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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

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Foreword

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The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

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.

ISO 8299 was prepared by Technical Committee ISO/TC 85, *Nuclear energy*, Subcommittee SC 5, *Nuclear fuel technology*.

This second edition cancels and replaces the first edition (ISO 8299:1993). which has been technically revised.

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 method applies to the measurement of the isotopic composition and the concentration of uranium and plutonium in input solutions 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 referenced documents are indispensable for the application 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 10980:1995, *Validation of the strength of reference solutions used for measuring concentrations*

ISO 11483, *Preparation of plutonium sources and determination of $^{238}Pu/^{239}Pu$ isotope ratio by alpha spectrometry*

3 Principle

The described method is based on isotope ratio measurements by thermal ionization mass spectrometry (TIMS). TIMS analysis requires separation of the element to be analysed from all other elements. Two methods of separation for Pu and U using anion exchange columns are described in Clause 7. Other separation methods may be used provided that they lead to a separation of similar quality. Column extraction chromatography described in ISO 15366 is an example of a suitable alternative.

The described method consists of two separate TIMS measurements.

a) One measurement is made to determine the isotopic composition of the element. 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) A second measurement is made on a mixture of the sample and a spike consisting of an artificially enriched isotope of the element to be analysed. 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 in the sample or not. The use of ^{233}U or ^{244}Pu spikes eliminates the need for an isotopic measurement in the unspiked 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 however more common to use the less expensive ^{239}Pu, ^{240}Pu and ^{235}U spike solutions., Accurate measurements

made on the weights of the sample and spike that are mixed is required for the IDMS method. It is necessary that the isotopic composition and the concentration of the spike be known or measured accurately. The IDMS calculations are described in 11.6

The IDMS method includes the following steps:

— dilution by mass, if the dilution precedes the spiking;

— 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.

1) Total evaporation (TE), multi-Faraday collector measurements. This method consumes the whole sample. Each of the isotopic ion currents is collected from the beginning of the ion emission until it ceases. There are several advantages with this method and it allows for precise measurements of small sample amounts and is easily adopted for automatic measurements.

2) Conventional multi-Faraday collector measurements. In the conventional method, the ionization of the sample is optimized to yield a long-lasting ion beam of stable intensity. The data are collected in blocks, typically containing 10 sets (scans) of measurements. This method is mainly favoured when there is only one detector or when there is the possibility to normalize unknown ratios relative to a known isotopic ratio in the sample. In the case of nuclear samples, this is mainly the case when a double spike has been used, as for example a uranium $^{233}U/^{236}U$ spike. In this case, it is possible to analyse the sample more precisely than with the TE method. Otherwise, the TE method normally returns a better precision and accuracy. With the conventional method, it is possible to calculate the internal precision of the measurement as a quality assessment of the measurement. The TE method relies almost entirely on separate measurements on standards to derive the external precision and accuracy in the measurements.

4 Reagents and materials

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

4.1 Spikes and reference materials

4.1.1 Uranium standard reference solution, prepared from natural uranium metal of purity with an elemental concentration certified to 0,05 % (2σ) or better, such as NBL-CRM-112A (ex NBS-960D), EC-101, CEA-MU-2, JAERI-U4. See Annex A and ISO 10980 for the preparation and validation of this solution.

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

— plutonium metal with an elemental concentration certified to 0,05 % (2σ) or better, such as NBL-CRM-126, EC-201, CEA-MP-2 or NBS-949, with a ^{239}Pu isotopic abundance of 97 % or more, known also to 0,05 % (2σ) or better, if ^{240}Pu, ^{242}Pu or ^{244}Pu is used as 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.

Consult Annex A and ISO 10980 for the preparation and validation of this solution.

4.1.3 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.

4.1.4 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) or CEA-MP-2 (97 % enriched ^{239}Pu metal).

4.1.5 Mixed uranium/plutonium spike solution of certified isotopic and chemical composition, such as IRMM-046 (mixed ^{233}U/^{242}Pu spike).

4.1.6 Large-size dried spike of certified isotopic and chemical composition, such as IRMM-1027, containing about 50 mg of 20 % enriched ^{235}U and 1 mg or 2 mg of 97 % enriched ^{239}Pu spikes.

4.1.7 Mixed uranium/plutonium spike, containing 0,2 mg/g to 0,3 mg/g of ^{235}U and 1 µg/g to 2 µg/g of ^{242}Pu in nitric acid, 7 mol/l, prepared from certified materials such as NBL-CRM-135 or NBL-CRM-U930D, and IRMM-049 or NBL-CRM-130.

NOTE If certified spikes 4.1.3, 4.1.4, 4.1.5, 4.1.6 or 4.1.7 are not available, the desired spikes can be prepared and standardized in accordance with ISO 10980. Suitable procedures are described in Annex A.

4.1.8 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-137 (ex NBS-947), NBL-CRM-144, NBL-CRM-122, CEA-MIRF-01, AEAT-UK-Pu3 for plutonium, and IRMM-072, IRMM-199, NBL-CRM-117, NBL-CRM-U005A to NBL-CRM-U930D, CEA-MIRF-02, AEAT-UK-U2 for uranium.

4.2 Other chemical reagents

4.2.1 Nitric acid solutions, $c(HNO_3) = 0{,}3$ mol/l, 1 mol/l, 3 mol/l, 4 mol/l, 7 mol/l.

4.2.2 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.

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

4.2.4 Hydroxylamine nitrate, $c(NH_2OH) = 0{,}019$ mol/l, in nitric acid, 0,3 mol/l.

4.2.5 Silver nitrate.

4.2.6 Analytical grade polystyrene-quaternary ammonium anion exchange resin beads, with 4 % cross linkage and a mesh size of 100/200, conditioned in 7 mol/l nitric acid solution.

EXAMPLE When starting with a resin in HCl form, proceed as described below:

In a 1 000 ml beaker, wash 500 ml of resin, successively

— twice with 500 ml water;

— twice with 500 ml of nitric acid, 0,3 mol/l (4.2.1);

— twice with 500 ml of nitric acid, 4 mol/l (4.2.1);

— five times with 500 ml of nitric acid, 7 mol/l (4.2.1), until a sample of the supernatant solution no longer yields a chloride precipitate after addition of silver nitrate (4.2.5).

Store the resin in a tightly capped conical flask. Use the resin within a few days. The resin may be stored for a month, provided that it is rinsed with water after the above treatment. After this time, wash the unused resin with water and discard it.

An alternative qualified procedure may be used and involve applicable national or international standards, a facility-specific procedure or the use of a commercially converted nitrate form of the resin, provided that it has been demonstrated to produce equivalent results.

WARNING — Resin should be rinsed with water after its use for the separation because storage of the resin for more than a few days in 7 mol/l nitric acid can lead to explosive decomposition.

4.2.7 Hydrofluoric acid, $c(\mathrm{HF}) = 0{,}01$ mol/l.

4.2.8 Aluminium nitrate, $c[\mathrm{Al_2(NO_3)_3}] = 0{,}004$ mol/l.

5 Apparatus

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

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

5.3 Analytical balance, with 0,1 mg accuracy, installed in a shielded cell or a glove box.

5.4 Pipeting stand, with disposable pipette tips, installed in a shielded cell or a glove box.

5.5 Hot plate, with vapour condensing system, in a glove box, to fume diluted solutions.

5.6 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.

5.7 Common laboratory ware, consisting of disposable plastic pipettes and containers, hot plates, flasks and beakers.

6 Apparatus for mass spectrometry

6.1 Computer-controlled TIMS, designed for precise measurement of isotopic composition having at least the following features.

6.1.1 General specifications

— Mass range: 10 to 280 units of atomic mass.

— Resolution: $>$ 380 at 1 % of the peak height; this resolution should be measured at the 235 and 238 uranium masses.

— Peak top flatness: less than 10^{-4} relative change in the signal for a change of $\pm$ 0,025 mass unit with a Faraday cup detector; less than 10^{-3} relative change with an electron multiplier detector.

— Abundance sensitivity: $< 5 \times 10^{-6}$ at mass 237 relative to mass 238.

— Sensitivity and transmission: $>$ 1 ion collected for 500 uranium atoms on the sample filament.

6.1.2 Ion source, consisting of a thermal ionization source with single and double or triple filament assemblies.

6.1.3 Pyrometer, consisting preferably of an optical or infrared pyrometer to determine the temperature of the ionizing filament.

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

6.1.5 Detector system, consisting of a Faraday multi-detector assembly with a minimum of six detectors that can analyse the uranium isotopes 233, 234, 235, 236, 238 and the plutonium isotopes 238, 239, 240, 241, 242, 244. It is also recommended that the instrument be equipped with either a secondary electron multiplier (SEM) 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 latter detector is also important for making background measurements on filament blanks, etc.

6.2 Filament preheating and degassing device, for cleaning the unloaded filaments.

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

7 Sampling

7.1 Subsampling and spiking

Two alternative procedures are described below.

7.1.1 Subsampling and spiking after dilution

The following procedure applies to solutions containing plutonium with a ^{239}Pu isotope abundance of 85 % or more, as encountered for example in solutions of natural uranium nuclear fuel irradiated in graphite-moderated and gas-cooled reactors.

a) Weigh to $\pm$ 0,1 mg about 2 ml of the sample of concentrated nuclear fuel solution, containing between 0,5 g and 0,6 g of uranium and between 4 mg and 6 mg of plutonium, into a tared 100 ml flask. Record the mass, m_1, of the sample. Take the precautions needed to avoid evaporation of the sample solution during the weighing.

b) Dilute to 100 ml with nitric acid, 7 mol/l (4.2.1), measure and record its mass, m_2 , to the nearest 10 mg, and mix well.

c) In another tared 100 ml flask, transfer 5 ml of the above solution, weighed to $\pm$ 0,1 mg, and record the mass, m'_1, of the aliquot.

d) Dilute to 100 ml with nitric acid, 7 mol/l (4.2.1) to obtain a solution containing 0,2 mg to 0,3 mg of uranium and 2 µg to 3 µg of plutonium per millilitre. Measure and record the mass m'_2 of the diluted solution to the nearest 10 mg, and mix well. Calculate the dilution factor, F, in accordance with Equation (1):

$$F = \frac{m_2 \cdot m'_2}{m_1 \cdot m'_1} \quad (1)$$

e) Pipette 1 ml or 2 ml of the diluted sample solution into a 60 ml disposable beaker and use this aliquot to determine the isotopic composition of the uranium and plutonium in the sample.

f) Weigh 1 ml or 2 ml of the spike solution (4.1.7) and 1 ml or 2 ml of the diluted sample solution to $\pm$ 0,1 mg into a tared 60 ml disposable beaker. Record the masses, m_S and m_C, of the aliquots of the spike and the diluted sample solutions, respectively.

g) Tip and swirl the beaker carefully to wet the inner walls and to ensure that all the liquid is quantitatively mixed. Use this mixture for the determination of the uranium and plutonium concentrations.

7.1.2 Spiking before dilution

This procedure applies to solutions containing plutonium with a ^{239}Pu isotope abundance below 85 %, as encountered for example in solutions of irradiated light water reactor nuclear fuels.

a) Weigh 1 ml or 2 ml of the sample of concentrated nuclear fuel solution to $\pm$ 0,1 mg into a vial containing a large-size dried nitrate spike (4.1.6) and add 7 ml of nitric acid, 7 mol/l (4.2.1). Record the mass, m_C, of the sample aliquot and the mass, m_S, of spike solution previously introduced in the vial and dried to prepare the large size dried spike.

b) Heat at 90 °C for 30 min to redissolve the dried spike quantitatively.

NOTE A Longer dissolution time can be necessary if the large-size dried spike contains some binding material(s) other than nitric acid.

c) Let the solution of spiked sample cool down to 30 °C or below, mix well, pipette an aliquot of 50 µl and transfer it into a 5 ml to 60 ml disposable vessel. Use this aliquot to determine the uranium and plutonium concentrations. In this case, the dilution factor, F, is equal to 1.

d) Pipette another 1 ml of the sample of concentrated irradiated nuclear fuel into an empty 10 ml vial, add 7 ml of nitric acid, 7 mol/l (4.2.1), mix well and pipette 100 µl of the diluted sample into a 5 ml to 60 ml disposable vessel. Use this aliquot for the determination of the isotopic compositions of uranium and plutonium.

7.2 Chemical valency adjustment and isotopic exchange

If there is the risk of a Pu polymer being present in the sample or in the spike, it is advisable to add hydrofluoric acid (4.2.7) and reflux the sample aliquots, and then to complex the excess fluoride with Al^{3+} before proceeding.

A redox valency cycle is performed to ensure that all plutonium isotopes are in the tetravalent state before the ion exchange separation is done.

a) Add 0,1 ml of ferrous solution (4.2.2) to each sample aliquot.

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

c) Add 0,1 ml of sodium nitrite solution (4.2.3) and mix 10 min to re-oxidize all plutonium to the tetravalent state.

7.3 Ion-exchange separation

a) Fill a chromatographic column (5.6) with a slurry of anion exchange resin (4.2.6) in nitric acid, 7 mol/L (4.2.1), to obtain a resin bed about 40 mm high. Verify that the acid flows at a rate of 0,2 ml/min to 0,5 ml/min through the column, after the resin has settled.

b) Transfer a sample aliquot onto the column.

c) Add 7,5 ml of nitric acid, 7 mol/l (4.2.1), i.e. 15 resin bed volumes, to the column to remove the fission products and the americium, and discard these effluents.

d) Continue the elution with 1,5 ml of nitric acid, 7 mol/L (4.2.1), i.e. 3 resin bed volumes, and collect this fraction in a 25 ml beaker for the uranium measurement.

e) Remove uranium tailings with 30 ml of nitric acid, 7 mol/L (4.2.1), i.e. 60 resin bed volumes, and discard these tailings.

f) Add 1,5 ml of the hydroxylamine nitrate solution (4.2.4), i.e. 3 resin bed volumes, and discard the effluents, which should contain very little plutonium.

g) Elute the plutonium with another 3 ml of the hydroxylamine nitrate solution (4.2.4), i.e. 6 resin bed volumes, and collect the plutonium eluate in a 25 ml beaker.

NOTE The above procedure allows for recovery of about 15 % of the initial amount of uranium and 80 % of the plutonium.

7.4 Replicate treatments

a) Repeat steps 7.1 to 7.3 to obtain duplicate separated unspiked and spiked fractions of uranium and plutonium.

b) Evaporate all collected fractions of uranium and plutonium just to dryness and redissolve them with an appropriate amount of nitric acid, 0,3 mol/l (4.2.1) or 4 mol/l (4.2.1), in order to obtain the following concentrations: 40 µg/ml to 1 000 µg/ml of uranium, and 10 µg/ml to 100 µg/ml of plutonium.

c) Transfer each fraction into a disposable polyethylene vial, cap it tightly and forward it to the mass spectrometer laboratory.

8 Preparation of the filaments

8.1 Degassing of filaments

It is recommended to purify the filaments, especially the ionization filament, before use by degassing them in a vacuum chamber (6.2). The amount of impurities remaining can be checked in the mass spectrometer by loading blank out-gassed filaments, which are heated to the normal operating temperature.

8.2 Normal sample loading

Mount a clean sample filament on the filament preparation device (6.3). 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 200 ng U or 5 ng to 50 ng Pu is favoured for a typical TE. Applying a small current through the filament then dries the sample solution. When the sample has dried, the current can 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 conventional multi-collector measurements, it should be noted that the different oxides could cause different fractionation rates.

8.3 Alternative sample loading techniques

Apart from the normal sample loading technique there are several other loading techniques that can be used. Two common methods are the following.

8.3.1 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 will help to attach the sample to the filament. The graphite will reduce the amount of oxides formed and decompose remaining nitrates. Typically there is also a better stability of the ion beam with the graphite. 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 the graphite loading.

8.3.2 Resin-bead loading on single filaments for Pu samples

The Pu can be absorbed on an anion-exchange resin bead that can be fixed with a colloid solution on 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.

8.4 Filament mounting

Mount the loaded sample filaments on the sample barrel, mount the ionizing filaments, and the other side filaments, when appropriate. Check the alignment of each filament assembly and cover it with a clean extraction lens. Check that each ionization filament is well aligned with the extraction slit. Introduce the sample barrel into the ion source, close the source and pump it down to reduce the pressure below 1×10^{-4} Pa.

9 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. For example, single detector measurements with an SEM or a Daly detector require a calibration of the dead time. When an SEM 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.

9.1 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. Depending on the stability of the instrument, this calibration needs to be updated at different intervals. For the measurements with methods using static Faraday multi-collectors, the mass calibration is normally not critical. Prior to a measurement, however, there should always be a fine adjustment using a peak centring routine.

9.2 Gain calibration for Faraday multi-detectors

The electronic gains of the different detector channels show typically 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, one can calculate the relative gain between each channel and a chosen reference channel and correct the signals measured during sample analysis. Commercial instruments normally have an automatic routine that can measure the relative gain prior to the sample measurements.

9.3 Faraday detector calibration

One of the main limitations in the accuracy of the described method is the cross calibration of the different Faraday detectors. Prior to measuring the differences in response between the detectors, one has to perform a gain calibration (9.2).

There are two methods for measuring the differences in response between Faraday detectors.

a) 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) By performing conventional static measurements 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 measurement methods, it is important that an assessment of the precision and accuracy of each method be made to establish the overall uncertainty of the calibration.

NOTE There is an ongoing development of new types of Faraday detectors that might eliminate the need for the Faraday response calibrations.

9.4 Mass discrimination calibration

There are several methods that can be used to assess the mass discrimination in conventional static multi-collector measurements.

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 and ^{238}U (e.g. IRMM-199), mixture of ^{233}U, ^{235}U and ^{238}U (e.g. IRMM072-1), and plutonium against a certified mixture of ^{239}Pu and ^{240}Pu (e.g. NBL-CRM-I37, 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).

As an example, n samples ($n > 10$) 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 nominator equal to Δm. This mean is compared to the certified value $R_{\text{certified}}$ of the isotope ratio, and a fractionation factor, K_{f}, per mass unit is calculated in accordance with Equation (2):

$$K_{\text{f}} = \left[\frac{R_{\text{measured}} - R_{\text{certified}}}{R_{\text{certified}}} \right] \Big/ \Delta m \qquad (2)$$

The calibration is repeated whenever a significant drift is detected in the course of quality control measurements, according to Clause 13, 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 235/238 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.

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

10 Isotopic mass spectrometric measurements

This clause describes two methods of analysing the samples using static multi-collector measurements.

Prior to both types of measurements, the sample in its filament assembly must 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.

10.1 Conventional static multi-Faraday collector measurement

a) Slowly heat up the ionization filament to approximately 2 000 °C.

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. Focus and optimize the voltage settings on the different lenses of the ion source.

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 made typically in blocks of 10 scans. Normally a minimum of 10 blocks of data is 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.

10.2 Total evaporation measurements using a multi-Faraday collector system

a) Slowly heat up the ionization filament typically to 2 000 °C.

b) Increase the sample filament current stepwise to yield a U^+ or Pu^+ signal that is just large enough to focus the pilot beam. If the instrument is equipped with a secondary multiplier detector or a Daly detector, it is normally an advantage to perform the focusing with this detector as this reduces the amount of material consumed prior to the measurement.

c) Measure the baselines and centre the peak with the ion beam in a reference detector.

d) Start the measurement and continue the measurement until virtually all of the sample material has been consumed. During the measurement, the sample filament current is continuously ramped up.

e) When the measurement is completed, the isotopic ratios are calculated by ratioing the summed-up signal of each isotope. 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 Calculation of the results

11.1 Calculation of ion current intensities

Ion current intensities are obtained by application of appropriate baseline corrections, scale, 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 spectrometric measurements are made, these are normally performed in blocks of 10 to 15 scans measuring all isotopes. For each scan k, a ratio $R_j(k)$ is calculated for each isotope j versus a reference isotope. Block means and standard deviations [11.2 a)] for each ratio should be calculated. As an end result, the weighted mean of all block means [11.2 b)] and the weighted standard deviation of the mean are recommended.

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

11.2 Calculation of mean, weighted mean and standard deviation on a set of ratios x_i, $(i = 1 \ldots N)$

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

$$mean = \overline{x} = \frac{1}{N}\sum_{i=1}^{N} x_i \qquad sd = \sqrt{\frac{1}{N-1}\sum_{i=1}^{N}\left(x_i - \overline{x}\right)^2} \qquad sd_{mean} = \frac{sd}{\sqrt{N}} \tag{3}$$

b) Weighted mean, standard deviation of weighted mean:

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

11.3 Mass discrimination correction

An isotope ratio corrected for fractionation effects R' can for the model described in 9.4 be calculated as follows:

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

where

K_{f} is the fractionation factor obtained through calibration step (9.4);

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 235/238 equals 1,0. Assume also that K_{f} has been calculated as described in the example of 9.4 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

11.4 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 %.

11.5 Calculation of the isotopic mass percent W_j

The conversion from atom percent is given by

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

where

M_i is the atomic mass of the isotope i, with [5]:

M_3 (^{233}U) = (233,039 628 ± 0,000 003) amu;

M_4 (^{234}U) = (234,040 946 ± 0,000 002) amu;

M_5 (^{235}U) = (235,043 923 ± 0,000 002) amu;

M_6 (^{236}U) = (236,045 562 ± 0,000 002) amu;

M_8 (^{238}U) = (238,050 783 ± 0,000 002) amu;

M_8' (^{238}Pu) = (238,049 553 ± 0,000 002) amu;

M_9 (^{239}Pu) = (239,052 157 ± 0,000 002) amu;

M_0 (^{240}Pu) = (240,053 807 ± 0,000 002) amu;

M_1 (^{241}Pu) = (241,056 845 ± 0,000 002) amu;

M_2 (^{242}Pu) = (242,058 737 ± 0,000 002) amu;

M_4' (^{244}Pu) = (244,064 198 ± 0,000 005) amu.

11.6 Calculation of concentration

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

$$C_{\mathrm{U}} = C_{\mathrm{U,S}} \cdot \frac{(G_u)_{\mathrm{S}}}{(G_8)_{\mathrm{C}}} \cdot \frac{M_8}{M_u} \cdot \frac{m_{\mathrm{S}}}{m_{\mathrm{C}}} \cdot \frac{1 - \dfrac{(R'_{u8})_{\mathrm{M}}}{(R'_{u8})_{\mathrm{S}}}}{(R'_{u8})_{\mathrm{M}} - (R'_{u8})_{\mathrm{C}}} \cdot F \tag{8}$$

$$C_{\mathrm{Pu}} = C_{\mathrm{Pu,S}} \cdot \frac{(G_p)_{\mathrm{S}}}{(G_9)_{\mathrm{C}}} \cdot \frac{M_9}{M_p} \cdot \frac{m_{\mathrm{S}}}{m_{\mathrm{C}}} \cdot \frac{1 - \dfrac{(R'_{p9})_{\mathrm{M}}}{(R'_{p9})_{\mathrm{S}}}}{(R'_{p9})_{\mathrm{M}} - (R'_{p9})_{\mathrm{C}}} \cdot F \tag{9}$$

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;

$C_{\mathrm{U,S}}$ and $C_{\mathrm{Pu,S}}$ 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;

$(G_u)_{\mathrm{S}}$ and $(G_8)_{\mathrm{C}}$ 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;

$(G_p)_{\mathrm{S}}$ and $(G_9)_{\mathrm{C}}$ 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 weights of the uranium spike isotope u, ^{238}U and plutonium spike isotope p, ^{239}Pu, as given in 11.5;

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 Equation (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 11.4, in the spiked mixture, in the spike solution and in the sample, respectively.

11.7 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 below [6]:

Isotope	Half life (in years)
^{238}Pu	87,7 ± 0,30
^{239}Pu	24 110 ± 30
^{240}Pu	6 563 ± 7
^{241}Pu	14,35 ± 0,10
^{242}Pu	(3,733 ± 0,012) × 10^5
^{244}Pu	(8,08 ± 0,10) × 10^7

12 Blanks

To monitor the process, there should be blank measurements performed in addition to the sample measurements. The different types of blank measurements are the following:

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

13 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 as the unknown samples currently analysed.

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

c) Calculate the results of the analyses of the reference materials as described in Clause 11. Corrective actions should be undertaken if statistically significant differences are detected between the measured and the certified compositions.

14 Repeatability of the measurements

14.1 Elemental assay

The coefficient of variation of the repeatability of duplicate determinations of uranium and plutonium concentrations in light water reactor spent fuel solutions observed at an industrial plant over a typical reprocessing campaign is about 0,2 %, using conventional isotope ratio measurements, and about 0,1 % when using the method of total evaporation.

14.2 Isotopic analysis

The coefficients of variation of the repeatability to be expected under the above conditions for the isotopic analyses are listed in Table 1.

Table 1 — Expected coefficients of variation of repeatability and reproducibility of isotopic analyses and isotope dilution analyses by thermal ionisation mass spectrometry[7]

Isotope or element	Abundance or concentration (% by mass)	Repeatability[a]		Reproducibility[b]	
		Conventional method	Total evaporation	Conventional method	Total evaporation
^{235}U	0,2 0,7 3,0	0,70 0,50 0,20	0,50 0,20 0,10	0,90 0,70 0,30	0,50 0,20 0,10
^{238}U	97 to 99	0,01	0,005	0,015	0,010
^{238}Pu[c]	0,3 1,5	10 1,50	10 1,50	10 1,00	10 1,00
^{239}Pu	50 to 80	0,05	0,05	0,07	0,03
^{240}Pu	10 to 30	0,10	0,10	0,10	0,05
^{241}Pu	3 to 15	0,20	0,20	0,30	0,20
^{242}Pu	1 to 5	0,30	0,20	0,40	0,30
$^{239}Pu + ^{241}Pu$	65 to 83	0,10	0,07	0,15	0,10
U conc.	10 to 30	0,20	0,10	0,30	0,15
Pu conc.	0,10 to 0,20	0,20	0,10	0,30	0,15

[a] Coefficient of variation of replicate analyses (1σ) performed at the same time at a single laboratory.

[b] Coefficient of variation of replicate analyses performed at different laboratories or times, under the most different conditions possible.

[c] ^{238}Pu by alpha-spectrometry.

15 Accuracy of the method

15.1 Elemental assay

A plant laboratory analysed 21 solutions of plutonium nitrate by isotope dilution analysis, using the conventional method of measuring ion ratios described in the present document. The mean of two independent analyses was compared with the mean result of two independent potentiometric titrations, performed at the same laboratory.

The average relative difference between the results of the two methods was equal to 0,03 %. The standard deviation of the relative differences was equal to 0,27 %.

15.2 Isotopic analysis

The coefficients of variation of the reproducibility expected for the isotopic analyses are listed in Table 1. These values also represent a measure of the expected accuracy.

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 4.1.1, 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 down 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, m_4, in grams, of the solution to the nearest 0,01 %.

The concentration of uranium, U, in milligrams per gram, in the stock solution is

$$U = \frac{m_3}{m_4} \cdot P_S \qquad \text{(A.1)}$$

where P_S is the purity, expressed as a mass fraction of uranium element (grams of uranium per gram of standard), of the chemical reference material reported on the certificate.

Cap the flask tightly and homogenize the solution.

Select a cap having a very stable tare, within $\pm$ 2 mg.

Measure and record the gross mass of the capped flask so that evaporation losses on storage can be estimated. Verify the concentration of the stock solution with the most accurate analytical method available in the laboratory in accordance with ISO 10980. Estimate, preferably experimentally, the coefficient of variation, SP, of the errors, which might have occurred during its preparation.

A.3.2 Stock solution of plutonium standard reference solution

The following procedure applies to the use of reference materials distributed in units of certified masses.

Transfer one unit of a certified plutonium metal standard such as CEA-MP-2 or NBS-949 (4.1.2) into a glove box.

Record its mass, m'_3, in milligrams, given in the certificate.

Open the sealed vial and empty it into a tared and dry conical flask.

Measure immediately the gross mass of the flask and calculate the net mass of the metal, m''_3 collected in the flask (including air buoyancy correction); compare it to the certified value m'_3, to confirm the identity of the unit.

Rinse or leach the vial several times with 1 ml aliquots of 4 mol/l hydrochloric acid solution and collect the rinse into the conical flask.

Cap the conical flask with a reflux head and proceed with a gentle dissolution; avoid losing solution in the form of aerosols.

When the dissolution is complete, dilute to about 100 ml with 3 mol/l nitric acid solution and transfer into the balance box. Allow the solution to reach thermal equilibrium. Measure the gross mass of the flask to the nearest 10 mg or better and calculate the net mass m'_4, in grams, of the solution.

The concentration of plutonium, Pu, in milligrams per gram, in the stock solution is

$$Pu = \frac{m'_3}{m'_4} \cdot P'_S \qquad \text{(A.2)}$$

where P'_S is the purity, expressed in mass fraction of plutonium element (grams of plutonium per gram of standard), of the chemical reference material reported on the certificate.

Proceed as with the stock solution of uranyl nitrate (see A.3.1).

A.4 Preparation of spike solutions

A.4.1 Solution of U spike

Select a batch of a chemically-pure compound of separated isotope, U_S, sufficiently enriched, such as the ones mentioned in 4.1.3, so that its isotope ratio $^{238}U/U_S = (R'_{u8})_S^{-1}$ can be measured with an accuracy of ± 0,000 5 or better. A material with a U_S isotope abundance of 80 % or more is acceptable. Such materials may be obtained through National Atomic Energy Commissions or their contractors such as US-DOE or ORNL, UKAEA or Amersham, the Commissariat à l'Energie Atomique (CERCA LEA, Pierrelatte, France).

Dissolve this material if necessary and dilute it to the desired concentration in 3 mol/l nitric acid solution. Store in sealed ampoules or in tight glass vessels allowing measurement of evaporation losses.

If the purity of the source material is insufficient or unknown, purify the solution, for example by ion exchange, before dilution and standardisation.

If the U_S spike contains, for example, 200 µg of ^{239}Pu isotope per gram of U_S isotope, mixing it with the Pu_S spike in a ratio of 1:100 will increase the $^{239}Pu/Pu_S = (R'_{p9})_S^{-1}$ isotope ratio by 0,02.

A.4.2 Solution of Pu spike

Select a batch of a chemically-pure compound of separated isotope, Pu_S, sufficiently enriched such as the ones mentioned in 4.1.4, so that its isotope ratio $^{239}Pu/Pu_S = (R'_{p9})_S^{-1}$ can be measured with an accuracy of ± 0,000 5 or better. A material with a Pu_S isotope abundance of 80 % or more is acceptable. Such materials may be obtained through National Atomic Energy Commissions or their contractors.

Dissolve this material if necessary in 7 mol/l nitric acid solution (it can be necessary to dissolve some compounds such as PuO_2 in a mixture of 7 mol/l nitric acid solution and 0,01 mol/l hydrofluoric acid solution).

Dilute to the desired concentration in 3 mol/l nitric acid solution and store in the same way as the solutions of U_S spike (see A.4.1).

A.4.3 Mixed solution of U_S and Pu_S spikes

When both the uranium and plutonium concentrations are to be analysed routinely, it is convenient to use a solution for spiking containing a mixture of the uranium and plutonium spikes. The proportion of the two spikes should be similar to the proportion of uranium and plutonium elements in the samples.

A mixed spike solution is readily prepared by mixing suitable aliquots of the separate spikes and diluting the mixture with 3 mol/l nitric acid solution to the desired concentration.

The same precautions apply for the storage of mixed and separated spike solutions.

A.4.4 Preparation of large-size dried spikes

Large-size dried spikes, as described in 4.1.6, are preferably prepared from certified reference materials of natural uranium metal NBL-CRM-112A or CEA-MU2, highly enriched ^{235}U metal NBL-CRM-116, and plutonium metal NBL-CRM-126 or CEA-MP2.

Stock solutions are prepared in accordance with A.3 to contain accurately known concentrations in the range of 20 mg/l to 40 mg/l of natural uranium, 4 mg/l to 8 mg/l of highly enriched uranium and 1 mg/l to 2 mg/l of plutonium.

The uranium and plutonium concentrations, $C_{U,S}$ and $C_{Pu,S}$, are calculated using the certificate values, the masses of reference materials taken and the measured mass of the solution as done for the preparation of the standard reference solutions according to A.3, including consideration of the traces of uranium contained in the plutonium certified reference material.

The isotopic composition of the plutonium spike is taken from the certificate of the certified reference material.

The ^{235}U isotopic abundance and the isotope ratio $^{235}U/^{238}U$ are calculated using the certificate values and the masses of reference materials taken, including consideration of the traces of uranium contained in the plutonium certified reference material.

Aliquots of 1 ml to 2 ml of the stock solution are pipetted and transferred into tared vials of about 10 ml. The gross weights are measured and used to calculate the net masses of the aliquots, m_S.

The aliquots are carefully heated to dryness in a manner that avoids any loss of material as aerosols and leads to the production of a film of dried spike adhering firmly to the bottom of the vial.

A.5 Standardization of the dilute spike solutions by isotope dilution mass spectroscopy

A.5.1 Standardization of the uranium spike

From the stock solution of the uranium chemical standard, prepare, by mass, L diluted solutions containing the same concentration of uranium as the spike solution ($L = 4$).

A.5.1.1 Isotopic analysis of the diluted solutions of certified chemical standard

Take one aliquot from each of the L diluted solutions of certified chemical standard and treat it in the same way as the isotopic standards used for the calibration of the mass spectrometer and as the samples prepared for isotopic analyses. Prepare and measure one filament from each aliquot. Measure masses 233, 234, 235, 236 and 238.

The results of the measurements of the isotope abundance, G_{st}, of the major isotope U_{st} should all agree to ± 0,05 % or better with the abundance indicated on the certificate. The results of the measurements of the U_S/U_{st} isotope ratio should also agree within ± 0,000 5 with the certified value.

A.5.1.2 Isotopic analysis of the spike solution

Take three or more aliquots of the spike solution and treat them in the same way as the isotopic standards used for the calibration of the mass spectrometer and as the samples prepared for isotopic analyses. Prepare and measure two filaments from each aliquot. Measure masses 233, 234, 235, 236 and 238.

The results of the replicate measurements of the abundance of the spike isotope, U_S, should agree within ± 0,05 % or better. The results of the replicate measurements of the $^{238}U/U_S$ and U_{st}/U_S isotope ratios should all agree to ± 0,000 5 or better.

A.5.1.3 Standardization of the U_S isotope concentration in the spike solution

Pipette and weigh accurately N aliquots ($N = 1$) of about 1 ml from each of the L diluted solutions of the certified chemical standard. To each aliquot, add an accurately weighed aliquot, also about 1 ml, of the spike. Treat each mixture in the same way as the isotopic standards used for the calibration of the mass spectrometers, and as the spiked samples prepared for isotope dilution analysis.

Prepare and measure R filaments from each mixture ($R = 4$). The U_S isotope concentration in the spike solution, C_S, in micrograms per gram is calculated according to the following equation:

$$C_S = \frac{m_{st}}{m_S} \cdot \frac{G_{st}}{100} \cdot \frac{M_S}{M_{st}} \cdot \frac{(\bar{R}'_{u/st})_M - (\bar{R}'_{u/st})_{st}}{1 - \dfrac{(\bar{R}'_{u/st})_M}{(\bar{R}'_{u/st})_S}} \qquad \text{(A.3)}$$

where

m_{st} is the mass, expressed in micrograms, of uranium in the certified chemical standard mixed with a mass, m_S , expressed in grams of the spike solution;

G_{st} is the isotopic abundance, expressed as a mass percentage, of the major isotope, U_S, of the chemical standard;

M_{st} and M_S are the atomic masses of the spike isotope, U_{st}, and of the major isotope, U_S, of the chemical standard, respectively;

$(R'_{u/st})_i$ are the U_S/U isotope ratios measured in the diluted solutions of the uranium chemical standard, spike and mixture with $i =$ (st, S, M), respectively.

A.5.2 Standardization of the plutonium spike

The standardization of the plutonium spike is performed against diluted solutions of a plutonium metal chemical reference material. Proceed otherwise as for the standardization of the uranium spike, with the following changes.

A.5.2.1 Isotopic analysis of the diluted solutions of certified chemical standard

Measure masses 238, 239, 240, 241, 242 and 244. The results of the measurements of the isotope abundance, G'_{st}, of the major isotope, Pu_{st}, in the chemical standard should all agree to ± 0,05 % or better with the abundance indicated in the certificate of the reference material. The results of the measurements of the Pu_S/Pu_{st} isotope ratio should also agree within ± 0,000 5 or better with the value given in the certificate.

A.5.2.2 Isotopic analysis of the spike solution

Measure masses 238, 239, 240, 241, 242 and 244. The results of the measurements of the abundance of the spike isotope, Pu_S, should agree within ± 0,05 % or better. The results of the measurements of the Pu_{st}/Pu_S and $^{239}Pu/Pu_S$ isotope ratios should all agree to ± 0,000 5 or better.

A.5.2.3 Standardisation of the Pu_S isotope concentration in the spike solution

The concentration of the spike isotope, Pu_S, in the spike solution, C'_S, in micrograms per gram, is calculated according to the following equation:

$$C'_S = \frac{m'_{st}}{m'_S} \cdot \frac{G'_{st}}{100} \cdot \frac{M'_S}{M'_{st}} \cdot \frac{(\bar{R}'_{p/st})_M - (\bar{R}'_{p/st})_{st}}{1 - \frac{(\bar{R}'_{p/st})_M}{(\bar{R}'_{p/st})_S}} \qquad \text{(A.4)}$$

where

m'_{st} is the mass, expressed in micrograms, of plutonium in the certified chemical standard mixed with a mass, m_S, expressed in grams, of the spike solution;

G'_{st} is the isotopic abundance, expressed as a mass percentage, of the major isotope, Pu_S, of the chemical standard;

M'_S and M'_{st} are the atomic masses of the spike isotope, Pu_{st}, and of the major isotope, Pu_S, of the chemical standard, respectively;

$(R'_{p/st})_i$ are the Pu_S/Pu_{st} isotope ratios measured in the diluted solutions of the plutonium chemical standard, spike and mixture with $i =$ (st, S, M), respectively.

A.5.3 Standardization of mixed spike solutions

Mixed spike solutions are standardised in accordance with A.5.1 and A.5.2, after the uranium and plutonium spikes have been mixed and the final dilution of the mixture is carried out as described in A.4.3.

A.5.4 Standardization of isotope dilution analysis with joint spikes

Uranium and plutonium elemental assays may be performed on the same sample aliquot by mixing it with accurately weighed aliquots of separate solutions of uranium and plutonium spikes.

In this case, the standardization of the analysis shall be carried out by submitting similar mixtures of the separated spike solutions to the procedures specified in A.5.1 and A.5.2.

This is necessary to take accurately into account the traces of plutonium isotopes that can be present in the uranium spike solution and vice versa.

A.6 Validation of large-size dried spikes

A.6.1 Validation of the isotopic composition

L dried spikes ($L > 4$) are selected randomly from the batch of spikes to be validated. They are dissolved and treated as described in 7.1.2, 7.2 and 7.3. The isotopic compositions are measured using the most accurate mass and alpha spectrometry procedures available as described in the present document and in ISO 11483.

The repeatability of the measurements should comply with the values given in A.5.1.2 and A.5.2.2. The measurements of the isotope abundance of ^{240}Pu should agree also within $\pm$ 0,05 %, and the measurements of the isotope ratio $^{240}Pu/^{239}Pu$ within $\pm$ 0,000 5, with the values of the certificate of the plutonium metal reference material. The measurements of the isotope abundance of ^{235}U and the measurements of the isotope ratio $^{235}U/^{238}U$ should agree within $\pm$ 0,05 % with the values calculated in A.4.4.

A.6.2 Validation of the element concentrations

L' dried spikes ($L' > 8$) are selected randomly from the batch of spikes to be validated. They are dissolved and treated as described in 7.1.2 a) to 7.1.2 c). Half of the spikes are used to determine the uranium element content following the most accurate procedure available, for example ISO 7097. The other half of the spikes are used to determine the plutonium element content following the most accurate procedure available, for example ISO 8298 or ISO 12183.

The measured values should agree within $\pm$ 0,10 % with the values calculated in A.4.4.

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