

TABLE 6a – Isotope ratio measurement of uranium and plutonium

NOTE: Description of the methods applicable for Table 6a: MC ICPMS.

Description of TIMS method is in preparation.

Method/measurement system (including software): Multi-Collector Inductively Coupled Plasma Mass Spectrometry (MC ICPMS)

Application: Measurements of uranium and plutonium isotope ratios and assay in nitrate solutions of U and Pu and in dissolved solid samples (e.g., metals, oxides, mixed oxides)

Short Description of the method/measurement system and typical measurement conditions (shielding, measurement time, etc.)
The first magnetic sector ICPMS with a multi-collector array was introduced in 1992 [1]. This instrument is dedicated for precise isotope ratio measurements for a large range of applications including the nuclear field. The source of this instrument is an argon plasma source (ICP) with the capacity to ionize with high efficiency all the elements of the periodic table. The energy dispersion of the source must be matched to that of the magnetic sector and this is done using an electrostatic filter located between the source and the magnet (double focusing mass spectrometer). A collision reaction cell can also be included on the most recent generation of MC ICPMS instruments. After separation of the ions, the detection is performed using a multi-collector system including Faraday cups and ion counters. Multiple collection allows the simultaneous measurement of the different isotopes of an element, thereby removing source instability. The samples are introduced in liquid form in 0.3 M nitric acid at concentration around 200 ng.g⁻¹ using a conventional introduction system, including a nebulizer associated to a nebulization chamber. Alternatively, a de-solvating nebulizer may be employed. Detector calibrations, included in the software of the instrument, are performed each day. Each analysis is preceded by a washout of around 5 to 10 minutes. All sample measurements must be associated with the measurement of a reference material in order to take into account the mass -dependent fractionation ("mass bias effect") inherent to ICPMS techniques. For each sample or standard, measurement times were around 10 minutes. The technique is also used for U and Pu isotopic ratios and for the determination of U and Pu assay using isotopic dilution (ID-MC ICPMS) in the same way as thermal ionization mass spectrometry (TIMS).
Factors affecting the method performance
A major factor affecting method performance is isobaric interference including ²³⁸U-²³⁸Pu and ²⁴¹Pu-²⁴¹Am. Before measurements, except for pure U solutions, uranium and plutonium must be purified, in the majority of cases by liquid chromatography, in order to avoid isobaric interferences or matrix effects. Concerning instrumental performance, due to mass bias effect, isotope ratios must be corrected using certified isotopic reference materials. In nuclear samples the correction is performed using sample standard bracketing (SSB) technique. Each sample is bracketed by certified isotopic standards and the average mass bias correction factor, calculated on these two standards, is applied to the sample. This correction is the major source of uncertainty on isotope ratio measurements, since it includes the uncertainty on the reference material used. All other sources of uncertainties including gain calibration, blank corrections, and counting statistics must also be taken into account.

Source of top-down value and ITV applicability
The ITVs were evaluated using a top-down approach. Evaluation was based on historical paired measurement data obtained from the Agency's measurements database. Data evaluation methodology included the following steps: data quality check, outlier detection and removal, application of the Analysis of Variance with Random Effects for the differences in paired data, calculation of random $u(r)$ and short-term systematic $u(s)$ uncertainties. The ITVs are applicable for measurements taken: for safeguards purposes, in safeguarded facilities, with measurement procedure and instrument specification equivalent to the one described in the "Short description" and the "Factors affecting the method performance".
Source of bottom-up value (only for prospective ITV not based on historical data)
N/A
Method references
[1] Walder A.J. et Freedman P.A. (1992) Isotopic ratio measurement using a double focusing magnetic sector mass analyzer with an inductively coupled plasma as an ion source. JAAS, 7, pp. 571-575.

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Date: Rev. 0 2023.09.5 (initial draft)

Date: Rev. 1 2023.10.21 (H. Isnard, F)

Date: Rev. 2 2024.02.14 (S. Woodbury, NNL, UK)

Date: final 2024.01.14 (E. Zuleger)

Method/measurement system (including software): Total Evaporation Thermal Ionization Mass Spectrometry (TE-TIMS), using a multi-collector thermal ionization mass spectrometer

Application: Measurement of uranium and plutonium isotope ratios in uranium or plutonium nitrate solution samples and in dissolved solid samples (e.g., metals, alloys, oxide powders, oxide pellets, mixed oxides)

Short Description of the method/measurement system and typical measurement conditions (shielding, measurement time, etc.)

TE-TIMS is an analytical method for the measurement of uranium and plutonium isotope ratios in uranium or plutonium nitrate solutions for safeguards purposes ^[1,3,4]. The same method is also applicable to determine the elemental content by isotope dilution of a spiked sample (see narratives Table 4 a, b). Measurements can be performed either directly in solutions or in dissolved solid samples (e.g., metals, alloys, oxide powders, oxide pellets, mixed oxides). However, to measure uranium and plutonium isotopes in mixtures of U and Pu with high precision a separation of uranium from plutonium and a separation of the fission products and minor actinides from the plutonium samples need to be performed prior to the measurements ^[2,3,4]. In TE-TIMS purified uranium or plutonium nitrate solutions are deposited onto a metal filament and the filaments holding the dried sample are placed in the mass spectrometer, which is subsequently evacuated. Under computer control, ion currents are generated by heating of the filament(s). The ion currents are continually measured until the whole sample is exhausted. The measured ion currents are integrated over the course of the measurement and normalized to a reference isotope ion current to yield isotope ratios ^[3]. The TE method relies almost entirely on separate measurements of standards to calculate measurement uncertainty and precision ^[4]. The measurement of the ratio $n(^{235}\text{U})/n(^{238}\text{U})$ is routinely being performed with a combined standard uncertainty ($k=1$) of about 0.07 % to 0.7 % depending of the ^{235}U enrichment. Typical combined standard uncertainties ($k=1$) for the plutonium ratio $n(^{240}\text{Pu})/n(^{239}\text{Pu})$ can be achieved between 0.11 and 0.18 %.

The TE method ^[1,3] using a multi-collector ionization mass spectrometer is usually applied for analysis of uranium nitrate solutions containing 0.1 to 0.5 g/L U and for plutonium nitrate solutions containing 0.01 to 0.2 g/L Pu.

The method is installed and routinely used at IAEA's Nuclear Material Laboratory in Seibersdorf and network laboratories.

The key measurement steps and their purposes are outlined below:

- test samples are prepared from homogenous solutions volumetrically, preferentially in a matrix of about 1M nitric acid.
- Calibration standards and quality control samples are prepared with the same concentration and matrix.
- Up to 5 µl of solution containing U or Pu concentrations specified above are loaded on degassed Rhenium filaments or non-degassed Tungsten double filaments and then evaporate to dryness at 0.6 A (exact configurations and preparation conditions vary depending on the facility).
- The sample evaporation filaments are mounted on the sample turret as a double filament assembly with an empty degassed Re filaments for enhanced ionization.
- The assembled turret is loaded into the TIMS instrument, the ion source chamber is pumped down, and a cooling trap is filled with liquid nitrogen to enhance the vacuum.
- At a vacuum in the source chamber better than 3×10^{-7} mbar the relevant instrument calibrations, such as gain and baseline calibration, can be started. Baselines can be automatically measured during the sample measurements.

- During the total evaporation process the signals of each isotope are collected in a different Faraday cup from the start to the end of the measurement.
- External (certified) reference materials with isotopic compositions preferably similar to the isotopic composition of the analyzed samples are measured under similar conditions as the samples for quality control (QC) purposes. Measurements are performed in manual or automatic sequences containing each sample and reference material for QC purposes. In addition, reference material can be loaded on the turret to check the performance of the instrument.
- The calculation of the isotope ratios is described in detail in ^[1,3,4].

Factors affecting the method performance

The primary factors impacting TE measurement precision and bias are:

- Sample isotopic composition;
- Dependence of the mass fractionation factor of the sample amount loaded;
- Sample matrix;
- Detector noises, gain and baseline calibration;
- Ensuring measurement control using traceable, uranium and plutonium quality-control reference materials;
- Mass fractionation effects, if not corrected for.

Source of top-down value and ITV applicability

The ITVs in Table 5a and 6a were evaluated using a top-down approach of all TE measurements. Evaluation was based on historical paired measurement data obtained from the Agency's measurements database. Data evaluation methodology included the following steps: data quality check, outlier detection and removal, application of the Analysis of Variance with Random Effects for the differences in paired data, calculation of random $u(r)$ and short-term systematic $u(s)$ uncertainties.

The ITVs are applicable for measurements taken: for safeguards purposes, in safeguarded facilities, with measurement procedure and instrument specification equivalent to the one described in the "Short description".

Source of bottom-up value (only for prospective ITV not based on historical data)

N/A

Method references

- [1] M. Romkowski, S. Franzini, L. Koch, Mass-Spectrometric analysis of subnanocurie samples of Uranium and Plutonium, in: Proceedings of the 8th Annual ESARDA Symposium, 1987, pp. 111-113.
- [2] Morgenstern, A., Apostolidis, C., Carlos-Marquez, R., Mayer, K., Molinet, R.; *Single-column extraction chromatographic separation of U, Pu, Np and Am*; Radiochimica, vol. 90, p. 81, 2002.
- [3] ASTM Standard Document C1672, Standard Test Method for Determination of Uranium or Plutonium Isotopic Composition or Concentration by the Total Evaporation Method Using a Thermal Ionization Mass Spectrometer. Available through the ASTM website: <https://www.astm.org/c1672-17.html>

[4] ISO 8299:2019(E), Nuclear fuel technology - Determination of the isotopic and elemental uranium and plutonium concentrations of nuclear materials in nitric acid solutions by thermal-ionization mass spectrometry.

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