
**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**

iTeh STANDARD PREVIEW

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

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

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

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

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

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

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

- the procedure for the preparation of resin used for separation and purification of the samples has been added in [5.3](#);
- sample preparation procedure from pellet, powder and other material forms to the solution has been added in [8.1](#);
- uncertainty of the measurement is considered in [Clause 15](#) instead of repeatability and accuracy.

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

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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

1 Scope

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

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

2 Normative references

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

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

3 Terms and definitions

No terms and definitions are listed in this document.

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

- ISO Online browsing platform: available at <https://www.iso.org/obp>
- IEC Electropedia: available at <http://www.electropedia.org/>

4 Principle

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

The described method consists of two separate TIMS measurements:

a) Isotopic measurement

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

b) Element concentration measurement

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

The IDMS method includes the following steps:

- sample dilution by mass if necessary;
- aliquoting and spike addition by mass;
- valency adjustment and isotope-exchange chemistry resulting in an isotopically equilibrated mixture;
- chemical purification/separation;
- sample loading and oxidation on filaments;
- isotope ratio measurements by TIMS on spiked and non-spiked fractions.

This procedure describes two methods of TIMS measurements:

- Total evaporation (TE), multi-Faraday collector measurements. This method consumes the whole sample. The ion beam of the element is totally collected. There are several advantages with this method. It allows precise measurements of small sample amounts, can easily calculate the mass discrimination factor and is easily adopted for automatic measurements. The TE method relies almost entirely on separate measurements of standards to calculate measurement uncertainty and precision.
- Bias correction method (conventional multi-Faraday collector measurements). In the bias correction method, the different isotopes are collected in a limited period of the sample evaporation. The data are collected in blocks, typically containing 10 to 20 sets (scans) of measurements. With the bias correction method, it is possible to calculate the precision of the ratio measurements within each block and between blocks and to use the internal precision data to assess measurement quality on a filament-by-filament basis.

5 Reference materials and reagents

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

5.1 Spikes and reference materials

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

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

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

- from other uranium metal, powder or pellet with an elemental concentration certified to 0,05 % ($k = 2$) or better, such as NBL-CRM-116-A (HEU metal), CRM-125-A(UO₂ pellet) and CRM-129 (U₃O₈ powder).

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

- plutonium metal with an elemental concentration certified to 0,05 % ($k = 2$) or better, such as NBL-CRM-126 or 126-A, EC-201, CETAMA-MP2 or NBS-949, with a ²³⁹Pu isotopic abundance of 90 % or more, certified to 0,05 % ($k = 2$) or better; the same isotopic abundance requirements apply if ²⁴⁰Pu, ²⁴²Pu or ²⁴⁴Pu is used as the spike isotope;
- certified plutonium standard solution enriched in ²⁴⁰Pu, ²⁴²Pu or ²⁴⁴Pu isotope in case where 97 % enriched ²³⁹Pu is used as a spike.

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

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

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

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

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

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

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

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

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

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

5.2 Other chemical reagents

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

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

5.2.2 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.

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

5.2.4 Hydrogen peroxide solution, $c(\text{H}_2\text{O}_2) = 10 \text{ mol/l}$.

5.2.5 Silver nitrate, $c(\text{AgNO}_3) = 0,01 \text{ mol/l}$ or, suitable for precipitation method.

5.2.6 Ascorbic acid, $c(\text{C}_6\text{H}_8\text{O}_6) = 0,1 \text{ mol/l}$ in nitric acid $0,1 \text{ mol/l}$.

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

5.2.8 Sodium hydroxide, $c(\text{NaOH}) = 1 \text{ mol/l}$.

5.2.9 Ammonium sulfate, $c((\text{NH}_4)_2\text{SO}_4) = 0,5 \text{ mol/l}$.

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

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5.3.1 General

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

5.3.2 Preparation of resin

5.3.2.1 Anion exchange resin¹⁾

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

- a) Twice with the equivalent resin bed volumes of distilled water;
twice with the equivalent resin bed volumes of $0,3 \text{ mol/l}$ nitric acid (5.2.1);
twice with the equivalent resin bed volumes of 4 mol/l nitric acid (5.2.1);
with the equivalent resin bed volumes of 7 mol/l to 8 mol/l nitric acid (5.2.1) until a sample of the supernatant solution no longer yields a chloride precipitate after addition of silver nitrate (5.2.5) or confirm by Cl test paper.
- b) With 20 times the resin bed volumes of 1 mol/l sodium hydroxide (5.2.8) and then wash by distilled water;
2 times the resin bed volumes of $0,5 \text{ mol/l}$ ammonium sulfate (5.2.9) and then wash by distilled water;
10 times the resin bed volumes of $1,3 \text{ mol/l}$ nitric acid (5.2.1) and then wash by distilled water;

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

3 times the resin bed volumes of 1 mol/l sodium hydroxide (5.2.8) and then wash by distilled water;
 3 times the resin bed volumes of 1,3 mol/l nitric acid (5.2.1) and then wash by distilled water;
 3 times the resin bed volumes of 1 mol/l sodium hydroxide (5.2.8) and then wash by distilled water;
 3 times the resin bed volumes of 1,3 mol/l nitric acid (5.2.1) and then wash by distilled water.

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

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

with the equivalent resin bed volumes of distilled water;

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

5.3.2.2 Extraction separation resins²⁾

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

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

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

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6 Apparatus <https://standards.iteh.ai/catalog/standards/sist/baa0c317-643a-46d3-942f-0fb468cdc57c/iso-8299-2019>

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

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

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

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

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

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

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

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

7 Apparatus for mass spectrometry

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

7.1.1 General specifications

- Mass range: 10 amu to 280 amu.
- Resolution: > 380 % at 5 % of the peak height; this resolution should be measured at the ^{235}U and ^{238}U masses.
- Peak top flatness: Less than 10^{-4} relative change (300 ppm by mass) in the signal for a change of $\pm 0,025$ mass units 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 5 000 uranium atoms on the sample filament.

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

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

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

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

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

8 Sample preparation

8.1 Subsampling and spiking

Spikes isotope composition should differ significantly from the samples in order to obtain enough isotope dilution effect for accurate IDMS measurement. The spike should be selected based on previous evaluation of suitable mixing ratio^[2]. Other conditioning steps, acid concentrations and heating temperatures should also be optimized depending on the sample types. Examples of subsampling and spiking procedures are listed below.

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

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