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Thermal ionisation mass spectrometry (TIMS) in nuclear science and technology – a review

Suresh K. Aggarwal†

The advances which have taken place during the last four decades in the instrumentation and applications of thermal ionisation mass spectrometry (TIMS) particularly of relevance to nuclear science and technology are highlighted. These include the measurements at different stages of the nuclear fuel cycle including nuclear material accounting, nuclear safeguards and nuclear forensics. The present day availability of fully automated TIMS instruments equipped with multi Faraday cup detectors has enhanced the capabilities of providing answers to many of the previous un-solved problems, but at the same time, these instruments are being treated as magic black boxes by operators performing routine analysis. The advances in the instrumentation as well as in the software available with the present TIMS machines allow us to venture into hitherto unexplored areas of R&D including the precise and accurate determination of ultra-trace amounts of different isotopes. TIMS along with isotope dilution will continue to be a gold standard and reference analytical method for various applications in nuclear science. MC-ICP-MS will play a complementary role to the present TIMS measurements, especially for routine analysis of actinides at different stages of nuclear fuel fabrication, burn-up determination and at the reprocessing plants.

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1. Introduction

Mass spectrometry (MS) is a versatile analytical tool for high precision and accuracy in the determination of isotopic ratios and concentrations. The inherent capabilities like high sensitivity and applicability to all the elements of the periodic table as well as for large molecules like proteins make these

Formerly at Fuel Chemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400085, India. E-mail: skaggr2002@gmail.com

† Present address: Neelkanth Gardens, 1006 Sunflower, Govandi-E, Mumbai 400088, India.

instruments ideal for understanding a wide range of natural phenomenon. It plays an important role in providing data on the isotopic composition and concentration of different elements required in nuclear, geological, environmental and biological sciences. In fact, MS based analytical techniques like secondary ion mass spectrometry (SIMS) and stable isotope ratio mass spectrometry are some of the very few available analytical techniques which have the potential to determine hydrogen isotopic abundances in various materials. In addition, depth analysis and lateral resolution achievable by MS are excellent and are being used in the materials research *e.g.* in the semiconductor industry.



Prof. Suresh Kumar Aggarwal worked at Bhabha Atomic Research Centre (BARC), Trombay, Mumbai, India from 1973 until January, 2015. He superannuated as Associate Director of the Radiochemistry and Isotope Group (R), Head of the Fuel Chemistry Division (FCD) and as Distinguished Scientist (DS). He obtained his Ph.D. in 1981 from Mumbai University, Post-doctoral training at University of Virginia at Charlottesville, USA (1987–89), stayed for six months at University of Antwerp, Belgium (1982–1983), spent 4 months at International Atomic Energy Agency (IAEA) laboratories at Seibersdorf, Vienna (1997) and was at National Cheng Kung University, Tainan, Taiwan for three months (2009). He is an internationally known expert in the field of elemental mass spectrometry. He was honoured with two gold medals by Guru Nanak Dev University, Amritsar (1972), Homi Bhabha Medal by BARC (1973), and "EMINENT MASS SPECTROMETRIST" award by the Indian Society for Mass Spectrometry (ISMAS) in 1996. He guided 17 Ph.D. students from Mumbai University and at Homi Bhabha National Institute (HBNI), Mumbai and has 230 papers published in international peer reviewed journals. Currently, he is the President of ISMAS. He is also a co-author of the book entitled "Introduction to Mass Spectrometry"

published by ISMAS. He represents India in IMSF and has organized a number of International Mass Spectrometry Conferences in India under the aegis of ISMAS. He is also the founder-President of Indian Society for ElectroAnalytical Chemistry (ISEAC).



With the growing world population, increasing demand for electricity, ever-growing concern of environmental greenhouse effect from fossil fuels and renewed interest in the utilisation of nuclear energy, mass spectrometry will play an increasing role at various stages of nuclear fuel cycle including safeguards, nuclear material accounting, environmental monitoring, and nuclear forensics. A variety of mass spectrometric techniques have to be used to meet the challenges of the nuclear science and technology in future. The different mass spectrometric techniques include TIMS, gas source electron impact ionisation mass spectrometry (GS-EIMS), gas chromatography-mass spectrometry (GC-MS), glow discharge mass spectrometry (GDMS), inductively coupled plasma source mass spectrometry (ICPMS), SIMS, knudsen effusion cell mass spectrometry (KCMS), resonance ionisation mass spectrometry (RIMS), accelerator mass spectrometry (AMS), electrospray ionisation mass spectrometry (ESI-MS), etc. These MS techniques are used to obtain highly precise and accurate data on the isotope-amount ratios, concentration (amount) at bulk, minor, trace and ultra-trace levels, and speciation of different elements like hydrogen, lithium, boron, lanthanides (La, Ce, Nd, Sm, Gd, etc.) and actinides (Th, U, Pu, Am, Cm, etc.) present in different matrices including fuel materials, irradiated fuel, dissolver solution at the reprocessing plant, environmental samples (biological, geological, food, etc.) and nuclear forensic samples. Amongst the large number of mass spectrometric techniques mentioned above, TIMS has been internationally recognised as the gold standard for obtaining data on the isotope amount ratios and concentrations of different elements, in particular U and Pu, in nuclear fuel samples. This manuscript gives a brief introduction to TIMS and presents its application in nuclear science and technology. In this review, the important applications of TIMS in nuclear industry are summarized. An attempt is made to highlight the major developments which have taken place during the present decade. A few thoughts are also included for the future outlook of this important and invaluable analytical tool. Since Th, U and Pu are the important actinide elements in nuclear science and technology, most of the discussion focuses on these three actinides. Though a number of excellent books1-8 and review articles9-16 on inorganic mass spectrometry, actinides and radioactive elements analysis are available, there is no comprehensive review on TIMS for nuclear science and technology. It may be noted that laser ablation ICPMS and SIMS play an important role in nuclear science and technology for the direct micro-analysis of solids, but these are beyond the scope of this review and, therefore, will not be discussed in this review.

2. Principle of thermal ionisation mass spectrometry (TIMS)

Thermal ionisation mass spectrometry involves vaporisation and ionisation of the element loaded and dried on the filament surface by resistive heating. The filament materials generally used are high purity rhenium, tantalum, tungsten and platinum. The filament material should have high melting point as well as high electronic work function since the formation of positive ions in TIMS is based on the Saha–Langmuir equation, given below, which includes an exponential of the difference between the work function (φ) of the filament material and ionisation potential (I) of the element.

$$\frac{n_+}{n_0} \propto \mathrm{e}^{(\varphi - I)/k}$$

Generally positive atomic or molecular ions are employed for TIMS analysis of elements of interest in nuclear science and technology. At times, the negative ions are also employed e.g. for boron, BO_2^{-} ion gives the highest sensitivity in negative TIMS $(N-TIMS)^{17-19}$ compared to $Na_2BO_2^+$, $Rb_2BO_2^+$ or $Cs_2BO_2^+$ ions in positive TIMS (P-TIMS).²⁰⁻²² The generation of negative ions in surface ionisation requires high electron affinity of the element or molecule and low work function of the filament material. A single or a multiple (double or triple) filament assembly is used.^{17,21,23} The use of double or triple filament assembly allows decoupling of the evaporation and ionization processes and gives flexibility to the analyst to adjust filament temperatures to carry out oligo-element analysis from the same filament assembly and also to control the formation of atomic and/or molecular ions (see below for U and Pu) to account for the isobaric interferences using interfering element correction (IEC) methodology. About 0.5 to 1 μ L of the solution in 0.5 to 1 M HNO₃ containing 250 ng to 5 µg of the element is transferred onto the sample filament and dried by passing a current of about 1 A. Sometimes, ionisation enhancers like silica gelphosphoric acid and additives like graphite or silicic acid are also loaded onto the sample filament to enhance the ionisation of the particular species of interest (*e.g.* UO_2^+ in U).²⁴ The ions generated are collimated, accelerated and focused into the mass analyser through an entrance slit. The low energy spread of the ions generated in thermal ionisation source allows the use of only magnetic analyser which provides direction focusing. Ions of different mass to charge ratios travel through the analyser in different trajectories. These ions, which consist of different isotopes of a given element, pass through an exit slit and are detected and collected in a multi-Faraday cup detector system. All the commercial TIMS systems available these days also incorporate a secondary electron multiplier (SEM) for measuring isotope-amounts of minor isotopes leading to ion currents less than 10^{-15} A. The gains of the different amplifiers used for various Faraday cups must be determined experimentally and differences, though small, need be accounted for during the determination of isotope amount ratios. One of the suppliers (Thermo Fisher Scientific) has invoked the concept of virtual amplifiers where all the amplifiers are involved in measuring each of the isotopes and this takes care of the differences in the amplifier gains. Ion counting systems (e.g. Daly detector) are also available in the commercial TIMS systems. The conversion gain ratio of SEM to Faraday cup needs to be determined when using both the detectors in an isotope amount-ratio experiment e.g. if ²³⁶U is measured on SEM or Daly and other U isotopes including ²³⁴U are measured using Faraday cups.

For minor isotope amount ratios *e.g.* 230 Th with an abundance of less than 1 ppm, the ion beam after the magnetic analyser passes through another energy filter (retarding potential quadrupole RPQ in Thermo Fisher Scientific TRITON PLUS or wide aperture retarding potential (WARP) filter in Isotopx PHOENIX) to improve the abundance sensitivity from 1 ppm to about 10 ppb, measured at mass 237 with respect to *m/z* of 238. The advent of these energy filters has allowed the accurate determination of isotope amounts with extremely low abundances. It may be noted that presently, all the three commercially available TIMS instruments are with a sector magnetic analyser having an extended geometry. An attempt was made by Thermo Fisher Scientific quite some time back to incorporate a quadrupole analyser with a thermal ionisation source, but this option met with a limited success and was discontinued.

The element to be analysed by TIMS should be in a chemically pure form to eliminate the suppressive effect of ion formation by other impurity elements present in the sample. This requirement often demands the chemical separation and purification of the samples. This is usually done with anion exchange resin, which absorbs both U and Pu, and trivalent actinides and other fission products are washed out with 7 M HNO₃. Uranium and Pu are sequentially eluted from the ion exchange column with 3 M HNO₃ and about 0.3 M HNO₃, respectively. Extraction chromatography with commercially available resins (TEVA, UTEVA and TRU from EiChrom Inc., Darien, Illinois, USA) is useful for various samples and is quite popular these days.^{25,26} In fact, this separation chemistry is one of the bottlenecks discouraging the use of TIMS in earthsciences and biological fields where the MC-ICP-MS instruments have been widely accepted and are being used routinely. However, for the analysis of radioactive elements like Pu, Am, Cm, etc., TIMS instruments still remain a work-horse and a gold standard in view of their high sensitivity, absence of any memory or carry over effect and elimination of the risk of generating any radioactive vapors as in ICP-MS. But MC-ICPMS is quite popular for the determination of trace amounts of actinides in biological and environmental samples.

In TIMS, during sample loading on the filament, ionisation enhancers are also used sometimes to perform mass spectrometric analysis from samples (e.g. environmental) containing small amounts of U or Pu.24,27 As an example, carbon in some form or the other (e.g. graphite) is added to the sample filament for isotopic analysis of small amounts of uranium. It was shown by extensive studies performed using X-ray photoelectron spectroscopy (XPS), scanning electron microscopy, and KCMS that the formation of U⁺ ions proceeds via the formation of uranium carbide.²⁸ A surface ionisation-diffusion type ionisation source (SID) using a rhenium filament overplated with platinum was also shown to give high sensitivity for Pu and Np.^{29,30} For Pu, a sensitivity of 0.5 to 2 ng with precision and accuracy of 0.07% was quoted and a detection limit of 10⁵ atoms of neptunium was determined using the SID source. For thorium, an ionisation efficiency of 4% was reported using the carburised filament and employing charge collection in TIMS.³¹ The combination of silicic acid and dilute phosphoric acid was found to produce a strong and stable ion beam of UO2⁺ in TIMS

analysis of natural samples.²⁴ A hot cavity source for improving the surface ionisation efficiency is also proposed.^{32,33}

3. Isotope dilution – thermal ionisation mass spectrometry (ID-TIMS)

Isotope dilution in TIMS is used to determine the concentration or total amount of an element present in a given matrix or solution.12 It involves the addition of a known amount of the pre-calibrated spike solution of enriched stable or long-lived isotope of the same element, whose concentration needs to be determined, to the unknown solution or solid. Subsequently homogeneous mixing between the sample and the spike isotopes is ensured e.g. by a redox treatment in case of Pu. This is followed by chemical separation, if required. Knowing the isotopic composition of the element in the unknown sample and the spike, the concentration of the element in the spike solution, the weights or volumes of the sample and the spike solution mixed, the concentration of the element in the unknown sample can be determined. Since the determination of concentration or amount in isotope dilution mass spectrometry (IDMS) depends only upon the change in isotopeamount ratio, the data are not affected by incomplete recovery of the analyte in chemical separation and purification. However, it is recommended to adopt a separation and purification procedure with high yield to minimise the isotope effects, if any, during chemical steps, particularly when dealing with light elements like boron, magnesium, etc. This is also important in samples containing very small amounts of the element to be determined. In view of the inherent advantages of IDMS, isotope dilution-thermal ionisation mass spectrometry (ID-TIMS) is termed as a definitive analytical methodology and is used as a reference technique to calibrate other analytical methodologies.5

The choice of the spike isotope of an element is governed by many factors. The spike isotope should preferably be absent or least abundant in the given sample. It should not have any isobaric interference from the adjacent or other elements. It should be easily available and should not be very expensive. It should preferably be in the same chemical form as the element in the sample for easy homogenisation or mixing. For U and Pu, the most commonly used spikes are ²³³U and ²⁴²Pu, respectively, since ²³⁸U and ²³⁹Pu are the two isotopes which have the highest abundances in most of the nuclear fuel samples of U and Pu.34 Alternate spiking mechanisms for U had been tried and proven to work.35 These authors have shown that U-IDMS works with spikes other than ²³³U. In the recent years, the²³³U and ²⁴²Pu spikes have been replaced with ²³⁵U (about 20% enriched) and ²³⁹Pu (about 99 atom%), respectively. A mixture of these two spikes, called large size dried (LSD) spike, is routinely employed by International Atomic Energy Agency (IAEA), at Seibersdorf, Vienna for nuclear safeguards applications at the reprocessing plants.³⁶⁻³⁸ This spike mixture was selected due to the relatively low cost of ²³⁹Pu compared to that of enriched ²⁴²Pu, and this spike eliminated the need to dilute the solution at the reprocessing plant by the operator/inspector. A number of studies are reported in the literature to evaluate and compare the use of different Pu isotopes as spikes in ID-TIMS of Pu. In our laboratory, it was shown that Pu with ²³⁹Pu about 70 atom% (*e.g.* from pressurised heavy water reactors PHWRs) can be used as a spike for determining the Pu concentration in samples with ²³⁹Pu about 95 atom% (*e.g.* Pu from research reactors) and *vice versa*. This development to use indigenously available spikes circumvented the problem of non-availability of enriched ²⁴²Pu from overseas laboratories.

The spike solutions are calibrated/certified using reverse isotope dilution TIMS using a chemical assay standard. A high purity metal characterised for impurities and isotopic composition is the ideal choice for this chemical assay reference material. A comparative evaluation of different spikes viz. ²³⁹Pu, ²⁴⁰Pu and ²⁴²Pu was reported for Pu concentration determination by ID-TIMS.³⁹⁻⁴¹ An inter-calibration campaign was also taken up using different selected Pu spike isotopic reference materials viz. ²³⁹Pu, ²⁴⁰Pu, ²⁴²Pu and LSD.⁴² In case of Pu, the radioactive decay of Pu isotopes (mainly ²⁴¹Pu, ²³⁸Pu) requires the certified values of Pu concentration in spike to be corrected regularly. This correction adds to measurement uncertainty in the Pu concentration of unknown Pu solution and this obviously would depend on the isotopic composition of Pu in the spike. Moreover, in case of Pu, there are chances of Pu spike being unstable due to radiolysis and polymerisation which requires a suitable chemical treatment for isotopic homogenisation of Pu isotopes between the sample and the spike solutions. These problems are not very serious in case of Th and U.

It may be mentioned that mono-isotopic elements cannot be determined by TIMS since evaporation and ionisation efficiency varies significantly from one filament loading to another and also from one element to another element. Efforts are required to prepare spikes for all the elements to be determined by ID-TIMS. For example, ²²⁹Th, ²³⁶Np and ²⁴³Am have been used as spikes in ID-TIMS for determining ²³²Th, ²³⁷Np and ²⁴¹Am, respectively, in nuclear fuel samples *e.g.* in dissolver solution of irradiated fuel. Recently, ICP-MS has been proposed⁴³ to produce ultra-high purity single isotopes or tailored isotope mixtures of high purity (>99.99%) in spite of low deposition rates (about 10 ng h⁻¹).

4. Isotope fractionation in TIMS

It is well known to the practitioners of TIMS that the evaporation process in thermal or surface ionisation source leads to preferential evaporation of the lighter isotope and the process is known as normal fractionation. This delineates into change (decrease) in the isotope ratio of the lighter isotope to that of the heavier isotope with time, during thermal ionisation mass spectrometric analysis. It is a mass-dependent fractionation phenomenon which depends upon a number of parameters like mass difference between the isotopes of an element, amount loaded on the evaporation filament, chemical form of the element, filament assembly (single or multiple), heating temperatures of the filaments and ionisation enhancers added on to the filament during sample loading, and rate of evaporation. Thus it is difficult to reproduce all these parameters from one TIMS analysis to the next. Therefore, isotope fractionation is recognised as a source of variable systematic error and this variation contributes to uncertainty in isotope amount ratio measurements.

In the early days of TIMS (during 1970s), the TIMS instruments were available with a single Faraday cup and an SEM. It was customary to first optimise the different parameters for achieving a stable ion beam and then evaluate the mass discrimination factor for each element by analysing the isotopic reference material. This approach was known as external normalisation and could yield precision and accuracy of about 0.5% on different isotope ratios of U and Pu. This approach is also referred to as the conventional method of MS analysis and involves acquisition of data for a given number of blocks (typically 3 or 5), with each block of 10-12 scans. The advent of multi-Faraday cup collectors where ion beams of different isotopes could be simultaneously collected revolutionised the TIMS applications and significantly improved the precision and accuracy of data on isotope ratios.44 This also reduced the time of analysis particularly for elements like Nd with a large number of isotopes. A number of methodologies have been developed in the past as well as in recent years to minimise the variable systematic error arising from isotope fractionation.45-52 These can be classified into two approaches: one to use internal normalisation either based on an invariant isotope amount ratio of two isotopes of the element (e.g. in Nd) or by external addition of a pre-calibrated double spike (e.g. $^{233}U + ^{236}U$ for U, $^{242}Pu +$ ²⁴⁴Pu for Pu) on the filament during sample loading,^{45,46} and secondly with total evaporation (TE) and ion current integration.46-53 The internal normalisation approach can only be used for elements with at least four stable or long-lived isotopes and cannot be applied to elements like Li, B with only two isotopes. Also the methodology of double spike cannot be adopted by various laboratories worldwide due to the high cost and limited availability of the enriched isotopes as well as inaccessibility to these isotopes due to restrictions in supplies. Therefore, many of the nuclear laboratories (IAEA, Vienna; IRMM, Belgium; NBL, USA; ITU, Germany) developed and adopted the TE approach to circumvent the problem of isotope fractionation.46-53 This TE approach minimises the isotope fractionation effects because the ion currents are integrated till the sample is completely exhausted from the sample filament. TE helps in improving the repeatability of isotope amount ratio data in any laboratory but does not fully account for isotope fractionation since the overall efficiency *i.e.* ions detected per atom loaded on the filament is limited to only 0.03% to 0.10% for U and Pu.53 Presently, TE and double spike have both been used by a few of the laboratories involved in preparing and characterising certified isotope amount ratio reference materials with a view to achieve overall uncertainties of 0.01 to 0.02% in the certified isotope amount ratios.52-56

The total evaporation method uses the double filament (high purity zone refined rhenium) assembly to decouple evaporation and ionization processes. The two filaments *-viz.*, ionisation filament and evaporation (sample) filament are heated independently. Firstly, the ionisation filament is heated to a current of 5–5.5 A to obtain sufficient signal for ¹⁸⁷Re (200–500 mV) and this is used for focusing and peak-centering. This is followed by controlled heating of the sample filament to obtain 50-100 mV signal of the major uranium isotope. The focusing and the peak centring are checked once again on the U isotope peak. This is followed by data acquisition when the pre-defined summed signal intensity of U isotopes is attained. Heating the sample filament and integration of the ion current of each isotope is continued under computer control till the sample is completely consumed or the signal intensity drops to a pre-defined value (50 mV). This TE approach is quite satisfactory for major abundant isotopes but is of limited success for the minor abundant isotopes (e.g. ²³⁴U, ²³⁶U in U). The data obtained for minor isotopes like 234U and 236U in U TIMS analysis were observed to be positively biased by TE approach. This limitation was attributed to the fact that these minor isotope peaks were not corrected for peak tailings (abundance sensitivity of TIMS), and also any changes in peak centring and focusing due to heating of the sample filament could not be corrected for during data acquisition in TE. In addition, internal calibration of SEM versus Faraday cup was also not possible. A modified total evaporation (MTE) method was, therefore, developed which involves the interruption of the total evaporation process regularly to allow for correction due to background from peak tailing.54-58 This interruption is also used to check for peak centring as well as ion-beam re-focusing due to the increased sample filament temperature. These modifications have significantly improved the accuracy and measurement uncertainty on the minor isotope abundances. Recently, natural U metal⁵⁹ and depleted U metal⁶⁰ were characterized by MTE. These are some of the characterizations that firmly established the advantages of the MTE method that also proved that improvement in the quality of the minor ratio data is achieved without compromising the quality of the major ratio data, in comparison to TE. One of the commercial instrument manufacturers (Thermo Fisher Scientific) has now incorporated software for MTE in their system. However, one of the limitations of MTE is that it requires a large amount (say 5 μ g) of the element to be loaded on the filament compared to 250-500 ng of U generally used in the TE method. Also the analysis time increases significantly in MTE due to regular interruptions for 10% of the time. The MTE methodology has been successfully used in recent years for the certification of minor as well as major isotopes for the isotopic reference materials of uranium. However, this MTE methodology may not be used regularly for the routine analytical work due to the increased analysis time, lower throughput, large amount of the sample to be loaded on the filament and due to the routine requirement of data on major abundant isotopes of U and Pu.

5. Applications of TIMS in nuclear fuel cycle

5.1. Isotopic composition and concentration determination

Data on the isotope amount ratios of U isotopes are needed at the ²³⁵U enrichment facilities. Though it is determined

routinely by GS-EIMS using UF₆ gas and measuring the ion currents of UF₅⁺ at m/z 330 and 333, TIMS is employed to check for the memory effects in GS-EIMS as well as for characterising the working standards to be used for GS-EIMS. Also when small changes in the ²³⁵U/²³⁸U amount ratios need be measured during the initial stages of the R&D work by various enrichment methodologies, TIMS is highly useful though MC-ICPMS can also meet this requirement.⁶¹ The data on ²³⁵U, ²³⁹Pu and ²⁴¹Pu in U and Pu bearing nuclear fuels are obtained by TIMS to certify the fissile content as a part of chemical quality assurance of fuels. In the irradiated fuel, data on the isotopic composition and concentrations of U and Pu are determined to calculate the burn-up from changes in the heavy element isotope amount ratios as well as for nuclear material accounting at the reprocessing plants.

A simple method using a mixed spike of ${}^{233}\text{U} + {}^{235}\text{U}$ was developed to determine simultaneously the $n({}^{235}\text{U})/n({}^{238}\text{U})$ amount ratio as well as the total amount of U present in the sample from the same filament loading.⁶² For the same reason, during initial stages of Pu ID-TIMS work, ${}^{244}\text{Pu}$ was proposed and used as a spike, which was discontinued probably due to its high cost and limited availability. Studies were also reported for the analysis of U and Pu from the same filament loading.⁶³⁻⁶⁵ as well as for determining traces of U in Pu.⁶⁶

Studies are reported on the ion source chemistry of U + Pu⁶⁷ and Th + U⁶⁸ using a double rhenium filament and by preparing synthetic mixtures of the two elements, by a thermal ionisation source. It was shown that UO⁺ ions are produced at lower ionisation and vaporisation filament temperatures compared to U⁺, Pu⁺ and PuO⁺. This observation along with interfering element correction (IEC) methodology using ²³⁵U as a monitor isotope was exploited for developing a novel methodology for the accurate determination of ²³⁸Pu in Pu samples circumventing the ubiquitous isobaric interference of ²³⁸U during TIMS analvsis.⁶⁹ The methodology was used to prepare and characterise the ²³⁸Pu working reference materials which are not available to nuclear community throughout the world.^{70,71} Recently, the same methodology has been used by a Group from Korea using ²³³U as a monitor isotope to determine ²³⁸Pu in Pu samples by TIMS.⁷² In the case of U-Th ion source chemistry, it was observed that the presence of thorium oxide on the filament enhances the stability of UO⁺ in TIMS. Further, it was stated that for TIMS analysis of Th, ThO⁺ ion is preferred whereas for TIMS analysis of U, either U^+ or UO^+ ion can be used.

ID-TIMS was also employed for the determination of Zr in alloy fuels⁷³ as well as recently in the irradiated fuel.⁷⁴ TIMS has also been applied to the determination of U, Th and Ra isotope ratios with high dynamic range and U minor isotope amount ratios with a secondary electron multiplier.^{75,76}

5.2. Burn-up determination of irradiated nuclear fuels

TIMS has been used for more than 4 decades and is still used at present to obtain the most reliable experimental data on the burn-up of the irradiated fuels as well on the depletion and build-up of U and Pu isotopes.^{34,77-81} These data along with concentrations of U, Pu and Nd (stable ¹⁴⁸Nd used as a burn-up

monitor) determined by triple spike ID-TIMS provide data on the burn-up. Burn-up can be calculated either from changes in the heavy element isotopic composition or by determining the total number of fissions using a suitable burn-up monitor *e.g.* ¹⁴⁸Nd for U + Pu fuels. The triple spike ID-TIMS provides the best possible data on burn up with minimum uncertainty. These experimental data are very useful to check and develop computer codes for the build-up and depletion of different heavy element isotope amounts as well as for reactor fuel management during reactor operation.

Burn-up studies are reported for irradiated fuels of natural U, MOX fuels containing both natural U and Pu as well as for thoria fuel bundles irradiated in research reactors.^{34,77-79} Recently, burn-up was reported for carbide fuels and for an experimental fuel of 233 U + 239 Pu where 145 Nd + 146 Nd together were used as a burn-up monitor.^{80,81} It is important to ensure that U blanks are checked and kept under control when determining the isotopic composition of U from irradiated Th since in this case, 233 U is the major isotope and a small amount of natural U introduced from reagents, apparatus or laboratory atmosphere will give erroneous data on the isotope amounts of different U isotopes.

5.3. Accountability of Pu and U at reprocessing plants

Determination of total Pu and U in the input accountability tank of a reprocessing plant is performed by the volume-concentration method where the concentrations of Pu and U are determined by ID-TIMS in an accurately measured aliquot of the solution. This involves uncertainties in the total volume or weight of solution in the tank and the aliquot size. A novel approach using a suitable tracer was developed and tried by several researchers.82-100 This involves the addition of a known amount of tracer element to the input accountability tank, suitable homogenisation and mixing of the tracer with the solution in the tank and taking any unknown aliquot from the solution. By determining tracer to Pu and tracer to U amount ratios by ID-TIMS, and knowing accurately the amount of tracer added, the total amount of Pu and U in the tank can be determined. This methodology eliminates the need to know the total volume of solution in the tank as well as the aliquot size. In addition, independent verification of volume/weight calibration of the tank, if required, is possible.

A number of tracers were proposed and tried starting from Li, Mg, Pb, Nd, Gd, Lu, Er, U and deuterium. The final choice of the tracer is governed by the cost and availability of the enriched isotope to be used as a spike in ID-TIMS, accuracy in the measurement of isotope ratios by TIMS and the blank levels in the dissolver solution of irradiated fuel. To circumvent the problem of blank build up, when using the same tracer repeatedly, it was proposed to employ two tracers alternately *e.g.* in the MAGTRAP (Magnesium Tracer for input Accountability of Pu) and LEADTRAP (Lead Tracer for input Accountability of Plutonium), during studies carried out by us at Tarapur.^{84,85} Subsequently, the European Community tried different tracers (Nd, Lu and Pb) in RITCEX (Reprocessing Input Tank Calibration Exercise) at Eurochemie Reprocessing Plant with different tracers yielding similar results.^{89-91,95} Another exercise CALDEX (Calibration Demonstration Exercise) was also taken up in the framework of European collaboration and evaluation of the tracers methodology.^{98,100} Due to the high cost of natural Lu and its enriched isotope ¹⁷⁶Lu to be used as a spike for ID-TIMS experiments, Er was considered to be an economically viable tracer for input accountability experiments. It is important to design the input accountability tank of a suitable shape allowing easy accessibility of the tracer addition point followed by homogenisation of the tracer.

6. Determination of half-lives

TIMS has played an important role in the determination of precise and accurate half-life values of different *trans*-actinium isotopes.^{94–115} A number of methods *viz.* parent decay, daughter growth, specific activity and relative activity were used to experimentally re-determine the half-life values and minimise the uncertainties in the data.

Half-life of ²³⁵Np was determined by the parent decay method by measuring the changes in the $n(^{235}Np)/n(^{236}Np)$ ratio periodically for about 630 days, using TIMS.¹⁰² The ²³⁵Np/²³⁶Np isotope amount ratio decreased from 4.342 to 1.445 in 630 days and a half-life value of 396.1 \pm 1.2 days was calculated. It was predicted that this methodology may be used, in future, to determine half-lives of radionuclides upto about 70 years, since this would give a change of about 1% per year in the isotope amount ratio. Aggarwal et al.^{103,104} determined the beta decay half-life of ²⁴¹Pu (14.4 years) using the same approach by preparing a synthetic mixture of Pu isotopes with almost equal amounts of ²³⁹Pu, ²⁴⁰Pu, ²⁴¹Pu and ²⁴²Pu. Isotope amount ratios $n(^{241}Pu)/n(^{239}Pu)$, $n(^{241}Pu)/n(^{240}Pu)$ and $n(^{241}Pu)/n(^{242}Pu)$ were determined periodically by TIMS. Further these ratios were internally normalised (double ratio or ratio of ratios method) with respect to $n(^{240}Pu)/n(^{242}Pu)$, $n(^{240}Pu)/n(^{239}Pu)$, $n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{241}Pu)/n(^{24$ $n(^{240}\text{Pu})$, respectively, to account for any differences due to the variable isotope fractionation pattern over the entire period (about 5 years) of the experiment. Recently, Wellum et al.^{105,106} reported a new measurement for the half-life of 241 Pu (14.325 \pm 0.024 years) by employing the data on isotope amount ratios determined over a period of about 30 years. Enriched ²⁴¹Pu (92.7 atom%) was used in this work which decreased to about 74.5 atom% after 30 years. The availability of present generation high sensitivity TIMS instruments holds the potential to employ this method to re-determine precise and accurate half-lives of other radioactive isotopes e.g. ²³⁸Pu (87.7 years), ²⁴⁴Cm (18 years), ²³²U (70 years), etc. which are of interest in nuclear science and technology. It is advisable to follow the decay over a period of more than one half-life to confirm the absence of any isobaric interference.

The daughter growth method¹⁰⁷ was used to determine the half-lives of ²³⁹Pu and ²⁴¹Pu. The in-growth of daughter nuclides *viz.* ²³⁵U from alpha decay of ²³⁹Pu and ²⁴¹Am from beta decay of ²⁴¹Pu was also determined by isotope dilution-TIMS. This approach also demands the determination of daughter nuclide initially present (at zero time) in the solution of the parent radio-nuclide.

The specific activity method¹⁰⁸ depends upon the availability of highly enriched isotope of the radionuclide with high radiochemical purity. The number of atoms present in a given mass are determined by ID-TIMS or can be known gravimetrically if the radionuclide is well characterised with respect to its purity, stoichiometry, *etc.* This method has been used for determining the half-lives of several U, Pu, and Am isotopes. In this method, the total number of disintegrations (radio-activity) per unit mass is obtained by using a suitable radiometric method like alpha counting.¹¹⁰

The relative activity method is based on using another isotope of the same element as a reference isotope and determining the isotope amount ratio and the alpha activity ratio of the two isotopes by TIMS and alpha spectrometry, respectively. The methodology has been successfully applied to the redetermination of half-lives of 242Pu,109 232U110 and recently for $^{243}\mathrm{Am^{111}}$ and $^{244}\mathrm{Pu.^{112}}$ As an example, the two different lots of highly enriched ²⁴⁴Pu available at International Atomic Energy Agency's (IAEA) laboratories at Seibersdorf were used, without mixing with the other Pu isotopes, for precise and accurate determination of the half-life of ²⁴⁴Pu taking both ²³⁹Pu and ²⁴²Pu, already present in the enriched ²⁴⁴Pu, as reference isotopes in the relative activity method. This methodology is very useful to re-determine precise and accurate half-lives of different transactinium isotopes of an element e.g. the longlived isotopes of Cm. A novel double dilution approach was developed by Aggarwal et al.¹¹³ during the initial stages of using the relative activity method, to obtain the isotope amount ratio as well as the alpha activity ratio close to unity in the synthetic mixture, with an objective to determine them with high precision and accuracy.

It may be noted that the different approaches mentioned above have also been used for precise and accurate determination of the half-lives of many other radioactive isotopes useful in geo-chronology and other fields. Cheng *et al.*¹¹⁴ reported, using TIMS, the half-lives of ²³⁴U (245 250 ± 490 years) and ²³⁰Th (75 690 ± 230 years) which are 0.3% and 0.4% higher, respectively, than the commonly used half-life values for these isotopes. These were further improved, in terms of precision, recently in 2013 to 245 620 ± 260 years and 75 584 ± 110 years by the same group using MC-ICPMS.¹¹⁵

7. Nuclear safeguards and nuclear forensics

Nuclear forensics and safeguards have gained lot of importance after the Gulf War in 1990 and splitting of the former Soviet Union.⁶³ International Atomic Energy Agency (IAEA), Vienna is the prime agency promoting the know-how in this particular field. TIMS is only one of the techniques used in addition to other mass spectrometric techniques like ICP-MS and SIMS. SIMS is very important for particle analysis of environmental samples to detect any undeclared activity of the nuclear fuel cycle. A book on nuclear forensics and several reviews and popular articles have appeared during the last couple of years on the growth and development of nuclear forensics.¹¹⁶⁻¹²⁷ TIMS is a unique analytical tool in nuclear forensics to find out the origin of the interdicted material and the age of the material.¹²⁸⁻¹³⁹ The latter means the time elapsed after the latest purification of U and/or Pu. Efforts are going on world-wide in different international laboratories to develop and confirm the suitability of different methodologies using TIMS to find out the accurate age of the old materials. Different parent-daughter chronological couples *e.g.* ²³⁵U-²³¹Pa, ²³⁹Pu-²³⁵U, ²⁴¹Pu-²⁴¹Am have been used to validate the analytical methodology.¹³³⁻¹³⁶ Efforts are also going on to produce certified reference materials of known age. Excellent reviews are available in the literature unravelling the intricacies involved in nuclear forensics. IAEA has also been conducting coordinated research programs (CRPs) for developing expertise in this branch of nuclear science and technology.

The age of any radioactive sample can be determined by measuring the daughter/parent ratio as a function of decay time.120 Since the age of nuclear materials will not exceed a few decades compared to the long half-lives of radioactive isotopes of U and Pu, the amounts of daughters grown are quite limited. This demands chemical separation followed by mass spectrometric or radiometric measurements. Age determination of uranium and plutonium refers to "Model ages" since it is assumed that (i) complete separation of the daughters was achieved at the time of initial preparation/purification of the material and (ii) the system has remained closed after that. Any deviation from these two assumptions would lead to erroneous results on the age. If possible, it is preferred to determine the age of the material by using two independent chronometers. Good agreement (concordance) in the data obtained by two independent radio-chronometers enhances the confidence in the results. In case of disagreement, the lower age is taken since the initial presence of some of the daughter nuclide would give a longer age in the calculation.

Isotope ratio measurements on Sr, Nd and Pb present in uranium ore concentrate or any uranium sample can also be used to trace the origin of uranium.^{137,138} This is due to the fact that there would be small differences in the contents of ⁸⁷Sr (daughter of ⁸⁷Rb), ¹⁴³Nd (decay product of ¹⁴⁷Sm, $T_{1/2} = 1.06 \times 10^{11}$ years) and radiogenic lead isotopes (*viz.* ²⁰⁶Pb, ²⁰⁷Pb and ²⁰⁸Pb) arising due to the geological history of the mine. The measurements require chemical separation of these elements in the purest form using suitable ion exchange procedures and highly precise determination of isotopic composition by either TIMS or multi-collector high resolution inductively coupled plasma source mass spectrometry (MC-HR-ICPMS).

The ¹⁴³Nd/¹⁴⁴Nd isotope ratio is a useful signature to assess the origin of uranium ore concentrates.¹³⁷ This ratio provides a robust signature since it is less prone to weathering. Significant differences in the ¹⁴³Nd/¹⁴⁴Nd isotope ratio have been observed between different uranium mines. This ratio depends upon the age of the minerals present and the initial Sm/Nd amount ratio of uranium ore. For determining the ¹⁴³Nd/¹⁴⁴Nd ratio, the purification of Nd from Ce and Sm needs to be done to avoid isobaric interferences at Nd mass numbers. The ¹⁴³Nd/¹⁴⁴Nd isotope ratio was shown to vary from 0.51068 to 0.51470 (1% only) with Sm/Nd amount ratios ranging from 0.17 to 1.96 in various uranium ores and ore concentrate samples. This can also be measured with high precision using TIMS or magnetic sector multi-collector ICPMS.¹²⁰

The ¹⁸O/¹⁶O isotope amount ratio in the actinides compounds is also proposed as a useful indicator for tracing their origin.¹³⁹ Small changes in the ¹⁸O/¹⁶O isotope amount ratio were observed in uranium oxide samples of different origins using SIMS and TIMS. The small differences (less than 3%) originated due to variations in the oxygen isotopic content of air and ground water at various geographical places as well as chemicals and water used to process the uranium ore into uranium ore concentrate. TIMS was used to monitor UO⁺ ions from solution deposited on the filament for determining ¹⁸O/¹⁶O isotope amount ratios. The use of magnetic sector SIMS was also demonstrated for the determination of the ¹⁸O/¹⁶O isotope amount ratio in uranium dioxide micro particles using carbon disks and gold substrates and performing the measurements on O⁻ ions using Cs⁺ as the primary ion beam.

8. Environmental and biological applications

TIMS has been used extensively for the determination of Pu and U isotopic amount ratios in a large number of environmental, biological and geological samples.^{134–138,140–144} However, the advent of MC-ICP-MS is quite attractive for obtaining these data in such samples containing less than microgram amounts of U and Pu. This is mainly because ICP-MS does not require the U and Pu to be in highly pure form and this eliminates the need to perform complex chemistry separations and purifications. At the same time, this reduces the time of analysis, providing data on a large number of routine samples in relatively less time. The unfortunate accidents of Chernobyl and Fukushima have given impetus to the development of different mass spectrometric techniques to provide the data on the isotopic abundances and amounts of U, Pu and other actinides present in a variety of soil samples and effluents from accident reactor sites.

9. Other interesting applications of TIMS

TIMS has been used for determining the fission yields of stable isotopes of many elements (*e.g.* lanthanides) during the thermal neutron induced fission of 233 U, 235 U, 239 Pu and 241 Pu.

The discovery of natural nuclear reactor (Oklo phenomenon) in 1972, which was solely due to the consistent small changes noted by one of the alert scientists (0.717 atom% *versus* 0.720 atom% of ²³⁵U) in samples received from uranium mines from Gabon Republic in West Africa by a French Company, provided a lot of opportunity to the users of TIMS to generate useful data.¹⁴⁵ Studies performed showed some regions of the mines with ²³⁵U down to 0.44 atom%. Some regions showed slightly enriched ²³⁵U also which was explained on the basis of alpha decay of ²³⁹Pu formed during nuclear reactor operation. This natural nuclear reactor was in operation about 2 billion years ago when the abundance of ²³⁵U was about 3 atom%. Double beta decay half-life of 96 Zr was determined by determining the positive anomaly (*i.e.* excess) of 96 Mo by TIMS in a zircon sample.¹⁴⁶ The data obtained were consistent (considering correlation between the half-life and the decay energy) with the double beta decay half-life values determined previously from the decay of 82 Se and 130 Te and by measuring the excess of 82 Kr and 130 Xe, respectively, by gas source mass spectrometry.

10. Developments in TIMS instrumentation and suppliers of TIMS

There are three commercial TIMS instruments available from three different vendors. These are (i) TRITON PLUS from Thermo Fisher Scientific, Germany; (ii) PHOENIX from Isotopx, UK; and (iii) Nu TIMS from Nu Instruments, UK. Each of these mass spectrometers is equipped with multi Faraday cup detectors that allow simultaneous acquisition of data of various isotopes (static collection) which eliminates the time dependent fluctuations in the ion currents encountered during measurements in the dynamic mode. The SEM/Daly detector with ion counting is also available. Analysis and data acquisition using positive or negative ions is possible. High abundance sensitivity (10 ppb or 10⁸) necessary to determine accurately the low abundant isotopes (e.g. ²³⁰Th and ²³⁶U) is achievable by including the energy filter options of RPQ or WARP filter. Efforts are on to explore the usage of amplifiers with $10^{13}\Omega$ resistors with Faraday cups and the results obtained at Thermo Fisher Scientific are quite encouraging.147 Table 1 presents a comparison of the salient features of TIMS instruments available from various vendors.

11. Certified reference materials

Certified reference materials (CRMs) are required to calibrate the thermal ionization mass spectrometer and also to check routinely the performance of the system. A variety of CRMs are available from Institute for Reference Materials and Measurements (IRMM), Geel, Belgium for Th, U, and Pu. These different reference materials are certified for isotope abundance ratio, isotope amount content, or element amount content. A few reference materials are certified for the production date, for age dating, in nuclear forensics applications. Many of these materials are prepared by gravimetrically mixing the highly pure and well-characterized metals or compounds, whereas others are certified with data from well-calibrated equipments and techniques.

12. Critical discussion and future outlook

At the outset, one may feel that the potential applications of TIMS in nuclear science and technology, summarised in Table 2, have nearly got saturated and nothing exciting needs be done further. However, a more critical look is warranted to discover the unknowns. Though accuracy to determine minor isotope-

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Table 1 🛛	A comparison of	f salient features o	TIMS instruments av	ailable from	various suppliers
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Parameter	Thermo Fisher (TRITON Plus)	Isotopx (Phoenix)	Nu instruments (Nu-TIMS)
Samples in Turret/Carousel Abundance sensitivity at 237 from m/z 238	21 (double/single filament) 2 ppm; 20 ppb with RPQ	20 (triple/double/single filament) 2 ppm; <10 ppb with WARP filter at axial Daly/SEM	20 (single/double filament) 2 ppm, 20 ppb with filter
Multi-collector Faraday cups	7, movable, option of upto 10	Individually movable and motorized 9 Faraday cups	Fixed (cups used for various masses with variable dispersion zoom optics), upto 16
Acceleration voltage (KV)	10	8	8 to 10
Ion counting (SEM/Daly)	SEM and MIC	Axial Daly, option for SEM, optional 6 ion counting multipliers	Up to 5 including 3 Daly
Resistors (Ω)	$10^{11}, 10^{12}, 10^{13}$	10 ¹¹	10 ¹¹ , others available
Negative ions	Y	Y	Y
Mass range	3 to 310	3–280, UO_2^+ can be monitored in static mode	3-300
Dynamic range	50 V (+ve ion), 15 V (-ve ion)	10 V (+ve ion), 10 V (-ve ion)	55 V (+ve ion), 12 V (-ve ion)
Switchable amplifiers	(Y) virtual amplifiers	Gain stable, but calibration to be done periodically	Gain calibration required
Magnet	Laminated	Solid electromagnet	Fully laminated, 30 cm radius
Focal plane	Inclined at 45°	Perpendicular to ion beam path	Perpendicular to ion beam path
Pumping system	Turbo + ion pumps	700 l s ⁻¹ TMP, backed with scroll pump, 40 l s ⁻¹ and 70 l s ⁻¹ ion pumps, optional rear 300 l s ⁻¹ TMP to replace rear 70 l s ⁻¹ ion pump	400 l s ⁻¹ TMP at source, two 75 l s ⁻¹ ion-pump on analyser
Data acquisition (static/dynamic/ multi-dynamic)	Y	Y	Y
Total evaporation and MTE	TE and MTE available	TE and MTE available	TE available
Country of origin	Germany	UK	UK

amount ratios in U has been shown to improve significantly with dynamic range of eight orders of magnitude, it is important that more international laboratories using different commercially available instruments should evaluate the full potential of MTE methodology in TIMS. The advent of fully automated high sensitivity TIMS instruments has made the operators to treat these machines like black boxes, but these high sensitivity equipments are capable of providing high precision in the data and offer a unique opportunity to unravel the ion source chemistry of different elements when present alone or in a mixture. The author believes that TIMS will continue to play a pivotal role for routine applications in safeguards as well as for other applications for nuclear fuels because of the risk and hazards associated with toxic vapors of actinides generated in the plasma source of ICP-MS. Further, the problem of carry-over or memory effect in ICP-MS, particularly during analysis of unknown samples of widely varying isotope amount ratios, will necessitate the use of TIMS for such applications. With the further introduction of $10^{13} \Omega$ resistors in the amplifiers of different Faraday cups, this would further enhance the sensitivity of TIMS and obviate the need to use SEM thereby eliminating the problems of (i) inter-calibration of SEM and Faraday cup, (ii) non-linearity of SEM, and (iii) decrease in the gain of SEM with time necessitating the replacement of SEM. The laboratories with access to enriched isotopes of U and Pu should prepare synthetic mixtures gravimetrically to unravel the mysteries of even and odd isotope effects in TIMS as observed for other elements (e.g. Pb).148,149 The interesting and puzzling phenomenon of reverse fractionation and normal

fractionation in TIMS, as observed in case of Nd isotopeamount ratios^{150,151} and explained on the basis of mixing of different domains on the sample filament, needs be critically evaluated for U and Pu using ²³³U/²³⁸U and ²³⁹Pu/²⁴⁴Pu isotopeamount ratios and at the same time, performing measurements on other U and Pu isotope amount ratios by gravimetric preparation of synthetic mixtures using enriched isotopes. As mentioned above, there are concerns about the half-life values of some of the isotopes *e.g.* ²³⁴U, ²³⁰Th which are important for nuclear forensics as well as geo-chronology.

The novices in the field of mass spectrometry should not carry the impression that MC-TIMS or MC-ICPMS is the panacea to all the requirements in nuclear science and technology. On the contrary, SIMS is an important analytical tool for particle analysis, depth profiling and surface analysis with high lateral resolution. RIMS and AMS are the ultra-sensitive mass spectrometric techniques used to determine femtogram amounts of Pu, U and other radioactive elements in food, soil, sea-water samples, etc. GDMS and LA-ICPMS are equally important to determine different elements (impurities) in high purity materials and to characterise highly enriched isotopes used to prepare certified isotopic reference materials. GC-MS is a routinely used technique for characterising different extracting agents for nuclear fuel reprocessing and waste handling. GC-ICPMS and GC-ICPMS/MS are promising for the determination of non-metals e.g. S, P, O required for various applications. ESI-MS and MALDI-TOF have great potentials for speciation studies particularly with reference to nuclear waste management and studies on the mobility of actinides and other

Table 2 Different Applications of TIMS in Nuclear Science and Technology

Stage	Measurement	Remarks
Mining	Isotopic composition of U	Build-up national and international libraries for data on useful signatures from different mines; discovering natural reactor
Enrichment	$^{235}\text{U}/^{238}\text{U}$ isotope amount ratio	235 U enrichment R&D studies and at plant
Fuel fabrication	Isotopic composition data of U and Pu	Chemical quality assurance of fuel materials in nuclear fuel cycle; to determine fertile and fissile content
Reactor (for fuel)	Burn-up determination, build-up and depletion of different isotopes of U, Pu	Post-irradiation studies for developing and verifying theoretical reactor codes; for developing isotope correlations
Reactor (for moderator/coolant)	Isotopic composition and concentration of boron, Gd	B ₂ O ₃ mixed with D ₂ O added in PHWRs, periodic determination required; Gd in coolant for fuel failure
Reactor for burnable poison	Isotopic composition of Gd, Dy etc.	For determining depletion in neutron absorbing isotopes
Reprocessing plant	Concentration and isotopic amount ratio data on U, Pu	Nuclear material accounting, input accountability at reprocessing plant
Nuclear forensics	Isotopic composition, amount, age determination	Isotope amount ratio data for Th, Pa, U, Np, Pu, Am, Sr, Nd, Pb, O <i>etc.</i> , amount ratio of daughter to parent
Environmental and biological samples	Isotopic composition and amount (concentration) of actinides	For accidental releases and nuclear tests
R&D studies	Half-lives, fission yields of stable isotopes, cross- sections <i>etc.</i>	Fundamental nuclear data required for various applications
Enriched stable and radioactive isotopes	Isotopic composition	For preparing isotopic reference materials gravimetrically and for characterisation of isotopes to be used as spikes in ID-TIMS
Round-robin experiments	Isotopic composition and concentration	For proficiency testing of different international laboratories

radioactive elements. TIMS and MC-ICP-MS should be considered as two complementary analytical techniques in nuclear science and technology.

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