

**PERFORMANCE EVALUATION OF INDIGENOUS THERMAL IONIZATION
MASS SPETROMETER FOR DETERMINATION OF $^{235}\text{U}/^{238}\text{U}$
ATOM RATIOS**

by

**D. Alamelu, A.R. Parab, K. Sasi Bhushan, Raju V. Shah, S. Jagdish Kumar,
Radhika M. Rao and S.K. Aggarwal**

Fuel Chemistry Division

and

R.K. Bhatia, V.K. Yadav and Madhavi P. Sharma

Technical Physics Division

and

Puneet Tulsyan, Pradip Chavda and P. Srinivasan

Machine Dynamics Division

GOVERNMENT OF INDIA
ATOMIC ENERGY COMMISSION

**PERFORMANCE EVALUATION OF INDIGENOUS THERMAL IONIZATION
MASS SPECTROMETER FOR DETERMINATION OF $^{235}\text{U}/^{238}\text{U}$
ATOM RATIOS**

by

**D. Alamelu, A.R. Parab, K. Sasi Bhushan, Raju V. Shah, S. Jagdish Kumar,
Radhika M. Rao and S.K. Aggarwal**

Fuel Chemistry Division

and

R.K. Bhatia, V.K. Yadav and Madhavi P. Sharma

Technical Physics Division

and

Puneet Tulsyan, Pradip Chavda and P. Srinivasan

Machine Dynamics Division

BHABHA ATOMIC RESEARCH CENTRE
MUMBAI, INDIA

2014

BIBLIOGRAPHIC DESCRIPTION SHEET FOR TECHNICAL REPORT
(as per IS : 9400 - 1980)

01	<i>Security classification :</i>	Unclassified
02	<i>Distribution :</i>	External
03	<i>Report status :</i>	New
04	<i>Series :</i>	BARC External
05	<i>Report type :</i>	Technical Report
06	<i>Report No. :</i>	BARC/2014/E/004
07	<i>Part No. or Volume No. :</i>	
08	<i>Contract No. :</i>	
10	<i>Title and subtitle :</i>	Performance evaluation of indigenous thermal ionization mass spectrometer for determination of $^{235}\text{U}/^{238}\text{U}$ atom ratios
11	<i>Collation :</i>	25p., 7 figs, 8 tabs.
13	<i>Project No. :</i>	
20	<i>Personal author(s) :</i>	1. D. Alamelu; A.R. Parab; K. Sasi Bhushan; Raju V. Shah, S. Jagdish Kumar; Radhika M. Rao; S.K. Aggarwal 2. R.K. Bhatia; V.K. Yadav; Madhavi P Sharma 3. Puneet Tulsyan; Pradip Chavda; P. Srinivasan
21	<i>Affiliation of author(s) :</i>	1. Fuel Chemistry Division, Bhabha Atomic Research Centre, Mumbai 2. Technical Physics Division, Bhabha Atomic Research Centre, Mumbai 3. Machine Dynamics Division, Bhabha Atomic Research Centre, Mumbai
22	<i>Corporate author(s) :</i>	Bhabha Atomic Research Centre, Mumbai - 400 085
23	<i>Originating unit :</i>	Fuel Chemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai- 400 085
24	<i>Sponsor(s) Name :</i>	Department of Atomic Energy
	<i>Type :</i>	Government

Contd...

30	<i>Date of submission :</i>	June 2014
31	<i>Publication/Issue date :</i>	July 2014
40	<i>Publisher/Distributor :</i>	Head, Scientific Information Resource Division, Bhabha Atomic Research Centre, Mumbai
42	<i>Form of distribution :</i>	Hard copy
50	<i>Language of text :</i>	English
51	<i>Language of summary :</i>	English
52	<i>No. of references :</i>	11 refs.
53	<i>Gives data on :</i>	
60	<i>Abstract :</i>	A magnetic sector based Thermal Ionization Mass Spectrometer (TIMS) designed and developed at Technical Physics Division, B.A.R.C., was evaluated for its performance for the determination of $^{235}\text{U}/^{238}\text{U}$ atom ratios in uranium samples. This consisted of evaluating the precision and accuracy on the $^{235}\text{U}/^{238}\text{U}$ atom ratios in various isotopic reference materials as well as indigenously generated uranium samples. The results obtained by the indigenous TIMS were also compared with those obtained using a commercially available TIMS system. The internal and external precision were found to be around 0.1% for determining $^{235}\text{U}/^{238}\text{U}$ atom ratios close to those of natural uranium (i.e. 0.00730).
70	<i>Keywords/Descriptors :</i>	MASS SPECTROMETERS; PERFORMANCE TESTING; URANIUM 235; URANIUM 238; SPECIFICATIONS; DATA ACQUISITION; SENSITIVITY; FARADAY CUPS; MAGNETIC FIELDS; ISOTOPE RATIO
71	<i>INIS Subject Category :</i>	S46
99	<i>Supplementary elements :</i>	

Performance Evaluation of Indigenous Thermal Ionization Mass Spectrometer for Determination of $^{235}\text{U}/^{238}\text{U}$ Atom Ratios

**D.Alamelu, A.R.Parab, K.Sasi Bhushan, Raju V Shah, S. Jagdish Kumar,
Radhika M Rao and S.K.Aggarwal**

*Fuel Chemistry Division, Bhabha Atomic Research Centre,
Trombay, Mumbai – 400 085*

R.K. Bhatia, V.K.Yadav and Madhavi P Sharma

*Technical Physics Division, Bhabha Atomic Research Centre,
Trombay, Mumbai – 400 085*

Puneet Tulsyan, Pradip Chavda and P. Srinivasan

*Machine Dynamics Division, Bhabha Atomic Research Centre,
Trombay, Mumbai – 400 085*

Abstract

A magnetic sector based Thermal Ionization Mass Spectrometer (TIMS) designed and developed at Technical Physics Division, B.A.R.C., was evaluated for its performance for the determination of $^{235}\text{U}/^{238}\text{U}$ atom ratios in uranium samples. This consisted of evaluating the precision and accuracy on the $^{235}\text{U}/^{238}\text{U}$ atom ratios in various isotopic reference materials as well as indigenously generated uranium samples. The results obtained by the indigenous TIMS were also compared with those obtained using a commercially available TIMS system. The internal and external precision were found to be around 0.1% for determining $^{235}\text{U}/^{238}\text{U}$ atom ratios close to those of natural uranium (i.e. 0.00730).

1. INTRODUCTION

Thermal Ionization Mass Spectrometry (TIMS) is an internationally recognized and accepted technique for precise and accurate atom ratios measurements of different elements for applications in the fields of nuclear technology, geochronology, biomedical etc [1-2]. Technical Physics Division (TPD) at BARC has been developing TIMS systems [3-6] for more than three decades to meet the demands of various units

of Department of Atomic Energy (DAE). TPD had previously developed TIMS systems for many user departments of DAE which include RMP, Mysore; KARP Kalpakkam; AFFF Tarapur; HWB in Talcher and Manuguru. The latest version of TIMS (Fig.1) has been developed incorporating several additional features which include (i) a turret housing 12 filament assemblies for increasing the sample analysis throughput, (ii) a modified ion source to improve sensitivity, (iii) collector system equipped with variable dispersion zoom optics with fixed collectors having wider apertures for improved collection efficiencies and a flat topped peak shape, (iv) a fast response analyser electromagnet with modified boundaries to rotate the focal plane along a line normal to principal beam axis, (v) compact and reliable electronics housed in a single table top rack, thus reducing the overall footprint of the instrument, and (vi) improved version of software to perform ratio measurements in multi-dynamic mode. Table-1 gives the important specifications of the indigenously developed instrument. This report discusses the design features and performance evaluation of this TIMS instrument.

1.1 Principle of TIMS

The ionisation in TIMS is achieved by surface ionisation of the sample on a metallic surface of high work function (Rhenium, Tungsten etc). The ionisation efficiency is governed by Saha Langmuir equation:

$$n^+/n_0 = g_i/g_o [(1-r_i)/(1-r_o)] \exp \{(W-I)/KT\}$$

where n^+ & n_0 are the number of positive ions formed and neutral species evaporated, r_i & r_o are reflection coefficients and g_i & g_o are the statistical weights of the ionic and atomic states, W is the work function of the filament material, I is the ionisation energy of the element, T is the temperature of the filament surface and K is the Boltzmann constant.

Generally high purity Re filament (single or multiple) is used for ionization because of its high work function (~5.2 eV) and high melting point (3180° C). The singly charged ions produced are collimated, accelerated and pass through a magnetic field of suitable geometry where they are deflected and separated according to their mass to charge ratios as shown in Fig.2. Subsequently, the separated ion beams corresponding to different isotopes are collected by Faraday collectors electrically connected to electrometer amplifiers for ion current measurements.

The design of the ion optical elements viz. ion source, analyser magnet and the Faraday cup collectors were optimized using software SIMION 7.0. The different subsystems of the indigenously developed TIMS are discussed below.

1.2 Sample Introduction and Ion Source

The sample introduction system consists of a circular wheel (called as turret) with 12 filament assemblies. The filament assembly has alumina base with three pairs of stainless steel (SS) pins on which three filaments can be spot welded. This can be used for isotopic analysis with triple filament assembly which uses two side filaments for sample loading and the centre filament as ionization filament. Each filament assembly is mounted in SS enclosure called shield cup having exit aperture of 1.5 mm (width) x 10 mm (height) for ion extraction. Ions are produced by heating the side filaments to a current of 2–2.8 Amp and centre filament to 5-6 Amp and are extracted out of shield cup by potential gradient produced by voltage applied on draw out (D) plate (Fig.3). Y focus (Y_1/Y_T) and ground (G) plates are used to focus, accelerate and steer the ion beam in horizontal plane for its alignment with the final slit of size 0.3 mm (width) x 6 mm (height). The vertical alignment of ion beam is achieved by optimizing potentials of Z_u/Z_d plates. R plate is used to enhance the insulation of the ion source without affecting the focusing. For high transmission of the ion source, the ion beam should focus properly at the source slit which requires the mechanical fabrication and assembly tolerances to be within 10 micron. To achieve this, all electrodes were fabricated by electric discharge machine (EDM)/wire cutting technique and assembled using dowel pins.

1.3 Magnetic Analyser

The main specifications of the magnetic analyser magnet are given in Table – 1. It is a water cooled electromagnet with fast response (1 decade per second) with maximum achievable field of 1 Tesla. The field is controlled by current source with stability better than 5ppm. Field homogeneity within the pole gap is better than 500 ppm in the median plane of the magnet. The exit angle of the magnet is mechanically adjustable by $\pm 5^\circ$ to finely adjust focusing position of the ion beam at the collector. The entry and exit boundaries of the poles of magnet are curved with suitable radii [3] so as to rotate the focal plane of the magnet along a line normal to the principal beam axis. This helps in reducing the difficulties in proper placement of collectors at respective locations while

performing atom ratio measurements for different elements of interest. For example, the strontium isotopic dispersion is drastically different from that of uranium isotopes. In this case, the placement of collectors and deflection optics (used in variable dispersion zoom optics) have to be inclined so that focal points for all the isotopes are at the entry of the respective collectors. This requirement would result into an unwieldy and cumbersome collector system. The rotated plane helped in eliminating all these difficulties.

1.4 Detector/ Collector System

It consists of five Faraday cups each having aperture of 3mm (width) x 15 mm (height). All the collectors are fixed on single SS plate as shown in Fig. 4. The collector system consists of variable dispersion zoom optics [4] which includes the dc quadrupole and deflection optics. The dc quadrupole is used to adjust the dispersion of the ion beams passing through it so that each ion beam is aligned properly to the aperture of the deflection optics. Deflection optics deflects the ion beams (by –ve potentials applied on deflection plates) outwards with respect to the centre aperture so that the dispersion among the beams increases while they are collected by the respective collectors. Since the dispersion is adjustable, the cups are mounted directly on the SS plate with single screw at backside. This feature helps in eliminating rotation motion feed-throughs which require mounting ports on the chamber walls and this is an undesirable requirement in a UHV system. The increased dispersion also helps in using wider slits of the collectors which lead to more peak flatness for the peak shapes resulting into better collection efficiency. Each Faraday cup (Fig. 5) is equipped with the entrance aperture having double slits with a depth of 10mm. This is followed by secondary electron suppressor (SES) floated at a negative potential of 150 V for suppressing the secondary electrons generated within the cup due to the impact of high energy ions on main collector. The main collector cup (1.2 mm wide x 18 mm deep x 16 mm high) is placed behind SES at a depth of 25 mm from the entrance slit using Teflon mounting arrangement. The whole assembly is insulated by Teflon sheet (0.1 mm thick) from the outer grounded body. All the above parts of collector were fabricated using Electric Discharge machine (EDM) / wire cutting method with mechanical tolerance of ± 10 micron.

1.5 Vacuum System

The turret chamber is pumped by a turbo molecular pump (TMP) with a pumping speed of 500 L/s. This is backed by a rotary pump with speed of 200 L/min. The amplifier chamber is pumped by a separate dry pump with a pumping speed 30 L/min. The collector side has one TMP with pumping speed of 200 L/s and one ion pump (35 L/s) is mounted just before the analyser tube. The collector and the source side are separated by an electro-pneumatically controlled gate valve. A vacuum level of 1.5×10^{-7} torr is maintained in source chamber (turret) and 2×10^{-8} torr in the collector system.

1.6 Electronics and Software

The electronics used in this instrument is similar to the one described elsewhere [7]. The filament currents are controlled through high stability (better than 10 ppm) filament current regulators (range 7Amps; compliance voltage 7 V). Independent high voltage power supply modules of 10 kV and 1 kV (stability <25ppm and ripple <50mV) were used for accelerating and focusing the beam by different electrodes (Shield, D, Y, Z etc.). The electromagnet is controlled by a current regulated DC power supply with output currents up to 150 A which corresponds to 1 Tesla magnetic field. Regulator module uses op-amp based proportional and integral controller, Isolated gate bipolar transistor (IGBT) bank, DC current transformer (DCCT), micro controller (μ C), Analog to digital converter (ADC), Digital to analog converter (DAC) and wireless link to PC and Teslometer. Beam current is measured by using electrometer amplifier and Field programmable gate array (FPGA) based data acquisition card. Electrometer amplifier can measure currents down to 10^{-15} A with time constant (τ) of less than 50 msec and noise of $40 \mu\text{V}_{\text{rms}}$ (for integration time of 5 sec). Data acquisition software supports multiple analysis modes, automated ratio calculation, optimized data presentation, back-ground correction, amplifier calibration and rejection of outliers during data analysis. Intermediate results are also displayed at the end of every scan and block.

2. EXPERIMENTAL

2.1 Testing and Evaluation of Indigenous TIMS

For the precise and accurate isotope ratio measurements, it is essential that the ion beam should properly focus at the collector aperture and collect well within the collector. To verify this, the ion beam was scanned across the collector by varying

magnetic field in steps of 0.2 gauss and the peak shape was recorded. A well-focused ion beam with a cross section smaller than the collector aperture should produce a flat top peak in a scan. Beam width was measured using this scan by measuring the flat top width and base width which was used to calculate the resolution of the instrument.

Sensitivity was measured by taking 1 microgram of the uranium and integrating the signal on amplifier till the complete sample was consumed. This gives the total number of ions collected on Faraday collector. The ratio of total number of atoms deposited on the filament and the ions measured is termed as sensitivity of the instrument.

2.2 Sample Preparation and Loading

High purity zone refined rhenium was used as the filament material. Triple filament assemblies were employed in both the instruments. In case of the indigenous TIMS, sample was loaded on both the sample filaments of the triple filament assembly while in case of commercial TIMS system, the sample was loaded on one of the sample filaments (pseudo-triple filament assembly). The filament assembly, after welding, was washed thoroughly with acetone before mounting on the sample loading assembly. For the indigenous TIMS, the filaments were boiled for 10 minutes in de-mineralized water before washing with acetone. About 3 microgram of uranium was loaded for each of the TIMS instruments for analysis. The indigenous uranium samples were first evaporated and treated with high purity concentrated nitric acid to remove fluoride and other organic impurities (if present).

2.3 Sample Loading Procedure

About 1 microlitre of sample solution was placed at the centre of the sample filament. The sample filament current was fixed at 0.7 Amperes for 2 minutes to dry the solution on the filament. The filament current was then increased to 1.4 Ampere and maintained at the same current for about 1 minute and was immediately reduced to zero. The same procedure was employed for both the instruments. Suitable dilution for samples was done so that the amount of sample loaded was around 3 microgram.

2.4 Procedure for Isotopic Analysis of Uranium Standards

To obtain the data on $^{235}\text{U}/^{238}\text{U}$ atom ratios in a reproducible manner, the experimental conditions namely the filament heating conditions were optimized and the same were employed for analysis of isotopic standards as well as other uranium samples.

2.4.1 Filament Heating Procedure

Due to variations in the thickness of the filaments, the temperature of the ionization filament can be different for different samples for the same heating current. Hence for reproducing analysis conditions for different samples, the heating temperature of the ionisation filament was fixed based on the $^{187}\text{Re}^+$ signal obtained during the analysis.

The ionisation filament was heated up to 4.5 Ampere in 10 minutes. Focusing parameters were adjusted to maximize the $^{187}\text{Re}^+$. The current was further increased to such a level so that the $^{187}\text{Re}^+$ signal was about 200 mV. In all the analyses, this procedure was employed and it took about 15 minutes to optimize this condition of analysis.

After fixing the $^{187}\text{Re}^+$ signal, the sample filament was slowly heated to 1.5 Ampere in 10 minutes. The magnet mass was taken to the Uranium range and $^{238}\text{U}^+$ signal was monitored. The focusing parameters were adjusted to maximise the $^{238}\text{U}^+$ signal. The sample filament was then heated slowly so as to obtain a signal of 50 mV for $^{235}\text{U}^+$ signal (which corresponds to about 4 - 5 V for $^{238}\text{U}^+$ signal) at the Faraday cup. This procedure of optimizing the U^+ signal for analysis took about 15 minutes.

Before acquisition of data, in the case of the commercial TIMS instrument, the high voltage was adjusted suitably so that the isotopic mass of the isotope of interest is at the centre of the peak scan (peak centering). In the case of indigenous TIMS, the same was achieved by slight adjustment of the magnetic field.

2.4.2 Data Acquisition Procedure

After optimizing the signals of $^{235}\text{U}^+$ & $^{238}\text{U}^+$, the data were obtained in static mode of multicollection. In this methodology, the ions corresponding to two isotopes of uranium (i.e. ^{235}U & ^{238}U) were focused onto two different Faraday cups and the ion current was integrated for a fixed time without changing either the acceleration voltage or the magnetic field.

Before acquisition of the data, it is necessary to correct for the base-line (i.e. the background current measured by the amplifier system). In the indigenous machine, the magnetic field is only displayed; the baseline is obtained by integrating the ion-current at a magnetic field of 5350 gauss for 25 seconds. The ion intensities of the two uranium isotopes were measured and integrated in two Faraday cups for a predetermined time

(i.e scan) and ion intensity ratio was calculated. For commercial TIMS, the measurement procedure consisted of acquiring 3 blocks, each block consisting of 12 scans. In the indigenous TIMS, a total of 36 scans were taken and the ratio was calculated at the end of the scans cycle. The details of the acquisition parameters as well as the cup-configuration employed for determining $^{235}\text{U}/^{238}\text{U}$ atom ratios are given in Table-2 for both the TIMS systems. In Indigenous TIMS, the internal precision for each data was calculated as relative standard deviation on 36 ratios. External precision was calculated as relative standard deviation on averages ratios of independent filament loadings of same sample on different filament assemblies.

3. RESULTS AND DISCUSSION

3.1 Comparison of Results Obtained for ISU-09 Uranium Isotopic Reference Material

To compare the precision as well as fractionation factor for uranium isotopic analysis by the two instruments, multiple filament loadings of isotopic reference material **ISU-09 (M/s. COMPAGNI GENERALE DES MATIERES NUCLEAIRES GROUPE, CEA ETABLISSEMENT DE PIERRELATTE LABORATOIRES, FRANCE)** were used for analysis. The results of the analyses are given in Tables 3 & 4. The data for the commercial TIMS are a compilation of values obtained for a period of 4 months, while the data for the indigenous TIMS were obtained over a period of 10 days from samples loaded on 4 turrets. It can be seen that the $^{235}\text{U}/^{238}\text{U}$ atom ratios obtained by the two machines are comparable and the K factor for 3 amu is comparable for the two machines. However, the precision of analysis (denoted as % RSD) for indigenous machine is poorer by a factor of 2, which needs further investigations, with regards to the amplifier noise, variation in the signal during the period of analysis etc.

3.2 Statistical Evaluation of the Data obtained by Indigenous TIMS on Uranium Isotopic Reference Material

The results of the statistical evaluation of the data obtained by the two TIMS machines are given in Table 5. It is seen that the measured $^{235}\text{U}/^{238}\text{U}$ atom ratio is higher than the certified ratio (which is due to the fractionation effect, i.e preferential evaporation of lighter isotope in thermal source). The K-factor, ie. ratio of the observed to the certified ratio is almost similar in both the instruments. However, the

relative standard deviation of the data on the isotopic Reference Material obtained over a period of 4 months by commercial TIMS is about two times better than that obtained by indigenous TIMS machine (obtained over a short span of 10 days). This needs further detailed studies. The Box plot for data on the isotopic standard is shown in Figure 6. It can be seen that the data obtained by the commercial and indigenous TIMS machine are not statistically different.

3.3 Analysis of Indigenous Uranium Samples

The performance of the TIMS machines for determining $^{235}\text{U}/^{238}\text{U}$ atom ratios of uranium close to the natural ratio was evaluated by analyzing uranium samples. For commercial TIMS, only one filament loading was done, while in case of indigenous TIMS, multiple (triple & double) as well as single filament loadings were employed.

Tables 6 & 7 give the consolidated data on the analysis of uranium samples. No correction for fractionation was applied to data obtained by the two machines. The average of the results of replicate filament loadings are given in Table 6. The $^{235}\text{U}/^{238}\text{U}$ atom ratio obtained by Indigenous TIMS is higher [(average: 1.0037 (duplicate) & 1.0015(triplicate))] than that obtained by commercial TIMS machine. Similar trend is observed for the single filament loading also (Table 7). However, since the difference among the values obtained by indigenous and commercial TIMS is almost similar in all the samples, the indigenous TIMS can be employed for determining the trend in the variation of $^{235}\text{U}/^{238}\text{U}$ atom ratios in a particular series of samples.

3.4 Statistical Analysis of the Data for Uranium Samples

The results obtained by the two TIMS instruments for uranium samples were statistically evaluated by Mann-Whitney-Wilcoxon test (also known as Mann-Whitney U test). It is a non-parametric test that can be performed on the data and the test checks whether the two independent sample sets come from distributions with equal medians. The test is useful for comparison of two sets when one of the sets has slightly higher value than the other. The output of the test is the probability value (p) and it is the probability of observing the given result, or one more extreme, by chance if the null hypothesis is true, i.e., if the medians are equal. The low values of p mean that the medians are not equal. The test was performed in Matlab. Table 8 lists the probability values for the three sets (single, duplicate and triplicate). Since the probability is

sufficiently higher (more than 0.5), it can be assumed that the medians of the two sets of data are similar.

In addition to this test, the data obtained by the indigenous TIMS were graphically compared with those obtained by Commercial TIMS using the Bland-Altman Difference plot shown in Figure 7. It is a graphical method to compare the two measurements/techniques. In this method, the differences between the two methods are plotted against the data of the Commercial TIMS machine (assuming the data obtained by Commercial TIMS as the standard). It can be seen that all data fall within 1.96 sigma (95 %) confidence limit w.r.t. the data obtained by the commercial TIMS.

4. CONCLUSION

The performance of a magnetic sector based thermal ionization mass spectrometry system designed and developed indigenously was evaluated for the determination of $^{235}\text{U}/^{238}\text{U}$ atom ratios. Isotopic reference material and other indigenous uranium samples were analysed by the two machines. The data obtained by the indigenous machine were compared with those obtained by the commercial TIMS machine. The sensitivity of the indigenous machine was found to be satisfactory for analysis of uranium. Though no significant difference was observed between the results for the isotopic reference material, slight difference in the isotope ratios was observed for other uranium samples, though statistically insignificant. Statistical tests were performed on the results and no significant difference was noted between the data obtained by the two TIMS machines.

5. ACKNOWLEDGEMENTS

The authors sincerely thank DrS.K.Gupta, Head, Technical Physics Division, B.A.R.C. and Mr. G.Gouthaman, Ex-Head, machine Dynamics Division, B.A.R.C. for their constant encouragement and support to the T.I.M.S. Development activity. The authors are also thankful to Mr. V.Nataraju, Head, Advanced Mass Spectrometry Section (AMSS), T.P.D., B.A.R.C., and all the members of the AMSS and Digital Control Section, T.P.D., B.A.R.C. for their keen interest and support in the development of T.I.M.S.

6. REFERENCES

1. Improved Techniques for High Accuracy Isotope Ratio Measurements of Nuclear Materials using Thermal Ionization Mass Spectrometry
S. Richter and S.A. Goldberg, International Journal of Mass Spectrometry, 229 (2003) 181-197.
2. Modern Isotope Ratio Mass Spectrometry by I.T.Platzner, John Wiley & Sons, 1997.
3. Rotation of Focal Plane of Magnetic Analyzer in an Isotope Ratio Mass Spectrometer using Curved Shims
Rajender K. Bhatia, Yogesh Kumar, K. Prathap Reddy, V.K. Yadav, E. Ravisankar, T.K. Saha, V. Nataraju, V.K. Handu, International Journal of Mass Spectrometry, 313 (2012) 36–40.
4. A Novel Variable Dispersion Zoom Optics for Isotope Ratio Sector Field Mass Spectrometer
R.K. Bhatia, V.K. Yadav, V.M. Mahadeshwar, M.M. Gulhane, E. Ravisankar, T.K. Saha, V. Nataraju, S.K. Gupta, International Journal of Mass Spectrometry, 339–340 (2013) 39–44.
5. Thermal Ionisation Mass Spectrometer for the Isotopic Analysis of Lithium and Boron
S.N.Bindal, K.V.Kurup, K.A.Sayed, R.G.Ochani, A.R.Parkar, V.B.Reddy, P.Raju, T.K.Saha, N.V.Rao, V.K.Handu, S.R.Halbe and V.V.K.Rama Rao, Proceedings of 8th ISMAS Symposium on Mass Spectrometry 1999, p. 761-766, Edited by S.K.Aggarwal.
6. Design Enhancements of TIMS for Geochronology Applications at AMD, Hyderabad
Rajender K. Bhatia, R. Datta, Rekhu Chandak, M. M. Gulhane, Pratap R. Kasina, A. M. Kasbekar, N. Ved, M. Gopalakrishna, E. Ravisankar, T. K. Saha, V. Nataraju, and V. K. Handu,
Proceedings of 11th ISMAS Triennial International Conference on Mass Spectrometry- TRICON 2009, Paper No.CP-78, p. 493-495, Edited by S.K.Aggarwal, P.G.Jaison, Arnab Sarkar and Pranaw Kumar.
7. Design and Development of Electronics for Dual Source Mass Spectrometer
R.Chandak, R. Datta, M. M. Gulhane, V. K. Handu, V. B. Reddy and T. K. Saha

- Proceedings of 13th ISMAS-WS 2008, Paper no. CP-12, p. 155-159, Edited by S.K.Aggarwal, P.G.Jaison, D.Alamelu.
8. Mass Spectrometric Analysis of Uranium and Plutonium
S.A.Chitambar, V.D.Kavimandan, B.Saha, S.K.Aggarwal, G.Periaswamy, K.Bhagyalakshmi, P.M.Shah, P.A.Ramasubramanian, A.I.Almaula, H.C.Jain, C.K.Mathews and M.V.Ramaniah, B.A.R.C. Report – 865 (1976).
 9. Determination of K-factors for Isotope Abundance Measurements of Uranium and Plutonium by Thermal Ionisation Mass Spectrometry
S.K.Aggarwal, A.I.Almaula, P.S.Khodade, A.R.Parab, R.K.Duggal, C.P.Singh, A.S.Rawat, G.Chourasiya, S.A.Chitambar and H.C.Jain, J. Radioanal. Nucl. Chem.- Letters, 87 (1984) 169-178.
 10. Isotope Fractionation Factors in Thermal Ionisation Mass Spectrometric Analysis of Uranium and Plutonium
S.A.Chitambar, P.S.Khodade, A.R.Parab and H.C.Jain, Preprint Volume of the Fourth National Symposium on Mass Spectrometry, IISC, Bangalore, January 4-6, 1988, Paper no.NT-8.
 11. Determination of Uranium Isotope Ratios by Thermal Ionisation Mass Spectrometry: Precision and Accuracy
S.K.Aggarwal, P.M.Shah, M.K.Saxena, Sanjai Kumar and H.C.Jain, DAE Symposium on Nuclear and Radiochemistry, Dec. 21-24,1992, Andhra University, Waltair, NT-1, p. 265-269.

Table 1. Specifications of the TIMS Instruments

Parameter	Indigenous TIMS	Commercial TIMS
Resolution (M/ Δ M at 10 % valley)	418	450
Sensitivity (sample required)	1 ion per 580 atoms of uranium (1 – 2 μ g)	1 ion per 500 atoms of uranium (\leq 1 μ g)
Precision	0.1% for natural U, 8 ppm for Sr	0.05% for natural Uranium
Abundance sensitivity	30 ppm at 237 for ^{238}U	2 ppm at mass 237 w.r.t 238; 10 ppb with WARP Filter or RPQ
Mass range	Upto 550 amu @ 8 kV acceleration	Upto 310 amu @ 8 kV Acceleration
Acceleration Voltage	Upto 10 kV	Up to 8 kV
Ion source & Filament assembly	Thermal ionization with triple filament assembly	Thermal Ionization with triple filament assembly (present study used pseudo triple assembly)
Turret	12 filament assemblies	20 filament assemblies
Analyser	Stigmatic geometry, sector magnet with 300 mm radius, 90° deflection (modified boundaries to rotate focal plane normal to principal beam axis)	Stigmatic geometry, sector magnet with 620 mm radius, 90° deflection (modified boundaries to rotate focal plane normal to principal beam axis)
Collector system	Five Faraday collectors (all fixed collectors) with zoom optics	Nine motorized Faraday cups (No zoom optics); One SEM and One Daly detector at axial

Table 2. Parameters employed during data acquisition in the TIMS instruments

Sl No.	Parameter	Indigenous TIMS	Commercial TIMS
1	Filament assembly	Triple filament assembly	Pseudo triple filament assembly
2	Filament material	Zone refined rhenium	Zone refined rhenium
3	Acceleration voltage (V)	7000	8000 (typical)
<i>4. Baseline Measurement</i>			
a	At field/mass	At 5350 gauss	Average of background at ± 0.5 amu of the mass of interest
b	Integration time	25 seconds	10 seconds
5	<i>Acquisition Details</i>		
a	Cup configuration	235U : LM-1 238U : HM-2	235U : Axial 238U : H1
b	No. of scans per block	-----	12
c	Total number of scans	36	36
d	Integration time	10 seconds	5 seconds

Table 3. Results of analysis of ISU-09 Isotopic Reference Material by Commercial TIMS

Sl No.	²³⁸ U signal (Volts)	²³⁵ U/ ²³⁸ U ratio measured	Precision of measurement (%)	K factor *
1	4.32	0.010989	0.036	1.002
2	2.52	0.010989	0.066	1.002
3	4.83	0.010994	0.032	1.003
4	3.0	0.010986	0.064	1.002
5	2.3	0.011000	0.072	1.004
6	6.21	0.011004	0.02	1.004
7	2.84	0.011001	0.11	1.004
8	2.74	0.010982	0.05	1.002
9	4.73	0.011000	0.04	1.004
10	2.88	0.010987	0.061	1.002
11	4.68	0.010990	0.026	1.002
12	2.76	0.010998	0.058	1.004
13	3.42	0.010996	0.057	1.003
14	3.6	0.011009	0.086	1.004
	Mean	0.010994	0.056	1.003 \pm 0.07 %

* Certified value of the ²³⁵U/²³⁸U atom ratio in ISU-09 isotopic reference material = 0.01096 \pm 0.09% (1 sigma)
k-factor = (observed/certified) atom ratio

Table 4. Results of Multiple Turret Loadings of ISU-09 Isotopic Reference Material by Indigenous TIMS

17/04/13 to 18/04/2013			19/04/2013 to 22/04/2013			23/04/2013 to 25/04/2013		
Set No. 1			Set No. 2			Set No. 3		
²³⁵ U/ ²³⁸ U Ratio	% RSD	K Factor	²³⁵ U/ ²³⁸ U Ratio	% RSD	K Factor	²³⁵ U/ ²³⁸ U Ratio	% RSD	K Factor
0.010996	0.12	1.003	0.010981	0.07	1.002	0.010987	0.09	1.002
0.011015	0.15	1.005	0.010981	0.09	1.002	0.010977	0.09	1.002
0.010985	0.11	1.002	0.010985	0.1	1.002	0.011002	0.08	1.004
0.011008	0.12	1.004	0.010993	0.08	1.003	0.010987	0.12	1.002
0.010985	0.1	1.002	0.011011	0.1	1.004	0.011013	0.12	1.004
0.011014	0.12	1.004	0.010988	0.1	1.002	0.010979	0.1	1.002
			0.010989	0.1	1.002	0.011007	0.12	1.004
			0.010981	0.1	1.002	0.010991	0.13	1.002
			0.011008	0.1	1.004	0.010993	0.1	1.003
			0.010999	0.1	1.004	0.010989	0.2	1.002
			0.010965	0.09	1.000	0.011016	0.09	1.005
0.011000	0.12	1.003	0.010989	0.09	1.002	0.010994	0.11	1.003

Table 5. Statistical Evaluation of the Data on ISU-09 Isotopic Reference Material

	Commercial TIMS	Indigenous TIMS		
		Set - 1	Set - 2	Set - 3
Mean ²³⁵ U/ ²³⁸ U	0.010994	0.011000	0.010989	0.010994
Standard deviation	7.77E-06	1.38E-05	1.32E-05	1.31E-05

Certified ²³⁵U/²³⁸U atom ratio ratio : 0.01096 ± 0.09% (1 sigma)

Table- 6. Results of Analysis of Uranium Samples by the two TIMS Machines

Date of analysis (in Indigenous machine)	Sample Code	Analysed by Commercial machine		Analysed by Indigenous machine (developed by TPD, BARC)		b/a
		$^{235}\text{U}/^{238}\text{U}$ atom ratio(a)	RSD (%)	$^{235}\text{U}/^{238}\text{U}$ atom ratio(b)	RSD (%)	
02/07/2013	MDD/P5-2/6706	0.00599	0.15	0.00605	0.12	1.010
02/07/2013	MDD/P5-2/6707	0.00848	0.07	0.008525	0.13	1.005
02/07/2013	MDD/P5-2/6708	0.00604	0.06	0.00607	0.09	1.004
02/07/2013	MDD/P5-2/6709	0.00803	0.06	0.008065	0.11	1.004
03/07/2013	MDD/P5-2/6710	0.00611	0.07	0.00614	0.10	1.004
05/07/2013	MDD/P5-2/6711	0.008	0.05	0.00806	0.09	1.008
05/07/2013	MDD/P5-2/6712	0.0061	0.06	0.00612	0.10	1.003
05/07/2013	MDD/P5-2/6713	0.00835	0.06	0.0084	0.10	1.006
05/07/2013	MDD/P5-2/6714	0.00638	0.10	0.006385	0.06	1.000
05/07/2013	MDD/P5-2/6715	0.00835	0.04	0.0084	0.20	1.006
01/05/2013	MDD/MD-4/617	0.00815	0.05	0.00817	0.10	1.002
01/05/2013	MDD/MD-4/618	0.00631	0.05	0.00631	0.08	1.000
02/05/2013	MDD/MD-4/619	0.00825	0.06	0.00825	0.09	1.000
02/05/2013	MDD/MD-4/620	0.00638	0.06	0.00638	0.09	1.000
26/04/2013	MDD/P5/6717	0.0083	0.05	0.008306	0.10	1.000
26/04/2013	MDD/P5/6718	0.00637	0.06	0.00638	0.10	1.002
29/04/2013	MDD/P5/6719	0.00831	0.07	0.00832	0.10	1.001
01/05/2013	MDD/P5-C/6720	0.00635	0.05	0.00637	0.06	1.003
		Mean	0.065		0.10	1.0032± 0.30%

Table - 7. Results of Analysis of Uranium Samples by the two TIMS machines

Date of Analysis	Sample details	Analysed by commercial machine		Analysed by Indigenous machine (developed by TPD, BARC)		b/a
		$^{235}\text{U}/^{238}\text{U}$ atom ratio(a)	RSD (%)	$^{235}\text{U}/^{238}\text{U}$ atom ratio(b)	RSD (%)	
14/06/2013	MDD/P5-2/6701	0.00863	0.04	0.00869	0.12	1.007
14/06/2013	MDD/P5-2/6702	0.00596	0.05	0.00596	0.10	1.000
17/06/2013	MDD/P5-2/6703	0.00862	0.06	0.00864	0.08	1.002
08/07/2013	MDD/P8-C/93	0.0079	0.07	0.00794	0.12	1.005
08/07/2013	MDD/P5-2/6737	0.00883	0.08	0.00884	0.20	1.001
08/07/2013	MDD/P5-2/6738	0.00605	0.12	0.00611	0.10	1.010
09/07/2013	MDD/P5-2/6739	0.00881	0.04	0.00889	0.10	1.009
09/07/2013	MDD/P5-2/6740	0.00605	0.13	0.00606	0.10	1.002
03/10/2013	MDD-P6-21-7699	0.00867	0.10	0.00869	0.07	1.002
03/10/2013	MDD-P6-21-7700	0.00581	0.09	0.00582	0.1	1.002
03/10/2013	MDD-P6-21-7701	0.00858	0.08	0.00861	0.1	1.003
03/10/2013	MDD-P6-21-7702	0.00586	0.09	0.00588	0.13	1.003
04/10/2013	MDD-P6-21-7703	0.00857	0.04	0.00858	0.13	1.001
04/10/2013	MDD-P6-21-7704	0.00587	0.07	0.00588	0.12	1.002
15/10/2013	MDD-P5-2-6809	0.00848	0.04	0.00848	0.11	1.000
15/10/2013	MDD-P5-2-6810	0.00615	0.09	0.00618	0.09	1.004
15/10/2013	MDD-P5-2-6811	0.00847	0.1	0.00850	0.09	1.004
15/10/2013	MDD-P5-2-6812	0.00614	0.11	0.00618	0.09	1.006
15/10/2013	MDD-CS5-8-131	0.00854	0.08	0.00853	0.23	0.998
22/10/2013	MDD-CS5-8-132	0.00595	0.07	0.00597	0.07	1.003
17/10/2013	MDD-CS5-8-133	0.00825	0.05	0.00828	0.11	1.004
17/10/2013	MDD-CS5-8-134	0.00612	0.05	0.00613	0.12	1.002
22/10/2013	MDD-CS5-8-135	0.00816	0.05	0.00818	0.1	1.002
17/10/2013	MDD-CS5-8-136	0.00623	0.04	0.00625	0.13	1.003
22/10/2013	PDS-MD4-639	0.00827	0.09	0.0083	0.09	1.004
18/10/2013	PDS-MD4-640	0.00637	0.09	0.0064	0.14	1.004
18/10/2013	PDS-MD4-641	0.0082	0.06	0.00821	0.11	1.001
18/10/2013	PDS-MD4-642	0.00632	0.04	0.00634	0.1	1.003
Mean			0.072		0.112	1.0032 ± 0.25%

Table 8. Probability of the Mann-Whitney-Wilcoxon Test of the $^{235}\text{U}/^{238}\text{U}$ atom ratio Data Obtained by Commercial TIMS and Indigenous TIMS

Sl No.	No. of filament loadings in Indigenous TIMS	Probability
1	Single	0.7307
2	Duplicate	0.6621
3	Triplicate	0.5429



Fig. 1. Photograph of the latest version of indigenous TIMS Instrument

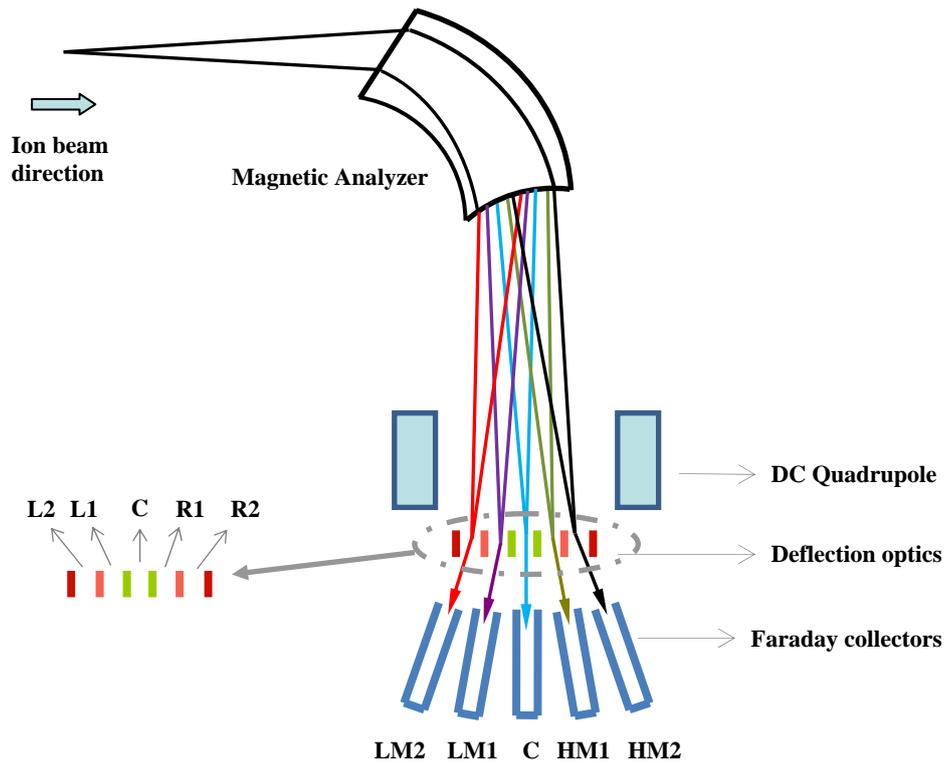


Fig. 2. Schematic of the TIMS Instrument

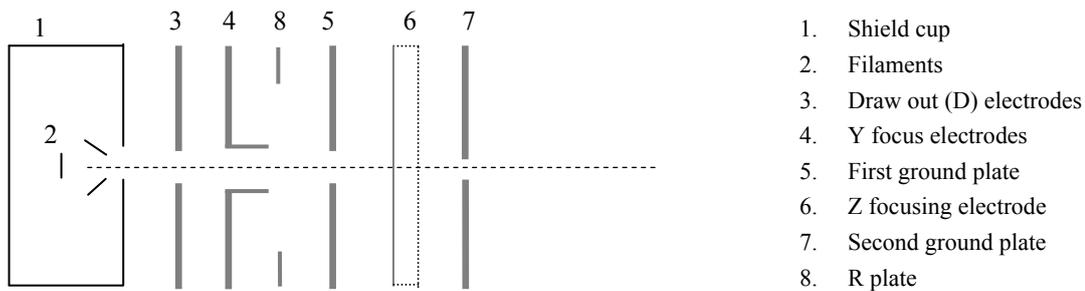


Fig. 3. Schematic of the Ion Source in TIMS

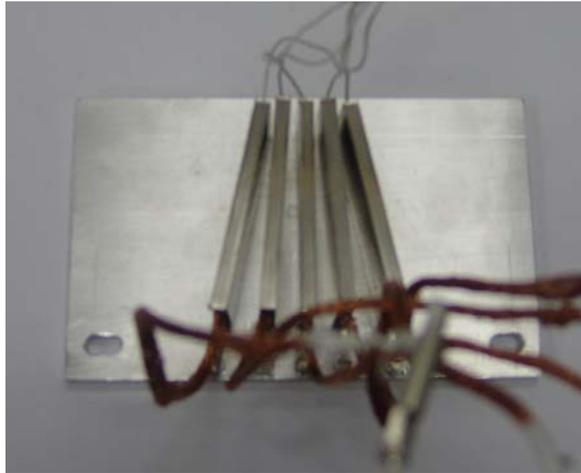


Fig. 4. Faraday collectors mounted on single SS plate in TIMS

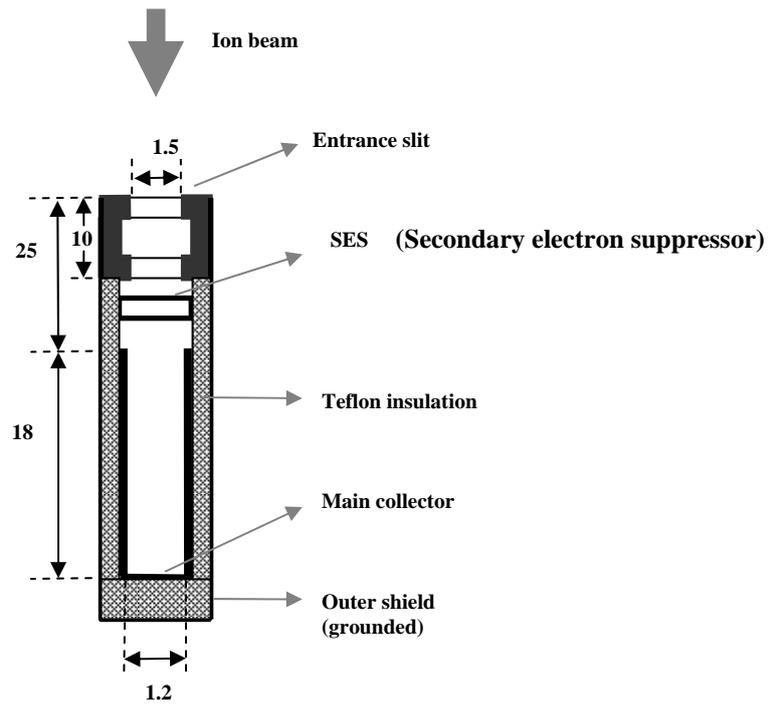


Fig. 5. Schematic of Faraday cup collector; all dimensions in mm

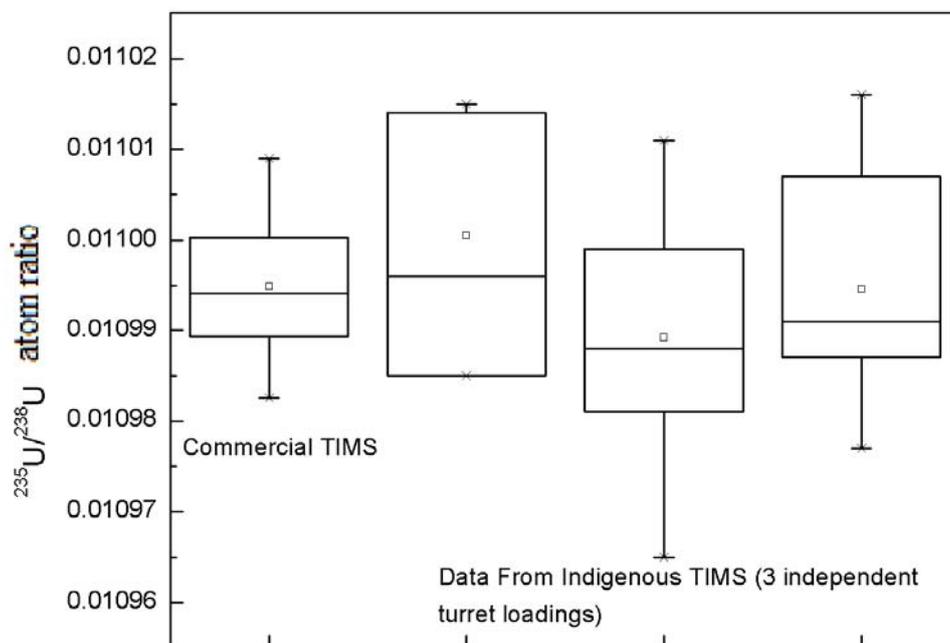


Fig. 6. Box – Whisker plot for the $^{235}\text{U}/^{238}\text{U}$ atom ratio determined in ISU-09 isotopic reference material by TIMS instruments

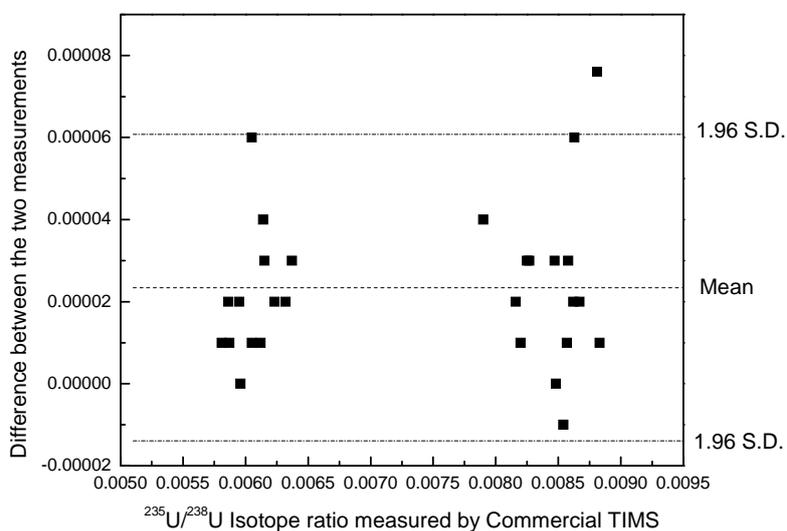


Fig. 7. Bland-Altman Plot for the data on the analysis of uranium samples (Single analysis)