

TABLE 4b – Plutonium Mass Fraction Measurements (DA)

NOTE: Description of the methods applicable for Table 4b: ALPH, COUL, MC ICPMS, HKED, KEDG and XRF. Description of GRAV and IDMS methods are in preparation.

Method/measurement system (including software): The method describes the determination of the plutonium mass fraction by Alpha Spectrometry

Application: Measurement of plutonium in low level radioactive solution resulting from the process of irradiated fuel dissolution

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

Plutonium is converted to tetravalent state and with TTA (thenoyltrifluoroacetone) forming a chelate complex that is separated from interfering alpha emitters, americium, neptunium (V) and curium, by extraction into xylene¹.

The tetravalent state of plutonium is obtained by an oxido-reduction cycle (acidity adjustment - reduction with Mohr salt $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ - oxidation by sodium nitrite) retaining only Pu(IV) in the organic phase. The stripping of plutonium out of the xylene with nitric acid prior to alpha counting is another option.

The separated plutonium solution to be analyzed by alpha counting is applied to a planchet (porcelain, stainless steel or platinum) as a thin layer using evaporation, ignition or electrolytic deposition techniques.

Alpha activity measurements of the background, reference standard and sample are required for the determination of the amount of plutonium in the sample. The measurements are carried out in a vacuum chamber with a semiconductor ion implanted detector (e.g., PIPS) with energy resolution (FWHM) 20 keV or better. Evaluations for gross alpha counts can be made on the whole spectrum, or at specific energies of plutonium isotopes $^{239+240}\text{Pu}$ (5.2 MeV) and ^{238}Pu (5.5 MeV).

Plutonium amount can be derived by two methods (i) comparison of radiation intensities emitted by a representative reference standard (freshly prepared to minimize interference with the growing alpha emitter ^{241}Am) and the sample respectively, or (ii) calculation by integrating chemical extraction recovery, counting efficiency and specific activity of individual plutonium isotopes. In both cases, chemical recovery, i.e., the ratio between the radionuclide amount present on the alpha planchet and the radionuclide content in the original sample before treatment, must be validated. In addition, the isotopic composition of plutonium must be known.

Spiking: the addition of a pre-calibrated spike (e.g., ^{238}Pu) to a known aliquot of the sample solution followed by direct source preparation, or using TTA/Xylene prior to alpha activity measurements can improve measurement performance.

The method applies to assay solutions containing 2 to 200 micrograms of plutonium per milliliter.

¹ Separation by ion-exchange is an alternative

Factors affecting the method performance
The primary factors impacting measurement precision and bias are: - inaccuracy in sample preparation (aliquoting, dilution); - unknown plutonium recovery in case the spike is not used; - quality, i.e., thickness and uniformity, of the sample material layer applied to the alpha planchet - counting statistics; - differences in plutonium isotope composition between the sample and the reference standard.
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] S. K. Aggarwal, G. Chourasiya, R. K. Duggal, C. P. Singh, A. S. Rawat, and H. C. Jain, Determination of the plutonium concentration by Isotope Dilution Alpha-Spectrometry without purification from americium-241 and a bulk of other impurities, Fresenius Z Anal Chem (1986) 323:148-152 [2] ISO 11483:2005 (E), Nuclear fuel technology - Preparation of plutonium sources and determination of ²³⁸Pu/²³⁹Pu isotope ratio by alpha spectrometry.

Prepared by: Georges Duhamel

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Date: Rev. 1 take inputs on S. Hara's scheme at RRP

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Method/measurement system (including software): COUL (CPC instruments, with custom instrument-control software, have been designed in the United States, France, and Russia)

Application: Measurement of plutonium nitrate in 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.)

CPC is an analytical method for the electrochemical measurement of pure plutonium nitrate solutions, with an expanded uncertainty not exceeding $\pm 0,2$ % at the confidence level of 0,95 for a single determination (coverage factor, $k = 2$). The method is suitable for aqueous solutions containing plutonium at more than 0,5 g/L and test samples containing plutonium between 4 mg and 15 mg. ^[1,2]

The key measurement steps and their purposes are outlined below:

- test samples are prepared from homogenous solutions by weighing and then fuming to dryness with sulfuric acid to achieve a stable anhydrous plutonium sulfate salt that is free from chloride, fluoride, nitrate, nitrite, hydroxylamine, and volatile organic compounds;
- if needed to remove interferences, dissolve test samples and purify by anion exchange, then fume the eluted plutonium solution in the presence of sulfuric acid to obtain the anhydrous plutonium sulfate salt;
- measure the supporting electrolyte blank and calculate the background current correction applicable to the electrolysis of the test sample from charging, faradaic, and residual currents;
- dissolve the dried test sample in the previously measured supporting electrolyte (the blank);
- reduce the test sample at a controlled potential that electrolyses the plutonium to a Pu^{3+} fraction greater than 99,8 % and measure the equilibrium solution potential at the end of this step by control-potential adjustment;
- oxidize the test sample at a controlled potential that electrolyses the plutonium to a Pu^{4+} fraction greater than 99,8 % and measure the equilibrium solution potential at the end of this electrolysis by control-potential adjustment;
- correct the integrated current (integrator output from the test sample) for the background current, including the residual current corrections, and for the fraction of plutonium not electrolysed;
- calibrate the coulometer using traceable electrical standards and Ohm's Law;
- use the measured value of the electrical calibration factor and the Faraday constant to convert the integrator output to coulombs and then to moles of plutonium measured by the coulometer;
- calculate the mass of plutonium by multiplying the moles of plutonium determined by controlled-potential coulometry times a molar mass of plutonium determined by other means, such as thermal ionization mass spectrometry, magnetic sector inductively coupled plasma mass spectrometry, or process knowledge.
- use quality-control standards with traceable plutonium quantity values to demonstrate independently the performance of the measurement system;
- periodically measure the formal potential of the plutonium couple, E_0 , which is user-specific based on the cell design, connections, reference electrode type, acid-type and molarity of the supporting electrolyte, and the presence of any complexing agents in the electrolyte.

These steps ensure that test samples are taken from reproducible and stable sample solutions and prepared for measurement. The test samples are measured using a protocol based upon first principles and a traceable, electrical calibration of the coulometer.

Factors affecting the method performance

The primary factors impacting CPC measurement precision and bias are:

- Accurate measurement of mass quantity values when preparing test samples for measurement;
- Low background current values and reproducible electrode performance;
- Stable control potentials to reduce and oxidize the plutonium ions in test sample solution;

- Accurate integration of the electrolysis during the oxidation of the plutonium; - Reliable electrical calibration of the integration system using traceable electrical standards, Ohm's Law, and the Faraday Constant; - Accurate measurement of trace iron amount of substance used to correct plutonium amount of substance results (trace iron typically measured by spectrophotometry, ICP-OES, or ICP-MS); - Periodic measurement of the formal potential of the plutonium couple; and - Ensuring measurement control using traceable, plutonium quality-control reference materials.
Source of top-down value and ITV applicability
The ITVs for the CPC measurement of plutonium were not evaluated using a top-down approach. CPC is not applied by member states or by the IAEA for safeguards purposes where paired measurement data are generated and tracked by the IAEA.
Source of bottom-up value (only for prospective ITV not based on historical data)
Conventional statistical analysis and the application of the GUM, JCGM 100:2008^[3] have been used to establish the ITV uncertainties $u(r) = 0.1 \%$ and $u(s) = 0.1 \%$. These uncertainty values have been derived from the measurement of plutonium certified reference materials. The standard uncertainties $u(r)$ and $u(s)$ were combined by propagations to generate a combined standard uncertainty, $u(c) = 0.14 \%$, which appears in Table 4b under the column header "ITV (% rel., $k=1$)." The typical purpose for the application of CPC by the IAEA is the characterization of plutonium amount of substance and/or plutonium mass fraction in solutions prepared from certified reference materials. These solutions are used for either quality control applications for CPC (or other plutonium measurements methods) or for the preparation of working reference materials such as large size spikes for isotope dilution mass spectrometry.
Method references
[1] ISO 12183:2016, "Nuclear fuel technology — Controlled-potential coulometric assay of plutonium". [2] Holland M. K., Weiss J. R., Pietri C. E., <i>Anal. Chem.</i> 1978, 50 p. 236. [3] JCGM 100:2008 (GUM 1995 with minor corrections), "Evaluation of measurement data – Guide to the expression of uncertainty in measurement". For additional references, see ISO 12183:2016.

Prepared by: Michael K. Holland, Omega Technical Services, Contractor to NBL Program Office NNSA, USA
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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 ^{238}U - ^{238}Pu and ^{241}Pu - ^{241}Am . 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.

Prepared by: Helen Isnard

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Method/measurement system (including software): HKED / KEDG / XRF**Application:** Measurement of Uranium and Plutonium in Solutions

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

K-Edge Densitometry (KEDG), X Ray Fluorescence (XRF), and their combination, Hybrid K-Edge (HKED), are techniques used to determine uranium and plutonium mass fractions or concentrations in dissolver, product, secondary flow, and waste solutions related to fuel reprocessing. A single measurement system, comprising of two High-Purity Germanium (HPGe) detectors, an X ray generator, shielding, collimators, data acquisition electronics, and computer, is typically deployed and capable of all three methods [1]. All three methods are rapid, non-destructive assay techniques, though they are typically listed among destructive assay techniques due to the low uncertainty of KEDG (< 1%). Samples are typically assayed with three (3) replicate measurements, each for a time of 1000 to 3000 s.

The KEDG method measures the X ray transmission discontinuity across K-edge energies for an absolute elemental concentration determination in highly concentrated uranium and plutonium solutions (> 50 g U per liter or > 50 g Pu per liter).

The XRF method determines the absolute elemental concentrations in pure or mixed solutions of uranium and plutonium in the range of 1 to 50 g per liter by quantifying the fluorescent X rays emitted due to excitation by the generator X rays.

The HKED method determines simultaneously uranium and plutonium in solutions where the uranium has higher concentrations, as in the case of dissolver solutions. The XRF portion of HKED quantifies the uranium to plutonium (U/Pu) ratio, and the KEDG portion measures the uranium concentration. The combination of two methods determines the absolute plutonium concentration. Typical uranium concentrations and U/Pu ratios are in the ranges of 150 to 250 g U per liter and 80:1 to 150:1, respectively.

HKED systems are installed primarily in on-site analytical laboratories associated with spent fuel reprocessing facilities.

Factors affecting the method performance

The main factors impacting measurement precision and bias of all three methods include the following [1]: counting statistics, X ray generator stability, detector and associated electronics stability, sample homogeneity, sample matrix, sample isotopic abundances, sample container dimensions, sample positioning, and sample temperature.

Some of these factors, such as sample temperature and sample isotopic abundances, are corrected for directly in the analysis software. X ray generator stability and sample positioning are typically monitored to be within certain control criteria for every assay or on a periodic basis. Detector electronics stability is also monitored and corrected for by using an in-situ energy calibration check source for each measurement. The radioactive decay of certain check sources, such as Cd-109, can also affect background evaluation in some KEDG algorithms over time. Its decay rate at the time of installation and sample measurement should be considered during the measurement evaluation. Sample container dimensions are typically measured for each container or monitored by a random sampling of a batch of containers.

Some factors, such as homogeneity and matrix effects, are specific to certain sample types and methods. For instance, high concentration Pu samples measured by KEDG should be performed as quickly as possible due to bubble formation and changing concentration from radiolysis effects. Samples containing suspended particles such as high active liquid waste need homogenization and correction factors, as the XRF calibrations are typically made with clean solutions. The XRF calibrations are also typically made with pure uranium or pure plutonium solutions, and mixed samples may need correction factors to account for attenuations of both the interrogating and fluorescent X rays. Similarly, hybrid-XRF calibrations are

typically made with mixed solutions containing no fission products. When present in dissolver solutions, fission products can change the background subtraction analysis and induce additional fluorescence not present in the calibration measurements. Corrective measures such as subtracting an additional passive spectrum measurement without the generator X rays or performing improved background and peak fitting algorithms may be employed.

For uranium assay using KEDG and HKED for the typical three replicate measurements (each of counting time between 1000 s and 3000 s), the ITV values are only valid for concentration levels above 150 g U per liter. When using the HKED technique for dissolved MOX pellets and powders, the uncertainties are typically higher than the ITV values. This is due to lower U/Pu ratios and lower uranium concentrations compared to dissolver solutions. Elemental concentrations below 1 g per liter can be measured by XRF, though with longer counting times and uncertainties larger than the ITV values.

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] H. Ottmar and H. Eberle, "The Hybrid K-Edge/K-XRF Densitometer: Principles – Design –Performance," Report KfK 4590, Karlsruhe, 1991.

Prepared by: Dante Nakazawa

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Method/measurement system (including software): The measurements are performed with the Total Evaporation-Thermal Ionization Mass Spectrometry method described for Table 5a and 6a using Multi-Collector Thermal Ionization Mass spectrometer.

Application: Measurement of plutonium and uranium mass fraction in 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.)

Isotope dilution mass spectrometry^[1] (IDMS) has been applied as a reliable analytical technique for accountancy measurements of uranium and plutonium contents in dissolved fuel when high accuracy is needed. Reference materials well characterized for their isotopic composition and their isotope content of uranium and plutonium called large-sized dried spikes (LSD) are used. Such spikes preferentially contain a high enrichment of an isotope that is not the main isotope of the element being measured in the sample. Typically, highly enriched ^{235}U and ^{239}Pu and certified reference metals with low uncertainty are used as starting materials for the preparation of LSD spikes. In addition, to avoid dilution steps for dissolver solutions in reprocessing plants these spikes contain milligram rather than microgram quantities of nuclear material in the dried form, often for stability and integrity covered with an organic material^[2]. Test samples are added to LSD spike vials^[3,4,5], dissolved and mixed to assume complete equilibration of spike with the analyte. Aliquots of the final solution are diluted and subjected to chemical separation^[6] and finally measured by Total Evaporation Thermal Ionization Mass Spectrometry TE-TIMS^[7]. With the isotopic composition of the test sample, the isotopic concentrations of the LSD spikes, weights of the sample and spike weight, the mass fraction of uranium and plutonium in the sample can be calculated^[3, 4, 5].

The key measurement steps and their purposes are outlined below:

- Test samples are typically dissolver solutions but also dissolved solid samples can be used.
- One aliquot has to be used to characterize the isotopic composition of the test sample.
- Another aliquot of the test sample is added to LSD spike vial by weighing. The mixture is heated for several hours to be assure that the LSD spike is dissolved, and aliquoted for further analysis.
- Uranium-plutonium mixtures of pure sample and sample-spike mixtures have to be separated and isolated, to perform U and Pu measurement by TE-TIMS. Therefore, the test samples are loaded onto evaporation filaments (Re or W) and to measure isotope amount ratios of U and Pu. For details see narrative of TE-TIMS and^[7].
- The mass fraction of U or/and Pu in the sample can be calculated using the isotopic composition of the test sample, the isotopic composition of the mixture and the isotopic composition and mass of the LSD spike and the test sample^[1].
- For quality assurance purposes suitable certified or well characterized laboratory reference materials are used as quality control samples.

Factors affecting the method performance
The primary factors impacting IDMS measurement precision and bias are: - Accurate measurement of mass quantity values when preparing test samples for measurement; - Precise determination of the isotopic composition of the test samples; - Use of well certified reference material or well characterized laboratory reference material (LSD); - Precise determination of the isotopic composition of the mixture; - Ensuring measurement control using traceable, uranium and plutonium quality-control reference materials; As direct use of the dissolver samples is possible, dilution steps can be avoided prior to mix it with the spike material, which results in lower uncertainties compared to the use of small spikes.
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] Quemet, Alexandre; Hubert, Amélie; Gourgiotis, Alkiviadis; Sanchez Hernandez, Ana Maria; Crozet, Marielle; Bailly, Guillaume; Dobney, Andrew; Duhamel, Georges ; Hiess, Joe; Repinc, Urška; Mialle, Sébastien; Boulet, Béatrice; Escoubé, Raphaëlle; Bouvier-Capely, C.; Pointurier, Fabien; Picart, Sébastien, An Isotope Dilution Mass spectrometry overview: tips and applications for the measurement of radionuclides. Journal of Analytical Atomic Spectrometry - JA-CRV-01-2024-000029.R1 [2] Toth K, Jakopič R, Bujak R, Bauwens J, Hennessy C, Kehoe F, Jakobsson U, Richter S, Aregbe Y, Preparation and Certification of Large-Size Dried (LSD) Spike: IRMM-1027v, EUR 30759 EN, 2021. http://dx.doi.org/10.2760/59260 [3] Rožle Jakopič, Kalman Toth, Jeroen Bauwens, Renata Buják, Carmel Hennessy, Frances Kehoe, Ulf Jakobsson, Stephan Richter, Yetunde Aregbe, 30 years of IRMM-1027 reference materials for fissile material accountancy and control: development, production and characterization. Journal of Radioanalytical and Nuclear Chemistry 330:333–345, 2021. [4] P. van Belle, E. Zuleger and L. Duinslaeger, An improved self-checking weighing practice and a method for contamination detection for use in IDMS nuclear material assay, Proceedings of the 49th INMM Annual Meeting, Tennessee, p 683-691, 2008. [5] Jakopič, R., Aregbe, Y., Richter, S., Zuleger, E., Mialle, S., Balsley, S. D., Repinc, U., Hiess, J.; <i>Verification Measurements of the IRMM-1027 and the IAEA Large-Sized Dried (LSD) Spikes</i>; J Radioanalytical and Nuclear Chemistry 311:1781-1791, 2017. [6] Morgenstern, A., Apostolidis, C., Carlos-Marquez, R., Mayer, K., Molinet, R.; <i>Single-column extraction chromatographic separation of U, Pu, Np and Am</i>; Radiochimica, vol. 90, p. 81, 2002.

[7] M. Romkowski, S. Franzini, L. Koch, Mass-Spectrometric analysis of sub-nanocurie samples of Uranium and Plutonium, in: Proceedings of the 8th Annual ESARDA Symposium, 1987, pp. 111-113.

Prepared by: Helene Schorle

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Method/measurement system (including software): The measurements are performed with the Total Evaporation -Thermal Ionization Mass Spectrometry method described for Table 5a and 6a.

Application: Measurement of plutonium and uranium mass fraction in 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
Isotope Dilution mass spectrometry using Thermal Ionization Mass Spectrometry (ID-TIMS) has been widely applied to analysis of safeguards nuclear material samples due to its high achievable precision and accuracy for isotope ratio measurements of uranium and plutonium. In most cases, sample dissolution procedures need to be applied to prepare a diluted test solution of a concentration, that is suitable for further analysis ^[1,2]. Isotope amount ratio measurement often needs to be performed on separate sample aliquots to determine the isotopic composition of the sample and chose the suitable spike isotope to use for isotope dilution analysis. As the mass fraction of the element (concentration of U or Pu) in the sample is unknown, aliquots of prepared sample solution are taken to be mixed with weighed amount of spike solution, that has well characterized isotope abundances and spike isotope concentration. As spike materials used often contain mg- to µg-amounts of elements, the naming of small size spikes was introduced. After the sample-spike mixture (blend) is equilibrated, losses of analyte do not affect the accuracy of the procedure. Therefore, blends can be subjected to extended sample preparation steps, to remove the matrix and isolate analytes of interests ^[3,4]. Analyte isolation steps for sample and blend aliquots are often mandatory to assure that Total Evaporation (TE) TIMS measurements remain largely unaffected by the sample matrix. The key measurement steps and their purposes are outlined below: — Weighed amount of the sample is dissolved to prepare a homogenous solution for further analysis. — Aliquots are taken to be able to determine the isotopic composition of the sample. — Weighed amount of either a commercially available certified spike material containing enriched spike isotope with suitable analyte concentration, or a well-characterized working reference material are added to separate aliquots of the test sample. Spikes are chosen to preferably contain high abundance of an isotope that is not present in a sample. Most commonly liquid spikes contain ²³⁵U, ²³³U and ²⁴⁰Pu, ²⁴²Pu (or even ²⁴⁴Pu) isotopes in high abundance, and are commonly applied in IDMS analysis of nuclear materials using small size spikes. — Complete equilibration of the sample-spike mixture. — Both un-spiked and spiked aliquots have to be chromatographically separated, to collect the U and Pu analytes separately and remove ²⁴¹Am ^[3,4]. For TE-TIMS measurements ^[5,6], small fractions of processed sample aliquots are loaded onto evaporation filaments (Re or W) for isotopic amount ratio measurements. — Using the isotopic composition of the test sample, blend and the certified value of the spike, the amount of test sample and the amount of the spike added to the test sample, the mass fraction of the element can be calculated. — Suitable certified or well characterized laboratory reference materials are used as quality control samples, for measurement, processes control and contamination control.

Factors affecting the method performance
The main sources impacting ID-TIMS method precision and bias are: - Weighing uncertainties (buoyancy, electrostatic charge, moisture content, stability of balances used) - Isotope ratio measurements of the sample and the blend (interferences, mass discrimination effects, contamination, abundance sensitivity) - Incomplete digestion, incomplete equilibration of sample-spike mixture, presence of interferences influencing mass spectrometry measurements or incomplete isolation of the analyte causing isobaric interferences, contamination effects. - Uncertainties of certified reference materials or well characterized laboratory reference materials, used as small-size spikes or measurement standards.
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] De Bièvre P, (1993) Isotope dilution mass spectrometry as a primary method of analysis. Anal Proc 30:328–333. [2] Sánchez Hernández AM, Andor C, Buda R, Commin L, d'Amati F, Horta Domenech J, Morel S, Nicholl A, Nourry C, Suurkuusk G, Vargas Zuñiga M, Wojnowski D, Zuleger E (2019) Optimising the use of reference materials for destructive analysis in nuclear safeguards. In: Proceedings of 41st ESARDA symposium, 188-199, 10.2760/159550. [3] Morgenstern A, Apostolidis C, Carlos-Marquez R, Mayer K, Molinet R, (2002) Single-column extraction chromatographic separation of U, Pu, Np and Am; Radiochimica, vol. 90, p. 81. [4] DMRC/CETAMA/NT/DO/2020/11/A (2020) Méthode CETAMA 397: Purification par chromatographie de U et de Pu en amount des analyses par Spectrométrie de Masse », Sous-groupe « Méthode » du GT03 « Analyses des actinides », diffusée le 28/07/2020. [5] Romkowski M, Franzini S, Koch L, (1987) Mass-Spectrometric analysis of subnanocurie samples of Uranium and Plutonium, in: Proceedings of the 8th Annual ESARDA Symposium, pp. 111-113, London. [6] C1672–17: Standard test method for determination of uranium and plutonium isotopic composition or concentration by total evaporation method using a thermal ionization mass spectrometer, ASTM International.

Prepared by: Ana Maria Sanchez Hernandez

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