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Determination of isotopic content and concentration of uranium and plutonium in nitric acid solution — Mass spectrometric method

Détermination de la teneur isotopique et chimique en uranium et plutonium d'une solution d'acide nitrique — Méthode par spectrométrie de masse

Reference number
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Foreword

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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.

International Standard ISO 8299 was prepared by Technical Committee ISO/TC 85, *Nuclear energy*, Sub-Committee SC 5, *Nuclear fuel technology*.

Annex A forms an integral part of this International Standard.

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Determination of isotopic content and concentration of uranium and plutonium in nitric acid solution — Mass spectrometric method

1 Scope

This International Standard specifies a method to determine the isotopic content and the concentration of uranium and plutonium in input solutions of irradiated fuels in light water reactors (boiling water or pressurized water) and in final products at spent fuel reprocessing plants. The method is applicable to other fuels, but the chemical separation and spike solution shall, if necessary, be adapted to suit each type of fuel.

2 Principle of the method

The method is based on isotope ratio measurements by thermal ionization mass spectrometry.

The isotopic composition of uranium and plutonium is determined through isotopic ratio measurements.

^{238}Pu is determined by means of alpha spectrometry if interferences from ^{238}U cannot be eliminated.

The sample is diluted in order to economize on the amount of spike needed and to minimize the level of biological protection which is necessary.

A highly accurate gravimetric dilution is necessary when elemental concentrations are measured.

Because plutonium tends to hydrolyse at low acidities, a solution of nitric acid (HNO_3) with a molarity greater than 1 mol/l should be used for the dilution of the sample.

When elemental concentrations are measured, accurately weighed quantities of spike isotopes are added in quantities comparable to the quantities of ^{238}U and ^{239}Pu isotopes in the diluted sample. Although ^{233}U and ^{242}Pu isotopes are normally used as spikes, other separated isotopes (e.g. ^{244}Pu, ^{239}Pu, ^{235}U and ^{236}U) can be used when available and appropriate.

The isotopic composition of the spikes and the isotopic abundance of the ^{238}U and ^{239}Pu isotopes in the sample shall be accurately known. If the ^{242}Pu and ^{236}U isotopes are used as spikes, it is also necessary to measure the isotopic abundance of these isotopes in the sample.

A chemical separation is necessary to eliminate interfering elements (e.g. ^{241}Am, fission products) following a reduction-oxidation cycle to ensure isotopic exchange between spikes and sample.

The isotopic composition of fresh product material is normally measured without purification.

Plutonium aged more than 1 week should be purified to remove ^{241}Am.

The method includes the following steps:

a) dilution by weight;

b) spike addition by weight;

c) isotope exchange chemistry;

d) ion exchange purification/separation;

e) preparation of filaments;

f) mass spectrometric measurements and calculation of isotopic and elemental concentrations.

Care shall be taken to avoid cross contamination. For this purpose, it is recommended that disposable laboratory ware (e.g. vessels and columns) be used. Throughout the method it is necessary to follow good analytical practices regarding cleanliness, accuracy of measurement, avoiding evaporation errors, etc.

3 Reagents

3.1 Isotopic reference materials, which cover the isotopic range of interest and are certified to 0,1 % or better for the major isotope ratios, such as CBNM-047a, NBL 128, CEA MIRF, NBL 137 (ex NBS Pu947) for plutonium and CBNM-072, CBNM-199, NBL 117, NBL U500 to NBL U930 for uranium.

3.2 Natural uranium metal, of purity certified to 0,05 % or better, such as NBL 112 (ex NBS U960), EC-101 or CEA-MU-2.

3.3 Plutonium metal, of purity certified to 0,05 % or better, such as NBL 126, EC-201, CEA-MP-2 or NBS 949, with a ^{239}Pu isotopic abundance of 90 % or more, known also to ± 0,05 % or better.

3.4 ^{233}U spike solution, of certified isotopic and chemical composition, such as NBL 111A, CBNM-040-1 or NBS U995.[1)]

3.5 Pu spike, of certified isotopic and chemical composition, such as CBNM-041-1 (^{242}Pu solutions) or NBL 131 (ex NBS Pu996) (^{244}Pu nitrate).[1)]

3.6 Mixed ^{233}U/^{242}Pu spike solution, of certified isotopic and chemical composition, such as CBNM-046-2 (may be used in place of 3.4, 3.5 or mixtures thereof).[1)]

3.7 Concentrated nitric acid (HNO_3), 14 mol/l solution.

3.8 Nitric acid, 7 mol/l solution.

3.9 Nitric acid, 4 mol/l solution.

3.10 Nitric acid, 3 mol/l solution.

3.11 Nitric acid, 1 mol/l solution.

3.12 Nitric acid, 0,2 mol/l solution, uranium-free.

3.13 Ferrous sulfate septahydrate ($FeSO_4.7H_2O$), 42,5 g/l solution in H_2SO_4 (0,05 mol/l), freshly prepared.

3.14 Sodium nitrite ($NaNO_2$), 250 g/l solution, freshly prepared.

3.15 Dowex AG 1 × 4 resin, 100/200 mesh (conditioned in 7 mol/l nitric acid solution).

In a 1 000 ml beaker, wash 250 ml of resin Dowex 1 × 4, successively with:

— 500 ml water: twice,

— 500 ml of 0,2 mol/l nitric acid solution (3.12): twice,

— 500 ml of 4 mol/l nitric acid solution (3.9): twice,

— 500 ml of 7 mol/l nitric acid solution (3.8): five times, until a sample of the supernating solution no longer yields a chloride precipitate after additon of silver nitrate.

Use the resin within 30 days. Beyond this time, wash the unused resin with water and discard.

A blank determination should be performed to show that the quantity of the uranium or plutonium present in the reagents or picked up during the separation procedure is less than 0,2 % of the uranium or plutonium expected to be present in a sample determination.

4 Apparatus and materials

4.1 Mass spectrometric equipment

4.1.1 Mass spectrometer, computer-controlled, thermal ionization type, designed for precise measurement of isotopic composition having at least the following features:

Resolution: greater than 400 at 1 % of the peak height. This resolution should be measured on the ^{235}U and ^{238}U masses.

Abundance sensitivity: less than 10^{-5} for ^{237}U.

Vacuum: pressures less than 10^{-4} Pa in the source and less than 10^{-5} Pa in the analyser. For instance, a modern apparatus can reach 10^{-5} Pa in the source and about 10^{-6} Pa to 10^{-7} Pa in the analyser.

Ionization: thermal ionization source fitted with two or three filament assemblies with disposable filament inserts. The ionization filament (50 µm thick and 0,75 mm wide) is made of rhenium, highly purified especially with respect to the alkali elements (see clause 11) and uranium. The sample filament(s) is (are) made either of rhenium like the ionization filament or tungsten (25 µm thick). Tantalum sample filaments may also be used when plutonium is analysed.

Detection: single or multidetector assembly preferably consisting of a Faraday cup detector or detectors, a secondary electron multiplier or Daly detector for the measurement of minor isotopes and one or several suitable voltage-to-frequency

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[1)] If certified spikes 3.4, 3.5 or 3.6 are not available, spike solutions may be prepared and standardized as described in annex A.

converter(s) and a high-precision digital measuring system for ion current integration.

4.1.2 Filament preheating and degassing device, for cleaning the mounted unloaded filaments, including if possible a small attraction plate to collect alkali ions.

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

4.1.4 Optical pyrometer, desirable to determine the temperature of the ionizing filament. Alternatively, the intensity of the $^{187}Re^+$ ions can be carefully calibrated as a function of the temperature of the ionizing filament; the $^{187}Re^+$ ion intensity can then be used to measure and control the temperature of this filament.

4.2 Instrument calibration

Use internationally accepted isotopic reference materials certified to 0,1 % or better for the ratio of the major isotopes.

Calibrate the analyses of uranium against a certified 1:1 mixture of ^{235}U and ^{238}U (e.g. NBL U500) or of ^{233}U and ^{238}U (e.g. NBL 117, CBNM-199) and plutonium against a certified mixture of ^{239}Pu and ^{240}Pu (e.g. NBL 137, ex NBS Pu947) or of ^{239}Pu and ^{242}Pu (e.g. NBL 128) or of ^{239}Pu and ^{244}Pu (e.g. CBNM-047a).

Treat, prepare and measure n samples of the certified reference material ($n \geqslant 10$) in the same way that unknown samples are analysed.

Calculate the arithmetic mean, $\bar{R}_{i/j}$, of the n measurements of the ratio of the ion currents produced by isotopes i and j. Compare this mean to the certified value, $R_{i/j}(s)$, of the isotope ratio and calculate a discrimination factor, B, equal to

$$B = [(\bar{R}/R_s)_{i/j} - 1]/(M_j - M_i) \qquad \ldots (1)$$

where M_j and M_i are the relative atomic masses (weights) of isotopes j and i.

The number of calibration measurements, n, is selected to ensure that the standard error on B is equal to or less than 0,000 1.

The calibration is repeated at least once a year or whenever a significant drift is detected, in accordance with 4.3, or suspected, for example after changing a major component of the instrument or the method of preparation of the samples.

4.3 Linearity of the method and stability of the calibration

Verify that the mass spectrometer and the method of analysis give linear response and accurate results over the range of isotopes and isotope ratios to be analysed.

For this purpose, regularly treat, prepare and measure samples of certified isotopic reference materials of different isotopic composition in the same way as the unknown samples currently analysed.

Calculate the results of the analyses of the reference materials as described in clause 8.

Statistically significant differences in time or in the range of isotope ratios between the measured and the certified isotope ratios indicate a drift of the calibration or a deviation from linearity.

In such cases corrective actions should be undertaken.

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

4.5 Glove box, for handling diluted solutions for operations of spiking and subsequent chemical treatment.

4.6 Analytical balances, for the gravimetric dilutions and spike additions.

4.7 Disposable plastic pipettes and containers.

4.8 Hot plate.

4.9 Flasks and beakers.

4.10 Disposable ion exchange column

The procedure specified in this International Standard is intended for use with a column made of a 16 mm diameter polyethylene tube, tapered at one end and filled with a 10 mm ± 1 mm high bed of Dowex 1 × 4 resin of 100/200 mesh (3.15). A column of different dimensions may be used, but the volumes of eluents must be adapted.

5 Chemical preparation

5.1 Spike preparation

Accurately prepare either

- two separate standardized spike solutions, one containing 150 µg/g to 200 µg/g of ^{233}U, the other 1 µg/g to 2 µg/g of ^{242}Pu, or
- a single standardized spike solution of mixed spike containing 150 µg/g to 200 µg/g of ^{233}U and 1 µg/g to 2 µg/g of ^{242}Pu.

The volume to be prepared depends on the availability of the isotopes. An example of preparation and standardization procedure is described in annex A.

5.2 Dilution of the input solution sample

A typical input solution contains 250 g/l to 300 g/l of uranium and 2 g/l to 3 g/l of plutonium when the burn-up is about 30 000 MWd/t. This highly radioactive solution is handled in a hot cell where it is diluted by weight 200- to 2 000-fold with 1 mol/l nitric acid (3.11).

Carry out at least two replicate dilutions on each batch of input solution.

As an example, a typical dilution procedure may be carried out as follows.

Transfer into a tared 100 ml flask, 2 ml of the input solution A, weighed to the nearest 0,1 mg (m_1) and containing 500 mg to 600 mg of uranium and 4 mg to 6 mg of plutonium.

Dilute to 100 ml with 1 mol/l nitric acid, determine the mass, m_2, of the diluted solution B to the nearest 10 mg and mix well.

Into another tared 100 ml flask, transfer 5 ml of solution B, weighed to the nearest 0,1 mg (m'_1).

Dilute to 100 ml with 1 mol/l nitric acid, determine, to the nearest 10 mg, the mass, m'_2, of the diluted solution C which is obtained, and mix well.

The dilution factor, F, is equal to

$$F = \frac{m_2 m'_2}{m_1 m'_1} \quad \ldots (2)$$

Transfer a sample of about 6 ml of solution C to a suitable facility.

5.3 Preparation for content assay

The following operations are performed at least once after each replicate dilution of the input solution in accordance with 5.2.

5.3.1 Spiking

The quantity of ^{233}U (and ^{242}Pu) added shall be comparable to the quantity of ^{238}U (and ^{239}Pu) present in solution C.

Transfer into a tared 60 ml plastic container 2 ml of the spike solution, weighed to the nearest 0,1 mg (m_S).

Add 2 ml of solution C, weighed to the nearest 0,1 mg, (m_C), and mix thoroughly without splashing. Ensure that all liquid is included in the mixing by wetting the interior container walls.

5.3.2 Isotopic exchange

If there is a possibility of Pu polymer being present in the sample or in the spike, it is advisable to add a drop of 0,1 mol/l hydrofluoric acid and reflux the spiked sample and then to complex excess fluoride with Al^{+++} before proceeding (for example, with aluminium nitrate).

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

Add 1 ml of the ferrous sulfate solution (3.13) into the 60 ml container.

Mix and wait 5 min for a complete reduction of Pu(VI) to Pu(III) or Pu(IV).

Add 1 ml of sodium nitrite solution (3.14) to reoxidize all plutonium to the tetravalent state.

Stir for 5 min.

5.3.3 Ion exchange separation

Add 8 ml of concentrated nitric acid (3.7) into the 60 ml container and mix to obtain 14 ml of solution D in 7 mol/l nitric acid (3.8).

Transfer solution D onto the ion exchange column, filled with 2 ml of ion exchange resin conditioned in the 7 mol/l nitric acid solution.

Wash the column three times with 15 ml of 4 mol/l nitric acid solution (3.9). Discard the eluate which contains americium and fission products.

Wash again with 15 ml of 4 mol/l nitric acid solution. Collect the eluate D′ in a glass beaker; it will be used for the uranium assay.

Wash with 15 ml of 4 mol/l nitric acid solution and discard the eluate.

Then wash with 10 ml of 0,2 mol/l nitric acid solution (3.12), collect the eluate D″ in a glass beaker; it will be used for the plutonium assay.

Evaporate the eluates D′ and D″ to dryness.

Redissolve in 50 µl of concentrated nitric acid and fume to dryness to eliminate organic residues. Repeat once or twice.

Redissolve finally with a few drops of 0,2 mol/l nitric acid solution. The solutions obtained are ready to be loaded on the filaments used for mass spectrometry.

Operations 5.2 and 5.3 are presented in the form of a diagram in figure 1.

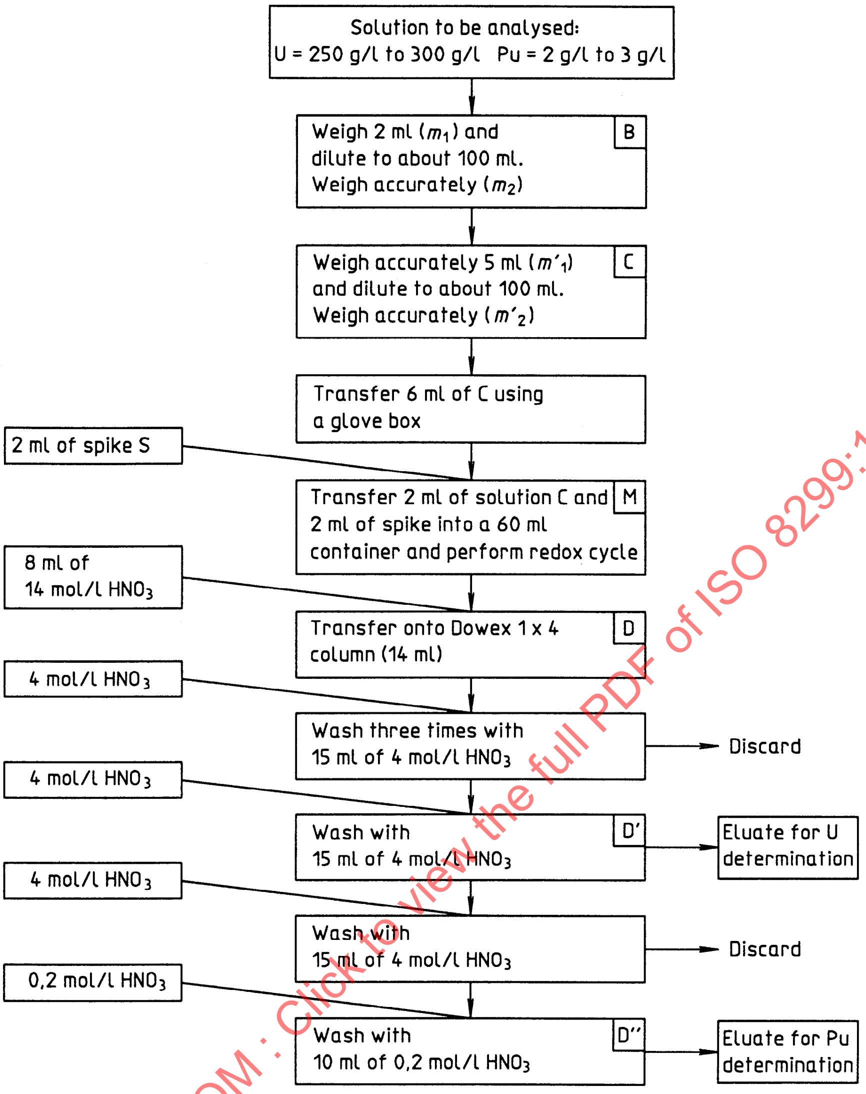

Figure 1 — U and Pu content assay

5.4 Preparation for isotopic assay

Carry out the operations described in 5.2.

Transfer 4 ml of solution C into a 60 ml plastic container.

Perform a redox cycle as described in 5.3.2.

Add 8 ml of concentrated nitric acid and mix.

Transfer the solution E obtained onto the ion exchange column.

Wash three times with 15 ml of 4 mol/l nitric acid solution and discard the eluate.

Wash again with 10 ml of 4 mol/l nitric acid solution and collect the eluate E′ in a glass beaker for the isotopic assay of uranium.

Wash four more times with 15 ml of 4 mol/l nitric acid solution to eliminate uranium and to avoid the interference of ^{238}U on the isotopic assay of plutonium. Discard the eluate. The repeated washings are necessary to achieve a decontamination factor of about 10^4 for uranium.

Now wash with 10 ml of 0,2 mol/l nitric acid and collect the eluate E″ in a glass beaker for the isotopic assay of plutonium.

Evaporate the eluates E′ and E″ to dryness.

Redissolve in a few drops of 0,2 mol/l nitric acid. The solutions obtained are ready to be loaded on the filaments used for mass spectrometry.

Operations 5.2 and 5.4 are presented in the form of a diagram in figure 2.

6 Preparation of filament

6.1 Purification of filaments

Purify the filaments by degassing in a vacuum chamber for 10 min to 30 min at approximately 2 000 °C.

6.2 Loading procedure

Load 5 µl to 10 µl of the uranium and plutonium solutions obtained in the ion exchange separation which is equivalent to 0,5 µg to 2 µg uranium and 0,05 µg to 0,5 µg of plutonium (the amount depends on the type of mass spectrometer used) onto a suitably prepared sample filament.

Try to deposit the sample in the centre of the filament in the form of a precise dot.

Heat the filament progressively, for example, by means of an electric current, to 90 °C to 100 °C in order to evaporate the solvent smoothly.

Then bring the filament to a dark red glow for 10 s to destroy the nitrate and to fix the oxides on the filament.

Avoid temperatures higher than 600 °C.

The temperature of the filament during the final stages of sample mounting is a critical factor and shall be carefully controlled to prevent significant variations in the fractionation between runs.

NOTE 1 It is important to reproduce closely all the parameters, which control the quality of the deposit, from one analysis to another: acidity, element concentrations (± 30 %), chemical purity especially with regard to the alkali elements, amount (± 30 %) and position of deposit and heating procedure.

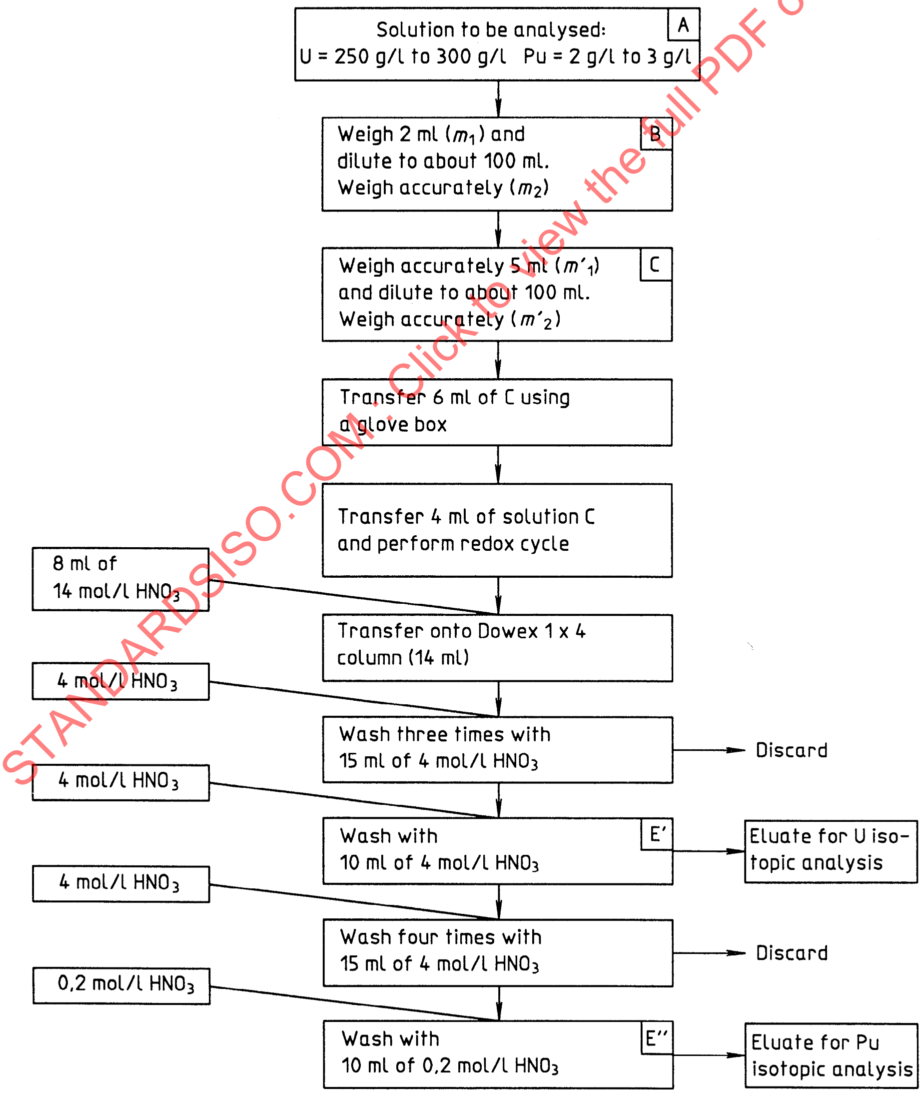

Figure 2 — U and Pu isotopic assay

7 Isotopic mass spectrometry measurement

7.1 Position the filament assemblies in the mass spectrometer source (most modern instruments allow the simultaneous installation of several assemblies in the source), close the source and pump down to obtain a source pressure of less than 10^{-5} Pa (10^{-7} torr).

7.2 Perform the measurement according to the instruction manual of the mass spectrometer.

7.3 Degas the sample by heating the sample filaments at a preselected temperature. Turn off heating of all filaments after 15 min and pump without heating for about 30 min for accountability analysis and about 15 min for process control measurements. Degassing is considered essential for measurements with high-sensitivity electron detectors where low-level interference from organic and inorganic molecules is a major problem. Degassing is also essential with conventional Faraday cup detectors when there are small amounts of organic impurities in the sample.

NOTE 2 Sample degassing may be considered optional for U and Pu isotopic analysis, but is strongly recommended for most accurate analyses.

7.4 Resume heating of the ionization filament to obtain the signal of the main isotope of the filament (e.g. the ^{187}Re peak) and focus to obtain maximum intensity.

7.5 Adjust the temperature of the ionization filament to 2 080 °C ± 50 °C. Control the temperature using an optical pyrometer or by measuring the ^{187}Re$^+$ ion current. If, at this stage, the ion current of the main isotope of the ionization filament (e.g. the ^{187}Re ion current) is unstable, interrupt the analysis here.

7.6 Otherwise, increase the sample filament current stepwise to yield a preset U$^+$ or Pu$^+$ signal.

Focus for maximum signal intensity.

7.7 Wait 20 min to 30 min to obtain a steady emission and readjust the sample filament heating currents to maintain the U$^+$ or Pu$^+$ signal intensity.

Focus again for maximum intensity.

7.8 Adjust the sum of the ion currents of the isotopes to be analysed to a preset value equal to approximately 80 % of the range of the current amplifier system (e.g. about 10^{-12} A).

Start the measurement after the ion currents begin to decay in a slow and smooth fashion.

Use exactly the same time and collection schedules for the analyses of samples and for calibration measurements.

7.9 In single collector operation, the "peak-jumping" technique of ratio measurements is normally preferred to the "mass-scanning" technique. The baseline is therefore determined at least once per cycle of isotope ratio measurements.

7.10 The peak top observation time is governed by many factors including response of the measuring circuit, emission stability, rate of signal decay, settling time of the magnet switching circuit and desired precision and accuracy of the measurement. In general, there is a minimum delay of 2 s for circuits to stabilize after peak switching occurs when the isotope ratios range between 0,02 and 50. For accurate measurement of less abundant isotopes, longer delay times can be required to minimize the effects of system response and should be determined for each measuring circuit/mass spectrometer.

8 Calculation of the results

8.1 Calculation of isotope ratios

Average raw ion current ratios are obtained by interpolation and using appropriate scale 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 and $\overline{R}_{i/j}$ to designate the average raw isotope current ratio for isotopes i and j.

The isotope ratios $\overline{R'}_{i/j}$, corrected for mass discrimination, are calculated as follows:

$$\overline{R'}_{i/j} = \overline{R}_{i/j}\,[1 + (M_j - M_i)B]^{-1} \qquad \ldots (3)$$

where B is the mass discrimination factor.

8.2 Calculation of the isotopic abundance

The isotopic abundance A_i for the isotope i in a sample, is calculated as follows:

$$A_i = \frac{\overline{R'}_{i/j}}{\sum\limits_k \overline{R'}_{k/j}} \qquad \ldots (4)$$

where all isotope ratios are referred to the same base isotope j.

For example, in a uranium sample which is normally free from ^{232}U, ^{233}U and ^{237}U isotopes, the isotopic abundance of ^{235}U is given by

$$A_5 = \frac{\overline{R'}_{5/8}}{\overline{R'}_{4/8} + \overline{R'}_{5/8} + \overline{R'}_{6/8} + \overline{R'}_{8/8}} \qquad \ldots (5)$$

For a plutonium sample normally free from ^{236}Pu and ^{244}Pu isotopes, the isotopic abundance of ^{239}Pu is equal to

$$A_9 = \frac{\overline{R'}_{9/9}}{\overline{R'}_{8'/9} + \overline{R'}_{9/9} + \overline{R'}_{0/9} + \overline{R'}_{1/9} + \overline{R'}_{2/9}} \qquad \dots (6)$$

The atomic percentage, At_i, for isotope i is equal to

$$At_i = A_i \times 100 \qquad \dots (7)$$

NOTES

3 In case of an insufficient separation of U from Pu in samples containing both elements, the isotopic ratio $\overline{R'}_{8/9}$ should be determined by means of alpha spectrometry, because of possible interferences from ^{238}U in mass spectrometry. The alpha activity ratio of the isotopes ^{238}Pu and (^{239}Pu + ^{240}Pu) of the unspiked sample solution C should be measured within the week following the purification (see clause 5), especially if the abundance of ^{241}Pu is high, since ^{241}Am interferes and will grow in again from the beta decay of ^{241}Pu.

4 The isotopic ratio $\overline{R'}_{8/9}$ is calculated preferably as follows, using the ratio of the activities of the isotope ^{238}Pu and the isotopes (^{239}Pu and ^{240}Pu) measured by alpha spectrometry.

$$R'_{8'/9} = R(\alpha)T_{8'}\left(\frac{1}{T_9} + \frac{R'_{0/9}}{T_0}\right) \qquad \dots (8)$$

where

$T_{8'}$ is the half-life of the isotope ^{238}Pu ($T_{8'}$ = 87,7 yr);

T_9 is the half-life of the isotope ^{239}Pu (T_9 = 24 110 yr);

T_0 is the half-life of the isotope ^{240}Pu (T_0 = 6 563 yr);

$R'_{0/9}$ is the isotopic ratio of ^{240}Pu and ^{239}Pu obtained by mass spectrometry.

8.3 Calculation of the isotopic mass percentage

The conversion to isotopic mass percentage from atom percentage is given by

$$G_i = \frac{At_i M_i}{\sum\limits_k (At_k M_k)} \times 100 \qquad \dots (9)$$

where M_i is the relative atomic mass of the isotope i with

$M_3(^{233}\text{U}) = 233{,}039\ 6$

$M_4(^{234}\text{U}) = 234{,}040\ 9$

$M_5(^{235}\text{U}) = 235{,}043\ 9$

$M_6(^{236}\text{U}) = 236{,}045\ 6$

$M_8(^{238}\text{U}) = 238{,}050\ 8$

$M_{8'}(^{238}\text{Pu}) = 238{,}049\ 6$

$M_9(^{239}\text{Pu}) = 239{,}052\ 2$

$M_0(^{240}\text{Pu}) = 240{,}053\ 8$

$M_1(^{241}\text{Pu}) = 241{,}056\ 8$

$M_2(^{242}\text{Pu}) = 242{,}058\ 7$

$M_{4'}(^{244}\text{Pu}) = 244{,}064\ 2$

8.4 Calculation of content

The contents of uranium, C_A^U, and plutonium, C_A^{Pu}, in grams per kilogram of uranium and plutonium, respectively, are given by the following formulae:

$$C_A^U = C_S^U \times \frac{G_{3S}}{G_{8C}} \times \frac{M_8}{M_3} \times \frac{m_S}{m_C} \times \frac{1 - \dfrac{(\overline{R'}_{3/8})_M}{(\overline{R'}_{3/8})_S}}{(\overline{R'}_{3/8})_M - (\overline{R'}_{3/8})_C} \times F \qquad \dots (10)$$

$$C_A^{Pu} = C_S^{Pu} \times \frac{G_{2S}}{G_{9C}} \times \frac{M_9}{M_2} \times \frac{m_S}{m_C} \times \frac{1 - \dfrac{(\overline{R'}_{2/9})_S}{(\overline{R'}_{2/9})_S}}{(\overline{R'}_{2/9})_M - (\overline{R'}_{2/9})_C} \times F \qquad \dots (11)$$

where

C_S^U and C_S^{Pu} are the contents, in grams per kilogram, of total uranium and plutonium in the spike solution;

NOTE 5 The content in grams per litre is calculated using the accurately measured density of the original sample solution.

G_{3S} and G_{8C} are the isotopic mass percentages of the isotope ^{233}U in the spike solution S, and of the isotope ^{238}U in the diluted sample solution C and original sample solution A, respectively;

G_{2S} and G_{9C} are the isotopic mass percentages of the isotope ^{242}Pu in the spike solution S, and of the isotope ^{239}Pu in the diluted sample solution C and original sample solution A, respectively;

M_3, M_8, M_9 and M_2 are the atomic masses of ^{233}U, ^{238}U, ^{239}Pu and ^{242}Pu, as given in 8.3;

m_C and m_S are the masses of the diluted sample solution C and of the spike solution S, respectively, used to prepare the spiked sample solution M (mixture);

$(\overline{R'}_{i/j})_M$, $(\overline{R'}_{i/j})_S$ and $(\overline{R'}_{i/j})_C$ are the isotope ratios corrected for mass discrimination as described in 8.1 in the spiked sample solution M (mixture), in the spike solution S and the diluted sample solution C or original sample solution A, respectively;

F is the dilution factor on a weight basis.

8.5 Isotope decay correction

The report of the analyses of plutonium containing solutions or mixed samples of uranium and plutonium shall include the date of the mass spectrometric measurements in order to apply decay correction if necessary, e.g. for safeguards verification or umpire purposes. The decay of ^{241}Pu and other Pu isotopes requires the correction of changes in the element concentration and isotopic content of plutonium as well as uranium, because the uranium daughter growth should not be neglected. The analyses of reference materials also require appropriate decay corrections.

9 Repeatability of the measurements

9.1 Element assay

The coefficient of variation of the repeatability of duplicate determinations of uranium and plutonium contents in light water reactor spent fuel solutions observed at an industrial plant over a typical reprocessing campaign is about 0,2 %.

9.2 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.

10 Accuracy of the method

10.1 Element assay

A plant laboratory analysed 21 solutions of plutonium nitrate by the isotope dilution method described in this International Standard. 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 %.

Table 1 — Expected coefficients of variation of repeatability and reproducibility of isotopic analyses by thermal ionization mass spectrometry

Isotope	Abundance %	Repeatability[1)] (% relative)	Reproducibility[2)] (% relative)
^{235}U	0,2	0,7	0,9
	0,7	0,5	0,9
	3	0,3	0,4
^{238}U	97 to 99	0,01	0,015
^{238}Pu	0,3	2	3
	1,5	0,7	1
^{239}Pu	50 to 80	0,1	0,15
^{240}Pu	10 to 30	0,2	0,3
^{241}Pu	3 to 15	0,3	0,4
^{242}Pu	1 to 5	0,3	0,4
^{239}Pu + ^{241}Pu	65 to 83	0,1	0,15

1) Coefficient of variation of replicate analyses performed at the same time at a single laboratory (as defined in ISO 3724).

2) Coefficient of variation of replicate analyses performed at different laboratories or times, under the most different conditions possible (as defined in ISO 3724).

10.2 Isotopic analysis

The coefficients of variation of the reproducibility expected for the isotopic analyses are listed in table 1.

11 Interferences

Ions with mass 233, 234, 235, 236 and 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 emit hexa-atomic ions of mass 234 and 236.

Ions with mass 238 (particularly ^{238}U), 239, 240, 241 and 242 cause interference in the analysis of plutonium if they have not been completely removed during chemical treatment; ^{241}Am formed from ^{241}Pu shall be removed 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 volatilization of uranium and plutonium occurs. The degree to which such alterations occur depends on the technique selected for loading the sample on to the filament as well as the concentration of the interfering elements. It is recommended to test for these effects by addition of known amounts of the various elements to pure standard solutions of uranium and plutonium and to ensure that these impurities are removed to below the level at which these effects occur.

Annex A
(normative)

Preparation and standardization of spike solutions

A.1 Scope

This annex describes a procedure to prepare and standardize solutions of ^{233}U and/or ^{242}Pu spikes suitable for the isotope dilution analysis of the uranium and plutonium concentrations in spent fuel solutions or other industrial solutions.

A.2 Principle

Chemically-pure compounds of separated ^{233}U or ^{242}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 ^{233}U and ^{242}Pu stock solutions may be mixed to prepare diluted mixed spike solutions.

The diluted spike solutions are standardized by isotope dilution mass spectrometry against standard solutions of certified chemical reference materials.

A.3 Standard solutions of certified chemical reference materials

A.3.1 Stock solution of natural uranyl nitrate

Open a unit of the natural uranium metal standard (3.1) and clean it in ethanol.

Then rinse with distilled water and etch 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, P_1, in milligrams, to the nearest 0,1 mg immediately before the surface oxidizes again.

Transfer into a tared Erlenmeyer 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 recesses, 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, P_2, in grams, of the solution to the nearest 0,01 %.

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

$$U = \frac{P_1}{P_2} \times C_\mathrm{s} \qquad \ldots \text{(A.1)}$$

where C_s is the purity of the chemical reference material reported on the certificate and expressed in mass fraction of uranium element (grams of uranium per gram of standard).

Cap the flask tightly and homogenize the solution.

Select a cap having a very stable tare, within ± 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. Estimate, preferably experimentally, the coefficient of variation, S_P, of the errors which might have occured during its preparation.

A.3.2 Stock solution of plutonium nitrate

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

Transfer one unit of plutonium metal standard (3.3) into a glove box.

Record its mass, P'_1, in milligrams, given in the certificate.

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

Measure immediately the gross mass of the flask and calculate the net mass of the metal, P_1'', collected in the flask; compare it to the certified value P_1' to confirm the identity of the unit.

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

Cap the Erlenmeyer flask with a reflux head and proceed with a gentle dissolution; avoid losing solution aerosols.

When the dissolution is complete, dilute to about 100 ml with 3 mol/l nitric acid solution (3.10) 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 P'_2, in grams, of the solution.

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

$$Pu = \frac{P'_1}{P'_2} \times C'_s \qquad \ldots (A.2)$$

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

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

A.4 Preparation of spike solutions

A.4.1 Solution of ^{233}U spike

Select a batch of a chemically-pure compound of separated ^{233}U isotope sufficiently enriched so that its ^{238}U/^{233}U or ^{235}U/^{233}U isotope ratios can be measured with an accuracy of ± 0,000 5 or better. A material with ^{233}U isotope abundance of 80 % 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'Énergie Atomique (ORIS, Gif-sur-Yvette, France).

Dissolve this material if necessary and dilute it to the desired concentration in 3 mol/l nitric acid solution (3.10). Store in sealed ampoules or in tight glass vessels allowing measurement of evaporation losses.

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

If the ^{233}U spike contains, for example, 200 µg of ^{239}Pu isotope per gram of ^{233}U isotope, mixing it with the ^{242}Pu spike in a 1:100 proportion will increase the ^{239}Pu/^{242}Pu isotope ratio by 0,02.

A.4.2 Solution of ^{242}Pu spike

Select a batch of a chemically-pure compound of separated ^{242}Pu isotope sufficiently enriched so that its ^{239}Pu/^{242}Pu isotope ratio can be measured with an accuracy of ± 0,000 5 or better. A material with a ^{242}Pu isotope abundance of 80 % 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 (3.8) (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 ^{233}U spike (see A.4.1).

A.4.3 Mixed solution of ^{233}U and ^{242}Pu spikes

When both the uranium and plutonium concentrations are to be analysed in routine 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 separated 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.5 Standardization of spike solutions

A.5.1 Standardization of the uranium spike

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

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 ^{238}U isotope abundance should all agree to ± 0,05 % or better with the abundance indicated on the certificate. The results of the measurements of the ^{233}U/^{238}U isotope ratios should also agree within ± 0,05 % 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, 238.

The results of the measurements of the ^{238}U/^{233}U isotope ratio should all agree to ± 0,05 % or better.

A.5.1.3 Standardization of the ^{233}U concentration in the spike solution

Pipette and weigh accurately N aliquots ($N \geqslant 1$) of about 1 ml from each of the L diluted solutions of certified chemical standard. To each aliquot, add an accurately weighed aliquot of the spike, also about 1 ml. 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 ($R \geqslant 4$). The ^{233}U concentration in the spike solution, C_S^3, in micrograms per gram is calculated according to the following equation:

$$C_\mathrm{S}^3 = \frac{m_\mathrm{st}^\mathrm{U}}{m_\mathrm{S}} \times \frac{G_\mathrm{8st}}{100} \times \frac{M_3}{M_8} \times \frac{(\overline{R'}_{3/8})_\mathrm{M} - (\overline{R'}_{3/8})_\mathrm{st}}{1 - \dfrac{(\overline{R'}_{3/8})_\mathrm{M}}{(\overline{R'}_{3/8})_\mathrm{S}}} \qquad \ldots \text{(A.3)}$$

where

m_st^U is the mass of uranium of certified chemical standard, in micrograms, mixed with a mass m_S of the spike solution, in grams;

G_8st is the ^{238}U isotopic abundance of the chemical standard, expressed as a mass percentage;

$(\overline{R'}_{3/8})_\mathrm{st}$ is the ^{233}U/^{238}U isotope ratio measured in the diluted solutions of uranium chemical standard.

The other symbols have the same meaning as in equation (10).

Perform an analysis of variance of the results to obtain estimates of the coefficient of variation of the different sources of errors in the standardization process.

The coefficient of variation of the mass spectrometric measurements, S_I, should be about 0,2 % or less.

The coefficients of variation of the aliquoting, S_A, the dilutions, S_D, and the preparation of the stock solutions of certified chemical reference material, S_P, should all be smaller than 0,05 %. The best estimate of the ^{233}U concentration of the spike is the arithmetic mean of all LNR results.

Its coefficient of variation S_E is equal to

$$S_\mathrm{E} = \left(\frac{\overline{S}_\mathrm{I}^2}{LNR} + \frac{\overline{S}_\mathrm{A}^2}{LN} + \frac{\overline{S}_\mathrm{D}^2}{L} + \overline{S}_\mathrm{P}^2 + S_\mathrm{C}^2 \right)^{1/2} \qquad \ldots \text{(A.4)}$$

where S_C is the coefficient of variation of the chemical purity of the natural uranium metal standard, reported in its certificate.

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 ^{239}Pu isotope abundance 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 ^{242}Pu/^{239}Pu isotope ratios should also agree within ± 0,05 % 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 ^{239}Pu/^{242}Pu isotope ratio should all agree to ± 0,05 % or better.

A.5.2.3 Standardization of the ^{242}Pu concentration in the spike solution

The ^{242}Pu concentration in the spike solution, C_S^2, in micrograms per gram, is calculated according to the following equation:

$$C_\mathrm{S}^2 = \frac{m_\mathrm{st}^\mathrm{Pu}}{m_\mathrm{S}} \times \frac{G_\mathrm{9st}}{100} \times \frac{M_2}{M_9} \times \frac{(\overline{R'}_{2/9})_\mathrm{M} - (\overline{R'}_{2/9})_\mathrm{st}}{1 - \dfrac{(\overline{R'}_{2/9})_\mathrm{M}}{(\overline{R'}_{2/9})_\mathrm{S}}} \qquad \ldots \text{(A.5)}$$

where

$m_\mathrm{st}^\mathrm{Pu}$ is the mass of plutonium of chemical standard, in micrograms, mixed with a mass m_S of the spike solution, in grams;

G_9st is the ^{239}Pu isotopic abundance of the chemical standard, expressed as a mass percentage;

$(\overline{R'}_{2/9})_{st}$ is the $^{242}Pu/^{239}Pu$ isotope ratio measured in the diluted solutions of chemical standard.

The other symbols have the same meaning as in equation (11).

A.5.3 Standardization of mixed spike solutions

Mixed spike solutions are standardized 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 assay 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 given in A.5.1 and A.5.2.

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