

TABLE 5a – $^{235}\text{U}/^{238}\text{U}$ Isotope Ratio Measurement

NOTE: Description of the methods applicable for table 5a: GSMS, Q-ICPMS and MC ICPMS
Description of TIMS method is in preparation.

Method/measurement system (including software): UF_6 Gas Source Mass Spectrometry (GSMS)

Application: $^{235}\text{U}/^{238}\text{U}$ isotope ratio in Uranium hexafluoride gas

Short Description of the method/measurement system and typical measurement conditions (shielding, measurement time, etc.)
UF_6 is one of primary form of uranium in the nuclear fuel sample. Gas Source Mass Spectrometry (GSMS) is a technique used to determine the isotope composition in gaseous UF_6. Measuring UF_6 in gaseous form avoids the conversion of the gas into uranium solution and is therefore less time consuming than Thermal ionization mass spectrometry (TIMS) or inductively coupled plasma mass spectrometry (ICP-MS) for this kind of sample. In GSMS, UF_6 is ionized mainly as UF_5^+ by an electron impact source. The formed ions are separated by a magnetic field. The UF_5^+ species are detected at masses between 329 and 333 amu by a multi-collector. In this technique, the sample is measured is against reference materials (certified or not) which are isotopically well characterized. Several methods are described “single standard”, “double standard” and “memory corrected double standard” in the literature, but the most commonly used are the DS and MCDS method if reference materials (RM) are available to bracket isotopically the samples. DS methods are not based on the simple average using the reference materials but on a weighted average based on the “isotopic distance” between the sample and the two RMs. This allows the cancellation of the memory effect due to the introduction of different gases in the inlet line. Prior analysis, an adequate conditioning of all UF_6 container is important to remove gas or HF gas in order to optimize the sensitivity of the instrument. For the different methods, overall uncertainties are dominated by the reference material uncertainties and the memory effects; the reproducibility of a measurement is generally $< 0.01\%$. For the combined uncertainties for typical $^{235}\text{U}/^{238}\text{U}$ ratio measurements by GSMS the reproducibility is only a minor contribution. Most dominant uncertainty contributions are about the uncertainties of the two used certified bracketing standards and the two observed types of memory effects. These are related to the alternating measurements of the sample and the bracketing standards in the same ion source chamber, and to the memory effect caused by adsorption of UF_6 on the inner walls of the inlet system.
Factors affecting the method performance
Memory effect of the gas inlet and sensitivity loss between sample and reference materials can bias the measurement of the isotope ratio. In DS method, the “isotopic distance” between the sample and the standards has to be similar in order to avoid memory effect.

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
S. Richter et al "uranium hexafluoride (UF_6) gas source mass spectrometry for certification of the reference materials and nuclear safeguard measurements at IRMM", J. Anal. At. Spectrom., 2013,28, 536-548

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Method/measurement system (including software): Measurement system using quadrupole analyzer (Q-ICPMS)

Application: $^{235}\text{U}/^{238}\text{U}$ isotope ratio

Short Description of the method/measurement system and typical measurement conditions (shielding, measurement time, etc.)
ICP-MS is an elemental and isotopic analytical technique that uses an inductive coupled plasma (ICP) ion source to desolvate, vaporize, atomize and ionize a sample. Its simplest version makes use of a quadrupole analyzer to separate ions according to their mass to charge ratio and a secondary electron multiplier (SEM) to measure their intensities. An ICP is a high temperature plasma generated by flowing typically an ionized argon gas through a magnetic field induced by a load coil that surrounds the tubes carrying the gas. It can efficiently ionize nearly 95% of the elements of the periodic table. Samples can be dissolved, purified using an ion chromatography resin (if deemed necessary) and prepared with 2% HNO_3 at concentrations between 10 -100 100 ng.g^{-1}. Aqueous solutions are introduced into the ion source by direct nebulization.
Factors affecting the method performance
The following factors affect the quality of the measurement results: resolution, sensitivity and counting statistics, dead time, abundance sensitivity and mass bias. The former is corrected by the use of certified reference materials that bracket the sample's isotope ratios. At about five samples can be measured per hour using this measurement procedure. The accuracy of an isotope amount ratio depends mainly on its measurement precision and the mass bias correction. Typical standard uncertainties for $n(^{235}\text{U})/n(^{238}\text{U})$ are in the range 0.1 to 0.5 % of the ratio, depending on the instrument design, analytical procedure and ion beam intensity, the available reference material.
Source of top-down value and ITV applicability
N/A
Source of bottom-up value (only for prospective ITV not based on historical data)
N/A
Method references
1. Handbook of Inductively Coupled Plasma Mass Spectrometry, K. E. Jarvis, A. L. Gray and R. S. Hook, pages 310-337 2. Isotope ratio measurements using ICP-MS, by G. Price Russ III, pages 90-114, in Applications of inductively coupled plasma mass spectrometry, edited by A.R. Date and A. L. Gray

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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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Method/measurement system (including software): MTE-TIMS instrument-control software, has been designed in the United States, European Commission, and the IAEA, using a Triton TIMS, a multi-collector thermal ionization mass spectrometer manufactured by Thermo Fisher Scientific^[1,2]

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

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

MTE TIMS is an analytical method for the measurement of uranium isotope ratios in uranium nitrate solution samples and in dissolved solid samples (e.g., metals, alloys, oxide powders, oxide pellets). The measurement of the “major” ratio $n(^{235}\text{U})/n(^{238}\text{U})$ is routinely performed with an accuracy of 0.02% to 0.05% (expanded uncertainty corresponding to a 95 % level of confidence). In contrast to the total evaporation thermal ionization mass spectrometry (TE-TIMS) method (see narrative for TE-TIMS), the MTE method’s most significant improvement is in the measurement performance achieved for the “minor” ratios $n(^{234}\text{U})/n(^{238}\text{U})$ and $n(^{236}\text{U})/n(^{238}\text{U})$. The $n(^{234}\text{U})/n(^{238}\text{U})$ ratio is measured using Faraday cups only with the result that the (relative) measurement uncertainty ($k = 2$) is improved by a factor of about 5–10 compared to TE measurements. For routine MTE measurements a detection limit of 3×10^{-9} to 5×10^{-9} can be achieved in natural or low-enriched U samples using an SEM detector for the $n(^{236}\text{U})/n(^{238}\text{U})$ ratio, several orders of magnitude superior compared to the TE method.

The method is applied for measuring aqueous uranium solutions containing uranium, using a multi-collector thermal ionization mass spectrometer. A minimum loading of uranium per filament of at least 2.5 µg is recommended ^[2]. The MTE method is installed and routinely used at IAEA’s network laboratories. The MTE method is also frequently used at JRC.G.II.5 (Geel/Belgium), JRC.G.II.8 (Karlsruhe/Germany) and ORNL (US), but with sample loads between 3 and 6 µg).

The key measurement steps and their purposes are outlined below:

- test samples are prepared from homogenous solutions volumetrically to have a loading concentration between 3 and 6 µg in maximum 5 µl solution, preferential in a matrix of 1M nitric acid.
- Calibration and quality control standards are prepared with the same concentration and matrix.
- Up to 5 µL containing between 3 and 6 µg are loaded on degassed or un-degassed Rhenium or Tungsten double filaments (exact configurations vary depending on the facility) and then are evaporated to dryness at 1 A, heated to 2.0 A and then immediately reduced to 0 A (IAEA procedure: at 1 A for 400 s evaporated to dryness, heated to 2.4 A for 200 seconds immediately reduced to 0 A).
- These sample evaporation filaments are mounted as a double filament assembly with an empty degassed double Rhenium ionization filament and loaded onto the sample turret.
- The assembled turret is loaded into the TIMS instrument. Then once the source chamber vacuum is less than 3×10^{-6} mbar a cooling trap is filled with liquid nitrogen.
- At a source chamber vacuum better than 2×10^{-7} mbar the instrument calibration, such as gain and baseline calibration, can be started. Baselines are automatically measured during the sample measurements, but they have to be checked to evaluate the instrument performance.
- If a SEM is used the dark noise should be < 10 cpm. A control measurement performed for 5 minutes is recommended.
- If a SEM is used, the SEM yield calibration is performed before every sequence at a source chamber vacuum better than 3×10^{-7} mbar.
- In contrast to the TE method, the modified total evaporation process is interrupted on a regular basis to allow for correction of background from peak tailing, and internal calibration of a secondary electron multiplier (SEM) detector versus the Faraday cups, peak-centering, and ion source re-

focusing, which is included in the software script. Therefore, the sample amount loaded is higher and the measurement time longer compared to the TE method. However, no significant effects from these interruptions have been observed. — The ionization of the samples takes place at the surface of filaments at temperatures of about 1900°C. — An external (certified) reference material is measured under similar conditions as the samples for mass fractionation correction. Also, a second preferentially also certified reference material should be measured for quality control (QC) purposes. — Measurements are performed in automatic sequences containing five times an external certified reference material; each of the two samples analyzed are measured a total of six times, each sample is measured using two aliquots, each aliquot is measured three times; and additionally, the second certified reference material is measured four times for QC purposes. — A SEM is used for measuring ^{236}U in samples containing $^{236}\text{U} < 0.04$ atom %. A Faraday cup has to be used for measuring samples containing ^{236}U with higher abundance. — The calculation of the isotope ratios is described in detail in ^[2] and ^[3].
Factors affecting the method performance
The primary factors impacting MTE measurement precision and bias are: — Sample isotopic composition; — Dependence of the mass fractionation factor of the sample amount loaded; — Sample matrix; — Secondary Electron Multiplier (SEM) detector stability; — Detector noises, gain and baseline calibration; — Ensuring measurement control using traceable, uranium quality-control reference materials; — Mass fractionation effects that require correction.
<u>Source of top-down value and ITV applicability</u>
n/a
Source of bottom-up value (only for prospective ITV not based on historical data)
The uncertainties for the MTE measurement of uranium isotope composition were evaluated using a bottom-up approach. For more details concerning uncertainties see [3].
Method references
[1] S. Richter and S. A. Goldberg, Improved techniques for high accuracy isotope ratio measurements of nuclear materials using thermal ionization mass spectrometry, <i>Int. J. Mass Spectrom.</i>, 2003, 229, 181–197. [2] S. Richter, H. Kühn, Y. Aregbe, M. Hedberg, J. Horta-Domenech, K. Mayer, E. Zuleger, S. Bürger, S. Boulyga, A. Köpf, J. Poths and K. Mathew, Improvements in routine uranium isotope ratio measurements using the modified total evaporation method for multi-collector thermal ionization mass spectrometry, <i>J. Anal. At. Spectrom.</i>, 2011, 26, 550–564 [3] ASTM Standard Document C1832, available through the ASTM website: https://www.astm.org/c1832-23.html

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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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