INTERNATIONAL STANDARD

ISO 8299

Third edition
2019-01

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

Technologie du combustible nucléaire — Détermination de la teneur isotopique et des concentrations en matériaux nucléaires de l'uranium et du plutonium dans une solution d'acide nitrique par spectrométrie de masse à thermoionisation

Reference number
ISO 8299:2019(E)

ISO copyright office
CP 401 • Ch. de Blandonnet 8
CH-1214 Vernier, Geneva
Phone: +41 22 749 01 11
Fax: +41 22 749 09 47
Email: copyright@iso.org
Website: www.iso.org

Published in Switzerland

Contents

Page

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see www.iso.org/iso/foreword.html.

This document was prepared by ISO/TC 85, *Nuclear energy, nuclear technologies, and radiological protection,* Subcommittee SC 5, *Nuclear installations, processes and technologies*.

This third edition cancels and replaces the second edition (ISO 8299:2005), which has been technically revised.

The main changes compared to the previous edition are as follows:

— the procedure for the preparation of resin used for separation and purification of the samples has been added in 5.3;

— sample preparation procedure from pellet, powder and other material forms to the solution has been added in 8.1;

— uncertainty of the measurement is considered in Clause 15 instead of repeatability and accuracy.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

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

1 Scope

This document specifies a method for the determination of the isotopic and elemental uranium and plutonium concentrations of nuclear materials in nitric acid solutions by thermal-ionization mass spectrometry.

The method applies to uranium and plutonium isotope composition and concentration measurement of irradiated Magnox and light water reactor fuels (boiling water reactor or pressurized water reactor), in final products at spent-fuel reprocessing plants, and in feed and products of MOX and uranium fuel fabrication. The method is applicable to other fuels, but the chemical separation and spike solution are, if necessary, adapted to suit each type of fuel.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 10980, *Validation of the strength of reference solutions used for measuring concentrations*

3 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at http://www.electropedia.org/

4 Principle

The described method is based on isotope ratio measurements by thermal ionization mass spectrometry (TIMS). TIMS analysis requires isotope separation of different elements that have the same or similar masses as an isotope of the element being measured, such as ^{238}U and ^{241}Am influences ^{238}Pu and ^{241}Pu. Separation method for Pu and U using columns purifications are described in Clause 8. Other separation methods may be used provided that they lead to a separation of similar quality. Column extraction chromatography described in ISO 15366 (all parts) is an example of a suitable alternative.

The described method consists of two separate TIMS measurements:

a) Isotopic measurement

One measurement is made to determine the isotopic composition of the element in the sample. The ^{238}Pu isotope abundance is determined by combining mass spectrometry following the present method and alpha spectrometry as described in ISO 11483, if the interference of the isobar ^{238}U is not eliminated by chemical separation.

b) Element concentration measurement

A second measurement is made on a sample and a spike mixture consisting of an artificially enriched isotope of the element to be analysed. The sample element concentration is determined by calculating the difference of isotopic composition before and after the sample spike mixture. This method of measuring an element's concentration is called isotope dilution mass spectrometry (IDMS). The spiking can be made using a spike isotope that either is present, only minimally present, or absent in the non-spiked sample. The use of ^{233}U or ^{244}Pu spikes can eliminate the need for an isotope measurement in the non-spiked sample to determine uranium and plutonium concentration. Although it is normally of interest to measure both the isotopic composition and the element concentration. It is also more common to use a less expensive spike made from ^{239}Pu, ^{240}Pu, ^{242}Pu or ^{235}U. Accurate measurements made on the masses of the sample and spike in the mixture are required for the IDMS method. It is necessary that the isotopic composition and the concentration of the spike be known or measured accurately and has small uncertainties. The IDMS calculations are described in 12.6.

The IDMS method includes the following steps:

— sample dilution by mass if necessary;

— aliquoting and spike addition by mass;

— valency adjustment and isotope-exchange chemistry resulting in an isotopically equilibrated mixture;

— chemical purification/separation;

— sample loading and oxidation on filaments;

— isotope ratio measurements by TIMS on spiked and non-spiked fractions.

This procedure describes two methods of TIMS measurements:

— Total evaporation (TE), multi-Faraday collector measurements. This method consumes the whole sample. The ion beam of the element is totally collected. There are several advantages with this method. It allows precise measurements of small sample amounts, can easily calculate the mass discrimination factor and is easily adopted for automatic measurements. The TE method relies almost entirely on separate measurements of standards to calculate measurement uncertainty and precision.

— Bias correction method (conventional multi-Faraday collector measurements). In the bias correction method, the different isotopes are collected in a limited period of the sample evaporation. The data are collected in blocks, typically containing 10 to 20 sets (scans) of measurements. With the bias correction method, it is possible to calculate the precision of the ratio measurements within each block and between blocks and to use the internal precision data to assess measurement quality on a filament-by-filament basis.

5 Reference materials and reagents

The solutions listed below are prepared from analytical grade reagents unless it is specified otherwise.

5.1 Spikes and reference materials

Reference materials and reference solutions to confirm instrument performance and spikes for the isotope-dilution are shown below.

5.1.1 Uranium standard reference solution, prepared by one of the following methods:

— from natural uranium metal with an elemental concentration certified to 0,05 % (k = 2) or better, such as NBL-CRM-112A (ex NBS-960D), EC-101, CETAMA-MU-2;

— from other uranium metal, powder or pellet with an elemental concentration certified to 0,05 % (k = 2) or better, such as NBL-CRM-116-A (HEU metal), CRM-125-A(UO_2 pellet) and CRM-129 (U_3O_8 powder).

5.1.2 Plutonium standard reference solution, prepared by one of the following methods:

— plutonium metal with an elemental concentration certified to 0,05 % (k = 2) or better, such as NBL-CRM-126 or 126-A, EC-201, CETAMA-MP2 or NBS-949, with a ^{239}Pu isotopic abundance of 90 % or more, certified to 0,05 % (k = 2) or better; the same isotopic abundance requirements apply if ^{240}Pu, ^{242}Pu or ^{244}Pu is used as the spike isotope;

— certified plutonium standard solution enriched in ^{240}Pu, ^{242}Pu or ^{244}Pu isotope in case where 97 % enriched ^{239}Pu is used as a spike.

For both U and Pu standard reference solutions, other standard solutions traceable to these CRMs or verified by means of a laboratory intercomparison can also be used. See Annex A and ISO 10980 for the preparation and validation of these solutions.

5.1.3 Uranium spike, of certified isotopic and chemical composition, such as IRMM-040, IRMM-041, IRMM-042, NBL-CRM-111A (ex NBS-995), NBL-CRM-135 or NBL-CRM-U930D.

5.1.4 Plutonium spike, of certified isotopic and chemical composition, such as IRMM-041, IRMM-043, IRMM-044, IRMM-049, NBL-CRM-130 (^{242}Pu nitrate), NBL-CRM-131 (^{244}Pu nitrate, ex NBS-996), NBL-CRM-144 (mixture of ^{240}Pu, ^{242}Pu, and ^{244}Pu nitrates), NBL-CRM-126 (97 % enriched ^{239}Pu metal), NBL-CRM-126A (93 % enriched ^{239}Pu metal) or CETAMA-MP2 (97 % enriched ^{239}Pu metal).

5.1.5 Mixed uranium/plutonium spike solution, of certified isotopic and chemical composition, such as IRMM-046 (mixed $^{233}U/^{242}Pu$ spike). Also, nitrate solution containing 0,2 - 0,3 mg/g ^{235}U and 1 - 2 µg/g ^{242}Pu, prepared from reference materials such as NBL-CRM-135 or NBL-CRM-U930D and IRMM-049 or NBL-CRM-130.

5.1.6 Large-size dried (LSD) spike, of certified isotopic and chemical composition and dried, such as IRMM-1027 series, containing about 50 mg of 20 % enriched ^{235}U and 1 mg or 2 mg of 90 % or higher enriched ^{239}Pu.

5.1.7 Mixed uranium/plutonium spike, containing 0,2 - 0,3 mg/g of ^{235}U and 1 - 2 µg/g of ^{242}Pu in nitric acid, 7 mol/l, prepared from certified materials such as NBL-CRM-135 or NBL-CRM-U930-D, and IRMM-049 or NBL-CRM-130.

NOTE If certified spikes 5.1.3, 5.1.4, 5.1.5, 5.1.6 or 5.1.7 are not available, an in-house LSD spike, prepared by mixing uranium CRMs (such as NBL-CRM-112A (natural uranium) and/or NBL-CRM-116 or 116A) and plutonium CRM (NBL-CRM-126 or 126A or CETAMA-MP2) or by reference solutions (see 5.1.1 and 5.1.2) can also be applied.

The desired spikes can be prepared and standardized in accordance with ISO 10980. Suitable procedures are described in Annex A.

Hereafter, dried spike, solution spike and LSD spike are called spike.

5.1.8 Certified isotopic reference materials, covering the isotopic range of interest and certified to 0,1 % or better for the major isotope ratios, such as IRMM-290, NBL-CRM-128, NBL-CRM-136, NBL-CRM-137 (ex NBS-947), NBL-CRM-144, NBL-CRM-122, CEA-MIRF-01, AEAT-UK-Pu3 for plutonium, and IRMM-072, EC-NRM-199, NBL-CRM-010, NBL-CRM-030, NBL-CRM-117, NBL-CRM-U005A to NBL-CRM-U930-D, IRMM-183 to IRMM-187, CEA-MIRF-02, AEAT-UK-U2 for uranium.

5.2 Other chemical reagents

In principle, oxidation-reduction reagents should be prepared just prior to use.

5.2.1 Nitric acid solutions, $c(HNO_3)$ = 0,3 mol/l, 1 mol/l, 3 mol/l, 4 mol/l, 7 mol/l and other.

5.2.2 Ferrous sulfate, $c(FeSO_4)$ = 0,2 mol/l, in amidosulfuric acid, $c(NH_2SO_3H)$ = 0,2 mol/l, and sulfuric acid, $c(H_2SO_4)$ = 1 mol/l, freshly prepared.

5.2.3 Sodium nitrite, $c(NaNO_2)$ = 0,7 mol/l, freshly prepared.

5.2.4 Hydrogen peroxide solution, $c(H_2O_2)$ = 10 mol /l.

5.2.5 Silver nitrate, $c(AgNO_3)$ = 0,01 mol/l or, suitable for precipitation method.

5.2.6 Ascorbic acid, $c(C_6H_8O_6)$ = 0,1 mol/l in nitric acid 0,1 mol/l.

5.2.7 Hydrofluoric acid, $c(HF)$ = 0,001 mol/l, 0,05 mol/l or 27 mol/l. HF can mix with nitric acid solution before use.

5.2.8 Sodium hydroxide, c (NaOH) = 1 mol/l.

5.2.9 Ammonium sulfate, $c((NH_4)_2SO_4)$ = 0,5 mol/l.

5.3 Resin, applicable for separation/purification of Pu and U

5.3.1 General

Complete recovery (100 % separation) of plutonium or uranium is not required to perform IDMS. For mixed oxide samples, alpha spectrometry correction for ^{238}Pu isotopic composition is recommended. The following resins, or other materials and preparation procedures that obtain equivalent performance can also be applied.

5.3.2 Preparation of resin

5.3.2.1 Anion exchange resin[1)]

Resin in HCl condition should be reconditioned to nitric acid condition by one of the following procedures, or another which can lead to a separation of similar quality, and stored in distilled water.

a) Twice with the equivalent resin bed volumes of distilled water;

   twice with the equivalent resin bed volumes of 0,3 mol/l nitric acid (5.2.1);

   twice with the equivalent resin bed volumes of 4 mol/l nitric acid (5.2.1);

   with the equivalent resin bed volumes of 7 mol/l to 8 mol/l nitric acid (5.2.1) until a sample of the supernatant solution no longer yields a chloride precipitate after addition of silver nitrate (5.2.5) or confirm by Cl test paper.

b) With 20 times the resin bed volumes of 1 mol/l sodium hydroxide (5.2.8) and then wash by distilled water;

   2 times the resin bed volumes of 0,5 mol/l ammonium sulfate (5.2.9) and then wash by distilled water;

   10 times the resin bed volumes of 1,3 mol/l nitric acid (5.2.1) and then wash by distilled water;

1) Anion exchange resins AG1 or AG2 are examples of suitable products supplied by Bio-rad. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of the products named. Equivalent products may be used if they can be shown to lead to the same results.

3 times the resin bed volumes of 1 mol/l sodium hydroxide (5.2.8) and then wash by distilled water;

3 times the resin bed volumes of 1,3 mol/l nitric acid (5.2.1) and then wash by distilled water;

3 times the resin bed volumes of 1 mol/l sodium hydroxide (5.2.8) and then wash by distilled water;

3 times the resin bed volumes of 1,3 mol/l nitric acid (5.2.1) and then wash by distilled water.

c) Twice with the equivalent resin bed volumes of distilled water;

twice with the equivalent resin bed volumes of 1 mol/l sodium hydroxide (5.2.8);

with the equivalent resin bed volumes of distilled water;

with the equivalent resin bed volumes of 3 mol/l nitric acid (5.2.1) until a sample of the supernatant solution no longer yields a chloride precipitate after addition of silver nitrate (5.2.5) or confirm by Cl test paper.

5.3.2.2 Extraction separation resins[2)]

a) Conditioning: just before use, add approximate 3 mol/l nitric acid (5.2.1) for 3 to 4 times the resin volume to condition the resin into nitrate form. Other nitric acid concentration can be applied when enough efficiency is confirmed.

b) Storage: resins should be stored in a capped conical beaker and used within few days after conditioning. If rinsed with water after the above conditioning, it can be stored for a month.

WARNING — Resin should be rinsed with water after use for the separation, or after adjustment to nitric condition but unused. Storage of the resin for more than a few days in nitric acid can lead to explosive decomposition.

6 Apparatus

6.1 Shielded cells equipped with manipulators or tongs, for carrying out remotely the chemical preparations on highly radioactive solutions.

6.2 Glove boxes, for handling diluted spent fuel solutions or small plutonium samples free from fission products.

6.3 Analytical balance, with ± 0,1 mg uncertainty, installed in a shielded cell or a glove box.

6.4 Pipet and stand, with disposable pipette tips, installed in a shielded cell or a glove box.

6.5 Hot plate, in a glove box to fume diluted solutions or dissolving the spikes. Parallel use with vapour condensing system is recommended.

6.6 Disposable chromatographic columns, with approximate dimensions of 4 mm inner diameter, 45 mm height and a 10 ml capacity upper funnel. Columns of different dimensions may be used provided that the volumes of eluents are properly adapted.

6.7 Common laboratory ware, consisting of disposable plastic pipettes and containers, flasks, beakers and vials.

2) TEVA from Eichrom or Tristen are examples of suitable products available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of the products named. Equivalent products may be used if they can be shown to lead to the same results.

7 Apparatus for mass spectrometry

7.1 Mass spectrometers, designed for precise measurements of isotopic compositions having at least the following features.

7.1.1 General specifications

—	Mass range:	10 amu to 280 amu.
—	Resolution:	> 380 % at 5 % of the peak height; this resolution should be measured at the ^{235}U and ^{238}U masses.
—	Peak top flatness:	Less than 10^{-4} relative change (300 ppm by mass) in the signal for a change of ± 0,025 mass units with a Faraday cup detector; less than 10^{-3} relative change with an electron multiplier detector.
—	Abundance sensitivity:	< 5×10^{-6} at mass 237 relative to mass 238.
—	Sensitivity and transmission:	> 1 ion collected for 5 000 uranium atoms on the sample filament.

7.1.2 Thermal ionization source, consisting of a magazine (also called a turret) loaded with single, double or triple filament assemblies and covering shields. A stack of extraction lenses used to accelerate and focus the ion beam into the mass analyser.

7.1.3 Vacuum, with a capability of preferably less than 5×10^{-5} Pa in the ion source chamber and less than 5×10^{-6} Pa in the analyser. Specifications depend on the instrument.

7.1.4 Detector system, consisting of a Faraday multi-detector assembly with a minimum of six detectors that can analyse the ^{233}U, ^{234}U, ^{235}U, ^{236}U, ^{238}U and the ^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu, ^{242}Pu, ^{244}Pu. It is also recommended that the instrument be equipped with either a secondary electron multiplier or Daly detector. This detector can be used during automatic measurements with the TE method to focus the ion beams, and also for special cases where the sample is too small for normal analysis using the Faraday detectors. The detector is also important for making background measurements on filament blanks.

7.2 Filament preheating and **degassing device**, is recommended for cleaning filaments prior to loading sample if specifics are needed.

7.3 Filament preparation device, for loading the samples onto filaments and the reproducible drying and oxidation of the samples without cross-contamination.

8 Sample preparation

8.1 Subsampling and spiking

Spikes isotope composition should differ significantly from the samples in order to obtain enough isotope dilution effect for accurate IDMS measurement. The spike should be selected based on previous evaluation of suitable mixing ratio[7]. Other conditioning steps, acid concentrations and heating temperatures should also be optimized depending on the sample types. Examples of subsampling and spiking procedures are listed below.

Take the precautions needed to avoid evaporation of the sample solution during weighing and storage.

NOTE A longer dissolution time can be necessary if the spike contains some binding material(s) other than nitric acid.

8.1.1 Pellet or powder samples

a) If the sample is a pellet, crush before subsampling. Weigh to ± 0,1 mg in a tared flask or vial. Record the mass, m_1, of the sample.

b) Dissolve with 3 mol/l to 8 mol/l nitric acid (5.2.1). Add few drops of hydrofluoric acid (5.2.7) or dissolve with previously mixed nitric acid and hydrofluoric acid solution for Pu rich samples. Heat at approximately 100 °C on a hotplate.

c) Cool to room temperature and visually inspect if dissolution is complete. If undissolved sample remains, add 1 or 2 more drops of hydrofluoric acid (5.2.7) and heat. Dilute if necessary based on previous evaluation. Weigh and record the mass, m_2, to ± 0,1 mg.

d) Aliquot the sample solution to another tared bottle or vial, weighed to ± 0,1 mg, and record the mass, m'_1.

e) Add nitric acid to dilute if necessary. Measure and record the mass m'_2 of the solution and mix well. Calculate the dilution factor, F, in accordance with Formula (1):

$$F = \frac{m_2 \cdot m'_2}{m_1 \cdot m'_1} \tag{1}$$

f) Pipette the diluted sample, containing 0,1 mg to 0,3 mg of uranium and/or plutonium solution into a beaker or vial and use this aliquot to determine the isotopic composition of the uranium and/or plutonium.

g) Aliquot and weigh the spike and the above diluted sample solution to ± 0,1 mg in a tared beaker or flask. Record the masses, m_S and m_C, of the aliquots of the spike and the diluted sample solutions, respectively. Other spiking procedures are also applicable depending on spike type. One example is as follows.

If using dried spike, element amount, in the spike vial, m_S is known. Tare the spike vial, then add the above diluted sample solution based on previous evaluation and weigh m_C to ± 0,1 mg. Heat if necessary to dissolve dried spike. Complete transfer into cleaned and tared vial is recommended to recover all spike material. Use this mixture for the determination of the uranium and/or plutonium concentrations.

8.1.2 Concentrated nuclear fuel solution samples (such as reprocessing solution)

a) Weigh 1 ml to 2 ml of the concentrated nuclear fuel solution to ± 0,1 mg in a vial containing a LSD spike (5.1.6). Add 7 ml of 3 mol/l nitric acid (5.2.1). Record the mass of the sample aliquot and the mass of the spike solution introduced into the vial and dried to prepare the LSD spike.

b) Heat at 95 °C ± 5 °C to re-dissolve the dried spike quantitatively.

c) Let the solution of spiked sample cool to room temperature, mix well, pipette an aliquot of 0,2 ml to 0,5 ml and transfer it into another vial. Use this aliquot to determine the uranium and/or plutonium concentrations.

d) Pipette another sample, containing 0,2 to 0,3 mgPu of concentrated nuclear fuel solution into an empty vial, Use this aliquot for the determination of the isotopic compositions of uranium and/or plutonium.

8.1.3 Plutonium nitrate solution samples (such as product solution from a reprocessing plant)

a) Weigh at least 1 ml of the sample solution into a tared flask or vial. Record the mass of the sample to ± 0,1 mg.

b) Dilute if necessary and weigh and record its mass to ± 0,1 mg.

c) Aliquot sample solution into a vial containing a LSD spike (5.1.6) based on previous evaluation and weigh to ± 0,1 mg.

d) Dissolve the dried spike completely with 7 ml of 3 mol/l nitric acid (5.2.1) and heat at 95 °C ± 5 °C on a hotplate.

e) Cool to room temperature and visually inspect that dissolution is complete. Pipette an aliquot of 0,1 mg to 0,3 mg of plutonium into a beaker or vial. Use this aliquot to determine the plutonium concentration.

f) Pipette the diluted sample [8.1.3 b)], containing 0,1 mg to 0,3 mg of plutonium solution, into a beaker or vial and use this aliquot to determine the isotopic composition of the plutonium.

8.1.4 Dried nitrate samples

a) Dissolve the dried nitrate sample with 7 mol/l to 8 mol/l nitric acid (5.2.1), and heat at approximately 100 °C on a hotplate. Cool to room temperature and visually inspect to ensure that dissolution is complete.

b) Dilute if necessary, transfer completely into a cleaned and tared vial and weigh. Record the mass to ± 0,1 mg.

c) Follow same procedure from [8.1.1 d)] to [8.1.1 g)].

8.2 Chemical valency adjustment

If there is a risk of a Pu(IV) polymer being present in the sample or in the spike, it is advisable to add hydrofluoric acid (5.2.7) and reflux the sample aliquot, and to complex the excess fluoride with Al^{3+} before proceeding. If hydrofluoric acid (5.2.7) is used for dissolving the sample, it can be removed by drying the sample.

For samples that contain both plutonium and uranium, or plutonium containing ^{241}Am from ingrowth, separation/purification is required using one of the column purification options in 8.3. Valence adjustment should be performed before column purification to ensure that all plutonium isotopes are in the tetravalent state. One of the following procedures can be applied.

8.2.1 Valence adjustment with ferrous solution

a) Add 0,1 ml of ferrous solution (5.2.2) to each sample aliquot.

b) Mix and wait 15 min for complete reduction of plutonium to Pu(III) or Pu(IV).

c) Add 0,1 ml of sodium nitrite solution (5.2.3) and mix for 10 min to re-oxidize all plutonium to the tetravalent state.

Other condition is also applicable if same result can be obtained.

8.2.2 Valence adjustment with hydrogen peroxide

a) Add approximately 0,5 ml of 7 mol/l to 8 mol/l nitric acid (5.2.1) if the samples are dried and heat at 100 °C to dissolve.

b) Add 0,2 ml to 0,4 ml of hydrogen peroxide (5.2.4), cover with watch glass, mix and wait 15 min for a complete reduction of all plutonium to Pu(III) or Pu(IV).

c) Heat at 80 °C ± 5 °C for 90 min or 95 °C ± 5 °C for 5 to 10 min to re-oxidize all plutonium to the tetravalent state.

d) Remove the watch glass, then rinse and discard it (or thoroughly clean it before reusing).

8.3 Sample separation/purification

One of the following procedures can be applicable for sample separation and/or purification depending on the type of resin or sample. If the sample contains only uranium, separation/purification is not essential.

8.3.1 Ion exchange with anion-exchange resin

Example 1: Bio-rad AG-1x2

a) Fill a chromatographic column (6.6) with a 0,5 - 1 ml slurry of anion exchange resin (5.3.1.1), conditioned in nitric acid, 7 mol/l to 8 mol/l (5.2.1).

b) Transfer a sample aliquot onto the column.

c) Add 2,5 ml to 4 ml of nitric acid, 7 mol/l to 8 mol/l (5.2.1) several times i.e. 10 resin bed volumes, to the column to remove the fission products and the americium, and discard these effluents.

d) Continue the elution with 5 ml of nitric acid, 7 mol/l to 8 mol/l (5.2.1), or 2 ml of nitric acid, 3 mol/l to 4 mol/l (5.2.1), and collect this fraction for the uranium measurement.

e) Remove uranium tailings with 3 ml to 5 ml of nitric acid, 3 mol/l (5.2.1) and discard.

f) Elute the plutonium with another 5 ml of nitric acid, 0,2 mol/l to 0,3 mol/l (5.2.1), or 2 ml of nitric acid, 0,01 mol/l (5.2.1) and collect.

   Though this is enough to perform plutonium isotopic measurements, the following optional purification process can also be applied.

g) Adjust valence to tetravalent state (8.2) of the plutonium eluent [8.3.1 f)].

h) Transfer a sample onto the column filled with slurry of anion exchange resin [8.3.1 a)].

i) Remove uranium with 3 ml to 5 ml of nitric acid, 0,5 mol/l (5.2.1).

j) Elute the plutonium with 1,5 ml of ascorbic acid, (5.2.6) and collect the plutonium eluate for measurement.

k) Add concentrated nitric acid (5.2.1) and heat at 95 °C ± 1 °C until a glassy condition is achieved (just before dryness) to remove ascorbic acid (5.2.6).

Example 2: Bio-rad AG-1x8

a) Fill a chromatographic column (6.6) with a 0,5 - 1 ml slurry of anion exchange resin (5.3.1.1), conditioned in nitric acid, 7 mol/l to 8 mol/l (5.2.1).

b) Transfer a sample aliquot onto the column.

c) Add 3 ml of nitric acid, 7 mol/l to 8 mol/l (5.2.1) two times to the column to remove the fission products and americium, and discard these effluents.

d) Continue the elution with 3 ml of nitric acid, 7 mol/l to 8 mol/l (5.2.1) and collect this fraction for the uranium measurement.

e) Add 3 ml of nitric acid, 3,5 mol/l (5.2.1) four times to remove uranium tailings.

f) Add another 4 ml of nitric acid, 0,3 mol/l (5.2.1) containing 0,001 mol/l hydrofluoric acid (5.2.7) and collect the plutonium eluate for measurement.

g) Add concentrated nitric acid (5.2.1) and heat at 95 °C ± 1 °C until glassy condition (just before dryness) to remove ascorbic acid, (5.2.6).

If the sample contains only plutonium, discard the fission products as well as uranium eluate.

8.3.2 Purification with extraction separation resins (see 5.3.1.2)

a) Fill a chromatographic column (6.6) with 0,5 ml of solid phase extraction resin (5.3.1.2) and add nitric acid 3 mol/l (5.2.1) for 20 resin bed volumes.

b) Transfer a sample aliquot onto the column.

c) Add 1 ml of nitric acid, 0,5 mol/l (5.2.1) and collect this fraction for the uranium measurement.

d) Add another 0,5 ml of nitric acid, 0,5 mol/l (5.2.1) eight times to remove the fission products, americium and uranium tailing and discard these effluents.

e) Add 0,5 ml of nitric acid, 0,1 mol/l (5.2.1) containing ascorbic acid (5.2.6) three times and collect the plutonium eluate for measurement.

If the sample contains only plutonium, discard fission products as well as uranium elute.

8.4 Replicate treatments

It is recommended to repeat steps 8.1 to 8.3 to obtain duplicate (or more if necessary) separated non-spiked and spiked fractions of uranium and plutonium for reliable analysis.

9 Filaments preparation

9.1 Degassing of filaments

It is recommended to purify the filaments, before use by degassing in a vacuum chamber (7.2); this especially important for the ionization filaments. The amount of impurities remaining can be checked using the mass spectrometer by loading blank degassed filaments and heating to the normal operating temperature.

9.2 Sample loading

9.2.1 Normal sample loading

a) Evaporate all collected fractions of uranium and/or plutonium to dryness and re-dissolve with an appropriate amount of nitric acid, 1 mol/l.

b) Mount a sample filament on the filament preparation device (7.3). The sample in nitric solution is drop-loaded with a pipette onto the filament. The drop size should normally be as small as possible but with a sufficient amount of material for the measurement. A drop size in the range of 0,2 µl to 1,0 µl containing approximately 20 ng to 500 ng U or 5 ng to 200 ng Pu is favoured for a typical TE measurement. Equivalent or larger U or Pu amount in a drop is favoured for bias correction method.

c) Apply a small current, normally less than 1A through the filament to dry the sample solution. When the sample has dried, the current should slowly be increased to oxidize the sample. Dependent on the temperature, the sample can form different oxides on the filament. When using the TE method, this is of only small importance, but when using the bias correction method, the different oxides may cause different fractionation rates.

9.2.2 Graphite loading technique

A small amount of graphite is added on top of the sample after it has been drop-loaded onto the filament, which helps attach the sample to the filament. The graphite reduces the amount of oxides formed and decomposes the remaining nitrates. Typically there is also better stability of the ion beam with the graphite loading technique. In single filament measurements, one can also observe a better ionization efficiency. When using the normal multi-collector measurement technique, graphite loading is normally preferred. When using the TE technique, there is very little improvement with graphite loading.

9.2.3 Resin-bead loading on single filaments for Pu samples

The Pu can be absorbed onto an anion-exchange resin bead that can be fixed with a colloid solution into a boat-shaped single filament. The bead is often covered with an extra layer of graphite. This method is normally only applied for small Pu samples to improve the ionization efficiency.

9.3 Filament mounting (filament assemblies preparation)

Mount the loaded sample filaments and the ionization filaments on the magazine (turret). Check the alignment of each filament assembly and cover it with a clean cover shield. Check that each ionization filament is well aligned with the extraction cover shield slit.

Introduce the sample magazine (turret) into the ion source, close the source and evacuate to less than 5×10^{-4} Pa.

10 Instrument calibration

This clause lists and describes the most common calibrations that are made on TIMS instruments using multi-Faraday collector systems. The list does not cover all calibrations made for all types of TIMS analysis. When a secondary electron multiplier or a Daly detector is used in combination with a static Faraday detector system to measure one of the minor isotopes, it is necessary to cross-calibrate the detector amplification versus a Faraday detector.

If a variable multi-collector is used, it is also necessary to check the alignment of the different detectors.

10.1 Mass calibration

TIMS instruments require a calibration to be made between a known mass and the applied magnetic field to establish the mass/field relationship. It is recommended to perform a peak centering routine to finely adjustment the mass calibration for every measurement.

10.2 Gain calibration for Faraday multi-detectors

The electronic gains of the different detector channel amplifiers typically show small but significant differences. The difference in gain is normally measured by applying a calibration signal to the input of the different detector channels. From these measurements, the relative gain between each channel and a chosen reference channel can be calculated, to correct the signals measured during sample analysis. Commercial instruments normally have an automatic routine that measures the relative gain prior to the sample measurements.

10.3 Faraday detector calibration

One of the main limitations in the uncertainty of TIMS methods is the cross-calibration of the different Faraday detectors. The necessity of a Faraday detector calibration depends on the running frequency of the instrument and the type of samples (e.g. continuous measurement of samples with similar isotopic composition may cause memory effect and degrade the detector where high abundant isotopes are measured). Periodical calibration is recommended, also before measuring samples after moving the detectors, or when a bias in the result is identified.

Two methods for measuring the differences in response between Faraday detectors are described below. Prior to measuring the differences in response between detectors, a gain calibration should be performed (10.2).

a) Peak jumping: Switching a stable ion beam between a detector and a chosen reference detector can be used to determine the relative gain of the detector. This relative gain can be used in the same way as the measured electronic gain calibration to compensate for the difference in response.

b) Peak shifting: By performing bias correction method with a standard that allows for internal normalization (for example a $^{233}U/^{236}U$ spiked material). A set of measurements can be made using different cup configurations. From these high-precision measurements, one can calculate the different cup responses.

In both methods, it is important that an assessment of the precision and accuracy be made to establish the overall uncertainty of the calibration.

10.4 Mass discrimination calibration

Several methods can be used to assess the mass discrimination in bias correction method.

A common method is to use internationally accepted isotopic reference materials certified to 0,1 % or better for the ratio of the major isotopes. The following are examples of suitable reference materials: to calibrate the analyses of uranium against a certified mixture of ^{235}U and ^{238}U (e.g. NBL-CRM-U500), mixture of ^{233}U, ^{235}U and ^{238}U (e.g. IRMM072-1, IRMM074-1, EC-NRM-199), and plutonium against a certified mixture of ^{239}Pu and ^{240}Pu (e.g. NBL-CRM-l37, ex NBS-947), mixture of ^{239}Pu and ^{242}Pu (e.g. NBL-CRM-128), mixture of ^{239}Pu, ^{240}Pu and ^{242}Pu (e.g. IRMM-290), mixture of ^{240}Pu, ^{242}Pu and ^{244}Pu (e.g. NBL-CRM-144). Furthermore, the certified reference materials series IRMM-183 to IRMM-187 and the series IRMM-019-029[12] (to be converted from UF_6) is suitable for calibrating a mass spectrometer for isotope ratio measurements of uranium.

As an example, n samples of the certified reference material are treated, prepared and measured in exactly the same way as unknown samples. A calculation is made of the arithmetic mean, $R_{measured}$, of the n measurements of the isotopic ratio with the mass difference between denominator and numerator equal to Δm, atomic mass difference. This mean is compared to the certified value $R_{certified}$ of the isotope ratio, and a fractionation factor, K_f, per mass unit is calculated in accordance with Formula (2):

$$K_f = \left(\frac{R_{measured} - R_{certified}}{R_{certified}} \right) \Big/ \Delta m \qquad (2)$$

The calibration is repeated whenever a significant drift is detected in the course of quality control measurements, according to Clause 14, or suspected, for example after changing a major component of the instrument or the method of preparation of the samples.

EXAMPLE A set of measurements on the $^{235}U/^{238}U$ ratio on the NBL-U500 standard has the mean of 1,001. The certified ratio is 0,999 7 and the mass difference is 3.

$K_f = (1{,}001 - 0{,}999\ 7)/0{,}999\ 7/3 = 0{,}000\ 433\ 5$

11 Isotopic mass spectrometric measurements

This clause describes two methods of analysing the samples using static multi-collector measurements. Sequence may vary depending on measurement program by each instrument. It is recommended to perform duplicate measurement to increase reliability of measurement.

Prior to both types of measurements, the loaded turret shall be inserted into the instrument. A sufficient vacuum in the source housing, typically in the range of 5×10^{-5} Pa to 5×10^{-4} Pa shall be reached prior to the measurements. One should always use the same sample amount, the same time and collection schedules for the analyses of samples and reference materials, and for calibration measurements. Reference materials can be dispersed throughout the turret to bracket the samples and monitor any variation in performance.

11.1 Total evaporation measurements using a single or double filament assembly and a multi-Faraday collector system

a) Measure the baselines.

b) Increase the sample filament current stepwise to yield a U^+ or Pu^+ signal that is just large enough to focus the pilot beam.

c) Centre the peak with the ion beam in a reference detector.

d) The current is ramped until a predetermined Faraday cup signal is obtained. Start the measurement and continue until all of the sample material has been consumed.

e) When the measurement is completed, the isotopic ratios are calculated by dividing the integrated signal of each isotope by the integrated signal of one of the isotopes, typically the major isotope in the sample. A correction should be applied for the electronic gain. The total signal collected should be in the same range as the standard measurements performed.

11.2 Bias correction method using a double filament assembly and a multi-Faraday collector system

a) Slowly heat up the ionization filament to approximately 2 000 °C or to obtain 200 mV to 400 mV of ^{187}Re signal on the Faraday cup.

b) It is recommended to monitor the $^{187}Re^+$ ion to check that there is a good and stable ion beam (It is assumed that the ionization filament is made of Re).

c) Increase the sample filament current stepwise to yield a U^+ or Pu^+ signal between 10^{-12} A and 8×10^{-11} A or equivalent voltage on Faraday cup. Focus and optimize the voltage settings on the different lenses of the ion source. If monitored by voltage, it will be 8 V to 10 V signal using a 10^{11} ohm resistor on the amplifier but it depends on instrument.

d) Measure baseline and centre the peak with the ion beam in a reference detector.

e) Start the measurement at a pre-set time equal to the time used for measuring the fractionation correction. The data collection is typically made in blocks of 10 scans. Normally a minimum of 10 blocks of data are collected. There can be additional baseline and peak-centre measurements made between the different blocks of data.

f) When the measurement is completed, the data should be corrected for fractionation and electronic gain. The mean, standard deviation of the mean and the weighted standard deviation should be calculated for each isotopic ratio. The weighted mean is normally preferred if the signal has decreased during the measurement.

12 Calculation of the results

12.1 Calculation of ion current intensities

Ion current intensities are obtained by application of appropriate baseline corrections, scale, amplifier gain and cup efficiency factors. Use 3, 4, 5, 6, 8, 8', 9, 0, 1, 2, and 4' to designate the isotopes ^{233}U, ^{234}U, ^{235}U, ^{236}U, ^{238}U, ^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu, ^{242}Pu and ^{244}Pu, respectively.

When conventional mass spectrometry measurements are made, these are normally performed in blocks of 10 scans to 15 scans measuring all isotopes. For each scan k, a ratio $R_i(k)$ is calculated for each isotope j versus a reference isotope. Block means and standard deviations [12.2 a)] for each ratio should be calculated. As an end result, the weighted mean of all block means [12.2 b)] and the weighted standard deviation of the mean are recommended.

For a total evaporation measurement, the ratios are calculated as the integral of the measured signal, $I_j(k)$, for isotope j divided by the integral of reference signal, $I_r(k)$, for isotope r. In total evaporation measurements, there are no block means calculated.

12.2 Calculation of mean, weighted mean and standard deviation on a set of ratios x_i, (i = 1…N)

a) Mean, standard deviation and standard deviation of the mean:

$$\bar{x} = \frac{1}{N}\sum_{i=1}^{N} x_i \qquad \sigma = \sqrt{\frac{1}{N-1}\sum_{i=1}^{N}\left(x_i - \bar{x}\right)^2} \qquad \sigma_{\text{mean}} = \frac{\sigma}{\sqrt{N}} \tag{3}$$

b) Weighted mean, standard deviation of weighted mean:

$$<\bar{x}> = \frac{\sum_{k=1}^{N} W_k \cdot x_k}{\sum_{k=1}^{N} W_k} \qquad W_k = \frac{1}{\sigma_k^2} \qquad <\sigma> = \sqrt{\frac{1}{\sum_{k=1}^{N} W_k}} \tag{4}$$

12.3 Mass discrimination correction

For the model described in 10.4, an isotopic ratio corrected for fractionation effects R' can be calculated as follows:

$$R' = \frac{R}{\left[1 + \left(m_{\text{D}} - m_{\text{N}}\right) \times K_{\text{f}}\right]} \tag{5}$$

where

K_{f} is the fractionation factor obtained through calibration step (10.4);

m_{N} and m_{D} are the mass numbers for the numerator and denominator of the measured ratio R.

EXAMPLE Assume that a measured ratio of $^{235}U/^{238}U$ equals 1,0. Assume also that K_{f} has been calculated as described in the example in 10.4 as 0,000 433 5. This would give a corrected ratio of

R' = 1,0 / (1 + (238 − 235) × 0,000 433 5) = 0,998 7

12.4 Calculation of the atomic percent abundance A_i

Each of the n isotopes has an atomic abundance, A_i:

$$A_i = \frac{100 R_{ij}}{\sum_{i=1}^{n} R_{ij}} \tag{6}$$

R_{ij} is the isotope ratio for isotope i versus the reference isotope j.

EXAMPLE Assume that a measurement of a uranium sample results in two ratios, 235/238 = 0,999 7, 234/238 = 0,010 4 (and 238/238 = 1). The abundance of 234 = 100 × 0,010 4 / (0,010 4 + 0,999 7 + 1) = 0,52 % in the same way the 235 = 100 × 0,999 7 / (0,010 4 + 0,999 7 + 1) = 49,73 % and finally the 238 = 100 × 1 / (0,010 4 + 0,999 7 + 1) = 49,75 %.

12.5 Calculation of the isotopic mass percent W_j

The conversion from atomic percent is given by

$$W_j = \frac{A_j \times M_j}{\sum_{i=1}^{n}(A_i \times M_i)} \tag{7}$$

where M_i is the atomic mass of the isotope i, with Reference [8]: uncertainty estimates are expanded by a factor of six.

M_3 (^{233}U) = (233,039 64 ± 0,000 02) u;

M_4 (^{234}U) = (234,040 95 ± 0,000 02) u;

M_5 (^{235}U) = (235,043 93 ± 0,000 02) u;

M_6 (^{236}U) = (236,045 57 ± 0,000 02) u;

M_8 (^{238}U) = (238,050 79 ± 0,000 02) u;

M_8' (^{238}Pu) = (238,049 56 ± 0,000 02) u;

M_9 (^{239}Pu) = (239,052 16 ± 0,000 02) u;

M_0 (^{240}Pu) = (240,053 81 ± 0,000 02) u;

M_1 (^{241}Pu) = (241,056 85 ± 0,000 02) u;

M_2 (^{242}Pu) = (242,058 74 ± 0,000 02) u;

M_4' (^{244}Pu) = (244,064 21 ± 0,000 04) u.

u: stands for unified atomic mass unit

If other atomic masses are used, specify the source of value used for calculation in the report.

12.6 Calculation of concentration

The U and Pu concentrations in the sample are given by the following formulae:

$$C_U = C_{U,S} \cdot \frac{(G_u)_S}{(G_8)_C} \cdot \frac{M_8}{M_u} \cdot \frac{m_S}{m_C} \cdot \frac{1 - \frac{(R'_{u8})_M}{(R'_{u8})_S}}{(R'_{u8})_M - (R'_{u8})_C} \cdot F \tag{8}$$

$$C_{Pu} = C_{Pu,S} \cdot \frac{(G_p)_S}{(G_9)_C} \cdot \frac{M_9}{M_p} \cdot \frac{m_S}{m_C} \cdot \frac{1 - \frac{(R'_{p9})_M}{(R'_{p9})_S}}{(R'_{p9})_M - (R'_{p9})_C} \cdot F \tag{9}$$

where

C_U and C_{Pu} are the concentrations, expressed in grams per kilogram, of total U and Pu in the sample solutions. The concentration in grams per litre is calculated using the accurately measured density of the original sample solution;

$C_{U,S}$ and $C_{Pu,S}$ are the concentrations, expressed in grams per kilogram, of total U and Pu in the spike solution;

u and p are the spike isotopes in the uranium and plutonium spikes, respectively;

$(G_u)_S$ and $(G_8)_C$ are the isotopic abundances, expressed in mass percent, of the uranium spike isotope u in the spike solution, and ^{238}U in the sample, respectively;

$(G_p)_S$ and $(G_9)_C$ are the isotopic abundances, expressed in mass percent, of the plutonium spike isotope p in the spike solution and ^{239}Pu in the sample, respectively;

M_u, M_8, M_p and M_9	are the atomic masses of the uranium spike isotope u, ^{238}U and plutonium spike isotope p, ^{239}Pu, as given in 12.5;
m_C and m_S	are the masses of the sample solution and of the spike solution, respectively, used to prepare the spiked mixture;
F	is the dilution factor on a mass basis in accordance with Formula (1);
$(R'_{ij})_M$, $(R'_{ij})_S$ and $(R'_{ij})_C$	are the isotope ratios for isotope i versus reference isotope j, corrected for mass discrimination as specified in 12.3, in the spiked mixture, in the spike solution and in the sample, respectively.

12.7 Isotope decay correction

The report of the analyses of plutonium-containing solutions or mixed U/Pu samples shall include the date of the mass spectrometric measurements in order to apply a decay correction, if necessary. The element concentration and isotopic composition of plutonium shall be corrected for the decay of ^{241}Pu and other Pu isotopes, while the element concentration and isotopic composition of uranium shall be corrected for the in-growth of uranium isotopes. The analyses of reference materials also require appropriate decay corrections. The recommended values of the relevant half-lives are listed in Table 1, see Reference [9]: ± one standard deviations. For the ^{241}Pu, value refers to Reference [10].

Table 1 — Recommended values of the relevant half-lives

Isotope	Half-life values (in years) and uncertainties (k = 1)
^{238}Pu	87,7 ± 0,1
^{239}Pu	24 110 ± 30
^{240}Pu	6 561 ± 7
^{241}Pu	14,325 ± 0,012[10]
^{242}Pu	(3,75 ± 0,02) × 10^5
^{244}Pu	(8,0 ± 0,09) × 10^7

If other half-lives are used, specify the source of value used for calculation in the report.

13 Blanks

To monitor the process, blank measurement in addition to the sample measurement is recommended. The following are different types of blank measurements:

a) chemical blanks to monitor contamination coming from reagents used in the sample process;

b) room, glove-box and fume-hood blanks to monitor the cleanliness of the surrounding of the chemical preparation;

c) process, blank spike or chemical run through dissolution and separation process with samples;

d) filament blanks to monitor the cleanliness of the mass spectrometer ion source and the filaments.

14 Quality control

a) Verify that the calibration of the instrument remains stable and accurate over the range of isotopes and isotope ratios to be analysed. For this purpose, measure samples of certified isotopic reference materials of different isotopic composition in the same way the unknown samples are currently analysed.

b) Verify that the method of analysis gives accurate results by treating, preparing and regularly measuring samples of certified elemental and isotopic compositions in the same way the unknown samples are being analysed.

c) Calculate the results of the analyses of the reference materials as described in Clause 12. Corrective actions should be undertaken if statistically significant differences are detected between the measured and the certified compositions.

15 Measurement uncertainty

Laboratories should calculate measurement uncertainties for elemental assay and isotope ratios in accordance with an established and recognized methodology. Compliance with ISO/IEC Guide 98-3 is recommended.

The expected uncertainty of the plutonium and uranium elemental assay and isotopic analysis are listed in Tables 2 to 4 based on Reference [11] which gives International target values (ITV). The ITV (%rel.) are combined standard uncertainties calculated by propagating the random [u(r)] and the systematic [u(s)] uncertainty components.

15.1 Elemental assay

The expected uncertainty of the plutonium and uranium elemental assay and isotopic analysis are listed in Table 2.

Table 2 — Expected uncertainty of elemental assay by IDMS[11]

Element	Measurement condition	Uncertainty component		ITV
		u(r)	u(s)	(%rel.)
Pu assay	Glove box conditions	0,15 [a]	0,1 [a]	0,18
		0,2 [b]	0,2 [b]	0,28
	Hot cell conditions	0,2 [a]	0,2 [a]	0,28
		0,3 [b]	0,3 [b]	0,42
U assay	Glove box conditions	0,15 [a]	0,1 [a]	0,18
		0,2 [b]	0,2 [b]	0,28
	Hot cell conditions	0,2 [a]	0,2 [a]	0,28
		0,3 [b]	0,3 [b]	0,42

[a] Under conditions of sufficiently different isotopic compositions of spike and sample and near optimum sample to spike ratio, using large size spikes (such as LSD).

[b] Under conditions of sufficiently different isotopic compositions of spike and sample and near optimum sample to spike ratio, using small size spikes.

15.2 Isotopic analysis

The expected uncertainty of the isotopic ratio analyses are listed in Tables 3 and 4[11].

Table 3 — Expected uncertainty of plutonium isotope assay of Pu and Pu/U by TIMS[11]

Isotope ratio		Typical value for ratio (× 100)	Uncertainty component	
			u(r)	u(s)
High burn up Pu	$^{238}Pu/^{239}Pu$	1,7	1,5	1,0
	$^{240}Pu/^{239}Pu$	43	0,1	0,05
	$^{241}Pu/^{239}Pu$	13	0,2	0,2
	$^{242}Pu/^{239}Pu$	8	0,2	0,3

Table 3 *(continued)*

Isotope ratio		Typical value for ratio (× 100)	Uncertainty component	
			u(r)	u(s)
Low burn up Pu	$^{238}Pu/^{239}Pu$	0,02	10	10
	$^{240}Pu/^{239}Pu$	6	0,15	0,1
	$^{241}Pu/^{239}Pu$	0,2	1	1
	$^{242}Pu/^{239}Pu$	0,05	2	2

$^{238}Pu/^{239}Pu$ by alpha spectrometry/mass spectrometry combination.

Table 4 — Expected uncertainty of ^{235}U abundance by TIMS[11]

	Material	Uncertainty component		ITV
		u(r)	u(s)	(%rel.)
^{235}U	DU (<0,3 % ^{235}U)	0,5	0,5	0,7
	U (0,3 % < ^{235}U < 1 %)	0,2	0,2	0,28
	LEU (1 % < ^{235}U < 20 %)	0,1	0,1	0,14
	HEU (>20 % ^{235}U)	0,05	0,05	0,07

16 Interferences

Ions with an atomic mass of 233, 234, 235, 236 or 238 cause interference in the analysis of uranium if they have not been removed, or if they have been introduced as impurities during chemical treatment; potassium, for example, emits hexa-atomic ions of mass 234 or 236.

Ions with atomic mass 238 (particularly ^{238}U), 239, 240, 241 or 242 cause interference in the analysis of plutonium if they have not been completely removed during chemical treatment; it is necessary to remove the ^{241}Am formed from ^{241}Pu before Pu isotopic analysis is carried out.

In addition to the isobaric interferences, another class of interfering elements can alter the fractionation patterns. For example, thorium, zirconium, hafnium, rare earth metals, aluminium and titanium can increase the temperature required to volatilize and ionize uranium and plutonium. Iron, vanadium, copper and alkali metals can lower the temperature at which the volatilization of uranium and plutonium occurs. Carbon is said to disturb more than alkalis, Zr or Fe, when the measurements are done with the method of total evaporation. The degree to which such alterations occur depends on the technique selected for loading the sample onto the filament as well as the concentration of the interfering elements. It is recommended to test for these effects by the addition of known amounts of the various elements to pure standard solutions of uranium and plutonium and to ensure that these impurities are reduced below the level at which these effects occur.

Annex A
(normative)

Preparation and standardization of spike solutions

A.1 General

This annex describes a procedure to prepare and standardize or validate U and/or Pu spikes suitable for the isotope dilution analysis of the uranium and plutonium concentrations in spent fuel solutions or other industrial materials.

A.2 Principle

Chemically-pure compounds of separated U or Pu isotopes are dissolved to prepare stock solutions of spikes in 3 mol/l to 7 mol/l nitric acid to obtain a concentration close to the uranium or plutonium concentration in the solution to be analysed.

Aliquots of the U and Pu spike stock solutions may be mixed to prepare diluted mixed spike solutions.

Diluted spike solutions containing less than 1 g/l of spike isotope are standardized by isotope dilution mass spectrometry against standard solutions of certified chemical reference materials.

Large-size spikes containing 4 mg of spike isotope or more are standardized or validated preferably by titration or controlled-potential coulometry.

A.3 Standard solutions of certified chemical reference materials

A.3.1 Stock solution of uranium standard reference solution

Open a unit of a certified uranium metal standard such as those mentioned in 5.1.1, and clean it in ethanol.

Then rinse it with distilled water and etch it in 1 mol/l nitric acid until the surface of the metal takes a uniform and bright metallic shine.

Rinse rapidly with distilled water, then with ethanol and dry quickly in air at room temperature. Measure its net mass, m_3, in milligrams, to the nearest 0,1 mg immediately before the surface oxidizes again. (Note that air buoyancy correction of weighing is required.)

Transfer into a tarred conical flask.

Cap the flask with a reflux head and add enough 1 mol/l to 3 mol/l nitric acid solution to cover the metal and start a gentle dissolution.

As the dissolution ceases, add 7 mol/l nitric acid solution in small portions to maintain a gentle reaction.

When the dissolution is complete, dilute with distilled water and/or nitric acid to obtain the desired volume of a 3 mol/l nitric acid solution.

Let the solution cool to room temperature and transfer it to the balance room. When it has reached thermal equilibrium with the local temperature, measure the gross mass and calculate the net mass,