporting equipment also includes a mini spot welder and the degassing unit and a sample-heating unit. The spot welder and the sample heating unit are kept inside the fume hood for the safe handling of uranium and plutonium, which is routinely analyzed using the instrument.

Table 1. Salient Features of TIMS-3

Mass Range	0 to 380 at 5 kV
Resolution	Approx. 500 at 10% Valley
Abundance Sensitivity	30 ppm at 237 by 238 mass.
Source	Thermal Ionization source with triple filament assembly. Sample turret with 16 positions for simultaneous loadings.
Analyzer System	Magnetic Sector Analyzer with 90 degree sector angle and 30 cm as radius of curvature.
Multicollector Configuration	HM$_2$ HM$_1$ FC LM$_1$ LM$_2$ For U 238 236 235 234 233 For Pu 244 242 241 240 239
Ion Optics	Stigmatic focussing with extended geometry. Angle of entry and exit of ion beam: 26.5°.
Peak Shape	Normal and Satisfactory
Multicollection	Adjustable multicollection with two cups on lighter mass side, two cups on higher mass side, and fixed cup at fixed plane.
Automatic Controls	Filament Current Regulation, Acceleration Voltage scanning, Magnetic current scanning, Recording of ratios and baseline correction.
Vacuum System	Two Rotary pumps, Three ion getter pumps (one each at source, Analyzer and collector) and one Turbomolecular pump (TMP)
Isotopic Ratio Measurement	0.05 to 0.1% (Precision for ratio of 1)

3. Pre-Shipping evaluation of TIMS-3

Evaluation of the instrument prior to pre-shipping including rigorous testing of parameters like ion-optics for resolving power and beam centering, testing of vacuum system, testing practical resolution with theoretical resolution and checking the peak shape using certified standards etc. were established developer's work place. After shipping to the user's laboratory at KARP, requirement installation like magnet positioning, ion-optics alignment, acquiring of vacuum, multicollection adjustment to suit the analysis of uranium and plutonium etc. were met. After installation, some of the teething problems observed were overcome by adjustment of multicollectors for obtaining desired peak shape, attainment of high vacuum, calibration of ion current amplifiers for attaining the required stability etc.

4. Analytical Protocol

After standardization of the instrument, an analytical protocol has been established for the operating parameters like slope of heating the center and side filaments (0.6 amp/min for the center filament and 0.1 amp/min for the side filament), testing and adjusting the plate potentials, required baseline correction, recording of ratios using the software etc. Generally ratios are obtained for five blocks of ten scans each and minimum of two runs of five blocks are recorded. (In total 100 scan statistics). Using the instrument, several isotopic determinations for the input samples, uranium product samples as well as the audit plutonium samples are routinely carried out. Trace Uranium concentration in plutonium product samples is determined by IDMS technique using ^{233}U as the spike.

5. Improvement in Gain Variation

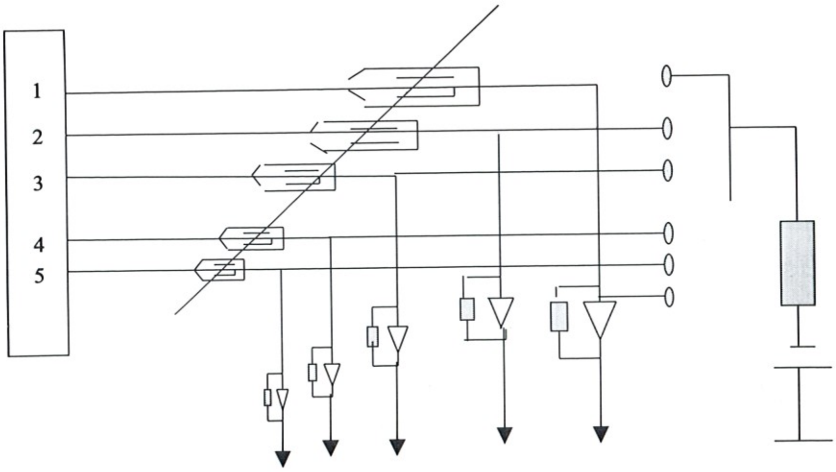

Fig. 3 Multicollector Faraday Cup arrangement in TIMS-3

During the operation of the instrument it was observed that the gains of the ion current amplifiers of the multi collector system [Fig. 3] were not the same and the analytical results obtained show a constant variation from the standard values. Since there was no in-situ calibration of amplifier gains, the gain factors of the amplifier cups were arrived at using the certified reference materials. Correction factors were accordingly affixed for the amplifier cups after doing the experiments using the certified reference materials and also using the natural uranium standards. The gain factors arrived at for the isotopic composition determination for uranium and plutonium are given in the Table 2. After fixing the gain factors for the amplifier cups, the isotopic composition determinations carried out using the instrument were in very good agreement with similar analyses carried out at BARC using an imported instrument.

TABLE 2: Gain variation correction incorporated using certified reference materials:

Sl. No.	Sample	Ratios for	Isotopic ratios		Correction factors applied	Isotopic ratios corrected
			expected	obtained		
1	Natural Uranium	234/238	0.00005	0.000055	0.9001	0.0000495
		235/238	0.00725	0.008635	0.8396	0.00725
2	SRM-U500 (Certified Ref. Material)	234/238	0.0104	0.0151	0.9001	0.013
		235/238	0.9997	1.1685	0.8396	0.9811
		236/238	0.00152	0.00195	0.8490	0.00165

6. Improvement in the design of the source chamber

While working with the cylindrical source chamber with 16 filament assemblies, it was observed that the variation in positioning of filament assemblies has resulted in poor external precision. Also, it was observed that the assemblies slip from their original position during the course of the analysis. This problem was taken to the manufacturers of the instrument and based on the feedback from KARP, a vertical source chamber was developed at MS & ESS, BARC, which involves linear movement mechanism for the filament assemblies. Through this improved design of the source chamber, the existing problems like positioning of the filament assemblies etc can be totally avoided. This improvement also avoids copper wire contacts in the filament assemblies that break due to the repeated heating in the source chamber. This also avoids cumbersome filament preparation and minimization of time for the preparation of reproducible filament assemblies. The vertical source chamber is in final stages of testing and is going to be installed at KARP shortly.

7. Improvements incorporated in electronics

New electrometer preamplifier cards were recently fixed in the instrument by modifying the old IC's to the latest ones for getting the required stability and to minimize the drift. These pre-amplifier cards were recently fixed with in the instrument, that has resulted in minimum noise and fluctuations in the ion current amplifiers. Similarly, the design of the filament current amplifier cards and the high voltage unit etc were suitably modified based on the problems encountered during the operation of the instrument.

With a view to improve the sensitivity of the instrument, a single filament assembly has been fabricated and tested at the developer's place. The same has been successfully tested at KARP and very encouraging results have been obtained with regard to the sensitivity and the peak shape. Improvements made with regard the stability of the high voltage unit and the source potential control unit has improved both the internal as well as external precision significantly.

8. Trace Uranium analysis in end product Plutonium

For the trace Uranium analysis in end product plutonium, prior to mass spectrometric analysis, an ion exchange separation method for the separation of Uranium from plutonium was followed using acetic acid medium. This has resulted into large column washes and long duration of ion exchange separation with nitrate-acetate-nitrate form conversion for final analysis.

Some improvement steps were introduced in this method for reducing the separation time and to minimize the waste volumes generated. Accordingly, bulk plutonium was separated from trace uranium using a solvent extraction procedure using Theonyl trifluoro acetone (TTA) prior to the ion exchange step. The aqueous, which is devoid of plutonium, is then subjected to the ion exchange separation as specified. The separated uranium was then determined using Isotopic Dilution method using ^{233}U as the spike.

The downtime of the instrument has been kept minimum by doing some of the preventive maintenance of the instrument like servicing of fore-vacuum pumps, sputter ion pump power supply units, maintaining the filament assemblies by ultrasonic cleaning, maintenance of the spot welding machine and sample heating unit. Some of the problems encountered like sensitivity, disappearance of signals during the analysis and difficulty in the preparation of filament assemblies etc are addressed to the manufacturers of the instrument. Single filament assembly source chamber has recently replaced the old turret assembly to check the improvement in sensitivity, signal stability etc. Better results with regard to the sensitivity have been achieved and efforts are on to make some of the modifications in the turret assembly so as to address some of the problems encountered during the operation of the instrument.

9. Conclusion

TIMS-3 has been in operation since the year 2000 and the manufacturers are sparing no effort in extending their services for the smooth running of the instrument. Some problems still exists related to the sensitivity of the instrument, peak shape etc which are being attended by VPID, BARC. The experience in operation of the instrument has further led to the development of new thermal ionization mass spectrometers at VPID division of BARC with 10kV acceleration voltage. The instrument is highly useful for catering the analytical requirements of the plant right from the installation and continues to provide valuable analytical outputs for the plant.

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__Shri. Hariharan Seshadri__ has been working with indigenous Thermal Ionization Mass Spectrometer (TIMS) at Kalpakkam Reprocessing Plant since its inception. He has been responsible for making several improvements in the performance characteristics of the instrument by coordinating with the developers of the instrument, VPID, BARC. His other interests are alpha spectrometry, potentiometry, radiometry etc pertaining to the analysis of Uranium and plutonium. He is a life member of ISMAS, IVS, AWARE etc. He is presently working in SRI, Kalpakkam.

Geochronological and Isotope Geochemical Studies using Multicollector Thermal Ionisation Mass Spectrometer: Implications in Uranium Exploration

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1. Introduction

Geochronology provides information on the age of the earth and related planetary systems including meteorites. It is the only tool by which we can get an absolute age of the Precambrian rocks which are devoid of fossils. The Precambrian stratigraphy is mainly based on the ages obtained by this technique.

Modern methods of geochronology are based on the principle of radioactive decay of long lived radionuclides viz ^{87}Rb, ^{147}Sm, ^{238}U, ^{235}U and ^{232}Th to their respective daughters viz ^{87}Sr, ^{143}Nd, ^{206}Pb, ^{207}Pb and ^{208}Pb and are widely applied in dating various rocks of the earth's crust and extra terrestrial bodies as well. The isotopic composition of the parent and daughter nuclides are measured. Thermal Ionization Mass spectrometer (TIMS) equipped with a multicollector system and their elemental concentrations are usually determined by Isotope Dilution Mass Spectrometry (IDMS).

2. Geochronology: Principles and Practices

2.1 Principle of Age Determination

Geochronological studies are carried out based on the principle of radioactive decay. The exponential law of radioactivity is represented by the equation.

$$N_t = N_0 e^{-\lambda t}$$

where N_0 = number of parent nuclide at time $t = 0$

N_t = number of parent nuclide remaining at anytime 't'

λ = decay constant of the parent nuclide

t = time in years

The age equation derived from above equation [Faure & Mensing, 2005] is

$$D_{rad.} = P\,(e^{\lambda t} - 1)$$

where, P = number of parent nuclide which is decaying

$D_{rad.}$ = number of daughter nuclide formed due to decay of the parent nuclide

In natural samples, daughter nuclides(D_p) include the daughters present initially (D_i) and those derived from the radiogenic decay of the parent (D_{rad}) i.e $D_p = D_i + D_{rad.}$

Accordingly, the age equation is given by

$$D_p = D_i + P\,(e^{\lambda t} - 1)$$

$$\Rightarrow \qquad \text{where} \qquad t = 1/\lambda \ln [\{ (D_p - D_i)/P \} + 1$$

As it is difficult to measure the absolute abundances of a given nuclide precisely by the Thermal Ionisation Mass Spectrometer, the above age equation is expressed in the form of isotopic ratios that are usually measured in TIMS by dividing a common non radiogenic nuclide (e.g ^{86}Sr, ^{144}Nd and ^{204}Pb etc.) which remains constant with time.

The above age equation is used to obtain both isochron ages and model ages.

2.2 Isochron age

The above derived age equation is in the form of equation for a straight line i.e. $Y = mX + C$. So in a XY plot, when the isotope ratios of the parent and daughter of a suit of co-magmatic and co-eval samples (8 to 10 numbers) are regressed, a straight line called as 'isochron' is obtained. The slope(m) of this line corresponding to the factor $e^t - 1$ yields the age of the suite of rocks and the intercept 'C' made by this isochron on Y-axis, gives the initial ratio. Thus the isochron method is applicable to those rocks which have attained isotopic homogenisation of its daughter element such that different samples of such rocks have similar initial ratio.

The goodness of the fit of the straight line obtained by least square regression [Williamson,1968] is indicated by a statistical parameter known as **M**ean **S**quared **W**eighted **D**eviates **(MSWD)** which is given by the formulae

$$[\Sigma W_i (Y_i - Y_i)^2] / (n - 2)]$$

Where W_i = Weight of each point i.e. 1/variance or $(1/\sigma^2)$

$Y_i - Y_i$ = The difference between the theoretical Y_i and experimental Y_i

$n - 2$ = Degree of freedom and σ = Standard Deviation

The commonly accepted values of MSWD are less than 2.5 for a suite of 5-10 samples which indicate that conditions of initial isotopic homogenisation and isotopic integrity of parent-daughter system are satisfied. MSWD values more than 2.5 are attributed to geological scatter apart from assigned analytical errors and the ages obtained with such values are referred to errorchrons instead of isochrons.

2.3 Model Age

When isochron ages are not obtained due to scatter of data points, model ages are determined by using initial ratios which is predicted by a model rather than measured directly.

2.4 Basic assumptions in Geochronometry

Geochronometry i.e radiometric dating of terrestrial and extra terrestrial rocks and minerals using the decay rates of long lived radio nuclides relies on the basic principle of radioactivity plus a couple of critical assumptions which are as follows:

- The rock or mineral(system) must have remained closed to the addition or escape of parent and daughter atoms since the time of it's formation except by decay of the parent to the stable daughter.
- It must be possible to correct for other atoms identical to daughter atoms (isobaric interferences) already present when the rock or mineral formed.
- The half life and decay constant of the parent isotope must be known accurately and the measurement of the daughter-to-parent ratio must be accurate because uncertainty in this ratio contributes directly to uncertainty in the age.
- Parent isotope should have half life of the same order as the range of time being measured and should be reasonably abundant in terrestrial rocks.

3. Thermal Ionisation Mass Spectrometry: Principles and Practices

Thermal Ionisation Mass Spectrometry has been the work horse for inorganic isotope ratio measurements since 1950's. It has seen spectacular progress over the past 50 years, brought about by automation, advances in solid state electronics, multi-collection techniques and filtering supported by advances in low-blank chemistry etc. It offers unparalleled accuracies and precision not only in the isotopic ratio measurements but also in the elemental abundance measurements of different elements too through isotope dilution techniques which are useful in geological, nuclear, environmental and life science applications. Despite the disadvantages that the method is not suitable for elements with ionisation potential exceeding 5.5 eV and moreover the methodology involves tedious and elaborate sample preparation and chemical separation protocols, TIMS instruments still have a significant role to play particularly for measurement of small samples (nanogram or less) and even for those elements which are the least abundant in nature. In addition, TIMS offer very little isobaric interferences which are overcome by good chemical separation and it has the ability to measure both positive and negative ions. Thus TIMS instruments remain the analytical mainstay in the field of geochronology.

Thermal ionisation Mass Spectrometers follow the basic geometry of the magnetic sector field mass spectrometers of Neir (1947) and essentially consist of an ion source, the mass analyser and the collector or detector assembly with adequacy in high vacuum systems. The schematic diagram of magnetic sector TIMS is shown in Fig. 1.

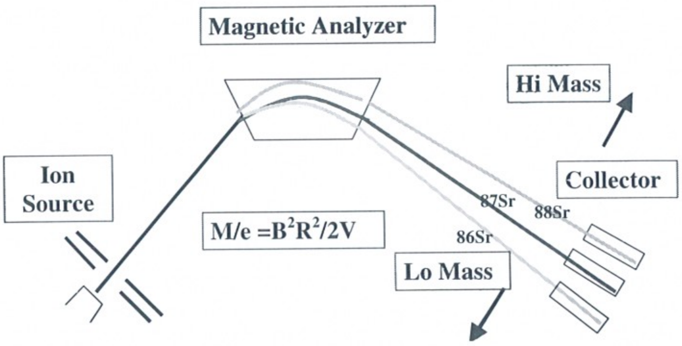

Fig. 1. Schematic of TIMS

3.1 Ion source : Ionisation and Acceleration

The ion source in a TIMS consists of either a single filament (for low ionisation potential elements like the alkalies and alkali earths) or multiple filament assembly(for Rare Earth elements) made up of ductile, refractory and high work function metals with high melting point and extremely high purity such as Rhenium(Re), Tantalum (ta), Platinum(Pt) or Tungsten (W) etc. The sample of the element to be analysed is placed on the surface of the filament (generally 0.01" thick, 0.03"wide and 0.4" long ribbons) as a solution of the chloride or nitrate of the element concerned. The solution containing the analyte element(s) are carefully dried and electroplated on to the ribbon before mounting in the mass spectrometer's ion source. The filament is heated by ohmic heating up to ~ 2000 K in the ion source under vacuum conditions (low pressure of 10^{-6} to 10^{-8} torr) which leads to evaporation and vaporisation of the sample. The high temperature of the evaporating element or of an adjacent filament (in case of multi-filament assembly) causes ionisation of the atoms either near completely or partly depending on its first ionisation potential (IP). The positive ions are accelerated from the ion source by applying high potentials typically in the range 5-10 KV across the filament plate and a series of slit plates help in collimating ions into a beam which is nearly monoenergetic in nature.

Ionisation is a function of the filament temperature, the work-function of the filament substance and the ionization potential of the element and is well explained in the Saha-Langmuir equation:

$$N_I / N_0 = (g_I / g_0)\ \exp\,[(\Phi - I)/kT$$

Where N_I/N_0 = ion to neutral ratio

g_I/g_0 = statistical weights of ion and neutral states (constant)

Φ = Surface work funcion (eV)

I = Element's first ionisation potential (eV)

K = Boltzman's constant

T = surface temperature in Kelvin

3.2 Mass Analyser : Deflection

The monoenergetic ions after being accelerated into a finely focused beam, enters a magnetic field generated by an electromagnet whose pole pieces are shaped and positioned in such a way that the magnetic field lines are perpendicular to the direction of travel of the ions. The magnetic sectors bend and deflect the trajectories of ions into circular path of radii that depend on the mass to charge (m/e) ratios of the ion which can be defined by the following equation:

$$m/e = (B^2R^2)/2V$$

where, m = mass; e = charge; B = magnetic field; R = radius of curvature; V = accelerating voltage

It is evident from the above equation that by changing the ion trajectories through variations of the magnetic field strength, ions of different m/e ratios can be focused on a detector.

Thus a magnetic sector mass analyser serves mainly two functions

(i) to resolve or separate the ion beams according to m/e ratio

(ii) to focus the ion beams on to the detector.

In practice, isotopic analyses is done by varying the magnetic field in certain automated steps to focus different ions onto the detector keeping the accelerating potential fixed. Hall effect measuring devices i.e hall probes are used to control and measure the magnetic field.

3.3 Collectors and Detectors : Ion collection and detection

The accelerating voltage in the source and the magnetic field are adjusted in such a way that one of the ion beams is focused through the collector slit and enters the detector cup positioned behind the slit plate while the other ion beams collide with a ground slit or with the metallic walls of the flight tube and are neutralised.

The modern TIMS is equipped with a computer controlled fully automated multicollector system consisting of faraday collectors fitted with an electron multiplier and Daly collector which detects ion beams that are too small to be measured with faraday cups.

The beam that enters the collectors are neutralised by electrons that flow from ground to collector through a highly stable large ohmic resistor (10^{11} ohms). A typical ion beam of 10^{-11} amps generates a potential of 1 volt. The voltage produced across the resistor is amplified and converted in to digital signals which are measured by electrometer valves / integrated circuits operational with Metal Oxide Silicon Field Effect Transistors (MOSFETS) etc which can be displayed in strip chart recorder / digital voltmeters (DVMs). The resulting signal consists of a series of peaks and valleys that form the mass spectrum characteristic of the element being analysed. The height of the peak is proportional to the relative abundance of the isotopes.

3.4 Vacuum

The TIMS (from source to collectorr) is pumped down to High Vacuum (HV) i.e 10^{-7} torr to minimise undesirable collision of ions of the ion beams with the ambient gas molecules/ background vapours which cause broadening of ion beams and degeneration of signals and to make the mean free path of the ions longer than the trajectory. Different types of vacuum pumps viz mechanical pumps, diffusion pumps, turbomolecular pumps, titanium sublimation pumps and cryo pumps etc. are used.

3.5 Fractionation

The isotopic fractionation occurs due to a variety of physico-chemical conditions in TIMS especially in the ion source during evaporation and ionisation of atoms from hot filaments which could yield unacceptable errors up to 1% in the measured isotopic ratios. So one of the most important tasks in TIMS is to correct for isotopic fractionation. For elements with two or more nonradiogenic isotopes, the fractionation factor is calculated from the following equation.

$$\textbf{True Isotopic Ratio} = \textbf{Observed Isotopic Ratio}\ (1 + F * \Delta m)$$

Where, F = fractionation Factor; Δm = mass difference of the two isotopes

3.6 Isotope Dilution Analysis : Principles and Practices

It is a technique used for the determination of concentration of an element using the selected isotope ratios in a mixture (M) of an unknown quantity of sample (S) and a known quantity of a 'spike' (T) i.e. a commercially available tracer of an element which is enriched in one particular stable minor isotope of the element.

According to IDMS principle

$$A\,(S)/A\,(T) = [R\,(M) - R\,(T)]/\,[R\,(S) - R\,(M)]$$

where A = Abundance of isotope of an element in Sample (measured) and in Tracer (known)

R = Isotopic ratios in mixture (measured)/tracer (known)/ Sample (known)

It is the most precise analytical technique for the estimation of a number of elements at nanogram or even at sub-nanogram level though it is time consuming and requires painstaking separation of the element of interest. A precision of 0.2% is attainable over a wide range of concentrations.

4. Different Systematics (Geochronometers) Their Applications and Significances

The details of the different parent and daughter isotopes, their mode of decay, half lives and decay constants which are useful for geochronometry using TIMS are given in Table 1.

TABLE 1: Different Geochronometers used for measuring the ages of terrestrial and extra terrestrial rocks using TIMS

Method/ systematics	Parent isotope	Daughter isotope	Mode of Decay	Half Life ($T_{1/2}$ in 10^9 years)	Decay Constant (λ in per year)	Suitable Rocks and Minerals
Rb-Sr	^{87}Rb	^{87}Sr	β^-	48.8	1.42×10^{-11}	Rocks and minerals with high Rb/Sr ratio e.g. granitic rocks and minerals like biotite, muscovite etc.
Sm-Nd	^{147}Sm	^{143}Nd	α	106	4.56×10^{-12}	Rocks and minerals with high Sm/Nd ratio e.g. basic and ultrabasic rocks and minerals like garnet, monazite
U/Th-Pb	^{238}U ^{235}U ^{232}Th	^{206}Pb ^{207}Pb ^{208}Pb	$8\alpha, 6\beta^-$ $7\alpha, 4\beta^-$ $6\alpha, 4\beta^-$	4.47 0.704 14.01	1.55125×10^{-10} 9.8485×10^{-10} 4.9475×10^{-11}	Uranium bearing minerals like uraninite, monazite, zircon, sphene and apatite etc.

4.1 Rb-Sr Systematics

The decay of ^{87}Rb (parent nuclei) and the growth of ^{87}Sr (daughter nuclide) in a rock or mineral since its formation, 't' years ago, is given by:

$$(^{87}Sr/^{86}Sr)_p = (^{87}Sr/^{86}Sr)_i + (^{87}Rb/^{86}Sr)_p\,(e^{\lambda t} - 1)$$

Where, $(^{87}Sr/^{86}Sr)_p$ = Present ratio (Measured)

$(^{87}Sr/^{86}Sr)_i$ = Ratio at the time of formation of the rock (intercept derived from the isochron plot)

$(^{87}Rb/^{86}Sr)_p$ = Present ratio (Measured)

$$\Rightarrow t = 1/\lambda \ln [\{ (^{87}Sr/^{86}Sr)_p - (^{87}Sr/^{86}Sr)_i \} / (^{87}Rb/^{86}Sr)_p + 1 \}]$$

The isotope ratio $(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})_\mathrm{p}$ is measured by the Thermal Ionisation Mass Spectrometer and the isotopic ratio $(^{87}\mathrm{Rb}/^{86}\mathrm{Sr})_\mathrm{p}$ is calculated from the weight ratio of Rb and Sr concentrations derived from IDMS. These ratios are regressed and plotted to obtain isochron ages and the intial $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$ from the slope and intercept respectively. When isochron ages are not obtained due to scatter of data points, the primordial $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$ ratio ($^{87}\mathrm{Sr}/^{86}\mathrm{Sr} = 0.69897$) called as 'Basaltic Achondrite Best Initial' **(BABI)** is used to obtain model ages which represent maximum possible age of the sample. The rocks or minerals having high Rb/Sr ratio (e.g. granitic rocks and minerals such as muscovite, biotite, K-feldspar phlogopite lepidolite, adularia and leucite) are suitable to obtain ages by this method.

4.1.1 Significance and application

- The Rb-Sr method is the most commonly used method which gives
- Age of emplacement of igneous rocks
- Age of major metamorphic event i.e. age of regional metamorphism.
- Age of diagenesis by analysing authigenic clay minerals (illite and glauconite) derived from shales and sandstones.
- Age of mineralisation in pegmatite by analysing co-genetic muscovite and biotite
- Thermal history e.g. age of metamorphism, cooling ages and time of the final exhumation of plutonic rocks etc. by dating minerals
- Samples having age as young as 10 Ma and as old as the age of the earth can be dated by Rb-Sr systematics.
- The initial $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$ ratio gives the idea about the petrogenesis i.e. whether the rock is derived from the crustal (0.708) or from the upper mantle source(0.702 and) and also gives an insight into contamination of the magma by crustal rocks.

4.2 Sm-Nd Systematics

The decay of $^{147}\mathrm{Sm}$ (parent nuclei) and the growth of $^{143}\mathrm{Nd}$ (daughter nuclide) in a rock or mineral since its formation, 't' years ago is similar to Rb-Sr systematics described above and is given by:

$$(^{143}Nd/^{144}Nd)_p = (^{143}Nd/^{143}Nd)_i + (^{147}Sm/^{144}Nd)_p\ (e^{\lambda t} - 1)$$

The Sm-Nd method is applied to chondritic meteorites in order to understand the evolution of the bodies in solar system because of their primitive nature. The isotopic composition of the chondritic meteorites is referred to as **CH**ondritic **U**niform **R**esorvoir (CHUR). The present day $^{143}\mathrm{Nd}/^{144}\mathrm{Nd}$ and $^{147}\mathrm{Sm}/^{144}\mathrm{Nd}$ ratio of CHUR is 0.512638 and 0.1967 respectively.

According to age equation,

$$(^{143}Nd/^{144}Nd)^t_{CHUR} = \mathbf{0.512638 - 0.1967}\ (e^{\lambda t} - 1)$$

The deviation of the terrestrial $^{143}\mathrm{Nd}/^{144}\mathrm{Nd}$ from that of the present day CHUR is given by a notation ε^t_{Nd} which is defined as

$$\varepsilon^t_{Nd} = [\ \{\ (^{143}Nd/^{144}Nd)^t_{sample} / (^{143}Nd\ /\ ^{144}Nd)^t_{CHUR}\ \} - 1\ ] \times 10^4$$

Positive ε_{Nd} value indicates depleted mantle sources where as the negative value shows enriched mantle sources for the rocks. The continental igneous rocks had $_{\mathrm{Nd}}$ values close to zero presumably because these rocks had been presumed to be derived from a reservoir similar to the chondritic reservoir that has largely remained unchanged since the formation of the earth.

When precise isochron ages are not obtained due to lack of spread in the $^{143}Nd/^{144}Nd$ and $^{147}Sm/^{144}Nd$ ratios, model ages are attempted using CHUR evolution line (T_{CHUR}) and depleted mantle evolution line (T_{DM}).

$$T_{CHUR} = 1/\lambda \ln [\{ \{ ^{143}Nd/^{144}Nd)_{sample} - (^{143}Nd/^{144}Nd)_{CHUR} \}/\{ (^{147}Sm/^{144}Nd)_{sample} - (^{147}Sm/^{144}Nd)_{CHUR} \} \} + 1]$$

4.2.1 Significance and application

- The average Sm/Nd ratio in crustal rocks is around 0.12. This ratio is around 0.15 in highly evolved granites whereas in ultramafic rocks it is up to 0.4. Due to similar geochemical properties of Sm and Nd (unlike Rb and Sr), large range of Sm/Nd ratio in natural rocks are rare and Sm and Nd generally does not get disturbed during post crystallization deformations and metamorphism. So the whole rock isochron ages can give the actual age of formation of the metamorphosed as well as undeformed rocks.
- This method is very useful for dating pre-metamorphic history in rocks which have undergone later deformation and metamorphism and where Rb-Sr and K-Ar methods had often failed to give precise age of crystallization.
- In case of high grade metamorphic rocks the whole rock Rb-Sr, U-Pb and Pb-Pb ages give age of peak metamorphism whereas Sm-Nd ages give the initial age of the formation of the rock.
- In Sm-Nd method, mineral isochrons have advantage in defining precise ages as they have large variation in Sm/Nd ratios, unlike whole rock systems where the spread in the Sm/Nd ratios is very less. Minerals like garnet and xenotime have very high Sm/Nd ratios (up to 2) and are quite favourable for dating by this method apart from basic and ultrabasic rocks.
- Due to difficulty in obtaining a wide range of Sm/Nd ratios and only a small change in the daughter ratio ($^{143}Nd/^{144}Nd$) together with the long half life of ^{147}Sm (106 Byr), the use of the Sm-Nd method is restricted to rocks older than 1000 Ma.
- The chondrtic model ages (T_{CHUR} and T_{DM}) give the crustal formation age provided sufficient fractionation in Sm-Nd occur as the crust evolved from the mantle. This method is most suitable for dating the protolith ages of rocks.
- Sm - Nd method thus is used to measure the crustal accretion ages and sediment provenance ages.

4.3 U-Pb Systematics

The decay of ^{235}U and ^{238}U (parent nuclei) and the growth of ^{207}Pb and ^{206}Pb (daughter nuclide) respectively in a rock or mineral since its formation, 't' years ago, is given by:

$$(^{206}Pb/^{204}Pb)_p = (^{206}Pb/^{204}Pb)_i + (^{238}U/^{204}Pb)_p * (e^{\lambda 8t} - 1)$$

$$(^{207}Pb/^{204}Pb)_p = (^{207}Pb/^{204}Pb)_i + (^{235}U/^{204}Pb)_p * (e^{\lambda 5t} - 1)$$

4.3.1 Significance and application

- The two chronometers ^{238}U - ^{206}Pb and ^{235}U - ^{207}Pb offer a simple method for testing the assumption of a closed U-Pb system in a rock by single analysis. If the two ages obtained by above two chronometers do not agree then they are termed as discordant ages and indicate that the rock has not remained as closed system since its formation. These discordant ages may be due to lead/uranium gain or loss during later geological events.
- In case of discordant ages U/Pb data are presented on a Concordia diagram where ratios of $^{206}Pb/^{238}U$ (*y*-axis) plotted against $^{207}Pb/^{235}U$ (*x*-axis). The Concordia curve is the locus of all the points for which $^{206}Pb/^{238}U$ ages are equal to the $^{207}Pb/^{235}U$ ages. In case of Pb loss/ U gain the discordant data points

will fall below the Concordia curve whereas in case of uranium loss data points shift above the Concordia curve. When the discordant data points from a suite of cogenetic samples fall on a line in the Concordia diagram the line is called the Discordia line. The upper intersection of the Discordia with the Concordia curve gives the age of crystallization for the suite of samples and lower intersection of this line give the secondary age or age of later event of Pb loss/U gain.

- Uranium is highly mobile in near surface conditions and isotopic disturbances due to uranium mobility is common in most of the rocks hence U-Pb isochron method is generally not applied to whole rock dating.
- Mostly, uranium rich minerals are suitable for dating by this method. The minerals like uraninite, brannerite, coffinite, zircon and monazite etc. can be dated to get the age of mineralisation by this method.

4.4 Pb-Pb Systematics

The age equations mentioned in U-Pb method can be rearranged to get the following equations:

$$({}^{207}Pb/{}^{204}Pb)_p - ({}^{207}Pb/{}^{204}Pb)_i = ({}^{235}U/{}^{238}U)_p * \{ (e^{\lambda 5t} - 1)/(e^{\lambda 8t} - 1) \} * \{ ({}^{206}Pb/{}^{204}Pb)P - {}^{207}Pb/{}^{204}Pb)_i \}$$

For a suit of 8-10 cogenetic samples, an isochron age can be obtained by plotting curve between ^{206}Pb/^{204}Pb (*x*-axis) and ^{207}Pb/^{204}Pb (*y*-axis).

4.4.1 Significance and application

- The common Pb-Pb method indicate the age of actual emplacement of the rocks, if they are undeformed.
- Most of the rocks specially sedimentary rocks like carbonates which are not suitable for dating by most of the other conventional methods can be dated by this method. This method gives the age of the formation of the carbonates in the sedimentary basin if it is undeformed otherwise it will give the age of the later event.
- The model % i.e. ^{238}U/^{204}Pb value indicates the nature of the source in which Pb evolved before its separation. μ values of > 8 and < 10 indicates crustal source and values indicates mantle source.

5. Geochronology Laboratory, AMD, Hyderabad: Existing Facilities And Methodology

5.1 Instrument

The geochronology Laboratory of AMD is centered round a sector 54 TIMS (VG 354 model) installed in 1984 supported by a class 100 clean chemical laboratory since 1997. The instrument was recently upgraded with new data acquisition system and new sector 54 software.

The detailed specifications of TIMS are given in Table 2 and the salient features are as under:

TABLE 2: Specifications of TIMS (VG 354)

Source	Thermal ionisation, 16 samples at a time
Analyser	90° Sector Magnet (Extended Geometry)
Detector	5 Faraday Cups (L_1, L_2, Axial, H_1, H_2 ($> 1 \times 10^{-3}$ and one Daly ($< 1 \times 10^{-3}$ A)
Precision	0.01 – 0.003%
Ab. Sensitivity	5 ppm at mass 237 with respect to ^{238}U peak
Sensitivity	1 ion per 500 atoms of 'U'
Resolution	370 at 10% valley
Background	$\sim 1 \times 10^{-15}$ A

The ion source has a turret carrying 16 samples (single and tripple filament) such that each filament can be preheated under computer control and the accelerating potential is maintained at 8 KV. After vacuum is restored, each filament holder is rotated by a carousel like movement into the correct ion source position ready for analysis.

The 90° magnetic sector analyser has a radius of 27 cms. However, the design of the magnetic pole pieces is such that the angle of incidence is 26.8^{0} with normal to the magnetic pole face and the mass resolution becomes equivalent to an anlyser of 54 cms radius. This design is known as extended geometry which enables Z focusing of the ion beams apart from X and Y directions.

The **multicollector system** include 5 Faraday cups (L_1,L_2, Axial, H_1, H_2) and one ion counting Daly detector which is used for signal multiplication in case of very small signals ($< 10^{-13}$ Amperes)

Vacuum in the source, analyser and collector regions is maintained by a set of pumps. A combination of 110 litre/sec triod ion pump and 3000 litre/sec titanium sublimation pump gives the source pump down to 2×10^{-7} torr within 30 minutes from insertion of the sample barrel. Initial rough pumping (upto 10^{-3} torr) from atmosphere is provided by a 100 litre/min two stage rotary pump. The pumpdown rate is enhanced through liquid nitrogen cold trap fitted in the roughing line close to the source housing. An all metal line of sight valve separates the source from the analyser. The pirani gauge and ion gauges are used to monitor the pressure.

Data acquisition in the upgraded version of TIMS is quite compact and consists of a single digital data acquisition system unit with 20 BIT AD converter and a display panel for simultaneous read out of all ion currents independent of data systems. This new unit has replaced the old six solarton digital voltmeters (DVMs) and shall be directly interfaced with the existing multiple interface unit.

The sector 54 software is written in Modula-2, developed by Prof Niklaus Wirth. The version of Modula-2 was specially developed for the MS DOS system by Logitech Inc. This software provides the interface between the TIMS and its users. This software replaces the manual controls and provides automatic control of virtually all operations and aspects of analysis. The software also provide the facility of saving the results from the main analysis program to the disk (Data dump files)

This mass spectrometer is capable of analysing Sr, Sm and Nd with a precision of 0.003% and Rb, Pb and U with a precision of 0.01%.

The errors (2σ) assigned based on the analyses of the standards and duplicates are 2% in Rb and 1% in U, Pb, Sr, Nd and Sm elemental concentrations, 0.2% in Pb isotopic ratios and 2%, 0.05%, 0.005% and 0.1% respectively for ^{87}Rb/^{86}Sr, ^{87}Sr/^{86}sr, ^{143}Nd/^{144}Nd and ^{147}Sm/^{144}Nd ratios.

The results of the standards and that of the blanks obtained during the analyses are in agreement with the prescribed limit and are given in Tables 3 and 4 respectively.

TABLE 3: Results of standard reference materials

Standards	Isotope ratio/ elemental abundances	Values obtained	Certified/ Recommended values
NIST (NBS) SRM 987 (Sr CO_3)	^{87}Sr/^{86}Sr	0.710245 ± 23	0.71025
JM(NDN-1) (Nd_2O_3)	^{143}Nd/^{144}Nd	0.511122± 10	0.511120
NIST (NBS) SRM 981	^{206}Pb/^{204}Pb	16.961	16.937
	^{208}Pb/^{204}Pb	36.853	36.721
USGS	Rb	170 ± 0.5 ppm	170
G-2 (granite)	Sr	480.5 ± 1 ppm	478
	Sm	7.18 ± 0.02 ppm	7.2
	Nd	53.88 ± 0.05 ppm	55
	^{87}Sr/^{86}Sr	0.70995 ± 8	0.7099
	^{143}Nd/^{144}Nd	0.70995 ± 13	0.51222
	^{147}Sm/^{144}Nd	0.1338	0.1309

TABLE 4: Results of blanks

Element	Value of blank (ng)
Rb	< 0.5
Sr	1.0
Sm	0.1
Nd	0.1
Pb	2

5.2 Methodology: Various stages in Geochronological Studies

The various stages in geochronological studies are described below:

5.2.1 Stage 1: Petrological studies

Petromineralogical studies are carried out to study the mineralogical and modal composition of the rock to know the correct nomenclature, to study the degree of alteration, weathering and deformation and to ascertain the suitability of rocks / minerals for dating, prior to the analysis of the sample. This study helps in selecting the mineral / rock to be dated and in the interpretation of the data as well.

5.2.2 Stage 2: Sample preparation and chemical processing

Whole rock samples are cleaned, broken and crushed in a Jaw crusher and ground to -200 mesh after quartering and coning in a shatter box. The representative samples are spiked with mixed tracers of Rb-Sr-U-Pb and Sm-Nd enriched in ^{87}Rb,^{84}Sr, ^{235}U, ^{206}Pb, ^{149}Sm and ^{146}Nd for the estimation of Rb, Sr, Sm and Nd respectively by IDMS and chemically digested in Teflon Bombs using 6ml 48% HF and 2ml 16M HNO_3 at 150°C for 48 hours and taken in 2.5 M HCl. Pb and U, after dissolution, are taken in 0.5 M HBr and U is further converted in HNO_3 prior to ion exchange separation. The mixed tracer solutions are calibrated using suitable standards. The unspiked powder samples are separately dissolved for the determination of isotopic ratios of Sr, Nd and Pb.

The desired elements are separated using conventional ion exchange columns. Rb, Sr and REE group are separated by AG 50 × 12 cation exchange columns whereas Nd and Sm are separated from REE group using **H**ydrogen **D**i-**E**thyl **H**exyl **P**hosphate (HDEHP) coated bio-bead columns. Pb and U are separated in AG 1 × 8 anion exchange columns (Column Volume 0.75 ml). The ion-exchange separation parameters has been given in Table 5.

TABLE 5: Elemental Separation through Ion-exchange

Sl. No.	Ion-exchange method	Elements	Eluant Acid	Elute vol.
1.	Cation (AG 50 × 12)	Rb	2.5 MHCl	14-20 ml
		Sr	2.5 M HCl	36-48 ml
		REE Group	5 M HNO_3	0-11 ml
2.	Cation (HDEHP coated bio beads)	Nd	0.25 M HCl	3.14 ml
		Sm	0.4 M HCl	3-14 ml
3.	Anion (AG 1 × 8)	Pb	1 N HNO_3	1.5 ml
		U	1 N HNO_3	1.5 ml

5.2.3 Stage 3: Analyses on TIMS (VG-354)

The pure separated elements are loaded on mass spectrometer. The details of the loading procedure for different elements have been described in Table 6. Rb and Sr whose first ionization potential are comparatively lower, are loaded on single tantalum filament along with orthophosphoric acid in chloride and nitrate form respectively whereas Sm, Nd and U with higher first ionization potential are loaded on the side tantalum filaments of the triple filament (Ta-Re-Ta) in nitrate form wherein ionization takes place indirectly through heating the centre rhenium filament. Pb is loaded in nitrate form on silica gel film on single rhenium filament along with orthophosphoric acid.

TABLE 6: Loading parameters of samples on TIMS

Sl. No.	Elements	Procedure of Loading and	Chem. form	Filament Type
1.	Rb	1 μ L of 0.5M H_3PO_4+ few hundred η g of Rb	Chloride	Single, Ta
2.	Sr	1 μ L of 0.5M H_3PO_4+ few hundred η g of Sr	Nitrate	Single, Ta
3.	Nd/Sm	1 μ L of 0.5M H_3PO_4+ few hundred η g of Nd/Sm (on each side filament)	Nitrate	Triple, Ta-Re-Ta/Re-Re-Re
4.	U	1 μ L sol. + 1 μ g of U on each side	Nitrate	Re-Re-Re
5.	Pb	Silica jel film + few hundred η g of Pb + 1 μ L of 0.5 M H_3PO_4	Nitrate	Re

The abundances of Rb, Sm, Sr, Nd, Pb and U are measured using IDMS and are analysed in peak jumping mode in single collector. The Sr, Nd and Pb isotopic ratios are analysed by dynamic multi collection mode typically involving nearly 150 cycles of measurements and simultaneous correction for mass fractionations, short time drift in ion beam intensities and electronic noises except Pb where mass fractionation corrections are applied externally. The Sr and Nd isotopic ratios were corrected for mass fractionation by normalizing to a value of 0.1194 for $^{86}Sr/^{88}Sr$ and 0.7219 for $^{146}Nd/^{144}Nd$ respectively.

The construction of isochron diagrams was based on the method using "ISOPLOT' of Ludwig(1993).

6. Implication of Geochronological Data in Uranium Exploration

Dating of rocks and minerals help in 'U' exploration since uranium deposits world over are time bound e.g. Quartz Pebble Conglomerate type of uranium mineralization:

(Witwatersrand, South Africa and Blind River, Canada)	2200-2800 Ma
Unconformity type uranium mineralization	
(Cigar lake Canada and Pine Creek, Australia)	1600-900 Ma
Triassic–Jurassic (Colerado, U.S.A)	250-150 Ma
Cretaceous-Tertiary (Domiasiat, India- 65Ma).	100-5 Ma

Therefore, the accurate age data can help in modeling for a particular type of deposit in a geological terrain.

The Pb isotope ratios like $^{206}Pb/^{204}Pb$ and $^{207}Pb/^{206}Pb$ help in delineating and distinguishing uranium mineralised zones, the details of which are given in Table 7. It is also well known that granites which are younger and derived by the partial melting of the pre-existing crustal rocks are the principal source rocks for uranium. The initial $^{87}Sr/^{86}Sr$ ratios, model μ and ε_{Nd} help in characterizing the different types of granites , the details of which are given in Table 8.

In India, U-Pb geochronological studies have revealed two distinct phases of uranium mineralisation viz 1700-1800 Ma event in Vempalli Dolostone, 1300-1400 Ma event in Lambapur and Gandi areas and one episode of remobilisation at 450-550 Ma in Lambapur and Gandi areas in and around Cuddapah basin, Andhra Pradesh (Cuddapah Supergroup).

TABLE 7: Pb isotope in uranium exploration

Pb isotope ratios	In uranium deposits	In normal crustal rocks
$^{206}Pb/^{204}Pb$	> 100	13-25
$^{207}Pb/^{206}Pb$	< 0.2	0.8 – 0.9

TABLE 8: Sr, Nd, Pb Isotope and granite petrogenesis (main source for uranium)

	M-Type granite	I-Type granite	S-Type granite	A-Type granite
$^{87}Sr/^{86}Sr$ Initial	< 0.704	< 0.706	$> 0.708 - 0.8$	0.703-0.712
ε_{Nd}	> 0 (+ *Ve*)	~ 0	< 0 (−Ve)	Variable
μ	< 8.0	7.5-8.0	$8 < / \mu < 10$	$8 < \mu < 10$

7. Conclusion

The role of geochronology and isotope geochemistry is of paramount importance in geological understanding in general and in uranium exploration in particular. The following are the important conclusions we can draw from the above studies which are all of utmost significance in modeling for uranium exploration.

- Time of emplacement of rocks viz. source rocks for uranium i.e. granite etc.
- Time of regional metamorphism which helps in mobilizing the uranium from the pre-existing rocks
- Time of thermal event which causes further concentration of uranium in the system
- Time of uranium mineralisation and remobilisation Petrogenesis of the source and the host rocks of the uranium
- Crustal evolution
- Chronostratigraphy of Precambrian terrain
- In conceptual modelling for 'U' Exploration

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An Overview on Sample Dissolution Techniques for Analysis of Geological and Environmental Materials by ICP-MS

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1. Introduction

The most important aspect on the success of any geological and environmental investigations primarily depends on proper collection of representative samples, contamination free pulverization, adopting specific sample dissolution technique and finally precise estimation of desired elements by standard instrumental techniques. Adequate attention should be paid for selection of instrument-specific dissolution techniques of various samples for specific investigations.

Choice of specific sample decomposition technique is a basic and integral step of various scientific investigations. This is because of the fact that this primary step is a limiting factor to generate precise data and sample throughput in the context of the recent development of the states-of-the-art multi-element-measurement instrumentation that can attain very low level of detection of most of the required elements in the samples. Due to complex character of geological materials, it is highly essential to choose specific dissolution technique that should be compatible with the objectives of the investigation, the chemical and mineralogical nature of the samples, the elements to be determined, sample throughput needed, desired precision and accuracy, availability of the instruments, skill of the analyst and time available for analysis.

Conventional methods of chemical analysis following simply acid dissolution, fusion with fluxes or other classical techniques that require tedious procedures cannot keep pace with the productivity of the latest microprocessor-based instrumental techniques presently available in the analytical fields.

2. Solution techniques

The plasma spectroscopic analysis of samples is primarily a solution technique for which any heterogeneous solid sample; whether these are geological, environmental, biological or nuclear requires to be brought into a chemically uniform & homogeneous solution using suitable contamination free dissolution technique before feeding into the plasma. However, direct slurry and suspension of fine solid particles nebulization, most complicated laser ablation and other techniques are being developed recently for solid fine powder-sample analysis by many workers using ICP-MS, but these techniques are complicated and require very skilled analyst.

2.1 Advantages of solution techniques

Advantage of direct solid sample analysis is that it avoids complicated sample dissolution steps, but the solution techniques possess several inherent advantages and the most important are [i] minimizes matrix interferences [ii]ensures complete decomposition of refractory materials [iii] aquaregia-based partial dissociation, used in mineral exploration and environmental studies, permits determination of elements in labile phases [iv] allows chemical separation and preconcentration processes [v] speciation studies and [vi] the most important one is analysis against artificial standard solutions.

Liquid samples such as ground water, hydrothermal fluids etc. can be analysed by direct aspiration into the spectrometer without any chemical manipulation, other than addition of few ml of high purity acid and normally does not pose any remarkable problem due to its homogenity and less matrix.

2.2 Pre-concentration techniques

Many elements in environmental samples are present at a very low concentration level (such as rain water, dry deposition etc.), which are below the detection limit of ICP-MS. These cannot be determined by direct aspiration and it needs to adopt various "pre-concentration techniques" to enrich selected analytes from a large volume of sample solution. This may be achieved using a single or combination of techniques. The most remarkable and acceptable techniques are; [i] ion -exchange [ii]chelating ion-exchange [iii] solvent extraction and [iv] co-precipitation. In many cases on-line flow injection preconcentration technique is also adopted for this purpose.

2.3 Classification of dissolution techniques

As ICP-MS technique is a solution technique, solid samples are to be treated adopting various dissolution techniques. Although dissolution of metals, alloys and some simple samples is comparatively easy and straightforward, the geological materials, being complex in nature due to the presence of varied type of resistant minerals, need special care and attention towards selection of dissolution technique that is compatible with the aims and objectives of the investigations. These techniques may be broadly grouped into three categories:

- Partial or complete dissolution of finely grounded samples with a single or combination of acids, other than hydrofluoric acid in open or close vessel.
- Partial or complete dissolution of finely grounded samples with varied type of acid mixtures in different ratios including HF in open and close vessel.
- Fusion of finely divided samples with single and combined fluxes in different ratios at a high temperature and dissolution of resulting mass with acid.

Depending on complex nature of the many samples and other special type of investigations, the above techniques need modifications either in the chemical steps or using special device. These are:

(i) Partial dissolution with mixture of acids followed by fusion of the unreacted mass with suitable flux and dissolution of resulting fused –mass with acid and finally combining of the two fractions.

(ii) Microwave-assisted decomposition of geological samples with acids and other reagents in closed vessels at higher temperature and pressure may be used for sample dissolution but there remain doubt about complete dissolution of resistant minerals which are common in most of the geological materials.

(iii) Selective extraction of elements where information on the associated elements with various phases i.e metals bonded in sulphides, oxides, silicate and amorphous oxyhydroxides coatings or even remains in metallic form are also done using selective extraction schemes of different phases with a variety of reagents, weak acids and oxidizing, reducing and complexing reagents. This practice is in vogue for many years in exploration geochemistry, and special type of analytical objectives and now also is in use in some environmental studies.

3. Dissolution of Geological and Environmental Samples

Although, HNO_3, HCl, HF, $HClO_4$, H_2SO_4, are good reagents for sample dissolution, but in plasma analysis, very few cases above acids are being used individually. However, HNO_3 matrices are considered as best acid medium for ICP-MS estimation of analytes.

Aqua-regia digestion is conveniently employed in most environmental studies and mineral surveys where total decomposition is not necessary as because trace-elements of interest are loosely bonded in clay minerals, adsorbed onto particle surface, trapped in various oxides or oxyhydroxides including associated with organic matter. This procedure could be employed in emission techniques successfully but due to presence of chloride ion and formation of polyatomic ion interference, use of aqua-regia for ICP-MS is not preferable. A mixture of acids such as HNO_3-HF-$HClO_4$ is most favoured combination for dissolution of geological materials for ICP-MS estimation of most of the trace-elements in 1 M HNO_3 final solution. The HNO_3-HF-$HClO_4$ system may cause interference problems with As and V and also to a lesser extent Cr, Fe, Ga, Se, Ti and Zn due to residual chloride ions from remnant $HClO_4$.

Samples containing resistant refractory minerals (Cassiterite, chromite, magnetitie, tourmaline, wolfroamite, beryl, columbite, corundum, chromite, garnet, ilmenite, kyanite, rutile, staurolite) could not be digested with 100 % efficiency with HNO_3-HF-$HClO_4$ in open vessel technique. Although " High Pressure Closed Digestion Vessels" (Microwave Digestion System) could be used successfully in complete dissolution of varied types of geological materials, but it does not seem to be completely effective in the case of samples containing above resistant minerals and this restricts the use of Microwave Digestion System particularly where objectives demands analysis of REE, HFSE and some strategic elements..

Alkali fusion using $LiBO_2$, mixture of meta and tetra borate, Na_2O_2 permits complete dissolution of the entire mass containing most refractory materials. The most disadvantage of fusion process is introduction of high matrix in the system, which need dilution of the final solution for analysis but may miss some trace elements.

It suggests that no single preparation technique is well suited for digestion of geological and environmental materials completely. However, combination of both the techniques i.e., open-vessel combined acids (HNO_3-HF-$HClO_4$) followed by mix of (lithium tetraborate + lithium metaborate) fusion permits estimation of wide range of elements including volatile hydrides, REE, Hf,Nb,Ta and Zr in most samples with desired precision and accuracy.

Excellent sensitivity of ICP-MS with simple nature of REE mass-spectrum with superior detection limit, the ICP-MS instrument allows complete separation-cum-estimation of all REE in geological and environmental samples without adopting any chemical separation technique at level down to about ten times of the chondritic distribution values with a dilution factor of about 400-500 on a sample solution. This is an excellent advantage of ICP-MS over other solution-technique measurements.

Although HNO_3-HF-$HClO_4$ dissolution permits estimation of all REE in samples, but many minerals such as Zircon, sphlene,garnet,apatite, monazite where majority of the REE resides are not completely dissolved by above acid-mixture in open vessel technique. My experience says that complete dissolution of unknown mineralogical composition sample requires combined decomposition technique i.e. HNO_3-HF-$HClO_4$ plus fusion of unreacted mass with suitable flux or direct fusion of entire sample with proper flux such as 1:1 mixture of lithium tetraborate and lithium metaborate followed by dilute HNO_3 leaching of the fused mass.

Due to low abundance and heterogeneous abundance of gold and PGEs (Au,Pt,Pd,Rh,Ru,Ir and Os), determination of the above precious metals in geological materials is very critical and needs special care during sample preparation and quantification precisely.

These elements can be determined usually only after separation from gangue material followed by adopting preconcentration technique either using Pb-fire-assay or NiS-fire-assay techniques. Performing several chemical treatment steps, the elements are measured by the ICP-MS.

The Pb-Fire-Assay preconcentration technique permits 100%recovery in case of Au, Pt and Pd whereas NiS-Fire-Assay method allows good recovery in the case of Au, Pt, Pd and highest recoveries for Ir, Os, Rh ans Ru.

The most striking advantage of ICP-MS technique is to estimate quantitatively the HFSE from a single-step dissolution technique using mixed acids (HNO_3-HF-$HClO_4$).

Recent development in the field of ICP-MS estimation of multielement is that a little or no sample preparation is required. With the invent of laser-ablation [LA] sample introduction system and its coupling with ICP-MS instrument, tedious sample preparation steps could be avoided where direct solid sample in the form of vapor generated through point excitement by a narrow laser beam on the surface of the powdered sample can be introduced into the plasma through this attachment. The combination of these two gave birth of new set, popularly known as ''LA-ICP-MS' to the geoscientists. However, there are lots of intricacies of this technique and need special care, attention and skilled analyst.

The most important aspect of elemental quantification is to use proper Standard Reference Materials [SRMs] in each batch of samples along with the actual samples for analysis by ICP-MS technique.

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Sample Introduction Methods in ICP-MS

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1. Introduction

Inductively coupled plasma mass spectrometry (ICP-MS), is the technique for ultratrace multi-elemental and isotopic analysis and sample introduction plays a major role in application of this technique to a wide variety of materials [1]. Generally, pneumatic nebuliser-spray chamber assembly is used to produce fine aerosol of the sample solution which is introduced into the plasma for analysis. The conventional pneumatic nebuliser-spray chamber system has the limitations of (i) necessity for dissolution of solid samples (ii) requirement of higher volume of solution (few ml) and (iii) difficulty in speciation studies. Such limitations have been overcome by various other methods of sample introduction such as high efficiency nebulisers, gaseous sample introduction, electrothermal vaporization, chromatographic separation techniques and laser ablation [2,3].

2. Nebulisers

Pneumatic nebuliser (either concentric or cross flow) in combination with spray chamber is generally used for introducing sample aerosol into the plasma. In Meinhard pneumatic nebuliser [Fig.1], the solution is generally passed through a capillary (~0.4mm dia) with the flow rate of ~ 1ml/min. Nebuliser agron flows through the outer tube (interannular area at the tip: 0.028 mm^2) with the pressure of ~ 40 psi resulting in the formation of droplets. Spray chamber allows droplets of <2 μm size to reach plasma. This results in the sample introduction efficiency of around 2%. When the available sample volume is as low as 10μl, a flow injection device has to be used with this nebuliser which results in transient signal. This causes difficulty especially in multi-elemental analysis. This problem has been overcome with the development of other nebulisers such as microconcentric nebuliser (MCN) and direct injection nebulisers [4].

In MCN [Fig. 2], the capillary diameter is reduced to 0.1 mm and gas outlet cross sectional area is also reduced (0.017mm^2) such that the nebuliser is operated with nebuliser pressure of ~ 80psi and solution flow rate of 10- 50 μl/min. This results in steady state signal with sample introduction efficiency of 50 %. Thus, MCN is very useful when the sample availability is limited.

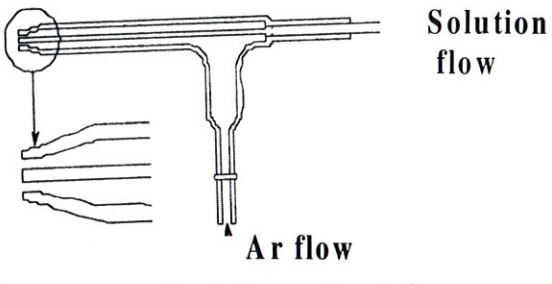

Fig. 1. Pneumatic nebuliser

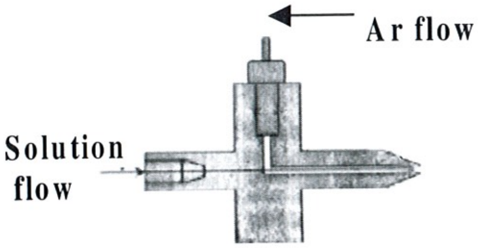

Fig. 2. Micro Concentric Nebuliser (MCN)

In Direct Injection High Efficiency Nebuliser (DIHEN), injector tube is replaced with the nebuliser and there is no spray chamber [Fig. 3]. Sample transport efficiency is ~ 100% and this nebuliser is very advantageous for small volumes of sample solution as it is normally used with 50μ l/min solution flow rate.

In ultrasonic nebuliser, solution passes through a piezoelectric transducer [Fig. 4]. Ultrasonic standing waves are generated on the surface of the solution giving rise to droplets. More droplets of smaller size (<2 μm dia.) are generated resulting in higher sample transport efficiency (20 -30 %) and thus better sensitivity.

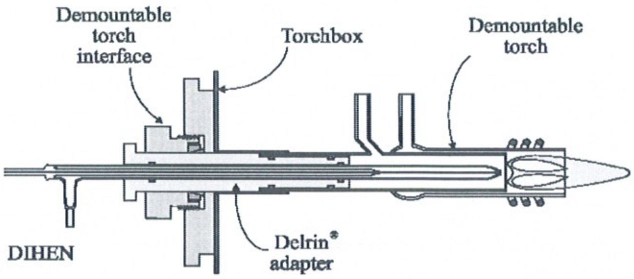

Fig. 3 Direct Injection High Efficiency Nebuliser

Higher sample transport efficiency increases the introduction of both analyte and matrix elements into plasma. Because of this, when the concentration of matrix element is high, matrix effect is increased. Therefore, ultrasonic nebuliser is preferred for solutions with low concentration of matrix.

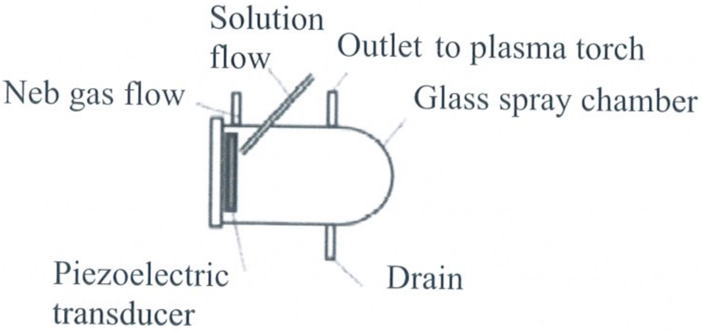

Fig. 4 Ultrasonic Nebuliser

Desolvation system is also used with nebulisers to minimise the interferences due to oxide ions. In membrane desolvation system, the spray chamber is heated to reduce the size of the droplets and the solvent vapours produced are removed by using membrane.

3. Hydride generation-ICP-MS

Conversion of analytes into suitable gaseous species improves the efficiency of introduction of analytes into the plasma. In hydride generation method, analytes which form volatile hydrides are converted to gaseous species by using a powerful reducing agent such as sodium borohydride. The gaseous species are separated using gas-liquid separator before their introduction into the plasma. High efficiency of analyte introduction results in better sensitivity and lower detection limits. Since the analytes get separated from matrix, this method is very useful in the analysis of high salt solutions especially those containing high concentration of alkali and alkaline earth elements as they do not interfere in the hydride generation.

In our laboratory, a simple hydride generation system was designed in-house and coupled with ICP-MS [5]. In this method, acidified sample solution and sodium borohydride solution are mixed in a glass mixing chamber generating gaseous hydrides. Separation of gaseous species from the solution was carried out by employing a simple modification in the nebuliser. In this modified nebuliser, to avoid nebulisation both capillary diameter and inter annular gap are increased to mm level and the outer diameter is kept the same as that of meinhard nebuliser so that it snugly fits in the end cap of the scott spray chamber. The HG-ICP-MS method was standardised for As, Bi, Sn, Sb, Se and Te. Though mercury forms mercury vapour with sodium tetrahydroborate, it was found to suffer from memory effect. The memory effect problem was overcome by carrying out a suitable modification in the experimental set up and adopting Flow injection (FI) mode of sample introduction [Fig. 5].

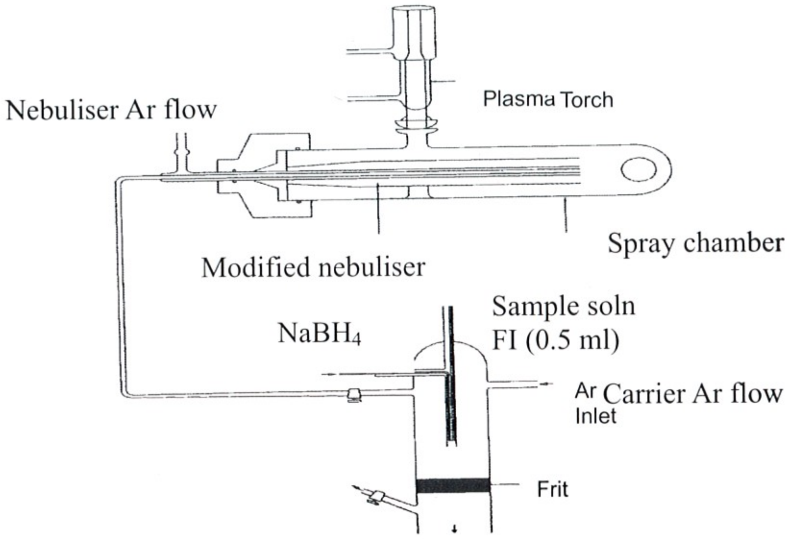

Fig. 5 FI-Cold vapour generation - ICP-MS

In FI-vapour generation-ICP-MS, plasma stability was maintained by using double argon flows i.e. carrier argon flow to carry the mercury vapour to the plasma and the nebuliser flow to ensure plasma stability during the draining of sample solutions. To overcome the memory effect, cysteine was also added to sample solutions. Cysteine forms complex with mercury species and thereby prevents them from sticking to the walls of the peristaltic pump tubing. On reaction with sodium tetrahydroborate, both inorganic and methylmercury species form gaseous species i.e. mercury vapour and methylmercury hydride respectively. Detection limit for both mercury species was found to be 0.1ng/ml.

4. Speciation studies using hyphenated techniques

The toxicity or bioavailability of an element depends on the chemical form in which it is present in the environment. Therefore, speciation plays a crucial role in environmental and biological studies. Generally, species are separated either by using off-line methods such as solvent extraction or online methods such as chromatographic techniques.

4.1 Gas Chromatography coupled with ICP-MS (GC-ICP-MS)

Gaseous species are separated using gas chromatographic column and the species are transported to the plasma [Fig.6]. Transfer line is generally an electrically heated silica tube kept inside the stainless tube and

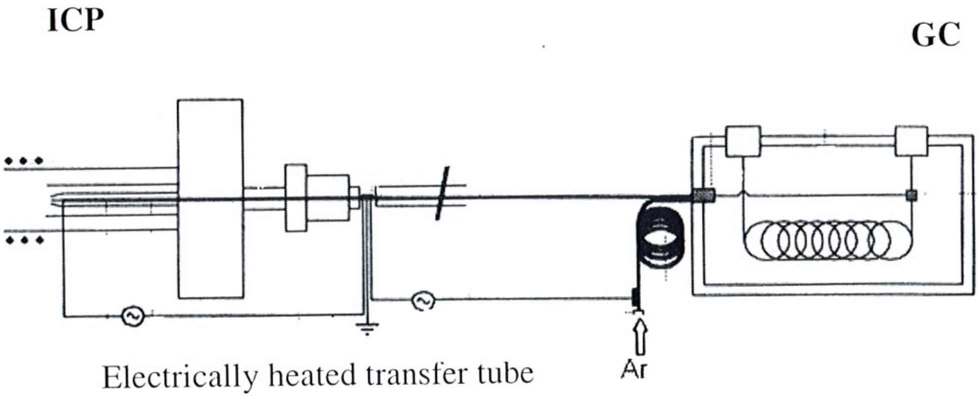

Fig. 6. GC-ICP-MS

extended to the end of the injector tube of the ICP. Argon gas is used as the transfer gas and is also preheated before entering the GC column.

GC-ICP-MS is very useful in speciation studies of organometallics of Sn, Pb and Hg where toxicity depends on the number and nature of alkyl groups. For speciation studies, ionic or insufficiently volatile forms are converted to suitable volatile species such as tetra alkyl forms before their separation by GC. Determination of 25 organometallic species of Sn, Hg and Pb by GC-ICP-MS has been reported [6]. This technique offers the advantage of complete sample transport efficiency (~100%) with the detection limit of pg level.

4.2 High performance liquid chromatography -ICP-MS (HPLC-ICP-MS)

HPLC is widely used for the separation of nonvolatile species of elements. It is generally used in the reverse phase mode i.e. mobile phase being polar and the stationary phase is non polar. Various species are separated using suitable column and mobile phase. The toxicity of arsenic depends on its chemical form and it is in the order: Arsenite> Arsenate>monomethyl arsenous acid (MMAA)> Dimethylarsenic acid (DMAA)> arsenobetaine. Speciation studies of arsenic in arsenic contaminated ground water samples of West Bengal and biological samples from the affected people of the same region have been reported [7]. Determination of Arsenic species by HPLC-ICP-MS in urine samples of the people affected by arsenic contaminated water has also been reported [8]. Arsenic species were separated using anion exchange column (Gel Pack G1-IC-A15) as the stationary phase and 0.38 g/L of phosphate buffer as the mobile phase employing100 µl injection volume [Fig.7].

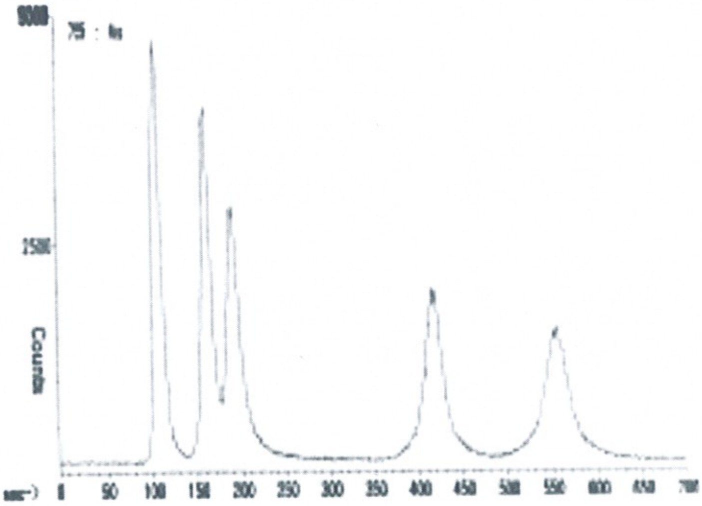

Fig. 7 Mass spectrum of Arsenic species after HPLC separation

4.3 Capillary Electrophoresis- ICP-MS (CE-ICP-MS)

Separation in capillary electrophoresis (CE) is due to the differential migration of species in a capillary tube under the influence of applied electric field. This most efficient separation technique has been employed with ICP-MS for speciation studies [9]. The basic instrumental set up of capillary electrophoresis is given in the Fig. 8. It consists of a high voltage power supply (0 to 30 kV), a fused silica (SiO_2) capillary (dia: 25-100µm,

Length: 20-100cm, two buffer reservoirs, two electrodes and the detector [Fig.8].

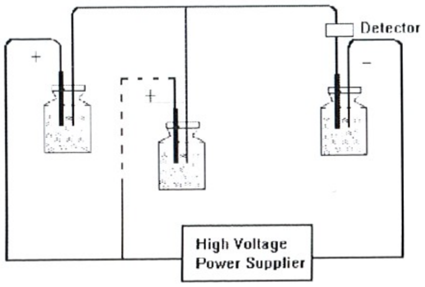

Fig.8 Capillary Electrophoresis

Sample injection is accomplished by temporarily replacing one of the buffer reservoirs with a sample vial. A specific amount of sample is introduced by controlling either the injection voltage or the pressure. The movement of analytes is due to the combined effect of electrophoretic mobility which is directly proportional to the charge and inversely proportional to the friction coefficient and electroosmotic mobility. Studies on interfacing of capillary electrophoresis with ICP-MS have been reported [9,10]. Major factors to be achieved in interfacing are (i) Effective electrical contact at the outlet end of the capillary (ii) minimum suction effect of the nebuliser (iii) minimum band broadening (iv) high transport efficiency to the plasma. CE interface to ICP-MS is given in Fig. 9.

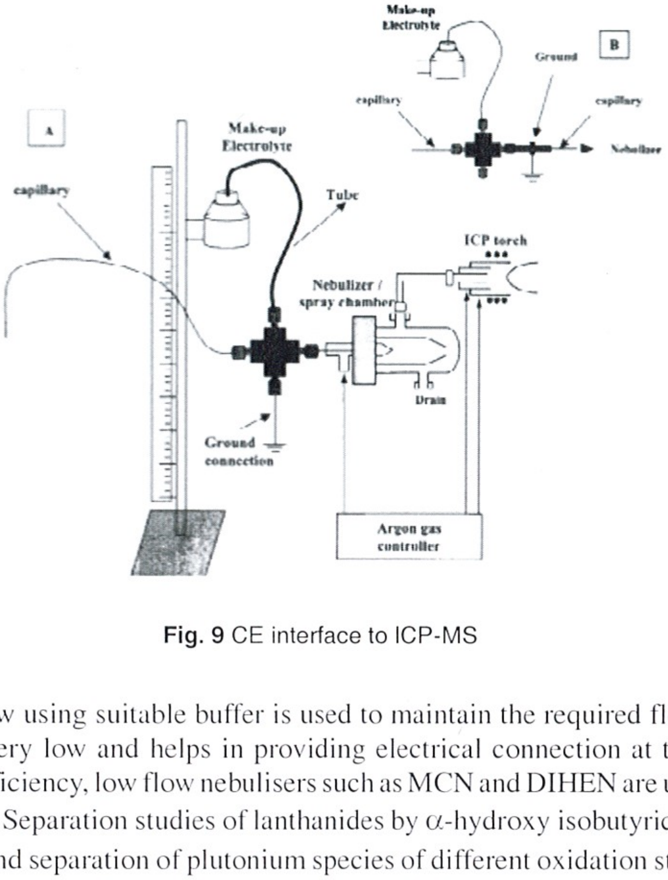

Fig. 9 CE interface to ICP-MS

Generally sheath flow using suitable buffer is used to maintain the required flow rate as the flow rate through the capillary is very low and helps in providing electrical connection at the end of the capillary through tee union. High efficiency, low flow nebulisers such as MCN and DIHEN are used for the introduction of sample into the plasma. Separation studies of lanthanides by α-hydroxy isobutyric acid, separation of Np, Am and U with α-alanin and separation of plutonium species of different oxidation states with α-alanin have been reported [11].

5. Electrothermal vaporization

Small volume of sample solution is introduced into a graphite tube or onto a metal filament. Drying, charring and vaporization stages are programmed suitably for the efficient removal of matrix. Argon flow carries the generated vapour into the plasma. This is very useful in the analysis of concentrated acids as the interfering chloride or sulphate species are removed during the charring stage. This is also useful in the analysis of solutions of limited volume (μl) and containing complex matrices requiring matrix removal.

6. Laser ablation-ICP-MS

Laser beam is focussed onto the solid sample and the resulting plume is swept into the plasma for analysis [12,13]. The signal depends on the properties of laser such as wavelength, irradiance, energy and repetition rate and also on the properties of materials such as density, specific heat capacity, boiling point and thermal conductivity. Laser ablation cell was designed and fabricated in our laboratory. LA-ICP-MS using Nd-YAG laser was standardised for the analysis of low alloy steels. Matrix matched standards are necessary for quantitative analysis to normalise the variation in ablation, transport and ICP processes. The major advantages of this technique are (i) direct solid sampling minimizes the sample preparation and contamination (ii)Wide dynamic range (ppm to % level) due to the possible adjustment of laser intensity (iii) analysis of both conducting and nonconducting samples are possible (iv) surface profile studies are also possible

7. Conclusions

Various sample introduction methods have widened the scope and application areas of ICP-MS. Capillary electrophoresis coupled with ICP-MS and laser ablation - ICP-MS using excimer lasers to minimize or avoid elemental fractionation are emerging as important strategies in biomedical, geological and nuclear applications.

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Plasma Source Mass Spectrometry for Concentration and Isotope Ratio Measurements: An Overview and Development at BARC

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1. Intoduction

The role of mass spectrometry for isotope ratio analysis, trace and ultra trace analysis and constituent analysis has been ever increasing in the fields of analytical sciences in general and nuclear sciences in particular. The growing demands from analytical community for a precise isotope ratio and concentration measurement has lead to significant improvement in mass spectrometer instrumentation with respect to sensitivity, detection limits, precision and accuracy. Among the many analytical techniques available, Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) is by far the most successful method because of its high detection power and true multi-element capabilities. For characterization of nuclear materials, efforts have been put in BARC towards the development of ICP-MS, using quadrupole mass analyzer (QMA). Design and development of Multi-collector ICP-MS (MC-ICPMS) using magnetic analyzer has also been initiated. The details are described in this paper.

Some of the limitations of this otherwise powerful multi element technique, are the spectroscopic and non-spectroscopic interferences which restrict the applicability of this technique to elements beyond a certain mass region. Most of the developments are directed towards reducing or eliminating these interferences. These developments employ use of (i) Cool plasma technique in ICP-QMS, (ii) Collision / Reaction Cell technology (CCT) and (iii) Medium to high resolution magnetic sector analyzer instead of QMA.

2. Development of Plasma Source Mass Spectrometers

2.1 Inductively Coupled Plasma Mass spectrometer (ICP-MS)

BARC has taken up the development of an ICP-MS in order to explore the potential of developing this technology indigenously. The complexity of the technology demands expertise from various fields. All the subsystems have been designed and developed in-house and evaluated for optimum performance individually, before integrating them into a prototype. The electronics systems viz. RF generator, ion optics supplies, precision RF and DC supplies for quadrupole mass analyzer, and data acquisition system, have all been developed in-house. Successful overcoming of many challenges that were encountered at different stages of this development and continued improvements in the subsystem designs, led to a prototype that routinely offered sensitivity of 1 MCPS per ppm and LODs of a few ppb for most of the elements. The potential of the instrument for trace and ultra trace analysis has been established by running laboratory standards. This development has given us confidence to take up the development of first engineered model of ICP-MS for use in boron enrichment project of Heavy Water Board, Mumbai. Development of this instrument is in progress.

With the expertise gained in development of magnetic sector instruments and ICP with QMA, design of a MC-ICPMS has also been completed. This instrument, once completed, is expected to offer the flexibility and sensitivity of ICP as an ion source and the single focusing multi collector arrangement for precise isotope ratio measurements. It also includes a collision cell for effective reduction of molecular ion interferences and higher transmission of analyte ions.

2.2 Quadrupole mass spectrometer (QMS)

Development of quadrupole mass spectrometers was taken up, initially, to support our ICP-MS program in making it fully indigenous. QMS systems using 16 mm and 19 mm rod diameters have been successfully developed. While the former is routinely being used for cluster studies and photolysis studies, the latter one is a development for RIMS applications at NCCCM, Hyderabad.

These have been characterized for their optimum performance in terms of sensitivity, resolution and mass range. An imported QMA and its electronics in prototype ICP-MS was replaced by an in house developed QMS with 16 mm diameter rod assembly. A similar QMS was used for ^{13}C enrichment studies in collaboration with L&PT Division. We also have a project on hand to develop a 16mm rod based QMS for ^{18}O enrichment studies being done in the Heavy Water Plant of HWB, Mumbai.

2.3 Magnetic Sector Analyser

The inadequate resolution offered by QMS, typically 0.7 to 1 amu, has led to the application of medium to high resolution magnetic sector technology to ICP-MS. In order to achieve isotopic ratio measurements that are comparable to those obtained in TIMS, four main difficulties have to be overcome. These are: (i) interfacing the atmospheric plasma to the ultra high vacuum required for collision free detection of the analyte ions, (ii) broad geometric nature of the ion source necessitates shaping of the ion beam into a narrow ribbon at the entrance to the magnet, (iii) the ion spread in the plasma source of the order of ~20eV which is rather high for efficient resolution by the magnet (energy focusing is essential) and (iv) inherently unstable nature of plasma source. This means that single detector systems are inadequate and one should employ simultaneous multi-collector method of detection.

2.3.1 MC-ICPMS

Commercially four different models of MC-ICPMS are available. Two different schemes are used in these instruments. In one scheme, while most of the instrument is maintained at ground potential, the ion source and its associated pumping system float at high potential. In the second scheme, the ion source is held at ground potential while lens system and analyser float at the accelerating potential. Shaping of the beam from circular cross section to a rectangular one is accomplished either by a set of DC quadrupoles or a set of electrostatic lenses or a combination of both. They all employ the double focusing technology with electrostatic analyzer and electromagnet analyzers, either in the forward or reverse geometry. In all models available there are multiple movable faraday collectors for simultaneous collection for isotope ratio measurements and an on-axis secondary electron multiplier for trace elemental analysis. The combination of ICP with multi-collector magnetic sector mass spectrometry has widened the applications base compared to TIMS because of the true multi-element nature of ICP source. MC-ICP-MS offers sensitivity of $>10^8$ cps/ppm for indium and the detection limits are down to ppt or sub-ppt levels, with good precision.

Keeping in view the requirement of precise isotope ratio measurements at very low concentrations and the successful development of TIMS, VPID has taken up the in-house development of an MC-ICPMS. The main design is conceived taking into consideration the main difficulties as indicated above. The scheme involves, apart from the conventional ICP source and two cone interface, a combination of collision cell technology, fast laminated electromagnet, and multiple faraday collectors. Simulation studies of some of the subsystems have been completed.

3. Development of Plasma Source for Elimination of Interferences

3.1 Cool Plasma Technique

This technique is useful for reducing the interferences by molecular ions arising out of the bulk plasma gas which is argon in most cases. This involves reducing the operating power of the plasma from ~1300 to ~700 Watts. However, it is sometimes difficult to optimize and is suitable only for few of the interferences. It is also susceptible to more severe matrix effects and switching the modes back and forth between normal and cool conditions is often time consuming.

3.2 Collision/Reaction Cells

The limitations of cool plasma technique mentioned above and the desire to improve performance led to the development of multi-pole (Quad/Hexa/Octo) Collision / Reaction cells. They can be used to remove the interferences by eliminating the source of the problem viz. the formation of the molecular species. The cell will normally be inserted between the ion-lens and the mass analyzer of a conventional ICP-QMS. When a collision gas is introduced into this cell, ion-molecule reactions take place and molecular ions are selectively removed from the ion beam. Though some unwanted molecular ions are generated during these reactions, they can be effectively eliminated by proper selection of the operating mode of the cell and the cell gas. The added advantage of using this cell is that the ion beam is thermalised, thereby reducing the energy spread, and also collision focusing is accomplished. The reduction in spectral backgrounds at the nominal mass of interest are as high as 10^7.

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Analysis of Structural Materials by ICP-MS

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1. Introduction

Reactor technology demands the use of a wide viety of materials for the various structural components of a reactor. Inductively coupled plasma mass spectrometry (ICP-MS), a sensitive multi elemental technique is widely applied for the trace and ultra trace level analysis of wide variety of materials [1]. In our laboratory, ICP-MS is being employed for the quality control, failure analysis and development work being carried out to enhance the reliability and safety of reactor components made out of these materials.

2. Analysis by ICP-MS

The elements in a material are classified into various levels depending upon their concentration. Generally, elements in the concentration range 1 – 100% are called as major elements and in the range 0.01 – 1% are called as minor constituents. Trace elements are those present in the concentration 1 ppb – 0.01% and ultra trace level elements are those present at 1 ppb level. Metallic concentration of various structural materials used for prototype fast breeder reactors (PFBR) are given in the Table 1[2].

TABLE 1. PFBR material specification (Concn.: wt %, single values : Max. permissible)

Element	D9 Core material	304L(N) SS	316L(N) SS	Mod. 316(N)SS electrodes	Mod.9 Cr-1Mo Steeltubes	Mod.9 Cr-1Mo filler wire	Mod.9 Cr-1Mo electrodes
Cr	13.5 – 14.5	18.5 – 20	17 – 18	18 – 19	8.0 – 9.0	8.0 – 9.5	8.0 – 9.5
Ni	14.5 – 15.5	8 – 10	12 – 12.5	11 – 12	0.20	0.6 – 10	0.6 – 10
Mo	2.0 – 2.5	0.5	2.3 – 2.7	1.9 – 2.2	0.85 – 1.05	0.85 – 1.05	0.85 – 1.05
Mn	1.65 – 2.35	1.6 – 2.0	1.6 – 2.0	1.2 – 1.8	0.30 – 50	0.5 – 1.2	0.5 – 1.2
Ti	5 – 7.5 × C	0.05	0.05	0.1(Ti +Nb +Ta)	–	–	–
Nb	0.05	0.05	0.5		0.06 – 1.0	0.4 – 0.07	0.04 – 0.07
Cu		1.0	1.0	0.5	–	–	–
Co	0.05	0.25	0.25		–	–,	
B	10 – 20 ppm	0.002	0.002	0.002	V:0. 18 – 0.25 , Al: 0.04, Sn: 0.02, Sb, Ti: 0.01	V:0. 15 – 02 Ni + Mn	V:0. 15 – 0.22 Al: 0.04 N + Mn 1.5
Misc	C: 0.035-0.05%						

Major elements are analysed by wet chemical methods and atomic absorption spectrometry (AAS) whereas minor and trace elements are analysed using ICP-MS and AAS. Standardization of analysis for minor and trace constituents of structural materials was carried out using ICP-MS.

Samples are analysed by introducing solution in the form of aerosol into the plasma. Spectral interferences are due to the isobaric and polyatomic species formed from argon, matrix and acids used for dissolution. Some of the typical interfering species are given in Table 2.

TABLE 2: Spectral interferences in ICP-MS

Isotope (abundance)	Interference		Isotope (abundance)	Interference	
	Species (abundance)	Type		Species (abundance)	Type
^{40}Ca (96.9)	^{40}Ar (99.6)	Isobaric	^{48}Ti (91.52)	^{32}S^{16}O	Polyatomic
^{114}Cd (24.1)	^{114}Sn (0.65)		^{51}V (91.52)	^{35}Cl^{16}O	
^{142}Nd (27.05)	^{142}Ce (11.07)		^{75}As (100)	^{40}Ar^{35}Cl	
^{11}B (81.02)	^{12}C (98.89)	Overlap	^{80}Se (49.96)	^{40}Ar^{40}Ar	
^{39}K (93.08)	^{40}Ar (99.6)		^{93}Nb (100)	^{58}Ni^{35}Cl ^{56}Fe^{37}Cl	

Though isobaric and some molecular interferences can be corrected by using interference equation, it is better to choose the isotope of an analyte that is free from interference. Therefore, an acid medium which causes no spectral interference is chosen for dissolution of solid samples. Hence, sulphuric acid is used in the determination of V, As and Nb whereas aqua-regia is used for Ti.

Suppression or enhancement effects by the sample matrix are more pronounced in ICP-MS as compared to ICP-OES. Ion extraction process i.e. space charge effects behind the skimmer are responsible for the matrix effect. Matrix effect is a mass dependent phenomenon. Hence, heavy matrix elements cause more signal suppression and the lighter analytes are suppressed to a higher degree. Hence, matrix concentration is generally limited to 0.1% m/V by suitable dilution of sample solution. Suitable internal standards are also used in the analysis to compensate drift. Matrix effect is also investigated by standard addition studies on samples.

2.1 Analysis of various steels and alloys

D9 and modified D9 are preferred materials for reactor core due to their radiation resistant behaviour. Low carbon 304 and 316 stainless steel are used in reactor assembly and in sodium circuits. In the steam generator modified 9 Cr – 1 Mo steels are used. Other materials like Nb stabilized steels, stellite and colmonoy are also used. The weld materials used in such applications are alloy 800 and inconel. Typically the samples were analysed for different elements such as Mn, Mo, Ti, Nb, V, W, Co, Cu, La, Ce, Sn, Sb, Al, B, Ta, and As.

Mn, V, Co, Al and B were determined using high resolution mode to avoid the overlap interference from the matrix elements and background spectral species. Analysis was carried out by employing calibration mode using Ga, Sb and Tl as the internal standards. Standard addition study was also employed to investigate the matrix effect. Analysis of standard reference material is also carried out to establish the precision and accuracy of the method [3]. Typical analytical results of some of the samples are given in Table 3.

TABLE 3. Analytical results for steels and alloys

Sample	V	Nb	Ti	Cu	Al
weld deposit (316 SS)	613 ppm	13 ppm	–	–	–
weld deposit 2.5 Cr-1Mo	626 ppm	72 ppm	–	–	–
weld metal Mod 9Cr-1Mo	0.2%	0.02%	–	0.03%	–
Alloy	0.21%	< 20 ppm	< 50 ppm	0.13%	
Alloy 800	–	–	0.64%	0.045%	
9Cr-1Mo	0.27%	0.04%	–	0.014%	0.024%
Electrode	–	–	810 ppm	–	62 ppm
Ti mod. SS	–	–	0.13%	–	–

2.2 Analysis of thoriated tungsten

The dissolution of thoriated tungsten using HF – HNO_3 led to precipitation of thorium fluoride. Therefore, fusion using sodium bisulphate was carried out for the analysis. Sample was fused with sodium bisulphate and to the fused mass, hydrochloric acid was added resulting in precipitation of tungstic oxide with thorium in solution. Ammonium hydroxide was added to dissolve the tungstic oxide and precipitate thorium as thorium hydroxide. The precipitate was filtered and dissolved in hydrochloric acid. The resulting solution was suitably diluted for analysis. Thorium in the thoriated tungsten was found to be 1.0 %.

2.3 Analysis of zircaloy

2.3.1 Determinationof U, Th in zircaloy

The coolant water in KAMINI (Kalpakkam mini) reactor was found to contain trace level of gaseous fission products viz. krypton and xenon after the reactor startup. Zircaloy, the clad material was analysed for U and Th, to investigate the origin of krypton and xenon. Zircaloy was dissolved using HF and HNO_3 acid mixture. U and Th in the sample was found to be less than the detection limit i.e. 2 ppm. Therefore, suitable matrix removal procedures were employed to improve the detection limits of U and Th.

Determination of uranium: Phosphoric acid was added to the Zircaloy solution precipitating zirconium and thorium as their phosphates. The supernantant solution containing uranium was analysed by standard addition method. Uranium was found to be below the detection limit of 0.5 ppm.

Determination of thorium: Dissolved Zircaloy solution was acidified with sulphuric acid and mandelic acid was added to precipitate zirconium as mandelate. The supernatant solution was analysed for thorium. Thorium was found to be below the detection limit of 0.5 ppm.

2.3.2 Determination of Co and other elements in Zircaloy

Zircaloy was used as coolant channel in Madras Atomic Power Station (MAPS). Due to the hydride embrittlement in Zircaloy, its life time in the reactor is around 10 years. Therefore, the coolant channel in MAPS was replaced with Zr – 2 – 3% alloy which has the average life time of 20 years. Cobalt content in the Zircaloy is needed to design the shielding flasks for its transportation. Concentration of Co, calculated from the dose is in the range of 0.2 – 2 ppm. The Zircaloy used for the coolant channel was analysed for Co, Mn, Cu and U using ICP-MS and confirmed the calculated concentration described above. Zr – 2 – 3% Nb alloy sample was also analysed. The results are given in the Table 4.

TABLE 4. Analytical results of Zr alloy samples

Element	Concn (ppm)		Reactor Specification Limits (ppm)
	Zircaloy – 2	Zr – 2 – 3% Nb	
Co	0.7	1.8	20
Mn	26	46	50
Cu	10.5	6	50
U	< 2	2	3.5

2.3.4 Analysis of other materials

Cadmium, the neutron absorber in KAMINI, boron, borated graphite and boron carbide were analysed for their impurities. Corrosion deposits from the valve, tube and pump materials have been analysed for their minor and trace elements. Residue samples from the turbine lubricating oil of MAPS were also analysed. Oxalic acid samples were analysed to determine their purity.

3. On-line solvent extraction - ICP-MS

Generally, the salt concentration in the sample solution is restricted to 1 mg/ml which results in sub ppm level detection limits. Hence, matrix removal becomes mandatory to determine the elements at ppb levels. On-line solvent extraction ICP-MS was developed for matrix removal and the technique was standardised for the determination of ultra trace impurities in uranyl nitrate [4]. In this technique, an acidified uranyl nitrate solution and 0.2M TOPO in cyclohexane were pumped into the T shaped capillary tube, resulting in the formation of alternating segments of aqueous and organic phase. They were made to pass through the Teflon tube for extraction. After the extraction, the phases passed through a microporous teflon tube for phase separation. Because of the hydrophobic nature of teflon, only TOPO containing uranium goes out through the micropores. The aqueous solution containing the trace elements was pumped by means of peristaltic pump into the plasma for analysis. The major advantages of this method of separation are minimum contamination and possible analysis of small volume sample solutions.

3.1 Laser ablation-ICP-MS

Laser ablation-ICP-MS is a direct solid sampling technique in which laser beam is focused on to the solid sample and the resulting vapour is swept in to the plasma using argon [5, 6]. The signal from analytes depends on the properties of laser such as wavelength, irradiance, energy and repetition rate and also on the properties of the material such as density, specific heat capacity, boiling point and thermal conductivity.

Laser ablation cell was developed in our laboratory. The schematic diagram of LA-ICP-MS is given in Fig. 1. Laser ablation cell made of Perspex is mounted on a x–y translator, which facilitates sample movement during the analysis for enhanced precision.

Analysis of low alloy steels using standards. The second harmonic (532 nm) of a Q-switched ND-YAG laser was used with an energy of 16mJ/pulse. Pulse repetition rate of 10 Hz and pulse width of 10nsec were employed. Variations in the laser energy were normalized using the matrix element, Fe, as the internal standard. Matrix matched standards are necessary for quantitative analysis so as to correct for the fractional vaporization in the laser ablation process and element dependent variation in transport processes.

Another significant feature of LA-ICP-MS is the possibility of its use as a semi-quantitative analytical procedure, even in the absence of certified standards. This aspect was investigated for the low alloy steels. Sensitivities of different elements differ in LA-ICP-MS due to the fractionation effects in ablation process, transport of ablated material to the ICP, ionization process within the ICP and transfer of ions to the analyzer and detector. Relative sensitivity factor (RSF) is defined as the ratio of sensitivities of two elements after incorporating the correction due to isotopic abundance. In LA-ICP-MS, overall relative sensitivity factor is considered to be a combination of two factors i.e. 1. fractionation in ablation and transport to the ICP and 2.difference in the behaviour of elements within ICP, ion transport and detection. Iron was chosen as the internal standard to correct for the variation in the laser parameters and was also taken as the element for calculating the RSF. The concentration of an element can be expressed incorporating the relative sensitivity

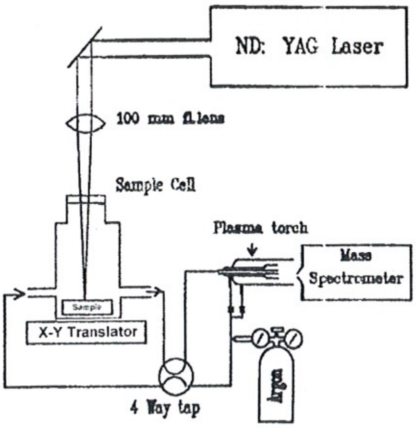

Fig. 1 Schematic Diagram of LA-ICP-MS

factor as $C_{Element} = K (I_{element}/Fe) C_{Fe}$, where K is the relative sensitive factor, $I_{Element}$ and I_{Fe} are the intensities of element and iron respectively in the LA-ICP-MS after the correction for isotopic abundance. C_{Fe} is the concentration of iron in the low alloy steel which is around 95%. Concentrations of elements were calculated by assigning the values to the relative sensitivity factor in the following ways:

1. Sensitivity of all the elements are assumed to be the same as that of Fe i.e. K = 1
2. Sensitivity difference in the ICP-MS was considered and therefore, sensitivity of all the elements was taken as the same as that of ICP-MS in the normal solution introduction mode
3. Apart from the difference in the sensitivities due to ICP-MS, additional correction for the variation between elemental sensitivities due to the ablation and transfer processes was included. Sensitivity was calculated from the measured signal of one matrix matched standard by LA-ICP-MS experiment.

The concentrations measured from various relative sensitivity factors and the certified values for a low alloy steel standard are presented (Fig. 2).

The concentration values show that only few elements i.e. Cr and V showed good agreement with certified values for K = 1, whereas other elements show large deviation as high as 300%. Incorporation of the relative sensitivity factors from solution studies, indicated reasonably good semi-quantitative estimates with the errors less than or around 20% for Mn, Ni, Cr, V and Cu and somewhat higher deviation of 200% for Mo and very large difference of 500 % and 700 % for Ce and Zr respectively. Use of one standard in LA-ICP-MS i.e. considering relative sensitive factor in LA-ICP-MS gives concentration values having very good agreement with certified values for all the elements except for V (difference of 20 %), Ce and Zr with the higher difference of 30% and 80% respectively. This may be attributed to the presence of considerable amount of Zr in particle phase of ablated plume as size influences particle transport. It is therefore concluded based on general behaviour, that at least one matrix matched standard is necessary for accurate semi-quantitative analysis.

Advantages of LA-ICP-MS

1. Direct solid sampling is an alternate method where dissolution becomes difficult. Contamination is minimized due to minimum sample handling
2. Wide dynamic range of ppm to % level is possible and amount injected into the plasma can be controlled by adjusting the laser intensity.
3. Analysis of both conducting and nonconducting solid samples.
4. Surface profile studies possible.

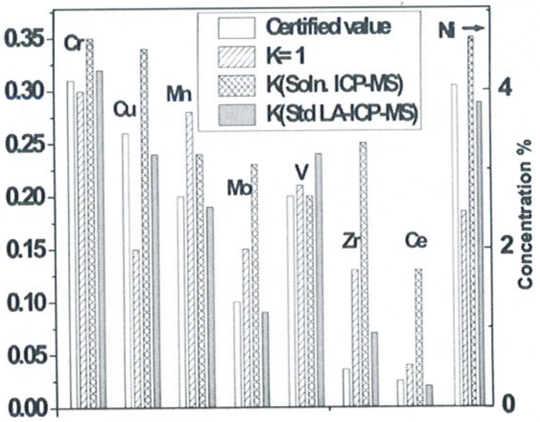

Fig. 2 Laser ablation ICP-MS as a semiquantitative tool

Acknowledgements

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ICP-MS for Exploration Studies in Nuclear Fuel Cycle

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1. Introduction

ICP-MS is a highly selective, sensitive and versatile technique in chemical analysis and hence occupied a major role in the analytical chemistry of the nuclear fuel cycle. Very recently in November 2005, AMD procured one ICP-MS of M/s.G.V. Instruments (micromass) platform model with collision cell technology for chemical analysis of variety of geological and hydrogeochemical samples for uranium exploration activities.

The ICP-MS was procured by AMD to facilitate the determination of REE, PGM and other refractory elements like Nb, Ta, Zr, Hf etc. in addition to U and Th at ppm to ppb levels (at chondrite levels) in rocks, ores, soils, sediments, water etc. which hitherto not possible by the existing AAS and ICP-AES. The analytical data will help understanding the different physico-chemical processes operating through geological timings like partial melting, fractional crystallisation assimilation, mixing of magmas in igneous rocks. In sedimentary and metamorphic rocks and ore deposits the analytical data will provide clues to the sources and processes related to their occurences. In addition, this data also helps in delineating mineralised zones and narrow down the target areas.

The ICP-MS after installation was standardised and calibrated for chemical analysis and the analytical data were reported from January, 2006.

2. Analytical Data:

- All the fifteen REEs were calibrated and then determined in four Geological Standard Reference Materials. The values obtained with this instrument are in coincidence with the recommended values. Soils, geological rock samples, beneficiation products and minerals were analysed for the REE.
- In various geological samples for uranium exploration, trace elements at ppb levels for Ga, Nb, Ta, Th, V, U etc. are determined. Before susbmitting the analytical data on real samples, eight SRM were analysed for these six elements (Table 1).

Table 1. Estimation of trace elements

	Uranium		Thorium		Gallium		Niobium		Tantalum		Vanadium	
	Rcmd Value	ICP MS	Rcmd Value	ICP MS	Rcmd Value	ICP MS	Rcmd Value	ICP MS	Rcmd Value	ICP MS	Rcmd Value	ICP MS
SY-3	650	676	1003	1004	27.40	- - -	150	166	30	28.1	50	51.30
SY-4	0.78	0.95	1.30	1.60	35	35.50	13	14.20	0.90	0.90	8.05	6.80
MRG1	0.22	0.26	0.96	1.15	17.20	16.50	20.0	18.50	0.80	0.65	527	- - -
JG-2	11.3	11.90	29.7	26.70	19.00	19.80	15.0	13.80	1.90	2.0	2.80	2.10
JG-3	2.0	2.10	7.80-	8.30	17.0	16.50	5.6	5.90	0.59	0.69	73	73
GXR1	35	35.0	2.44	3.00	14	12.9	0.80	0.65	0.18	0.20	80	85
GXR4	6.20	5.70	23	22.90	20	18.60	10	4.70	0.75	0.64	87	82
SO-4	2.80	2.70	8.60	10.00	10.70	11.80	10	11.60	0.62	0.50	85	86

- The ground water samples for hydrogeochemical survey of uranium to explore the underground uranium mineralisation were analysed in large numbers for V and Y.

- For the determination of PGM, the fire assay technique was used as a separation/preconcentration method followed by ICP-MS determination. The NIS fire assay was used for analysis. The values obtained for SRM and for samples doped with known concentration, showed that the recoveries are very good for Pt, Pd, Ru, Rh but for Au, Ir, Os, there is no qantitative recovery. Some more investigations are to be carried out in this direction by NIS and PbS fire assay methods.
- In geological and hydrogeochemical samples, uranium was determined by ICP-MS at ppm and ppb levels. Some of the values are cross checked with the fluorimetric values obtained after ethyl acetate extraction. Both the values are in very good agreement.

3. Research & Development

The ICP-MS cannot tolerate more than 0.1% dissolved salts in the sample solutions. For hydrogeochemical exploration of uranium, different ground water samples of varied total dissolved salts are to be analysed for major cations, anions and trace elements including uranium. In order to reduce the TDS levels below 0.1% for uranium estimation by ICP-MS, investigations have been carried out to separate and preconcentrate uranium by solid phase extraction. For this the biomass of bakers yeast is selected. All the parameters have been optimised for separation of uranium from high TDS followed by estimation by ICP-MS.

Dr. D.S.R. Murty *completed his Ph.D. degree in 1975, joined Atomic Minerals Directorate for Exploration and Research, Department of Atomic Energy in 1976 at Hyderabad. He has expertised in geoanalysis of a variety of geological samples, minerals, hydrogeochemical samples etc for more than 50 elements. he has mastered the most sophisticated instrumental techniques like Atomic Absorption spectrometry, inductively coupled Plasma emission spectrometry, microwave digestion etc., and published more than 60 research papers in national and international journals. As research guide he has guided three of his colleagues to get the Ph.D. degree under Bangalore University, and at present guiding one person for Ph.D. under J.N.T.U. Dr Murty is at present Officer-In-Charge, Chemistry Laboratory, AMD, Hyderabad.*

Isotopic and Chemical Studies conducted at PRL to understand Geological Processes

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1. Introduction

Geological processes like mountain building, metamorphism and its impact on weathering and its impact on climate change; time of evolution of life on the Earth have been studied by Thermal Ionization Mass Spectrometer at PRL. Highlights of the some important research work are given here.

2. Geochronology of the Himalaya

Geochronological studies of the Himalaya were undertaken in order to understand time-space relationship of different tectonic units in the Lesser Himalaya. The significant experimental results of this work are:

(a) Delineation of three prominent phases of magmatism/metamorphism in the Himalaya. One of them is related to the Himalayan Orogeny and the other two being Pre-Himalayan and are dated at 470-560 Ma and 1800-2000 Ma.

(b) Definitive evidence for the widespread occurrence of 1800 Ma old components in most of the Kumaun Lesser Himalayan material and their possible equivalents were obtained in the Peninsular region of India.

(c) The results enable identification of more than a dozen acidic igneous plutons intruded during Early Paleozoic time (~500 Ma) in different tectonic settings all along the Himalayan range. It is likely that these granitic activities represent a pre-Himalayan Orogeny.

The above studies enabled us to provide a comprehensive correlation between different tectonic units of Kumaun Lesser Himalaya and chronological frameworks for the evolution of the Himalayan region, especially in the respect of processes and time scales for magmatic/metamorphic events, were provided by the studies [1,2]

Geochemistry of Precambrian mafic magmatic rocks of the Western Himalayas and its Petrogenetic and tectonic implications. A gabbroic body, from Kumaun Lesser Himalaya, has been dated at 1907 ± 91 Ma with initial $^{87}Sr/^{86}Sr$ ratio 0.7022 ± 0.0008 by Rb-Sr whole rock method.

Concordance of ages (between 1800-2000 Ma) of the gabbros and granitods of the region probably indicate that this was a period of major crustal generation and evolution in a rift tectonic environment.

Similarity of chemical characteristics of the mafic magmatic rocks, exposed south of main central thrust, of the Lesser Himalayan samples are remarkably similar to the basal Aravalli volcanics of the NW Indian shield probably indicate the existence of a large Precambrian magmatic province at the northern margin of the Indian plate [3]

3. Strontium Isotope Geochemistry

Steady increase in $^{87}Sr/^{86}Sr$ observed for sea water during the past ~40 Ma (present day value of sea water is 0.7092). We have determined the Sr content and isotopic ratio of the Ganga-Brahmaputra river system to assess their role in the evolution of the Sr isotope fluxes in the oceans.The high $^{87}Sr/^{86}Sr$ (between 0.7300 to 0.7986) ratios obtained for Ganga source waters have been attributed to intense weathering of Precambrian granites and gneisses having high radiogenic Sr. Modelling on our data suggest that these river systems contribute ~30% to the Sr isotopic evolution of sea water during past ~20Ma. Our study demonstrated that the Himalayan Orogeny played an important role on the marine Sr isotope geochemistry in oceans during the past 20Ma [4,5].

4. Re-Os age of Vindhyan Black Shale

The time of the first appearance of multicellular organisms is fundamental question relating to biological evolution on Earth. We have studied black shale samples from Kaimur Group from Vindhyan sediments by the Re-Os method and our preliminary result yields an age of 1670 ± 60 Ma [6].

5. Sr isotopes in rivers of India and Pakistan

The study of dissolved Sr concentrations and $^{87}Sr/^{86}Sr$ of the major rivers draining India and Pakistan provide data on the flux of Sr isotope transported by these rivers to the ocean and their impact on the Sr isotope evolution of the oceans. The river basins sampled comprises diverse set of lithologic, tectonic and climate regimes which shows that almost all the rivers sampled have $^{87}Sr/^{86}Sr$ in excess of the global average, with head waters of Ganga and its tributaries having the most radiogenic Sr isotope composition. Studies on the source of radiogenic Sr to the Ganga system would help in understanding better the coupling between Himalayan tectonics, weathering and climate change [5]

6. Erosion distribution over Central and Eastern Himalaya

The Sr and Nd isotope composition of sediments of the Ganga and the Brahmaputra rivers show that the Higher Himalaya is the primary source for these sediments and that the Himalaya is undergoing differential erosion. It is seen that basins with high relief such as the Gandak in the Ganga Basin and the Eastern Syntaxis of the Brahmaputra are eroding very rapidly at rates of ~6 and 14 mm/y respectively compared to other regions of these basins which have erosion rates of ~2 mm/y. Such rapid erosion in these areas is causing rapid uplift resulting in the high peaks of the Namche Barwa, the Dhaulagiri and the Annapurna [7].

7. Cabonatites of India

Sr isotopic studies coupled with stable isotope were studied to get information on the Genesis and Evolution of the source region and the interaction between mantle derived carbonatite and the crustal rocks through time. Sung Valley carbonatite-alkaline complex has been dated to 107 Ma while, AmbaDongar complex has been dated to 65 Ma. The age shows spatial relationship with Deccan flood basalts and the initial strontium ratio supports the hypothesis of Reunion plume origin of this complex. This complex emplaced just at K/T boundary, could have enhanced the catastrophic effects leading to mass extinctions, by rapidly pumping a substantial amount of CO_2 in to the already disturbed atmosphere. The strontium isotopic study on carbonatite, associated alkaline rocks and country rocks of Amba Donger complex suggest that the liquid immiscibility had played a major role in the formation of this complex. Parent magma for Amba Donger was contaminated by the lower crustal granulite (~5%), the effect of which is clearly observed in initial $^{87}Sr/^{86}Sr$ of alkaline rocks but not in carbonatite. [8, 9].

8. Future scope

I propose to take up programmes

(i) that would exploit the Rb-Sr, Re-Os, Sm-Nd, U-Pb, Lu-Hf, Boron isotopes studies of mafic and ultra mafic rocks of the Himalayan Suture zones understand the crustal processes:

(ii) to use B and Fe Isotopic studies as biomarkers. These studies will contribute the PRL core programmes. These new avenues are possible because of the capabilities of the new TIMS, now available at our institute.

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Dr.J.R.Trivedi, *born in 1948, has taken his doctorate from Gujarat University in Physics and has been working on studies on meteorite to understand planetary processes and to understand evolution of Himalaya (timing of mountain building processes) and chemical weathering of Himalayan Rivers and its relation as the long term climate changes for the past several million years. These types of studies are done using various isotopic systems. He has more than 65 publications to his credit and he is a fellow of several national organisations. He is presently working for the Physical Research Laboratory at Ahmedabad.*

Research and Development Activities of Centre for Compositional Characterization of Materials using Inductively Coupled Plasma Mass Spectrometry

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1. Introduction

Inductively Coupled plasma-mass spectrometry (ICP-MS) is a multi-element technique that uses plasma to dissociate the ions contained in a sample. Ions are extracted from the plasma and passed through a mass spectrometer for detection based on mass to charge ratio. ICP-MS is a highly sophisticated analytical technique that is capable of sub-ppt (parts per trillion) detection limits. The lowest detection levels can only be achieved in a clean room environment. ICP-MS is an important analytical technique for the semiconductor, pharmaceutical, food and beverage, environmental and nuclear industries. The technique has a high sample throughput. ICPMS, when coupled to separation techniques like HPLC/IC, GC, Capillary Electrophoresis etc. provides valuable information on studies related to speciation. The presentation in the theme meeting covered our work related to ultra trace elemental analysis, speciation studies and isotope ratio determination as well as approach to element specific interferences. The analyses were done with the VG Plasma Quad 3, Inductively Coupled Plasma Mass Spectrometer housed in Class 100 area in Ultra Trace Analytical Laboratory of our Centre for Compositional Characterization of Materials (CCCM).

2. Ultra trace Elemental Analysis

2.1. Special sample introduction methods –Vapor generation – 'Collect and Punch' – ICP-MS method for Mercury and Selenium

2.1.1. Mercury

Mercury remains as one of the most often determined toxic element in the environment. There is a continuing need for the monitoring of mercury levels in the ecosystem. The entry of mercury, in organic and inorganic forms into the food chain has necessitated the development of analytical techniques for the determination of mercury at sub-ppb levels. Cold vapor generation is the most important form of sample introduction for the determination of (inorganic) mercury, for determination using AAS, AFS or ICP-MS. Continuous introduction of mercury vapor or its trapping on gold with subsequent release by heating has been practiced by many groups. A simple 'collect and punch' cold vapor inductively coupled plasma mass spectrometric (CV–ICP-MS) technique was developed for the determination of mercury directly at parts-per-trillion (ppt) levels [1]. It does not need any additional steps such as amalgamation or pre-coating or heating and is free from memory effects. Reduction to elemental mercury was carried out using a hydride generator with tin(II) chloride as the reductant. The mercury vapor was collected in a glass chamber and sent as a plug into the plasma, resulting in enhanced sensitivity. This arrangement provided a 10-15 fold enhancement of sensitivity compared to continuous transport method. Using the time resolved acquisition (TRA) mode of data acquisition, the direct determination of ng l^{-1} levels of mercury was achieved with good precision. The detection limit of the method is close to 6 ng l^{-1}. This method was validated through the analysis of NIST SRM 1566a Oyster tissue. Mercury at 50 ng l^{-1} level in aqueous solutions can be determined with a precision of about 2%.

2.1.2. Selenium

Selenium is used extensively in the manufacture and production of glass, pigments, rubber, metal alloys, textiles, petroleum, medical therapeutic agents, and photographic emulsions. Selenium dioxide is the most widely used selenium compound in industry. Selenium compounds are released to the air and water during the combustion of coal and petroleum fuels, and during the smelting and refining of other metals. Selenium dioxide is the primary source of problems from industrial exposures since the dioxide forms selenious acid with water or sweat, and the acid is an irritant.

The toxicity of selenium depends on whether it is in the biologically active oxidized form. It is known to be essential for biological systems, whilst, at levels only three to five times above bio-essential concentrations, it is toxic. It has the narrowest biological tolerance range of all of the elements [2]. The behavior and reactivity of Se depends on its oxidation state and, in general, inorganic forms of Se are more toxic than organic forms. Se(IV) and Se(VI) are the most common inorganic forms of Se. The selenium content of surface water is greatly influenced by pH, being high in acidic ($pH < 3.0$) and in alkaline waters ($pH > 7.5$). Traces of selenium ranging from ppb to sub-ppb levels are commonly found in community drinking water. These concentrations are close to or below, the limits of detection (LODs) of the most commonly used analytical methods, which lead to difficulties in quantifying individual species. Thus, the analyte has to be preconcentrated prior to its determination, in order to improve limits of detection.

For trace element analysis, ICP-MS, in comparison with other techniques possesses several advantages such as simultaneous multi-element capability and excellent detection limits. However, in the determination of selenium by ICP-MS, the two major isotopes ^{80}Se and ^{78}Se are severely interfered due to spectroscopic interference from argon dimers $^{40}Ar_2$ and $^{38}Ar^{40}Ar$ respectively. Hence, the lower abundant isotope ^{82}Se (9.2%) is generally used. Since the ionization potential of Se is very high (9.75eV) and a lower abundant isotope is used, determination of Se at ppb to sub-ppb levels in natural waters requires special sample introduction methods. A UV assisted vapor generation combined with the 'collect and punch'-ICP-MS method (similar to Hg vapor introduction) was developed for the determination of Se(IV) at ultra trace levels. Volatile Se species were formed by UV irradiation in the presence of low molecular weight organic acids. The vapors were collected in a glass chamber for a required amount of time before injecting into the plasma. This arrangement gave 7 times higher signal, when compared to continuous vapor injection. The detection limit was close to 0.4 μg/L. A precision of 1.2% (RSD, n=6) was obtained for 0.5μg/L of Se(IV) solution.

3. Characterization of Trace Elemental Impurities in High Purity Materials (As, Sb, Cd, Ga and Te)

An essential part of manufacturing semiconductors is based on the purity of the raw materials. Impurities even at ultra-trace levels can cause severe damage to the devices as they act as traps for the charge carriers, the chemical identity, concentration, spatial distribution and lattice position of each type of impurity are important parameters for the preparation of compound semiconductors. Hence, for most of the applications, the synthesis of the compound material requires the availability of the constituent elements of 6 N (99.9999%) level purity or better. Assessment of purity at improved detection limits is therefore essential.

CCCM has taken up the studies related to trace element characterization of high purity materials using multi element technique approach based on GFAAS, ICP-MS and GD-MS. The lack of suitable standard reference materials for the variety of matrices requires that the results be cross-validated using more than one technique. To a large extent, except in GD-MS, the solution-based techniques suffer from matrix suppression effects and hence appropriate chemical separation techniques need to be developed for the separation/preconcentration of the trace element impurities. High purity elements (4N-7N pure) like As [3], Sb [4], Cd [5], Ga [6], Te [7] have been characterized so far. Several approaches (i) Vapor phase dissolution followed by ion exchange, (ii) matrix volatilization and (iii) controlled dissolution have been developed and the concentration of trace elements determined using ICPMS and cross validated using GFAAS and GD-MS.

4. Direct determination of trace elements in Naphtha

Determination of trace elements in petroleum distillates is a challenging analytical problem.

Almost all the techniques require ashing the liquids to convert the trace elements into inorganic form for subsequent determinations. In addition, the low levels of trace elements in them require treatment of a large quantity of sample, which is quite cumbersome.

The requirement of trace element in naphtha arises because of the deleterious effect they have on the cracking catalysts even at very low concentrations of elements like V, Ni, As, Pb and Hg. The determination of trace elements after various microwave digestion and extraction procedures investigated by us, was limited by the process blank values. ICP-MS offers an attractive way for the direct analysis of such samples. By introducing the sample in low volumes into the plasma in the presence of oxygen and at high power, the organic molecules are destroyed and the inorganic trace elements in them can be determined. The carbon build-up on the sampling cone and oxygen level were required to be monitored and controlled. An emulsion based approach for the introduction of naphtha into the plasma has been developed [8]. The sample was emulsified with Triton-X 100 while stirring with a magnetic stirrer, for 20 minutes. The emulsified sample was directly passed along with the addition of about 8-9% of oxygen (relative to the nebuliser argon gas) into the plasma. Sub-ppb level detection limits were obtained by this method. This method is unique that it affords the use of aqueous standards (in the emulsified form) to be used for the analysis of organic liquids using ICP-MS.

5. Speciation Studies

Speciation analysis is the analytical activity of identifying and/or measuring the quantities of one or more individual chemical species in a sample (IUPAC). The toxicity and bioavailability depends on the concentration and form in which the species is present in the sample. Hence it is important to determine the individual species, in addition to the total elemental concentration. Liquid chromatography helps in the separation of various chemical species and when coupled to ICP-MS, provides a very sensitive technique for the determination of species at ultra trace levels.

5.1. Speciation of As [As(III) and As(V)] and Cr [Cr(VI) and Cr(III)] using Hyphenated Techniques IC-ICP-MS and FI-ICP-MS

5.1.1. Arsenic [As(III) and As(V)]

All arsenic compounds, which are soluble in acid or water, are poisonous. Arsenic oxide or the acids react with alkalis to form arsenates/arsenites. Calcium arsenate/arsenite, sodium arsenate/arsenite and lead arsenates are used as insecticides as are the copper compounds copper arsenite and copper-acetoarsenite. Other agricultural uses of arsenic compounds are as soil sterilants and fungicides. Di sodium methyl arsenate is used as a defoliant. Industrial processes such as copper and lead metallurgy are mainly responsible for the contamination of the natural water sources. Thus very large quantities of arsenic enter into the ecosystem through these anthropological and other natural activities (volcanic eruptions).

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 be tainted with much higher levels of arsenic than the World Health Organization (WHO) maximum permitted value of 50 $\mu g\ L^{-1}$. USEPA has recently lowered of permissible limit of arsenic concentration in drinking water from 50 $\mu g\ L^{-1}$ to a 10 $\mu g\ L^{-1}$, 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.

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. A very large number of research groups have been working on the remediation technologies for the removal of arsenic from the waters used for human consumption.

The determination of inorganic arsenic species As(III) and As(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 depend on the predominant chemical form in the particular water source.

Ion exchange and ion-pairing reverse phase chromatography coupled with ICP-MS or HG-AAS/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. In speciation studies it is important to maintain the integrity of the sample (i.e., prevent the interspecies conversion). Addition of acids / buffers to a sample is known to affect such equilibrium. In addition, these buffers are reported to clog and erode the nickel sampling cones in ICP-MS.

5.1.2 On-line Separation of As(III) and As(V) by IC-ICPMS

We have investigated two procedures [9] for the separation of As (III) and As (V) using Anion-Exchange Chromatography (AEC) and Reverse Phase Ion-Pair Chromatography (RPIPC) in combination with ICP-MS, 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. The separated species were determined by ICP-MS using Time Resolved Acquisition mode. Detection limits at parts per billion levels were obtained for the different 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.

5.1.3 Remediation of As in Groundwater

In addition, we have used this method to evaluate a procedure suitable for the remediation of arsenic in drinking water [10]. It is a two stage remediation procedure involving the use of Fenton's reagent (H_2O_2 and Fe(II)) followed by passage through zero valent iron. The efficiency of the process was investigated under various operating conditions. Potable municipal water and ground water samples spiked with arsenic(III) and (V) were used in the investigations. The species in the processed water samples were separated and determined using the HPLC–ICP-MS procedure mentioned in the above paragraph, to study the effectiveness of the oxidation step and the subsequent removal of the arsenic. The method is capable of removing arsenic to lower than the US Environmental Protection Agency (EPA) guideline value of 10 μg/L, from a starting concentration of 2mg/l of As(III). This approach is simple and cost effective for use at community levels.

5.1.4 Chromium [Cr(III) and Cr(VI)]

The wide industrial applications of the chromium compounds results in dumping of large quantities of chromium in the environment. Industrial effluents often contain significant quantities of Cr(VI) and are the main source of contamination in natural waters. Chromium occurs mainly in two oxidation states, as Cr(VI) and Cr(III) in nature. The existence of these two species in aqueous media is pH dependent. The two species differ significantly in their biological and toxicological aspects as well. Cr (III) is considered to be an essential element to activate insulin, while Cr(VI) is known to be carcinogenic to humans and other animals. Chromates easily permeates into biological cell membranes and it is reduced to Cr(III) in the cell, resulting in the formation of free radicals. Cr(III) formed there in a significant concentration can cause further adverse effects because of its high capability to coordinate various organic compounds resulting in inhibition of some metallo-enzyme systems.

Not only toxicity, but also the mobility and bioavailability of chromium, depend fundamentally on its chemical form. In many countries groundwater is the major source of drinking water. There is a significant problem of contamination of soil and groundwater by chromium. As a result, many agencies have developed treatment approaches for chromium contaminated soil and groundwater remediation strategies. Several approaches have been adopted such as isolation, immobilization, toxicity reduction, physical separation, extraction etc. Hence, it is essential to monitor the two chromium species in e.g., drinking water, occupational exposure or environmental samples and to study the efficacy of the above mentioned remediation approaches.

On-line separation and detection methods are preferred because sample pretreatment is minimal and consequently losses, contamination or chromium species conversion are reduced. Owing to its high sensitivity, ICP-MS has been widely used as the detection method by coupling it to HPLC. However, the detection of chromium by ICP-QMS using the two most abundant isotopes (m/z 52 and 53) is often interfered to varying degrees by the presence of molecular ions due to carbon ($^{40}Ar^{12}C^+$ and $^{40}Ar^{12}C^1H^+$) and chlorine ($^{37}Cl^{16}O^+$, $^{35}Cl^{16}O^1H^+$ and $^{35}Cl^{17}O^+$). The introduction of dynamic reaction or collision cell technique in recent ICP-MS instruments and High Resolution-ICP-MS has provided an effective method for alleviating these spectroscopic interferences. But in many quadrupole instruments without the collision or reaction cell, still in use in many laboratories, the problem of molecular ion interferences have to be tackled. Chromatographic separation helps in the isolation of these polyatomic interferences from Cr(VI) and Cr(III) species.

Methods for chromium speciation by IC-ICP-MS have been developed with single column possessing both anion exchange and cation exchange capabilities or on-line coupling of anion and cation exchange columns. Most use a complexing agent (EDTA, PDCA etc.) to impart a negative charge to the Cr(III) and subsequently use an anion-exchange column for separation. Speciation generally necessitate that samples be manipulated as little as possible to preserve the integrity of the original species. The use of a mobile phase with high salt concentration or an eluent containing carbon has to be avoided for Cr speciation by HPLC-ICP-MS. Dilute nitric acid has been preferred for elution, generally a gradient elution or a step elution using two different concentrations of nitric acid to elute Cr(VI) and Cr(III), is often reported.

5.1.5. On-line Separation of Cr(III) and Cr(VI) by IC-ICP-MS using a Single Column Approach under Isocratic Conditions

A method for the online separation and quantification of chromium species in waters by coupling ion-chromatography with inductively coupled plasma mass spectrometry was developed [11], using a single column approach under isocratic conditions and dilute nitric acid eluent for separation. The species were separated on a weak cation exchange column, Dionex Ion Pac CS12-CG12, also having reverse phase properties. A flow rate of 1ml min^{-1} was employed with a 25 μl sample loop for sample injection. The chromium species are well separated from the molecular ion interferences due to carbon ($^{40}Ar^{12}C^+$) and chloride ($^{37}Cl^{16}O^+$) on the two most abundant isotopes – ^{52}Cr and ^{53}Cr. The detection limits (3σ) for Cr(VI) and Cr(III) were 0.34 and 0.44 μg L^{-1}, respectively. The developed method was applied to a lyophilized certified reference material - BCR CRM 544. The concentration of Cr (VI) in the reconstituted CRM matched well with the certified value, but only 10% of Cr(III) could be recovered through the developed method. The laboratory Cr(VI) and Cr(III) standards (1mg L^{-1} intermediate standards) prepared in the bicarbonate buffer (pH 6.4) were found to be stable over a period of 12 months. The mixed standards of Cr(VI) and Cr(III) at μgL^{-1} levels prepared in the buffer from the intermediate standards gave peaks for both Cr(VI) and Cr(III) reproducibly on every sample injection. The procedure developed eliminates the need of a dynamic reaction cell or HR-ICP-MS to remove molecular ion interferences on the chromium isotopes.

5.1.6 Use of bio-sorbent for Cr Speciation

In addition to the usual analytical columns, the use of bio-sorbents (e.g. moss, after immobilization in a polysilicate matrix as substrate) was evaluated [12] for the separation of Cr(III) and Cr(VI) and in the selective pre-concentration of Cr(III), prior to their determination by Flow Injection-ICP-MS. Experiments were performed to optimize conditions such as pH, amount of sorbent and flow rate, to achieve the quantitative separation of Cr(III) and Cr(VI). During all the steps of the separation process, Cr(III) was selectively sorbed on the column of immobilized moss in the pH range of 4–8 while, Cr(VI) was found to remain in solution.

The retained Cr(III) was subsequently eluted with 2 mol l^{-1} HNO_3. A pre-concentration factor of about 20 was achieved for Cr(III) when, 200 ml of water was passed. The immobilized moss was packed in a home made mini-column and incorporated in flow injection system for obtaining calibration plots for both Cr(III) and Cr(VI) at low ppb levels that were compared with the plots obtained without column. After separation, the chromium (Cr) species were determined on-line by inductively coupled plasma mass spectrometry (ICP-MS) using TRA mode of acquisition. The sorption capacity of the immobilized moss was found to be ~11.5 mg g^{-1} for Cr(III). The effect of various interfering ions were also studied. The proposed method was applied successfully for the determination of Cr(III) and Cr(VI) in spiked and real wastewater samples and recoveries were found to be >95%.

6. Isotope Ratio Determination

6.1 Isotope Ratio Measurements of Boron for the Boron-10 Enrichment Program of DAE

Two different methods for the enrichment of B^{10} are being followed at Heavy Water Plant, Talcher and at IGCAR, Kalpakkam. Various anion-exchange resins are being tested at HWB, Manuguru to get better B^{10} enrichment. Our Centre has been providing analytical support in the determination of B^{10} enrichment. The boric acid compound, in both salt and solution form are obtained at different stages in the process of enrichment. The B^{10}/B^{11} ratio in the samples and standards were determined using ICP-MS. The B^{10}/B^{11} ratios obtained for the NIST 951 (standard boric acid) and NIST 952 (95% enriched B^{10} standard) standard reference materials was used for mass bias corrections in samples. The memory effects cause serious errors in B isotope ratio determination. Washing the nebuliser and spray chamber with ammonia-mannitol mixture and high purity water between successive sample acquisitions significantly reduced the memory effect and increased the rate of sample analysis.

6.2. Studies on the Removal of Spectral Interference of MoO on Cd Isotopes

The determination of cadmium at trace and ultra trace levels is important due to its toxicity. Inductively coupled plasma mass spectrometry (ICP-MS) is a highly sensitive and rapid technique suitable for the analysis of cadmium. But when a quadrupole analyzer is used isobaric interferences due to oxide ions of molybdenum can pose a problem and lead to erroneous results. A method was developed [13] to reduce the oxide interferences for the accurate determination of cadmium at ng/g levels in the presence of excess molybdenum. The addition of a little quantity of acetonitrile was shown to reduce the molybdenum oxide ions leading to accurate recoveries of cadmium values in the presence of molybdenum. The mechanism of the reduction in oxide ion interference may apparently involve a suppression of the oxide ion formation due to the oxygen scavenging capacity of the cyanogen radicals (of acetonitrile) rather than a competitive formation of molybdenum nitride or carbide ions. The developed method was validated by determining the cadmium concentration in an SRM, NIST 1568 a rice flour, and a sample, Algae 392, distributed by IAEA for inter laboratory comparison purposes which contain a cadmium concentration of 0.022 ± 0.004 and 0.0179 ± 0.0044 µg/g, respectively and a much larger molybdenum concentration. The concentrations obtained, 0.021 ± 0.004 and 0.026 ± 0.004 µg/g, respectively, by the developed method agreed very well with the certified values.

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Theme Meeting on
Mass Spectrometry in Nuclear Fuel Cycle
(MSINFC-2005)

December 21 –23, 2005

Convention Centre, Anupuram

ABSTRACTS*

**Abstracts of full-text articles have not been included.*

Mass Spectrometry in the Development of Control Rod MaterialS

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Boron carbide having different levels of enrichment in Boron -10 isotope is used as control rods in FBTR and PFBR because of its high neutron absorption cross section and high temperature stability. In the case of FBTR, the control rod material requires a 90% of ^{10}B isotope, where as PFBR requires a 65 % of ^{10}B isotope. The natural boron consists of two stable isotopes ^{10}B and ^{11}B with an abundance of 19.9 and 80.1 atom percent respectively. A plant has been designed and set up in IGCAR to produce enriched ^{10}B isotope of 90% to meet the requirements of FBRs. In the plant, ion exchange chromatographic process of separation is used to get ^{10}B isotope. Natural boric acid is used as the starting material and the borate ion is moved from one column to another in a battery of ion exchange columns using HCl as the displacing agent. Engineering experiments resulted in enriched boric acid with different levels of enrichment in ^{10}B isotope. In order to check the level of enrichment, it is essential to analyse the samples at various stages of the experiments. The enrichment obtained in the products was ascertained using an Inductively Coupled Plasma Mass Spectrometer. Recently, the plant has produced boric acid with 65% enrichment of ^{10}B isotope. The enriched boric acid is then used to produce elemental boron (^{10}B) using the electrochemical means and then the boron carbide ($^{10}B_4C$). It is also essential to know the impurity levels of the products obtained in every step, to meet the control rod grade specification of the boron carbide. The chemical assay of the enriched boric acid and also the enriched elemental boron were also carried out using ICPMS along with the various other analytical techniques. The talk will highlight the method used by us in getting the isotopic ratio of the samples with different enrichment of ^{10}B considering the fact of non-availability of Standard Reference Materials in the wide range ^{10}B enrichment.

Dr. K. Sankaran *received his Masters Degree in Chemistry from Madras University in 1981. He joined IGCAR after completion of his BARC training School in 1983 and is working in the Analytical and Spectroscopy Section of Materials Chemistry Division. He obtained the doctoral degree in 2000 from Madras University. His research interests include boron isotopic measurement and trace elemental analysis using ICPMS, experimental and computational studies of molecular structures, weak intermolecular interactions and high temperature species using Matrix Isolation Infrared spectroscopy.*

D_2/H_2 Measurements in Heavy Water

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The accurate determination of isotopic abundance D/D+H ratio during the initial stages of enrichment in heavy water plants has direct impact on power consumption in operating plant. This in turn influences the economy of operation of the plant, an important parameter in any commercial plant as well as the requirement of D_2O of specific grade needed for PHWRs. The accuracy of even 1 ppm in the measurement can lead to considerable economic losses per annum in the operation. Mass spectrometric technique is used for the measurement of isotope ratio. This presentation describes the measurements of D/D+H ratio starting from ppm to nuclear grade using various techniques involved during different stages of D_2O production.

Dr. Pandey *joined Chemical Engineering Division, BARC after graduating from the 26th Batch of Training School, in 1983. In the initial years, he acquired vast experience in employing various techniques like GC, IR and UV-Visible spectroscopy. Later he specialised in the development of techniques for the measurement of isotope ratios for light elements relevant to nuclear industry. His areas of interest include polymerisation, solvent development and development of scintillator chemicals. Recently he has shifted to Board of Research in Nuclear Sciences, BARC. He is actively involved in collaboration projects in the disciplines, physics, chemistry and biology with various institutions outside the DAE.*

Ultra Trace Elemental Analysis using ICP-MS and GD-MS

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Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) and Glow Discharge Mass Spectrometry (GD-MS) are the mainstay for ultra trace level elemental characterization in a variety of materials. The existing knowledge on the role of trace constituents in determining properties of materials as well as the need to know more, have resulted in the enhanced demand for the determination of trace and ultra trace level elemental constituents in all the fields. Recent advances in sample introduction and specifically tailored ion-molecular reactions have ensured interference free measurements for many isotopes down to ppq (10^{-15} g/g) levels, in ICP-MS. Sample preparation for analysis using GD-MS is relatively straight forward and analytes present at sub-ppm to ppb levels can be simultaneously analyzed along with minor and major constituents. But in ICP-MS, the total dissolved salt content is still a matter of concern and importance because of the suppression effects on ion intensities; the optimum matrix concentration being around 100 g/ml. This requires enormous dilution of the sample solution with the concomitant loss of sensitivity and creeping dilution errors in the final results computed. Novel and cost effective procedures for the removal of the major matrices have been developed at CCCM for the trace impurity characterization using ICP-MS. This lecture will detail the application of some of these approaches and also certain limitations of using low-resolution mass spectrometers like QMS.

Ultra Trace elemental analysis is a must for technological progress and it is time that highly focused indigenous initiatives in developing high performance analytical instruments like mass spectrometers are taken up by DAE and other departments.

Dr. Arunachalam *is from the 18th batch of the BARC training school, obtained his Ph.D., from University of Bombay. He was visiting scientist in Germany during 93-95 and presently the Head of CCCM, Hyderabad. His current research interests are: Development of methods for the determination of trace elements at ppb, sub-ppb levels in biological and environmental samples and high purity materials using ICP-MS and GD-MS and newer sample introduction techniques and speciation studies using hyphenated techniques like HPLC-ICP-MS. In addition he is interested in the preparation and distribution of (secondary) reference materials for analytical quality control and quality assurance in trace element determination in biological, environmental and food sciences and organizing Proficiency Testing (PT) programmes in trace element analysis. He is National Representative for Analytical Chemistry Division of IUPAC for 2004-2005. He is empanelled by NABL as an assessor. He has published over 60 publications in international journals on trace element characterization.*

Mass Spectrometry for Surface Characterization

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Secondary Ion Mass Spectrometry (SIMS) provides a unique capability for carrying out quantitative analysis of solid surfaces. Present day high technology materials often undergo degradation processes that are initiated at solid surface. Such deleterious processes include corrosion, erosion, wear, high temperature oxidation, surface damage induced by radiation, weld induced composition changes in alloys and thermally driven surface segregation of minor elements. These phenomena limit life of engineering components and needs to be assessed carefully. The remedial measures often involve surface modification strategies like hard facing, growth of nitrided over-layers, ion beam modification, multi-layer coating deposition and laser treatment. Evaluation of these processes needs quantitative assessment of surface composition profile.

SIMS instrument, in its dynamic operating mode, yields composition depth profile of constituents present in the top few layer of the specimen surface. Using this method, a number of material problems, pertaining to fast reactor in-core components, has been investigated. These include coolant side carburization of cladding tube, critical assessment of Heat Affected Zone (HAZ) in chrome-moly steels, segregation of carbon in grain boundaries of SS, surface melting of laser treated steel and dynamic strain ageing behaviour. The quantitative knowledge of small diffusion co-efficients available through calculations on SIMS data has been used to model long-term degradation behaviour. In static SIMS mode, the machine has been used to evaluate surface contaminants. The ion imaging capability of SIMS has been utilized to get three-dimensional elemental distribution in desired specimen volume exposed to service conditions.

In recent times, SIMS has been exhaustively used for studying problems pertaining to surface modification and engineering. Inter-diffusion in Zr/Fe layers, Al/Ge and Cu/Ni have been studied. Self-diffusion of ^{57}Fe and ^{15}N using tracer layers in amorphous and nano-crystalline phases of $Fe_{1-x}N_x$ multi-layers have been evaluated. Ion beam induced interfacial mixing of Co/Ag and Fe/Ag multi-layers have been studied. The interfacial compound formation driven by solid state reaction has been investigated in TM/Si systems. Study of sub-surface interfaces and acquisition of implantation profile in ion-irradiated specimen have been conducted.

The sensitivity and fast response characteristics of Quadrupole Mass Spectrometric systems have been exploited in synthesizing of nano-materials and transition metal carbide/nitride over-layers on structural alloys. A home built UHV compatible EGA-TGA-MS (Evolved Gas Analysis–Thermogravimetry-Mass Spectrometry apparatus) with controlled gaseous atmosphere and liquid injection capability have been built in-house. This machine, in temperature programmed decomposition mode, tracks evolved gases emitted from complex crystalline hydrates. Various steps encountered during decomposition can be delineated from the gas release / TG weight loss sequences. The end product of the decomposition process carried out in vacuum invariably results in formation of nano-crystalline phase. In addition to arriving upon stoichiometric evolution of nano-crystalline end products, the kinetic parameters are determined from fractional transformation plots. Using this procedure, a number of nano-crystalline oxides like CaO, Al_2O_3, ThO_2, CeO_2, ZrO_2, Cr_2O_3 and TiO_2 have been synthesized. The CrN and TiN nano-crystalline powders were obtained by subsequent gas phase nitridation experiments carried out in NH_3 atmosphere.

In gas-solid interaction mode, the EGA-TGA-MS has been very successfully used to grow stoichiometry-controlled over-layers like CrN and TiN on respective metals. The mass spectrometric gas consumption profiles are indicative of real time progress of surface nitridation. In every case, coherent, dense over-layers having a depth-varying composition and hardness gradient have been obtained. Such features are technologically important as compositionally graded over-layers achieve stress relaxation during service. Also efforts are under way to synthesize carbo-nitride over-layers using $CH_4 + NH_3$ mixture where surface hardness is a function of C/N ratio.

Obviously, such over-layers, exhibiting mechanical property gradients, need to be characterized for depth dependent composition by SIMS. The strategy of growing over-layers by gas-solid interaction through thermo-analytical means and subsequently examining them by surface analytical techniques like SIMS demonstrates Mass Spectrometry (MS) as a versatile front line technique for materials research.

Dr. Sitaram Dash *completed his post graduation in Physical & Nuclear Chemistry from the Utkal University, Bhubaneswar in the year 1979. He joined BARC Training school in 1981 and posted to IGCAR in 1982. He began his early career in the RCL and subsequently moved to MSD. He obtained his doctoral degree University of Madras. He worked as a guest scientist at Forschungszentrum Julich, Germany. Dr. Dash has built a thermal analysis-mass spectrometry for analyzing gases in solids which fetched him Kalpakkam Science and Technology Award. Presently he is working on synthesis of nano-crystalline hard coating by laser synthesis, magnetron sputtering, reactive evaporation and flame pyrolysis. His current interests are SIMS and nano-indentation studies on hard coatings.*

Dr. S. Rajagopalan *obtained his PG degree in Physics from American College, Madurai on 1976. Subsequently, he obtained his Ph. D in Physics from IIT, Delhi. He joined IGCAR and worked in Radiochemistry Programme on High Temperature X-Ray Diffraction studies of nuclear ceramics. Subsequently, he moved to Surface Science Section, Materials Science Division. Presently he is working on SIMS analysis of surfaces and interfaces of thin films and coatings fabricated by PVD techniques.*

Shri P.K. Ajikumar *has graduated in Physics from Mahathma Gandhi University, Kottayam in the year 1987, obtained M.Sc degree in Physics from Annamalai University, Chidambaram in the year 1996. He also acquired PG diploma in Digital Electronics and Computers from Madras Christian College. He joined IGCAR in the year 1989. His expertise is in the field of Ultra High Vacuum systems, Mass Spectrometry, Thermal Analysis, Hard coatings etc. He has worked as a guest scientist at Forschungszentrum, Julich, Germany. Currently he is pursuing synthesis and characterization of nitride and carbide overlayers on transition metals by controlled atmosphere exposure using the EGA-TGA-MS system. He has co-authored over 30 scientific publications.*

Mr. M. Kamruddin *is a senior scientist at MSD, IGCAR. He has graduated from 27th batch of training school and joined RCL, IGCAR and subsequently moved to MSD. He has worked as Guest Scientist at Forschungszentrum, Juelich, Germany. He has indigenously set-up an ultra high vacuum compatible, MS and TG based EGAs. He has used the MS data on decomposition of thermally less stable inorganic solids for controlled synthesis of nanocrystalline materials. He has co-authored more than 50 scientific publications. His specialization includes surface characterization, synthesis and characterization of nanocrystalline ceramics, surface analysis and nanocrystalline composite coatings.*

Dr. A.K. Tyagi, *is currently Head, Surface Science Section of the MSD, IGCAR. He did his M.Sc., from Meerut university, Meerut and M.Tech., and Ph.D. from IIT, Delhi. He joined the department through 22th batch of BARC training school in 1978. He specialized in the area of materials characterization, particularly surface/interface and thin film analysis using Secondary Ion Mass Spectrometry (SIMS). His other areas of interest are nanomaterials, protective coatings, ion implantation, surface modification, gas-solid interactions and scanning probe microscopy. Dr. Tyagi has worked as Guest Scientist at Hahn-Meitner Institute, Berlin, and Forschungszentrum, Juelich, Germany. He is a co-author of 185 scientific publications. Dr. Tyagi is a life member of ISMAS, MRSI, IIM and IPA.*

Development of Magnetic Sector Mass Spectrometers in BARC

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Mass Spectrometry is a crucial analytical tool for number of DAE's programs that require isotopic ratio measurements in samples of hydrogen, lithium, boron, uranium, plutonium etc. High sensitivity isotopic mass spectrometry plays a key role in this. Monitoring of deuterium, lithium-6 and uranium-235 in various enrichment processes as well as determining the overall plutonium produced in nuclear reactors are extremely important tasks for DAE. Realising the importance of mass spectrometric techniques in nuclear areas, BARC, since its inception in 1954, took up the development of technologies towards the underlying instrumentation programme in a major way. Expertise has been developed in the areas of HV/UHV technology, precision mechanical engineering and fabrication, magnet technology, ion optics, sensitive and stable analog and digital electronics, data systems etc.

Over the past three and a half decades BARC has developed several mass spectrometers suitable for needs of a number of programs in the Department of Atomic Energy. These include the mass spectrometers for 1) isotopic ratio measurements for hydrogen, lithium, boron, nitrogen, potassium, rubidium/strontium, uranium, and plutonium, 2) general purpose gas source based mass spectrometers for inorganic analysis, organic analysis and for gas content in certain nuclear materials, 3) inductively coupled plasma source mass spectrometer for elemental analysis, 4) quadruple mass spectrometers, and 4) double focusing mass spectrometer with a resolving power of about 6000.

During the last few years, triple collector gas source mass spectrometers have been built, installed and commissioned at RMP, Mysore for the isotopic analysis of UF_6 gas. Quadrupole mass spectrometer, using indigenously developed 16 mm and 19 mm rods as well as appropriate RF and DC supplies have been completed and successfully tested.

Under X plan, two magnetic sector mass spectrometers, with improvements, have been taken up for development to meet the increasing demand for high precision isotopic ratio measurements. One is a triple collector TIMS for Uranium isotopic analysis. The fabrication of its subsystems and their assemblies has been completed. Presently, it is undergoing testing. The second is a multi-collector inductively plasma ion source mass spectrometer (MC-ICPMS). This instrument has been designed and procurement of components is in progress. Work is also going on, under X plan, towards the development of an automated sample handling system for D/H mass spectrometer.

Another magnetic sector instrument that is under development is a TIMS with dual ion source for use in Heavy Water Board at their Heavy Water Plant, Manuguru. All its sub-systems have been designed and fabricated, and are presently being assembled. This mass spectrometer will have the facility to analyse $^{10}B/^{11}B$ in the form of sodium metaborate as well as $^{16}O/^{18}O$ in the form of carbon dioxide gas.

Shri V. K. Handu *has done his B.E (Electrical Engg.) from REC, Srinagar, and M. Tech from IIT, Kanpur. He is from the 16th batch of BARC training school. He has worked on the development of electronics for the D/H mass spectrometers for the analysis of water samples in Heavy Water Plants, isotopic ratio process gas mass spectrometers for the analysis of* UF_6 *gas in RMP, Mysore, thermal ionization mass spectrometers for isotopic analysis in solid samples in reprocessing plants like KARP, AFFF etc, and first prototype of ICP-MS mass spectrometer. During the last few years, he has been involved in the indigenously development of various subsystems of quadrupole mass spectrometer (QMS) viz. quadrupole rods, RF and DC supplies, and data system. These have been used in the prototype ICP-MS. Currently he is involved with the development of TIMS, ICP-MS, and QMS for Heavy Water Board for use in Heavy Water Plants. He is also involved in development of the advanced version of thermal ionization (TIMS) and multi-collector ICP (MC-ICPMS) mass spectrometers. Besides the design, development, and building of the mass spectrometer instrumentation required in DAE programmes, he is also currently involved in the design and development of special electronics systems like development of high power RF systems for high intensity proton accelerator under development in BARC.*

Vapour Pressure Measurements at Ultra High Temperatures using Laser Induced Vaporization Mass Spectrometry

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Off normal events in a nuclear reactor can take fuel materials to very high temperatures and vapor pressure data of these materials at such high temperatures (~ 5000 K) is required to analyze accident conditions. Conventional heating methods cannot be adopted for such high temperature studies due to difficulties in attaining very high temperatures and problems due to chemical interactions of the sample with the container material, if, indeed, a container can be used at these temperatures. An in-house developed Laser Induced Vaporization Mass Spectrometry facility is used to determine the vapor pressure of inactive fuel materials. A pulsed Nd-YAG laser is used in this facility as a heat source and as it heats only a small area (few mm^2 or less) and only transiently, there is no need for a container. The identity and density of the species formed are determined by the use of a quadrupole mass spectrometer (QMS). When tuned to the mass of a particular ion, the mass spectrometer provides an arrival time-resolved spectrum for each species, with time=0 being the time of incidence of the laser pulse. The peak surface temperature reached is determined from the measured time-of-arrival (TOA) profiles by fitting them to a sum of Maxwell-Boltzmann distributions after deconvoluting the amplifier time constant. From the temperature and the intensity of various species, the partial pressures are calculated. The observed intensity of C_3 species, detected in the vaporization of graphite at a peak surface temperature of ~ 4000 K is used for the determination of the calibration constant for the measurement. Vapor pressures of graphite, UO_2, UC, and ThO_2 are determined using this facility. This paper briefly summarizes these results.

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Mass Spectrometric Measurements of Hydrogen and Deuterium in Zirconium Alloys

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Presence of gaseous elements even in trace amounts in metals and alloys, either in free state or in combined form, has profound effect on their structural, mechanical and other properties. The presence of hydrogen in certain metals (e.g., Ti, V, Zr) and alloys (e.g., steel, zircaloy) beyond certain limit leads to embrittlement resulting in loss of structural integrity of the material. The hydrogen embrittlement in the coolant channels of Pressurized Heavy Water Reactors (PHWRs) has been identified as one of the major causes of coolant channel failure. The process involves absorption of atomic hydrogen (or deuterium) at the reactor operating temperature resulting in the precipitation of ZrH_2 as a separate phase. This occurs when hydrogen (or deuterium) concentration exceeds its solubility in zircaloy at that particular temperature. This insoluble and separate hydride (or deuteride) phase in zircaloy matrix makes the coolant channel brittle resulting in reduced lifespan for these coolant channels. The ageing management therefore requires that this deuterium pick-up rate should be quantified for the preventive measures to be taken for the smooth operation of the reactor. The whole exercise is to analyse hydrogen/deuterium pick up in wafer thin samples sliced from the interior of the coolant channels so that the integrity can be maintained for their continuous usage.

A number of parameters starting from sampling of zircaloy sliver samples from the pressure tubes, treatment of samples, extraction of hydrogen/deuterium from the samples, and finally measurement of isotopic composition, need to be evaluated critically for reliable assessment of hydrogen/deuterium pick-up by the pressure tubes. Some of the techniques identified for the determination of hydrogen in solid samples include inert gas fusion (IGF), differential scanning calorimetry (DSC), nuclear techniques involving neutron scattering as well as heavy ion induced reactions on hydrogen targets, hot vacuum extraction (HVE), and mass spectrometry. Among these, Hot vacuum extraction (HVE) technique has been reported to be a viable alternative for the determination of gases in metals and alloys. The technique is generally based on simple gas laws for the calculation of hydrogen concentration. In fact, if hydrogen is the only impurity to be determined, HVE has generally been preferred over other techniques. Mainly two variations of this technique are available in literature. In one, the evolved hydrogen is preferentially absorbed in a Pd filter while all other gases are removed. Subsequently the Pd foil is heated and the pressure due to evolved hydrogen is measured. In another variation, first the total pressure of the evolved gases is measured. Then hydrogen is oxidised to water on heated CuO and the moisture is preferentially absorbed in an anhydrone trap. The decrease in pressure is due to the hydrogen removed as moisture. These two variations, though simple, cannot be used for differentiating the liberated hydrogen as protium or its heavier counter part deuterium. Such information is useful in nuclear technology to identify the exact cause of corrosion as due to water or heavy water so that the appropriate corrective measures can be undertaken. A mass spectrometer coupled to a HVE system is an ideal combination for the determination of gases and their isotopic composition in metals and alloys. Isotopic composition of hydrogen, for instance would be useful in expressing the hydrogen+deuterium content as total hydrogen equivalent given as [H]+[D]/2. This paper reviews different mass spectrometric methodologies available for hydrogen determination in zircaloy and presents typical results obtained in author's laboratory.

Dr. K.L. Ramakumar *is currently the Head, Radioanalytical Chemistry Section, Radiochemistry and Isotope Group in BARC. He is a specialist in the fields of trace elemental analysis by Mass Spectrometry and ion chromatography, thermal analysis by differential scanning calorimetry as well as in analytical chemistry. These include determination of H and D by HVE-QMS, Separation of B, F and Cl by pyrohydrolysis followed by their determination using ion chromatography, C, N, and trace elements by instrumental methods including ICP-MS. Determination of heat capacity of thoria, thoria-urania and* $(U,Gd)O_2$ *by DSC. He has been a Peer Reviewer for International Science Foundation (USA) Program for providing research grants to Russian Scientists. He was also on an Expert assignment to IAEA's Safeguards Analytical Laboratory (SAL) at Seibersdorf, Austria. He has more than 180 publications to his credit.*

Theme Meeting on
Isotopic Ratio and Concentration Measurements
by TIMS & ICP-MS
(MSINFC-2006)

August 2-4, 2006
Convention Centre, Anupuram

ABSTRACTS[*]

**Abstracts of full-text articles have not been included.*

Isotope Dilution Mass Spectrometry (IDMS) for Measurement of Elemental Concentration

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IDMS is a well-known analytical method for measurement of concentration. IDMS is based on the measurement of isotope ratios in samples before and after the addition of a known amount of an isotopically enriched element. The element to be analysed must have at least two stable or long-lived radioactive isotopes able to be measured in a mass spectrometer. The abundance of the two isotopes and, hence, the isotope ratio in the mixture will be intermediate between those in the sample and the spike and it will depend both on the amount of spike added and on the initial amount of the element in the sample. The relationship for deriving concentration by IDMS is given below:

$$C_s = C_{Sp} \frac{m_{Sp}}{m_S} \frac{M_S}{M_{Sp}} \frac{A^b_{Sp}}{A^2_S} \left(\frac{R_{in} - R_{Sp}}{1 - R_{in} \cdot R_S} \right)$$

c_S and c_{Sp} the concentrations of the element in the sample and the spike, respectively, m_S and m_{Sp} the mass taken from sample and spike in the mixture, respectively, and M_S and M_{Sp} the atomic mass of the element in the sample and the spike, respectively. The concentration of the element in the sample, c_S, is determined by measuring R_m by mass spectrometry. The uncertainty in the concentration measurement depends only on the uncertainty in the measurement of the isotope ratios R_S, R_{Sp} and R_m as M_S and M_{Sp} are known and m_S and m_{Sp} can be gravimetrically determined. The only parameter that has to be experimentally determined is R_m, and this can be done with high accuracy and precision by using a thermal ionisation mass spectrometer.

In comparison to other methods such as external calibration or standard additions, there is no parameter regarding the instrumental sensitivity involved in arriving at concentration. Therefore, any variation of this parameter due to instrumental instabilities such as signal drift or matrix effects will have no influence in the final value for the element concentration in the sample (c_S). Another advantage of IDMS for total elemental analysis is that once complete isotope equilibration between the sample and the spike has been achieved, possible loss of substance of the isotope-diluted sample will have no influence on the final result. This is due to the fact that any aliquot of the isotope-diluted sample will contain the same R_m, and therefore, there is no need to know the pre-concentration or dilution factor of the sample or to take into account any non-quantitative separation or evaporation step. Due to many of these advantages, measurement of concentration by IDMS is internationally regarded as a reference or highly qualified primary method. IDMS is regarded as the recommended method for IAEA safeguards measurements of strategic materials of nuclear interest. The use of IDMS for total elemental determinations is well documented in the literature and several reviews and books have been written on this subject [1-3].

In the last years, we have seen the application of isotope dilution methodologies in some new analytical fields. One of those new fields is elemental speciation where the aim is the determination of the individual chemical species in which an element is distributed in a given sample. The current status of these applications was discussed by Pablo Rodriguex-Gonzalez et al.[4] in a recent review.

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Dr. M. Sai Baba *did his masters degree from Andhra University and obtained doctoral degree from University of Madras. Carried out postdoctoral work at Texas A&M University, USA and at Research Centre, Julich, Germany. Worked as guest scientist at Research centre, Julich, Germany. Has co-authored 37 journal publications. Authored the chapter on "Knudsen Effusion Mass Spectrometry", in the book "Introduction to mass spectrometry". He is a Member of several professional bodies. He has held the position of Vice-President of Indian Society of Mass Spectrometry. His research interests are mainly in the area of high temperature chemistry. Currently, he is heading Strategic & Human Resources Planning Section and Scientific Information and Resources Division, IGCAR.*

Indigenisation of Thermal Ionization Mass Spectrometers

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BARC has built several TIMS instruments for isotopic ratio analysis of nuclear materials like U, Pu, Li and B. These are under use in various units of DAE in Tarapur, Kalpakkam, Mysore and BARC. There is growing demand for such instruments especially for U and Pu for isotopic analysis but with higher sensitivity and better precision. Thus, the development of new TIMS instrument for U and Pu has been taken up under X plan.

The new triple collector TIMS comprises of symmetric stigmatic geometry with a central radius of 30 cm and 90 degree angle of deflection. Other important features of the instrument are:

- *10 kV accelerating potential for better focusing of the ion beam, which improves the characteristics of the instrument like sensitivity, resolution and abundance sensitivity.*
- *Improved ion source design equipped with einzel lenses for focusing in y and z directions to improve the transmission, which adds to the sensitivity of the system.*
- *Vacuum system using turbo molecular and ion pumps to maintain vacuum of* 10^{-8} *torr in the entire system to reduce the scattering of ions and hence improves abundance sensitivity.*
- *Improved electronics and data acquisition system for better stability of the ion beam.*
- *Analyzing magnet with better stability and field homogeneity, for improving directional focusing of the ion beam.*
- *Modified design of faraday cups using deeper collectors to avoid escape of ions and electrons.*
- *Improved mechanical fabrication of components so as to obtain better alignment.*

Moreover, simulation study was carried out for the incorporation of the einzel lenses in the ion source of this instrument. In this study the geometry of the einzel lenses was created with the ion source and the focusing of ions was studied with various potentials on its electrodes. This improves the transmission of the ions through magnetic analyzer. Practically also we have obtained ~30% more sensitivity with einzel lenses.

So far, various measurements have been carried out to obtain the parameters like precision, accuracy, sensitivity and resolution. This paper contains the description of these measurements and results obtained.

Apart from this, a new TIMS for isotopic analysis of boron in the form of Na_2BO_2 has been designed and built for use in Heavy Water Board. Description and results obtained on this instrument also will be discussed in this paper.

The main features of this instrument are:

• Central radius	15cm
• Geometry type	stigmatic
• Angle of deflection	90^{o}
• Angle of entry/exit of ion beam	26.5^{o} *(exit angle adjustable* $\pm 5^{o}$*)*
• Accelerating voltage	5KV
• No. of collectors	3
• Mass range	1-100 amu
• Resolution	200
• Filament assembly type	triple filament assembly

This instrument has been assembled and performance evaluation using boron samples is in progress.

Shri S.N.Bindal, *born in 1948, was working as a senior scientific officer in the Vacuum Physics & Instrumentation Division, BARC, Mumbai. After completing his B.Sc., he has joined the erstwhile Technical Physics Division of BARC. He has been associated with the developmental activities of Mass Spectrometry group. He made significant contributions to the programmes on Thermal Ionisation Mass Spectrometer, Inductively Coupled Plasma Mass Spectrometer and Process Gas Mass Spectrometer. He has worked on advanced version of TIMS for isotope ratio analysis.*

Data Acquisition and Handling in Thermal Ionization Mass Spectrometer

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The modern Thermal Ionization Mass Spectrometers (TIMS) are equipped with multi collectors and highly stable electronic signal processing circuitry. However, to take full advantage of these state-of-the-art equipments appropriate measures for data acquisition and treatment are necessary. This will enable us to take up problems (such as, timing and duration of core-mantle differentiation of the earth), that require very high order of precision.

Data acquisition must be planned considering number of isotopes to be measured, how many and what type of detectors are available, whether the measurement is to be done in peak jumping (dynamic) or static mode. It is advantageous to make measurements in the static mode if rotation of electronic amplifier channels is possible. Depending on the signal/noise ratio and intensity the integration time needs to be chosen. Each block can have 10 to 30 measurements and around 200 measurements per run are needed for meaningful statistical treatment of the data.

It is very essential to monitor isobaric interferences and to apply correction. Intensity of the interfering isobar must be in the order of 10^{-5} V or less relative to the isotope of interest for analysis requiring reproducibility at 10^{-6} (ppm) level. A separate Faraday cup / SEM could be employed to monitor the isobaric interference in the multi-collector TIMS.

The most difficult part of data handling is applying the fractionation correction on the measured isotope data. In the TIMS sample is deposited on a metal filament which is heated and ionized by evaporation. Although the vapor pressure is dependant on molecular weight, other factors, such as, fraction of the sample evaporated, ionization potential, work-function etc. which also influence extent of isotope fractionation Correction for fractionation could be applied externally or internally.

External fractionation correction is applied when only one or no stable isotope is present. In case of Pb or U the fractionation factor (α) is estimated on the basis of repeated analysis of standards and the same is applied to measurements on samples taken under similar if not identical conditions. Because, external fractionation correction can not be exact lower degree of accuracy and precision are achieved when compared to internal fractionation correction.

Internal fractionation correction involves estimation of the fractionation factor using two or more stable isotopes and using it to correct for fractionation effect on the isotope ratio of interest. There are three methods of applying such corrections and these are (a) linear law, (b) power law and (c) exponential law. The relative advantages of each of these methods will be discussed.

Prof.S.Balakrishnan *is currently the Dean of School of Earth Sciences, Physical, Chemical and Applied Sciences in Pondicherry University. He has obtained his Ph.D. from JNU, New Delhi and has served in University of Roorkee before moving to Pondicherry. He has several publications to his credit in national and international journals. His areas of specialization include Isotope Geology and Geochemistry.*

Geochronological Studies in TIMS at KDM Institute of Petroleum Exploration

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The evolution of any sedimentary basin is closely interlinked with global tectonics. Since geochemical and isotopic characteristics of the basement rocks provide the fingerprints of various paleogeological processes associated with basin formation and evolution, it is necessary to carry out in detail the multi-isotopic studies of the basement rocks. Further, the identification of the various basement thermo-tectonic episodes is of paramount importance in the formation of a comprehensive basin evolutionary model.

In this presentation I report the geochronological studies carried out on the Precambrian basement rocks from the wells *"A"* and *"B"* using Rb-Sr as well as ^{40}Ar-^{39}Ar dating methods to understand basement evolution of Western Offshore Basin of India. While the studied well *"A"* is located NWN of Bombay high filed, the well *"B"* is located south of Bombay high field. Five granitic basement samples from conventional core CC-3 (2054.3-2058.3 m) of well *"A"* has yielded whole rock Rb-Sr isochron age of 185576 Ma, which has been interpreted as the time of emplacement of granitic basement in this area. Further, the ^{40}Ar-^{39}Ar studies carried out on one sample (CC3B2B) of the basement has indicated subsequent thermal heating at around 600 Ma ago. The Rb-Sr studies carried out on conventional cores CC-5 (Depth: 1924.4-1931 m), CC-6 (Depth: 1931-1934.4 m), CC-9 (Depth: 1942.2-1948.6 m) and CC-11 (Depth: 1954.5-1961 m) of well *"B"* have suggested that the schistose basement in this well was metamorphosed around 1400-1450 Ma ago. The basement in this well must have been formed earlier, whose age, however, could not be construed.

The geochronological studies carried out on the Precambrian basement rocks of diverse composition from the Western Offshore of India suggest a complex emplacement and post crystallization tectono thermal history. Present study and earlier geochronological studies suggest that the granitic/gneissic/schist basement rocks of Western Offshore were emplaced at around 1700-2100 Ma and 1400-1450 Ma ago and were further subjected to secondary thermal activities between 1400-1450 Ma and 500-600 Ma ago. While the older thermal activity, observed in the well *"B"* and earlier partially studied well *"C"*, located WWS of Mumbai high, might be related to Middle Proterozoic granitic magmatism as reported from the wells *"E"* and *"F"* located in near vicinity south and SWS of Mumbai high respectively, the younger thermal event as observed in the well *"A"* as well as earlier studied well "G" are related to famous wide spread Pan-African thermo tectonic event spreading from the Arabian peninsula to eastern Africa covering Madagascar, southern India, Sri Lanka and east Antarctica. The results obtained in the present study in the light of those obtained earlier will be discussed and presented to understand basement evolution of western offshore basin of India.

Dr S. S. Rathore *completed his Ph. D. in geochronology from Physical Research Laboratory, Ahmedabad and has about 16 years experience in the field of mass spectrometry/geochronology. He joined ONGC in the year 1989 as graduate trainee and was posted at Geochronology Laboratory of KDM Institute of Petroleum Exploration, Dehradun from 1991 to 2000. For next three years, he was posted at Agartala (Tripura) to complete his NE tenure. Since 2003, he is again posted at Geochronology Laboratory, KDMIPE, Dehradun. Dr Rathore had established K-Ar and Ar-Ar dating facilities at KDMIPE and improved the technical capabilities of Rb-Sr dating facility which utilizes TIMS. He has published/presented more than 45 papers and has participated in several national and international seminars/symposia. Dr Rathore is presently working as Suptdg. Geologist.*

Studies on the Formation of Atomic and Molecular Ions of Actinides in Thermal Ionization Mass Spectrometry

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Thermal Ionisation Mass Spectrometry (TIMS) is the most popular technique for determining the isotope ratios and concentration, using isotope dilution, of the actinide elements. During TIMS analysis of an element, one can obtain atomic (M^+) and/or molecular ions (MO^+, MO_2^+) of different intensities, depending upon the sample loading procedures, type of the filament materials, filament geometry (single or multiple) and the heating temperatures of the filaments in the thermal source. This feature of TIMS can be exploited to perform the measurements with high sensitivity in cases when the amount of element is available in limited amounts (g or lower). Moreover, these studies can help in circumventing/minimizing the isobaric interferences by optimizing the suitable analysis conditions. Some of the examples are m/q 238 (^{238}U and ^{238}Pu), m/q 232 (^{232}Th and ^{232}U) and m/q 241 (^{241}Pu and ^{241}Am).

We performed studies on the formation of M^+ and MO^+ ions using synthetic mixtures of U and Pu as well as by taking an actual dissolver solution of irradiated thoria with Th/U amount ratio of about 70. Suitable filament heating conditions were identified to obtain data for ^{238}Pu using Pu^+ ion and correction for the isobaric interference from ^{238}U was applied based on the U isotope ratios pre-determined using UO^+ ion from the same filament loading. Similarly, U and Th could be determined sequentially from the same filament loading using U^+ or UO^+ for U and ThO^+ for thorium. The developed methodologies have been applied to the various real-life samples of Pu from PHWRs and of irradiated thoria samples. The results obtained have been encouraging. Based on these studies, a methodology for determining trace levels of U in Pu matrix has also been developed and has been applied to U determination in Pu chemical assay reference material.

A high purity rhenium double filament assembly was used in all the experiments. The samples were loaded from 1 M HNO_3 medium. The formation of atomic as well as the oxide ions was studied as a function of the vaporization as well as the ionization filament heating current. From this study, it is seen that the isotopic composition of U in a mixture of U and Pu can be obtained without any isobaric interference from ^{238}Pu, using UO^+ ions. The methodology was then implemented for the determination of ^{238}Pu by TIMS, accounting for the isobaric interference of Pu using UO^+ ions. The same methodology has also been applied for the determination of traces of U in the Pu chemical assay reference material.

From the studies on the formation of ions in the U + Th system, it is seen that one may attempt to determine ^{232}U by TIMS in presence of Th, using metal or oxide ions, at different filament heating conditions.

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Mrs. D. Alamelu *obtained her M.Sc. degree in Physics from Annamalai University. After graduating from 38th batch of Training School, BARC, she joined Mass Spectrometry Section of the Fuel Chemistry Division in 1995. Since then, she has been actively involved in the indigenous development of Time of Flight Mass Spectrometer. Her other areas of interest include Thermal Ionisation Mass Spectrometry and Alpha Spectrometry.*

Dr. S.K. Aggarwal, *is currently, Head, of the Fuel Chemistry Division, BARC, Mumbai. After completing the B.Sc. Honors degree with two gold medals he joined the 16th batch of BARC Training School in 1972 and received the Homi Bhabha Award. He did his Ph.D. from the Mumbai University in 1980. He did post-doctoral research in USA during 1987-89. During1992-2007, he has actively served ISMAS holding high positions. He is the co-author of a book entitled "Introduction of Mass Spectrometry" He has more than 350 publications in International and National Journal repute. He is a specialist in the field of Atomic Mass Spectrometry and Alpha Spectrometry and is interested in various mass spectrometric techniques. His other areas of interest include electrochemistry and solvent extraction.*

Isotope Ratio Measurement by Thermal Ionization Mass Spectrometry at PREFRE Plant,BARC, Tarapur

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PREFRE has been processing PHWR spent fuel for last 30 years. Accurate accounting of Special Nuclear Material (Uranium & Plutonium) is extremely important in a bulk handling facility like PREFRE. Isotope Dilution Thermal Ionization Mass Spectrometry (ID-TIMS) is the method employed in PREFRE Plant for the determination of SNM concentration at the input stage. Also the isotopic composition of plutonium and uranium at the input and product stage is obtained by employing TIMS and low level uranium present in the final plutonium product (PuO_2) is determined by employing ID-TIMS method.

In addition, mass spectrometry laboratory of PREFRE, Tarapur is providing services to FRD, Trombay as well for carrying out isotopic analysis of uranium in oxide

The Mass Spectrometer, MAT-261 presently in use at PREFRE is high precision, fully automatic machine capable of analyzing 13 loadings without operator intervention. It was procured and commissioned in 1984. Since then the instrument is in continuous operation and has performed isotope ratio measurements of about 25,000 filament loadings of U and Pu samples. Earlier to this, MS2790, a mass spectrometer designed and fabricated by TPPD was in use, which has rendered fairly good service for a period of about ten years.

After installation in 1984 the operation of MAT-261 was almost trouble free for a period of about 6 years. The mass spectrometer system was being controlled by HP 200 series technical computer 9845B with 896 KB RAM, HPIB interface, 15 MB Winchester, dual 8 inch floppy disk drive and thermal printer. Program language was BASIC in accordance with extended HP BASIC. The entire software package was stored on four tape cartridges (2 systems, 1 module, 1 TESTHELP). In middle 1990 the computer developed major problems like cartridge drive failure, floppy drive failure, CRT Control and graphic memory failure etc.

Very high rectification and maintenance charges were quoted by private firms. Hence, it was decided to replace the HP9845B with then available PC/XT. Computer Division of BARC, Trombay provided necessary help and guidance in interfacing the mass spectrometer with PC/XT. Related software translation into GWbasic language was carried out by Process Instrumentation Division and laboratory section of PREFRE plant. Essential software modules required for automatic measurement of isotope ratio in static and peak jump mode were translated. With the development of PCs and problems faced with the maintenance of older models, the required operating software has now been translated into window based VB language and the instrument is being controlled by a conventional PIII PC. This job has been completed in-house in PREFRE plant laboratory without outsourcing.

Major hardware replacements done to this date includes Isolation valve and turret mounting support rods which have gone bad due to wear and tear. Though functionally the instrument is in operating condition, there are certain failures like automatic magazine rotation, magnet's secondary coil and SEM which have over the years gradually restricted the availability of all the features available initially.

It has been observed that the instruments performance as measured in terms of resolution, abundance sensitivity, ion beam stability, peak shape and precision of isotope ratio measurement have gradually deteriorated. Since external precision of isotope ratio measurement has not worsened beyond 0.02%, the precision of elemental concentration measurement by ID-TIMS still remains in the acceptable range (0.2%).

Shri S.V. Udagatti *joined mass spectrometry group of PREFRE Lab. in 1981. Over the years he has specilised in maintenance of vacuum pumps and carries out preventive maintenance routinely. Presently he is co-ordinating the day to day routine work activities in M.S. Section.*

Mass Analysers and Detectors for ICP-MS

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Mass separation device is the heart of any Inductively Coupled Plasma Mass Spectrometer, where in the ions are separated as per the mass to charge ratio. The selection process is achieved in a number of ways depending upon the mass separation device used. Because of multi element capability, superb detection limits, wide dynamic range and high sample through put, ICP-MS is proving to be a compelling technique for more and more diverse applications. The different mass separation devices used are based on Quadrupole Technology, Magnetic sector technology, Time of flight technology or Collision/ Reaction cell technology. More than 90% of commercially available ICP-MS of today have quadruple as the mass separation device. The quadruple instrument is adequate for most routine applications. However this instrument suffers from well documented spectral and non spectral interferences. In order to overcome these problems, ICP-MS with other mass separations devices are developed. Another important component of the ICP-MS is the detector. The function of the detector in ICP-MS is to quantify the number of ions emerging from the mass analyzer by converting into electrical pulses. Over the years, lots of improvements have taken place in the detector technology that the detection limits are improving day by day. The talk will cover the principle involved in various mass analysers and detectors used in ICP-MS emphasizing the usefulness and weakness of these devices.

Dr. K. Sankaran *received his Masters Degree in Chemistry from Madras University in 1981. He joined Indira Gandhi Centre for Atomic Research after completion on his BARC training School in 1983 and working in the Analytical and Spectroscopy Section of Materials Chemistry Division. He obtained the Doctoral Degree in 2000 from Madras University. His research interest includes Boron isotopic measurement and trace elemental analysis using ICPMS, experimental and computational studies of molecular structures, weak intermolecular interactions and high temperature species using Matrix Isolation Infrared spectroscopy.*

Research Activities in IGCAR using ICP-MS

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Development of nuclear materials for variety of applications is one of the important on-going activities being pursued in various laboratories in IGCAR. Elemental characterisation of nuclear materials is an important aspect of analytical services supporting these activities. One of the characterization techniques is Inductively Coupled Plasma-Mass Spectrometry, for sensitive multi-element determination accomplishing trace element analysis as well as isotopic ratio measurements.

Standardisation of Analytical methods for various structural and nuclear materials involves selecting appropriate dissolution methods, study of spectral and matrix interferences and selection of suitable isotopic mass and resolution. The following is a list of analytical activities pertinent to ICP-MS technique carried out in our lab:

- Analysis of structural materials used for FBR, are SS 304L (N), SS 316L (N), Modified 9Cr-1Mo steel, Modified D9, Ti and Nb stabilised steel, satellite and Colmonoy.
- Analysis of weld materials like Alloy 800, Inconel and Thoriated tungsten.etc.
- Analysis of Boric acid, Boron, Boron Carbide , Borated Graphite for assay & impurities.
- Analysis of impurities in Uranium Oxide as a reference material for internal DAE Inter laboratory comparison exercise by solvent TBP-CCl4 extraction method.
- Laser Ablation -ICP-MS was developed for direct sampling and special profiling.
- Uranium matrix removal by on-line solvent Extraction followed by ICP-MS analysis.
- Various Raw materials for Sensor like Yttria stabilised zirconia, Citric Acid, Oxalic acid for impurities present in them.
- Routine analysis of impurities in primary and secondary sodium from FBTR .

Development of Nuclear materials like Enriched Boron and Boron Carbide has gathered momentum in research recently. Though the quadrupole ICP-MS is less precise than TIMS, it is a popular method for B isotope ratio determination because of its speed and convenience. To derive this benefit, huge quantum of samples were anlaysed for boron ratio measurements.

Different working standards of varying boron enrichment atom ratios were prepared and analysed both in TIMS and ICP-MS for precision and accuracy of our results.

Enrichment profile of Boric acid at different plant conditions was obtained using isotopic measurement results from ICP-MS.

Shri. J.K. Sekar *obtained his graduation in chemistry from Madras University and M.Sc Chemistry from Annamalai University. He joined in 1989 at RMP,BARC, Mysore and involved in isotopic ratio measurements in Uranium and its compounds. At present, He is in Analytical Chemistry and Spectroscopy section of MCD, IGCAR. He is working in ICP-MS and developed many methods of Analysis and Standardisation. He is currently involved in Boron Isotopic ratio measurements using ICP-MS.*

Operating Experience with Commercial ICP-MS

R. Krishna Prabhu
Fuel Chemistry Division, Chemistry Group, IGCAR, Kalpakkam - 603 102
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ICP-MS is a well established as a sensitive multi element technique for solving a variety of analytical problems. It is powerful laboratory tool for the rapid chemical analysis and isotopic ratio measurements. It is an asset to any advanced analytical laboratory especially in the nuclear industry. The first Inductively coupled plasma Mass spectrometer was installed in IGCAR in the year 1987. Since then the instrument has been extensively used for analytical proposes for different projects with in IGCAR and some of the outside institutions. Some of the analytical methods developed and area of work carried out using ICP-MS are described briefly. The difficulties encountered and maintenance for up keeping the ICP-MS instrument are also discussed.

The analytical methods for the characterisation of nuclear materials like sodium and uranium was developed during early 90's. ICP-MS is known for its matrix effects. It was necessary to remove these matrix effects by selectively removing the matrix element from the solution. Direct flow injection method, and online solvent extraction for the removal of uranium and analysis by ICP-MS were developed and demonstrated. Laser ablation and laser vaporization technique for solid samples and small volumes of solution were the other methods developed in our laboratory which were used for the solid surface profiling and determination of trace elements in of small volume of solutions.

In collaboration with Geological survey of India a method was developed for the determination of Platinum group elements in geological samples using the NI-S fire assay process. A large number of samples from GSI were analysed for platinum group elements using this method. In collaboration with Shree Chitra Institute for medical research and technology, Trivandrum and Kerala Agricultural University, a coconut root wilt disease that prevailed in Kerala was studied. To arrive at the base line data, Blood sample and food materials were characterized for their trace elements. These studies were carried out in collaboration with Post Graduate Institute of Bio-Medical Sciences, Chennai. The instrument was extensively being used for the isotopic ratio measurement of boron sample from enrichment plant since 1996 and giving full support to the enriched elemental boron preparation facility.

The indigenization activities of many parts of the instruments in absence of spare parts due to embargo/obsolete in nature were carried out successfully. Recently the instrument computer was replaced by an advanced P4 system. The interface was designed and fabricated in house using microcontroller and the instrument was successfully automated to its full capacity. A programme in Visual BASIC incorporating all the requirement were loaded which is more user friendly and having maximum flexibility.

Shri R.K. Prabhu *is working with the Materials Processing Chemistry Section of the Chemistry Group in IGCAR. He is actively engaged in research using ICP-MS.*

TECHNICAL PROGRAMME

Theme Meeting on
MASS SPECTROMETRY IN NUCLEAR FUEL CYCLE
(MSINFC-2005)

21 December, 2005 (Wednesday)

0900-1000 **REGISTRATION**

1000-1100 **INAUGURAL SESSION**

Welcome Address	**Dr. P.R. Vasudeva Rao** *Director, CG, IGCAR*
Opening Address	**Dr. Baldev Raj** *Distinguished Scientist, Director,IGCAR*
Vote of Thanks	**Dr. T.G. Srinivasan** *Head, FChD, CG,,IGCAR*

Plenary Talk-I: **Mass spectrometry in Nuclear Fuel Cycle: Historical Perspective** - *Dr.C.K. Mathews*

Plenary Talk-II: **Reminiscences of Applications of Mass spectrometry**- *Dr. H.C. Jain*

1100-1130 **TEA**

1130-1230 **SESSION I: MS in Enrichment studies**

1. Development of control rod materials
   Dr. K. Sankaran
2. D_2/H_2 measurements in heavy water
   Dr. G.N. Pandey

1230-1330 **LUNCH**

1330-1500 **SESSION II : MS for Ultra trace analysis and surface characterization**

3. Ultra-trace analysis
   Dr. J. Arunachalam
4. Surface characterization
   Dr. A.K. Tyagi

1500-1530 **TEA**

1530-1700 **SESSION III: Instrumentation**

5. Indigenous development of Magnetic sector instruments
   Shri V.K. Handu
6. Indigenous development of ICP-MS and QMS
   Shri V. Nataraju
7. Up-gradation and modernization of mass spectrometers
   Shri K.C. Srinivas

22 December, 2005 (Thursday)

0930-1115 **SESSION IV: MS in R & D of Fuel Cycle**

8. Studies on fuel-clad interaction in fast reactors
   Dr. M. Sai Baba

9. Vapour pressures at very high temperatures
   Dr. M. Joseph

10. Thermodynamic properties of fission product carbides
    Dr. Vidya Sundararajan

1115-1145 **TEA**

1145-1245 **SESSION V: MS in Reprocessing Studies**

11. Application of GC-MS in the Studying the Phenomenon of Radiolytic Degradation of Purex solvent
    Dr. S.C. Tripathi

12. Application in Reprocessing plants and for NUMAC
    Dr. A. Dakshinamoorthy

1300-1400 **LUNCH**

1400-1500 **SESSION VI: MS in Trace element characterization**

13. Application of thermal ionisation mass spectrometer for characterisation of PHWR and BWR fuels
    Shri R.B. Yadav

14. Characterization of structural materials
    Dr. S. Vijayalakshmi

1500-1530 **TEA**

23 December, 2005 (Friday)

0930-1100 **SESSION VII: MS in Post-Irradiation studies**

15. Studies on Irradiated Fuels
    Dr. M. Sai Baba

16. Determination of gases in solids with special emphasis on measurement of D_2/H_2 in Zircaloy
    Dr. K.L. Ramakumar

1100-1130 **TEA**

1130-1230 **CONCLUDING SESSION**
Panel Discussion on "Indigenous Development, Inter-comparison experiments and Potential areas of application of Mass Spectrometry"

Chaired by: **Dr. V. Venugopal**
Director, RC&I Group, BARC

1230 **LUNCH**

TECHNICAL PROGRAMME

Theme Meeting on
ISOTOPIC RATIO AND CONCENTRATION MEASUREMENTS BY TIMS & ICP-MS
(MSINFC-2006)

2 August, 2006 (Wednesday)

0900-0930 **REGISTRATION**

0930-1000 **INAUGURATION**

1000-1040 *Plenary Talk:* **Overview of Current status in TIMS**
Dr. K. Gopalan

1040-1110 **TEA**

1110-1240 **SESSION I**

1. Isotope Dilution Mass Spectrometry (IDMS) for measurement of elemental concentration
Dr. M. Sai Baba

2. Ion sources and sample preparation methods for TIMS
Shri R. Balasubramanian

3. Mass analyzers for TIMS
Dr. T.S. Lakshmi Narasimhan

1245-1345 **LUNCH**

1345-1455 **SESSION II**

4. Detectors for TIMS
Shri D. Darwin Albert Raj

5. Indigenisation of TIMS
Shri S.N. Bindal

1455-1520 **TEA**

1520-1700 **SESSION III**

6. Data Acquisition and handling in TIMS
Prof. S. Balakrishnan

7. Research activities using TIMS at PRL
Shri J.R. Trivedi

8. Geochronological studies in TIMS at KDMIPE
Dr. S.S. Rathore

3 August, 2006 (Thursday)

0930-1100 **SESSION IV**

9. Research activities using TIMS at IGCAR
Dr. M. Sai Baba

10. Geochronological and isotope geochemical studies using multicollector TIMS:A review of the activities of geochronology laboratory, AMD, Hyderabad
Dr. U.K. Pandey

11. Research activities in TIMS at FChD, BARC
Mrs. D. Alamelu

1100-1130 **TEA**

1130-1300 **SESSION V**

12. Isotope ratio measurements by TIMS at PREFRE Plant, Tarapur
Shri S.V. Udagatti
13. Operating experience with indigenous mass spectrometer at KARP
Shri H. Seshadri
14. Instrumentation aspects of TIMS at IGCAR
Shri R. Parthasarathy

1300-1400 **LUNCH**

1400-1510 **SESSION VI**

15. Current Status of ICP-MS –An overview
Dr. V. Balaram
16. Mass analyzers and detectors in ICP-MS
Dr. K. Sankaran

1510-1530 **TEA**

1530-1710 **SESSION VII**

17. An overview on sample dissolution techniques for analysis of geological and environmental materials by ICP-MS
Dr. D.K.Das
18. Sample introduction methods in ICP-MS
Dr. S. Vijayalakshmi
19. Research and Development activities of NCCCM using ICP-MS
Shri. K. Chandrasekharan

4 August, 2006 (Friday)

0930-1040 **SESSION VIII**

20. Plasma Source Mass Spectrometry for Concentration and Isotope Ratio Measurement - an overview and development at BARC
Shri V. Nataraju
21. ICP-MS for exploration studies in Nuclear Fuel Cycle
Dr. D.S.R. Murty

1040-1100 **TEA**

1100-1200 **SESSION IX**

22. Research activities in IGCAR using ICP-MS
Shri J.K. Sekar
23. Operating experience with ageing commercial ICP-MS
Shri R. Krishna Prabhu

1200-1300 **Concluding Session**

1300 **LUNCH**

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Shri K. Vijayakumar	
Dr. M. Sai Baba	**Convener**

About the Editors....

Dr. P.R.Vasudeva Rao graduated from BARC Training School in 1973, and did his Ph.D from Bombay University in 1979. His areas of interest include solution chemistry of actinides, novel separation techniques for actinides, chemistry of nuclear fuel materials and the development of materials for nuclear fuel cycle. He has authored more than 150 publications in journals of international repute. He is the President, Southern Regional Chapter of Indian Association of Nuclear Chemists and Allied Scientists. He is the Member of International Advisory Board of Journal of Nuclear Materials. He has been honoured with the MRSI Medal in 1998 and is an Elected Fellow of the Tamil Nadu Academy of Sciences. He is the Distinguished Scientist and presently the Director of Chemistry and Metallurgy & Materials Groups of IGCAR. He holds the position of Senior Professor in Homi Bhabha National University.

Dr. M. Sai Baba did his Masters degree from Andhra University, and obtained doctoral degree from University of Madras. Carried out post-doctoral work at Texas A&M University, USA and at Research Centre, Julich, Germany. Also worked as guest scientist at Research centre, Julich. Has co-authored 37 journal publications. Authored a chapter on "Knudsen Effusion Mass Spectrometry", in the book "Introduction to mass spectrometry". He is a member of several professional bodies. He has held the position of Vice-President of Indian Society of Mass Spectrometry. His research interests are mainly in the area of high temperature chemistry and mass spectrometry. Currently, he is heading the Strategic and Human Resource Planning Section and Scientific Information and Resources Division, IGCAR.

Dr.Vidya Sundararajan graduated from University of Madras in 1988 in Chemistry. After completing M.Sc. in chemistry in Indian Institute of Technology, Madras, she joined Training School, BARC in 1990. She has got her Ph.D. from the Indian Institute of Technology, Madras, in 2002. Her areas of research interest include high-temperature mass spectrometry, fission gas analysis by mass spectrometry and thermodynamic modeling of irradiated fuel. She is a senior scientist presently working in Strategic & Human Resource Planning Section, IGCAR.

Shri R. Balasubramanian graduated in chemistry from Madurai University in 1975, and joined Radio Chemistry Division, BARC in 1976. He moved to Radiochemistry Laboratories, IGCAR in 1980 and has been working in Mass Spectrometry Group since then. He became an Associate Member of the Institution of Chemists in 1992. His area of specialisation is in thermal ionisation mass spectrometry of nuclear materials. He has several publications in the field of thermal ionisation and Knudsen effusion mass spectrometry.