

NUCLEAR FORENSICS INTERNATIONAL TECHNICAL WORKING GROUP

ITWG GUIDELINE THERMAL IONISATION MASS SPECTROMETRY (TIMS)



EXECUTIVE SUMMARY

Thermal Ionisation Mass Spectrometry (TIMS) is used for isotopic composition measurement of elements having relatively low ionisation potentials (e.g. Sr, Pb, actinides and rare earth elements). Also the concentration of an element can be determined by TIMS using the isotope dilution technique by adding to the sample a known amount of a "spike" [1]. TIMS is a single element analysis technique, thus it is recommended to separate all other elements from the sample before the measurement as they may cause mass interferences or affect the ionisation behaviour of the element of interest [2].

This document was designed and printed at Lawrence Livermore National Laboratory in 2017 with the permission of the Nuclear Forensics International Technical Working Group (ITWG).

ITWG Guidelines are intended as consensus-driven best-practices documents. These documents are general rather than prescriptive, and they are not intended to replace any specific laboratory operating procedures.

1. INTRODUCTION

In TIMS, a liquid sample (typically in the diluted nitric acid media) is deposited on a metal ribbon (called a filament made of rhenium, tantalum, or tungsten) and dried. The filament is then heated in the vacuum of the mass spectrometer, causing atoms in the sample to evaporate and become thermally ionised. After the ionisation, the ions are accelerated, separated by mass to charge ratio, and detected. A TIMS instrument consists of three primary parts: the ion source, mass analyzer, and detector system (Fig. 1). The filament configuration in the ion source can be either single, double, or triple filament. In the single filament configuration, the same filament serves both for evaporation and ionisation. In the double and triple filament configurations, the evaporation of the sample and the ionisation take place in separate filaments (Fig. 2). Although, in principle, any mass analyzer can be used, most commercial TIMS instruments use magnetic sectors. The main difference in TIMS instrumentation, besides the number of samples that can be loaded in the sample turret, is usually the detection system. Current TIMS instruments usually provide an array of collectors in



Fig.1. Typical schematic of a TIMS instrument: ion source – thermal ionisation, magnet – 90° magnetic sector, analyser – combination of Faraday cups and ion counters.



Fig.2. Double filament unit in thermal ionisation source. contrast to the single collector systems used previously. The detector array can consist either of Faraday cups with a single ion counter (SEM or Daly) or a mixture of Faraday cups and miniaturised electron multipliers [3].

The isotope ratios measured directly by TIMS must be corrected for fractionation. Fractionation is a physical phenomenon that takes place in the ion source when the sample is heated. The heat induces preferential evaporation of the lighter isotopes causing time dependent fractionation (Fig. 3). The chemical form and size of the sample, the temperature, and the ribbon material may also affect the fractionation [4, 5]. If one uses the so-called total evaporation method, where the whole sample is evaporated and signals of each isotope are integrated over the entire analysis period, no fractionation correction is usually required [6-8]. There are two ways to correct the fractionation affected results: one can measure certified reference materials [9-10] and determinate a correction factor; or one uses an internal normalisation to an accepted ratio (e.g., ⁸⁶Sr/⁸⁸Sr = 0.1194 and ${}^{146}Nd/{}^{144}Nd = 0.7219$).

In addition to bulk analysis, TIMS can be used for isotopic analysis of particles [11-12]. It can also be combined with the fission track technique (FT-TIMS) in order to identify appropriate particles for analysis [13]. However, when using FT-TIMS it is not possible to perform chemical separation for the particles. Therefore, some level of mass interferences are likely to occur.

2. USE FOR NUCLEAR FORENSICS

Thermal ionisation mass spectrometry can be used to determine the isotopic composition of uranium and plutonium (as well as other actinides of interest).²³⁵U and ²³⁹Pu enrichments are important signatures providing an indication of the intended use of the material [14].

The minor isotopes of uranium, ²³⁴U and ²³⁶U, also contain useful information for nuclear forensic purposes. For instance, an elevated amount of ²³⁶U indicates the use of uranium recycled from reactor fuel and hence points at reprocessing activities. In natural uranium samples, variations in the ²³⁴U and ²³⁵U abundances have been recorded, a phenomenon that might provide an indication about the origin of the material [15-18]. In the case where several samples of identical enrichment of ²³⁵U have been seized together, minor isotopes may help to verify similarities and differences between the samples.

The isotopic composition of Pu can provide information about the type of reactor in which it was produced. Different reactor types (e.g., light-water reactors, heavywater moderated reactors, graphite moderated reactors, fast breeder reactors) have different neutron energy spectra (slow vs. fast) and fluxes, as well as different initial ²³⁵U enrichments of the fuel, resulting in unique Pu isotopic compositions [19]. If the Pu production reactor type can be determined, it can be used to narrow down the possible sources of the material.



Fig.3. Fractionation phenomenon of the thermal ionisation source.

Besides the isotopic analysis of uranium and plutonium, isotopic compositions of other elements, usually present in minor amounts in nuclear materials, may give useful information. This includes e.g. strontium, neodymium, and lead, which are found in nuclear materials as contaminants from the source material (i.e. U ore) or production processes, or fission products, which are found in spent fuel [20].

3. SAMPLE REQUIREMENTS

The sample should be "pure", i.e. chemically separated from other elements so that no mass interferences (e.g. ²³⁸U – ²³⁸Pu or ²⁴¹Pu – ²⁴¹Am) occur and any effect on the evaporation and ionisation processes is minimised. The sample may be deposited on the filament in a diluted salt matrix (usually in nitric acid) or it may be loaded on to a few ion exchange resin beads, which are then physically placed on the filament. Required sample amount depends on the measurement method (total evaporation vs. static measurement vs. peak jumping), on the detector type (Faraday cup vs. ion counter), and on the first ionisation potential of the element being analysed. Therefore, sample sizes may vary from picogram to microgram loading depending on the above factors.

4. PRO'S AND CON'S OF THE TECHNIQUE

Pro's:

- Of all the mass spectrometric techniques (as well as radiometric techniques), TIMS is still the most accurate and precise technique for isotopic analysis, however the introduction of multi-collection to the ICP-MS technique is narrowing the gap. Precision of <0.05% is usually achieved by TIMS for the main uranium ratio, i.e. the ²³⁵U/²³⁸U. New miniaturised ion counting detectors enable multi-collection of minor isotopes (²³⁴U and ²³⁶U) improving the precision also for the minor isotopes.
- TIMS suffers much less from molecular interferences compared to ICP-MS allowing e.g. very tiny abundances of ²³⁶U to be detected (²³⁶U/²³⁸U – 10⁻¹⁰).

Con's:

- Sample preparation is rather time consuming
- Expensive instrumentation

5. FAQ – COST, DO'S AND DON'T'S, COMMON MISTAKES

- Cost: Instrument > 700 000 Euro; filaments ~10 Euro/filament.
- Highly skilled operators required.
- In the case of high U/Pu ratio in the sample, the complete U/Pu separation is very difficult in practice, therefore the ²³⁸Pu abundance is usually determined by alpha spectrometry.
- Filaments made of rhenium or tantalum need to be "baked" (degassed) before use, tungsten usually does not.
- Lens systems (retardation or deceleration) can be inserted in front of an ion counter detector to improve the abundance sensitivity (from 10⁻⁷ to 10⁻¹⁰).

6. REFERENCES

- K.G. Heumann, "Isotope dilution mass spectrometry", Int. J. Mass Spectrom. Ion proc. 118/119, 1992, 575-592.
- 2. S.K. Aggarwal, M.K. Saxena, P.M. Shah, S. Kumar, U. Jairaman, H.C. Jain, *Int. J. Mass Spectrom*. "Studies on the evaporation and ionisation behaviour of uranium and plutonium in thermal ionisation mass spectrometry", Ion Proc. 139, 1994, 111-126.
- 3. I.T. Platzner, Modern Isotope Ratio Mass Spectrometry, *Chemical Analysis* 145, John Wiley & Sons 1997, 530 pp.
- K. Habfast, "Fractionation in the thermal ionisation source", *Int. J. Mass Spectrom*. Ion Phys. 51, 1983, 165-189.

- 5. L.J. Moore, E.F. Heald, J.J. Filliben, "An isotope fractionation model for the multiple filament thermal ion source", *Adv. Mass Spectrom.* 7A, 1978, 448-474.
- R. Fiedler, D. Donohue, G. Grabmueller, A. Kurosawa, "Report on preliminary experience with total evaporation measurements in thermal ionization mass spectrometry", *Int. J. Mass Spectrom*. Ion Proc. 132, 1994, 207-215.
- P. De Bièvre, "Accurate isotope ratio mass spectrometry: Some problems and possibilities", *Adv. Mass Spectrom*. 7A, 1978, 395-447.
- S. Richter, H. Kühn, Y. Aregbe, M. Hedberg, J. Horta-Domenech, K. Mayer, E. Zuleger, S. Bürger, S. Boulyga, A. Köpf, J. Poths, K. Mathew, "Improvements in routine uranium isotope ratio measurements using the modified total evaporation method for multi-collector thermal ionization mass spectrometry" *J. Anal. At. Spectrom.*, 26, 2011, 550-564.
- 9. https://crm.jrc.ec.europa.eu/
- https://science.energy.gov/nbl/certified-referencematerials/
- M. Kraiem, S. Richter, H. Kühn, E.A. Stefaniak, G. Kerckhove, J. Truyens, Y. Aregbe, "Investigation of Uranium Isotopic Signatures in Real-Life Particles from a Nuclear Facility by Thermal Ionization Mass Spectrometry", *Anal. Chem.* 83, 2011, 3011–3016.
- J.-H. Park, E.-J. Choi, "Simultaneous determination of the quantity and isotopic ratios of uranium in individual micro-particles by isotope dilution thermal ionization mass spectrometry ID-TIMS", *Talanta* 160, 2016, 600–606.
- 13. S. Baude, R. Chiappini, "Isotopic measurements on micrometric particles: The French experience to detect fissile material", IAEA-SM-367/10/05.
- 14. IAEA Nuclear Security Series No.2-G, Nuclear Forensics in Support of Investigations.
- S. Richter, A. Alonso, W. De Bolle, R. Wellum, P.D.P. Taylor, "Isotopic fingerprints for natural uranium ore samples", *Int. J. Mass Spectrom*. 193, 1999, 9-14.

- S. Richter, A. Alonso-Munoz, R. Eykens, U. Jacobsson, H. Kuehn, A. Verbruggen, Y. Aregbe, R. Wellum, E. Keegan, "The isotopic composition of natural uranium samples – Measurements using the new n(233U)/n(²³⁶U) double spike IRMM-3636", *Int. J. Mass Spectrom*. 269, 2008, 145-148.
- 17. G. A. Brennecka, L. E. Borg, I. D. Hutcheon, M. A. Sharp, A. D. Anbar, "Natural variations in uranium isotope ratios of uranium ore concentrates: Understanding the ²³⁸U/²³⁵U fractionation mechanism", *Earth and Planetary Science Letters* 291, 2010, 228–233.
- L. A. Meyers, S. P. LaMont, A. M. Stalcup, H. B. Spitz, "Uranium isotopic signatures measured in samples of dirt collected at two former uranium facilities", *J. Radioanal. Nucl. Chem.* 301, 2014, 307–313.
- M. Wallenius, P. Peerani, L.Koch, "Origin determination of plutonium material in nuclear forensics", *J. Radioanal. Nucl. Chem.* 246 2, 2000, 317-321.
- 20. K.J. Moody, P.M. Grant, I.D. Hutcheon, Nuclear Forensic Analysis, 2nd Edition, CRC Press, Taylor & Francis Group, 2015, 502 pp.

DOCUMENT REVISION HISTORY

Document INFL-TIMS			
Version No.	Version Date	Description of Changes	Changes made by
1	March 2012	Initial Draft	M. Wallenius (author)
2	February 2017	Revision	M. Wallenius (author)