
**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*

[ISO 8299:2005](https://standards.iteh.ai/catalog/standards/sist/6836d986-f769-423b-aa91-b3aef02b834d/iso-8299-2005)

[https://standards.iteh.ai/catalog/standards/sist/6836d986-f769-423b-aa91-
b3aef02b834d/iso-8299-2005](https://standards.iteh.ai/catalog/standards/sist/6836d986-f769-423b-aa91-b3aef02b834d/iso-8299-2005)



PDF disclaimer

This PDF file may contain embedded typefaces. In accordance with Adobe's licensing policy, this file may be printed or viewed but shall not be edited unless the typefaces which are embedded are licensed to and installed on the computer performing the editing. In downloading this file, parties accept therein the responsibility of not infringing Adobe's licensing policy. The ISO Central Secretariat accepts no liability in this area.

Adobe is a trademark of Adobe Systems Incorporated.

Details of the software products used to create this PDF file can be found in the General Info relative to the file; the PDF-creation parameters were optimized for printing. Every care has been taken to ensure that the file is suitable for use by ISO member bodies. In the unlikely event that a problem relating to it is found, please inform the Central Secretariat at the address given below.

iTeh STANDARD PREVIEW
(standards.iteh.ai)

[ISO 8299:2005](#)

<https://standards.iteh.ai/catalog/standards/sist/6836d986-f769-423b-aa91-b3aef02b834d/iso-8299-2005>

© ISO 2005

All rights reserved. Unless otherwise specified, no part of this publication may be reproduced or utilized in any form or by any means, electronic or mechanical, including photocopying and microfilm, without permission in writing from either ISO at the address below or ISO's member body in the country of the requester.

ISO copyright office
Case postale 56 • CH-1211 Geneva 20
Tel. + 41 22 749 01 11
Fax + 41 22 749 09 47
E-mail copyright@iso.org
Web www.iso.org

Published in Switzerland

Contents

Page

Foreword.....	iv
1 Scope.....	1
2 Normative references	1
3 Principle	1
4 Reagents and materials.....	2
5 Apparatus.....	4
6 Apparatus for mass spectrometry	4
7 Sampling	5
8 Preparation of the filaments.....	7
9 Instrument calibration	8
10 Isotopic mass spectrometric measurements.....	9
11 Calculation of the results	10
12 Blanks.....	13
13 Quality control.....	13
14 Repeatability of the measurements	14
15 Accuracy of the method	14
16 Interferences.....	15
Annex A (normative) Preparation and standardization of spike solutions.....	16
Bibliography	22

Foreword

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

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

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.

iTeh STANDARD PREVIEW
(standards.iteh.ai)

[ISO 8299:2005](https://standards.iteh.ai/catalog/standards/sist/6836d986-f769-423b-aa91-b3aef02b834d/iso-8299-2005)

<https://standards.iteh.ai/catalog/standards/sist/6836d986-f769-423b-aa91-b3aef02b834d/iso-8299-2005>

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 $^{238}\text{Pu}/^{239}\text{Pu}$ 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 $^{233}\text{U}/^{236}\text{U}$ 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 $^{233}\text{U}/^{242}\text{Pu}$ 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 $\mu\text{g/g}$ to 2 $\mu\text{g/g}$ 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 (standards.iteh.ai)

4.2.1 Nitric acid solutions, $c(\text{HNO}_3) = 0,3 \text{ mol/l}$, 1 mol/l, 3 mol/l, 4 mol/l, 7 mol/l.

4.2.2 Ferrous sulfate, $c(\text{FeSO}_4) = 0,2 \text{ mol/l}$, in amidosulfuric acid, $c(\text{NH}_2\text{SO}_3\text{H}) = 0,2 \text{ mol/l}$, and sulfuric acid, $c(\text{H}_2\text{SO}_4) = 1 \text{ mol/l}$, freshly prepared.

4.2.3 Sodium nitrite, $c(\text{NaNO}_2) = 0,7 \text{ mol/l}$, freshly prepared.

4.2.4 Hydroxylamine nitrate, $c(\text{NH}_2\text{OH}) = 0,019 \text{ mol/l}$, 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, $c(\text{HF}) = 0,01 \text{ mol/l}$.

4.2.8 Aluminium nitrate, $c[\text{Al}_2(\text{NO}_3)_3] = 0,004 \text{ mol/l}$.

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.

- 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.
- 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.
- 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.
- 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):

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

- 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.
- 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.
- 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.