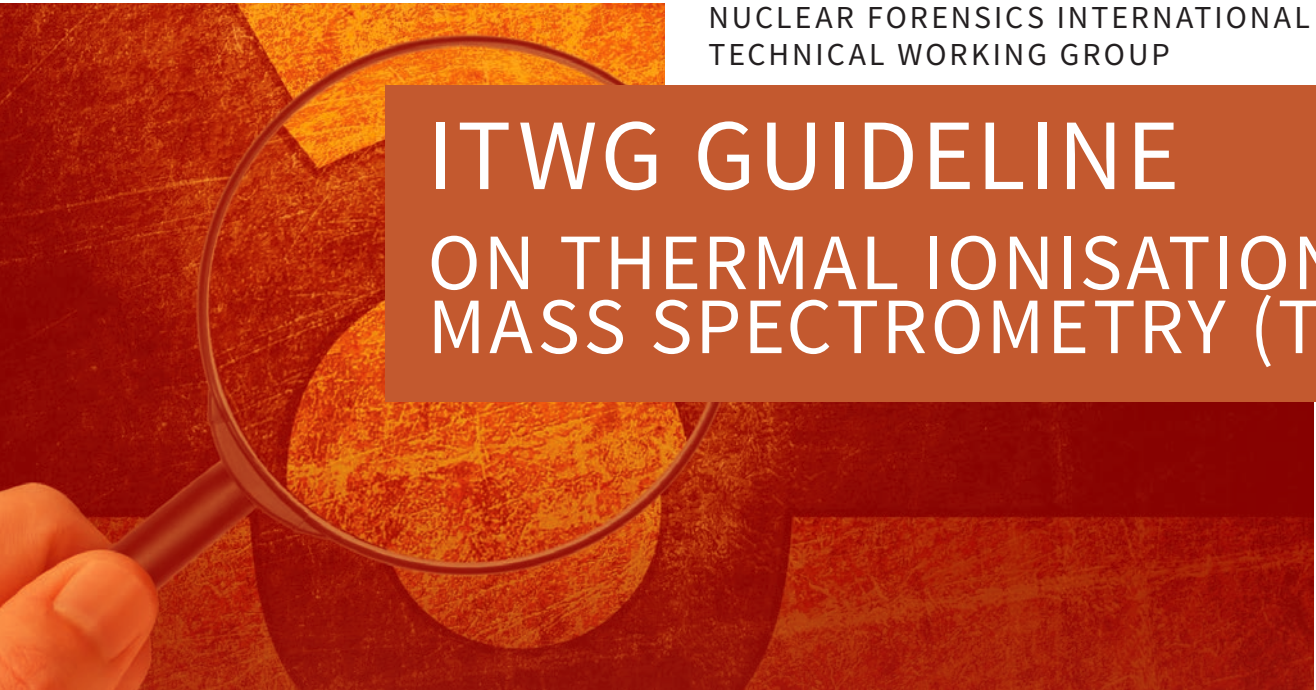




NUCLEAR FORENSICS INTERNATIONAL
TECHNICAL WORKING GROUP

A background image showing a hand holding a magnifying glass over a textured, orange-brown surface. The magnifying glass is positioned over a circular area, and the surface has a rough, crystalline appearance. The overall color palette is warm, dominated by shades of orange and brown.

ITWG GUIDELINE ON 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].

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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, the sample is deposited on a metal ribbon (called a filament, which is usually made of rhenium, tantalum or tungsten). 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 detector system. Current TIMS instruments usually provide an array

of collectors in 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 [6-9]. There are two ways to correct the fractionation affected results: one can measure certified reference materials and determinate a correction factor; or one uses an internal normalisation to an accepted ratio (e.g., $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$ and $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$).

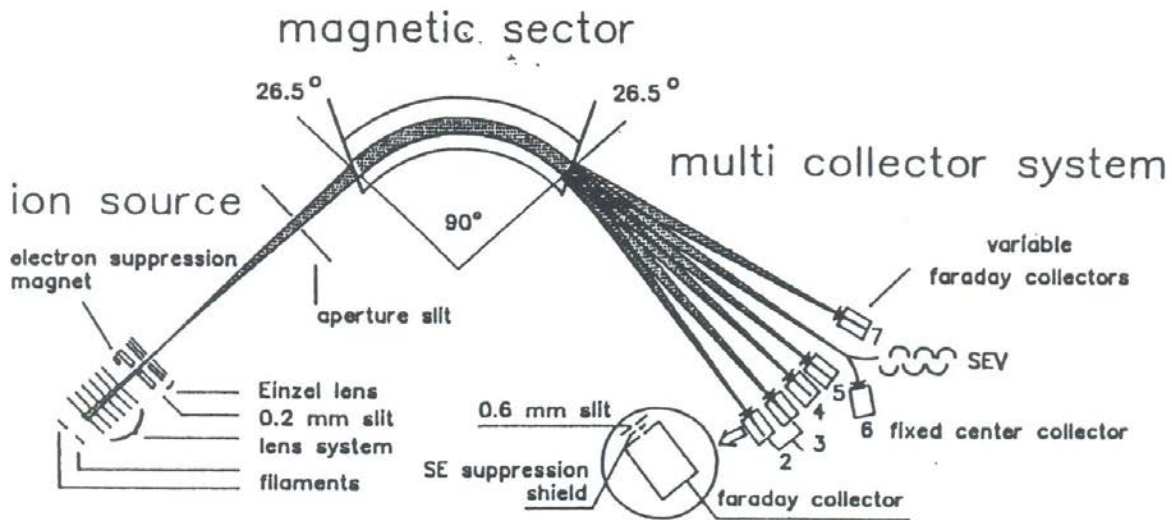


Fig. 1. Typical schematic of a TIMS instrument: Ion source – thermal ionisation, Magnet – 90° magnetic sector, Analyser – combination of Faraday cups and ion counters.

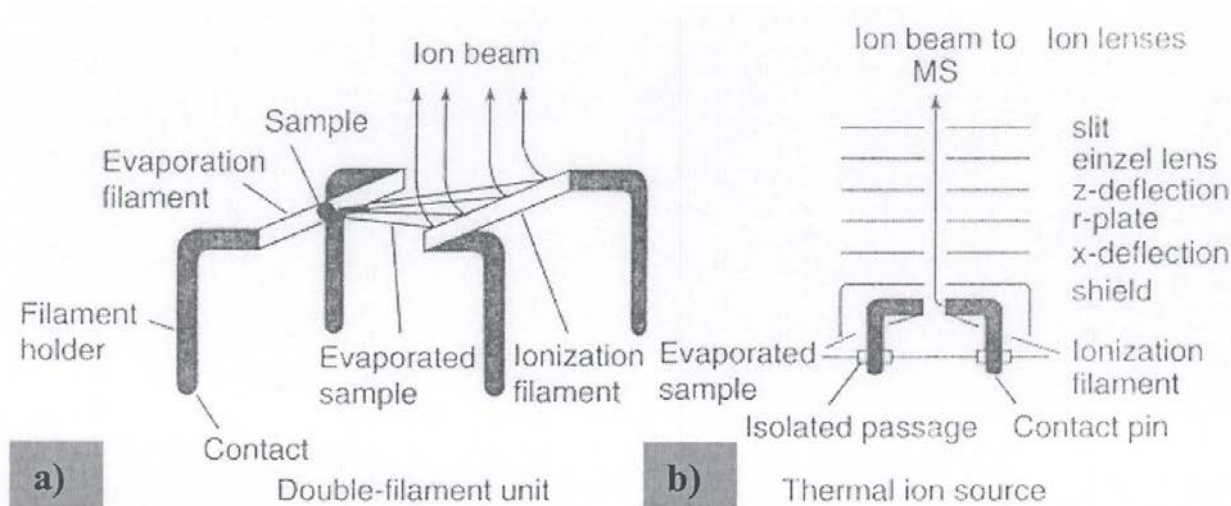


Fig. 2. Double filament unit in thermal ionisation source.

In addition to bulk analysis, TIMS can be used for isotopic analysis of particles, usually when combined with the fission track technique (FT-TIMS) in order to identify appropriate particles for analysis [10]. 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.

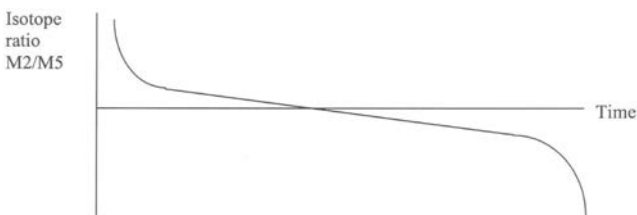


Fig. 3. Double filament unit in thermal ionisation source.

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). ^{235}U and ^{239}Pu enrichments are important signatures providing an indication of the intended use of the material [11].

The minor isotopes of uranium, ^{234}U and ^{236}U , also contain useful information for nuclear forensic purposes. For instance, an elevated amount of ^{236}U

indicates the use of uranium recycled from reactor fuel and hence points at reprocessing activities. In natural uranium samples, variations in the ^{234}U abundance have been recorded, a phenomenon that might provide an indication about the origin of the material [12, 13]. In the case where several samples of identical enrichment of ^{235}U 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, heavy-water moderated reactors, graphite moderated reactors, fast breeder reactors) have different neutron energy spectra (slow vs. fast) and fluxes, as well as different initial ^{235}U enrichments of the fuel, resulting in unique Pu isotopic compositions [14]. If the Pu production reactor type can be determined, it can be used to narrow down the possible sources of the material.

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 [15].

3. SAMPLE REQUIREMENTS

The sample should be “pure”, i.e. chemically separated from other elements so that no mass interferences (e.g. $^{238}\text{U} - ^{238}\text{Pu}$ or $^{241}\text{Pu} - ^{241}\text{Am}$) 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

+ 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 $^{235}\text{U}/^{238}\text{U}$. New miniaturised ion counting detectors enable multi-collection of minor isotopes (^{234}U and ^{236}U) 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 ^{236}U to be detected ($^{236}\text{U}/^{238}\text{U} \geq 10^{-10}$).
- Sample preparation is rather time consuming
- Expensive instrumentation

5. FAQ

- 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 ^{238}Pu 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}).

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DOCUMENT REVISION HISTORY

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