

FINAL  
DRAFT

INTERNATIONAL  
STANDARD

ISO/FDIS  
24459

ISO/TC 85/SC 5

Secretariat: BSI

Voting begins on:  
2021-07-06

Voting terminates on:  
2021-08-31

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## Determination of uranium content in samples coming from the nuclear fuel cycle by L-absorption edge spectrometry

*Détermination de l'uranium dans les solutions du cycle du combustible nucléaire par absorption de rayons X à la discontinuité L*

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Reference number  
ISO/FDIS 24459:2021(E)

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Published in Switzerland

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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](http://www.iso.org/directives)).

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This document was prepared by Technical Committee ISO/TC 85, *Nuclear energy, nuclear technologies, and radio protection*, Subcommittee SC 5, *Analytical methodology in the nuclear fuel cycle*.

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](http://www.iso.org/members.html).

# Determination of uranium content in samples coming from the nuclear fuel cycle by L-absorption edge spectrometry

## 1 Scope

This document specifies a method for the determination of uranium concentrations in nitric acid or TBP-DILUANT (for example TBP-kerosene) solutions coming from the nuclear fuel cycle.

The method is applicable

- for process control to solutions, free of suspension, which contain between 10 g/l to 300 g/l uranium, and
- for high accuracy purposes (Safeguards) to nitric acid solutions, free of suspension, which contain between 100 g/l and 220 g/l uranium.

Having

- the content of neptunium and plutonium impurities in the solution less than 1 % of the uranium content.
- the content of neutron poisons (gadolinium, erbium) less than 1 % of the uranium content to ensure the absence of significant interferences at the level of required precision, for high accuracy purposes.

The method is applicable to solid samples as well, provided that they can be fully dissolved in nitric acid.

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## 2 Normative references

There are no normative references in this document.

## 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 <https://www.electropedia.org/>

## 4 Principle

A highly collimated X-ray beam passes through a uranium solution with well-defined path length. The transmission spectrum is recorded with a solid-state detector. A sharp jump of the photon transmission, which is related to the concentration of uranium, occurs at the L-edge energy of uranium ( $E_{LIII} = 17,17$  keV). Uranium concentration is determined from the size of the jump using calibration and spectrum processing algorithms.

The proposed spectrum processing algorithms require the acquisition of reference spectrum to cancel out the influence of the matrix.

For high accuracy measurement, the isotopic composition of uranium and the temperature shall be known and corrections may apply.

The uncertainty of the number of counts in the channels before and after the L-edge is one of the main contributors to the measurement uncertainty.

The acquisition time needed to reach the necessary number of counts depends of the total count rate. The total count rate is a function of the intensity of the X-ray generator, of the characteristic of instrument, and of the concentration of uranium.

It is therefore specific to the laboratory, which shall evaluate beforehand the fit-for-purpose accuracy that will decide the target total count in the spectrum, the count rate and the acquisition time.

For high accuracy measurements, a minimum total number of counts of 2 000 000 in the fitting window is required to ensure satisfactory statistics around the L-edge. The count rates and measurement times given as indication in the document reflect this requirement. The reference, calibration and sample spectra shall be recorded with the same count rate and the same high voltage (HV) cut-off.

For process control purposes, the necessary total number of counts will depend of the needed accuracy. The measurement should be performed at the same HV cut-off and current.

## 5 Reagents and materials

Only analytical grade reagents shall be used.

All aqueous solutions shall be prepared with distilled water or deionized water.

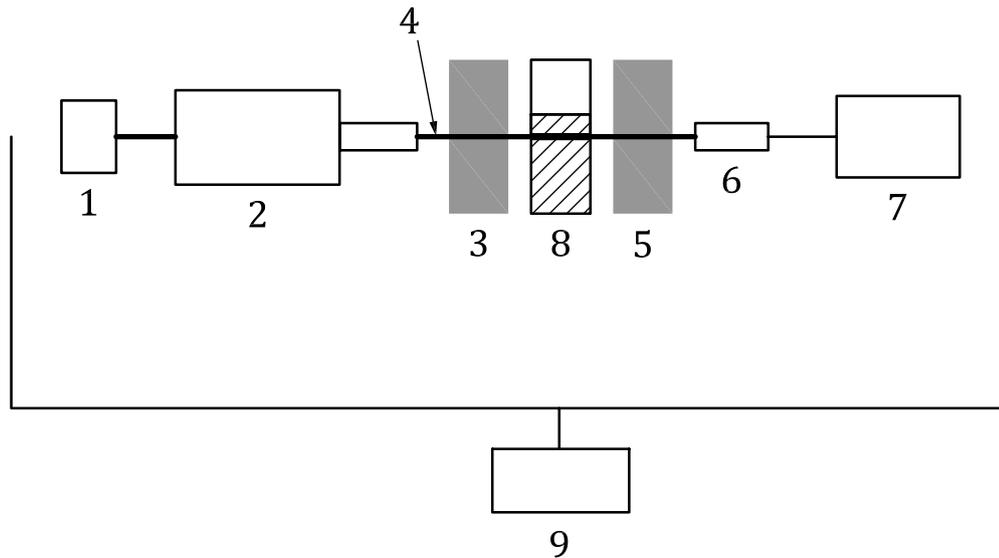
**5.1 Nitric acid solutions,**  $c(\text{HNO}_3) \approx 3 \text{ mol/l}$ , prepared from  $w(\text{HNO}_3) 65 \%$ ,  $\rho = 1,42 \text{ g/cm}^3$ .

**5.2 Uranium reference solutions.** (standards.iteh.ai)

These solutions are used for calibration and quality control purposes. They should ideally be prepared from a solid or liquid material with known uranium concentration, and known uranium isotopic composition for high accuracy purposes. The standard uncertainty of the uranium concentration should be equal or better than 0,06 %. The use of certified reference material traceable to SI units is recommended.

## 6 Apparatus

The L-absorption edge spectrometer consists of an X-ray tube, an X-ray detector, a multichannel analyser, a temperature sensor and software for data acquisition and processing. A principle diagram of the instrument components is shown in [Figure 1](#).

**Key**

1	HV controller	6	detector
2	X-ray tube	7	MCA
3	collimator	8	sample cell
4	temperature sensor	9	computer
5	collimator		

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**Figure 1 — Schematic of the instrument components**

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**6.1 X-ray tube.** <https://standards.iteh.ai/catalog/standards/sist/efbb2ec8-668e-45ad-be64-4a29350e71bd/iso-fdis-24459>

The maximum working voltage of X-ray tube is higher than 25 kV, voltage-controlled, current-controlled. It shall be stable over time and shall reach an intensity (adjustable, usually lower than 100  $\mu$ A) high enough to ensure satisfactory total count rate for fast and accurate measurement (as described in [Clause 4](#)).

**6.2 Shielding and collimator.**

The shielding body is made of brass or other shield materials. X-ray tube, X-ray detector and sample cell are directly mounted in the shielding body. The thickness of the shielding is chosen to ensure no X-ray leakage, and to satisfy the radioprotection requirements.

The collimator is made of tungsten, or other materials, whose fluorescence X-rays do not interfere with the region of interest.

**6.3 Sample cell.**

The sample cell can be made of glass or polycarbonate (PC), which can withstand nitric acid and TBP-DILUANT or in quartz that is resistant to nitric acid.

The optimum path length and the specifications of the cell depend on the characteristic of the apparatus and the analytical needs.

Examples of cell specifications:

- for process control purposes, disposable 4mm long PC cell;
- for high accuracy purposes, fixed flow-through cell with a path length of 2 mm and a volume of 125  $\mu$ l.

#### 6.4 X-ray detector and multichannel analyser.

The X-ray detector should have an energy resolution better than 135 eV (for the  $^{55}\text{Fe}$  peak at 5,9 keV). For example, a Peltier-cooled, high-resolution  $10\text{ mm}^2 \times 0,5\text{ mm}$  silicon drift detector.

#### 6.5 Software.

##### 6.5.1 For data acquisition.

Commercial or non-commercial spectroscopy software can be used to collect the X-ray spectrum.

##### 6.5.2 For data processing.

At the time of writing this document, no commercial solutions are available for the fitting of L-edge transmission spectrum. Examples of fitting algorithm are described in [7.5](#).

### 7 Method

#### 7.1 Pre-checks

Ensure that the temperature sensor is working properly and that the temperature is close to the temperature of reference.

Setup the multi-channel analyser:

- adjust the gain so that the peaks for energy calibration and the  $L_{\text{III}}$  edge of uranium are evenly distributed across the spectrum;
- perform the energy calibration by using induced X-rays in the spectrum, such as the characteristic lines of the X-ray tube target (silver or molybdenum) or the target positioned in a side path (germanium), and the collimator (titanium or brass).

Ensure that the HV cut-off and the total count rate are as expected. If not, adjust the voltage and the intensity of the X-ray generator.

#### 7.2 Reference spectrum

The matrix of the solution used to obtain the reference spectrum shall be similar to the one of the sample.

Prepare a solution with  $\text{HNO}_3$ , 3 mol/l using the reagents described in [5.1](#). For process control, 3 mol/l  $\text{HNO}_3$  can be used as the matrix solution for both nitric acid and TBP-DILUANT solutions.

Acquire the reference spectrum with a counting time long enough to ensure low statistical counting uncertainty. For high accuracy measurement, the count rate shall be similar to the one used to measure the samples and the reference solutions.

#### 7.3 Calibration

Prepare one or more uranium reference solutions with concentration close to the expected concentration of the samples. For process control, the uranium reference solutions also can be used to analyse TBP-DILUANT samples.

The solutions shall be prepared with the materials and reagents as described in [Clause 5](#). Dissolution and dilutions shall be performed gravimetrically on a calibrated analytical balance.

Measure the relevant reference solution(s) in replicates with a counting time long enough to ensure low statistical counting uncertainty.

## 7.4 Sample measurement

If feasible, and if there is prior knowledge of the concentration of uranium in the sample, the latter should be prepared with the materials and reagents (as described in [Clause 5](#)) to reach the optimum concentration between reasonable counting time and high enough L-edge.

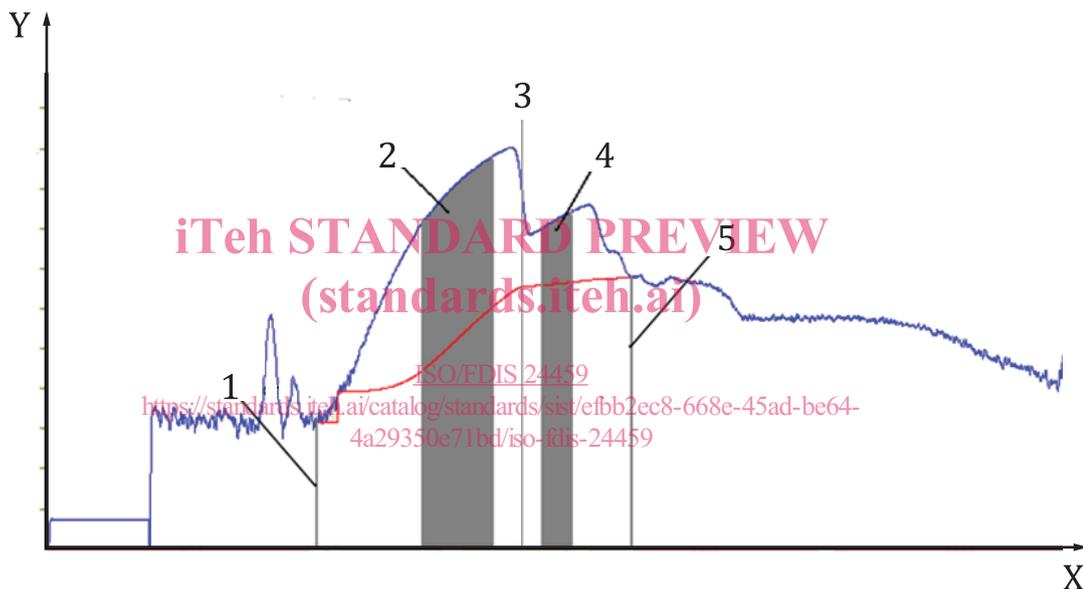
Dissolution and dilutions shall be performed gravimetrically on a calibrated analytical balance.

Measure each sample in replicates with a counting time long enough to ensure low statistical counting uncertainty. For high accuracy purposes, the count rate should be similar to the one used to acquire the reference and calibration spectra.

## 7.5 Spectrum evaluation

### 7.5.1 Region of interest

The regions of interest for extrapolation fitting are shown in [Figure 2](#).



#### Key

- X channel/energy
- Y counts
- 1 left bound of background region
- 2 below fitting region
- 3 L-absorption edge
- 4 above fitting region
- 5 right bound of background region

**Figure 2 — The fitting regions**

### 7.5.2 Smoothing (optional)

One of the possible approaches is the cubic smoothing algorithm with seven-point approximation to smooth the spectra as given by [Formula \(1\)](#):

$$Y_i = (-2 \times Y_{0,i-3} + 3 \times Y_{0,i-2} + 6 \times Y_{0,i-1} + 7 \times Y_{0,i} + 6 \times Y_{0,i+1} + 3 \times Y_{0,i+2} - 2 \times Y_{0,i+3}) / 21 \quad (1)$$

where

$Y_i$  is the counts at channel  $i$  after smoothing;

$Y_{0,i}$  is the raw counts at channel  $i$ .

All spectra are smoothed.

### 7.5.3 Background subtraction

The background counts at channel  $i$  is calculated following [Formula \(2\)](#):

$$Y_{i,b} = Y_l + (Y_r - Y_l) \left[ \frac{\sum_{j=l}^i Y_j}{\sum_{j=l}^r Y_j} \right] \quad (2)$$

where

$Y_{i,b}$  is the background counts at channel  $i$ ;

$Y_j$  is the counts at channel  $j$ ;

$l$  is the left bound of the background region;

$r$  is the right bound of the background region;

$Y_l$  is the average counts of left background region;

$Y_r$  is the average counts of right background region.

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The net spectra for both reference spectrum and sample spectrum are obtained by subtracting respective background spectrum as shown in [Formula \(3\)](#):

$$Y_{i,n} = Y_i - Y_{i,b} \quad \text{https://standards.iteh.ai/catalog/standards/sist/efbb2ec8-668e-45ad-be64-4a29350e71bd/iso-fdis-24459} \quad (3)$$

where  $Y_{i,n}$  is the net counts at channel  $i$ .

### 7.5.4 Calculation of the X-ray transmission

The background-corrected spectrum is divided channel by channel by the background-corrected reference spectrum yielding a transmission spectrum.

The transmission at each channel is calculated by [Formula \(4\)](#):

$$T_i = \frac{(Y_{i,n})_s}{(Y_{i,n})_r} \quad (4)$$

where

$T_i$  is the transmission at channel  $i$ ;

$(Y_{i,n})_s$  is the net counts at channel  $i$  of sample spectrum;

$(Y_{i,n})_r$  is the net counts at channel  $i$  of reference spectrum.

Linear regression is performed respectively on both fitting intervals below and above the L absorption edge, according to [Formula \(5\)](#).

$$\ln \left[ \ln \left( \frac{1}{T_i} \right) \right] = c \ln(E_i) + d \quad (5)$$

where