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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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# Foreword

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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*.

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# 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 of 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.

## 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 ($E_{\mathrm{LIII}}$ = 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.

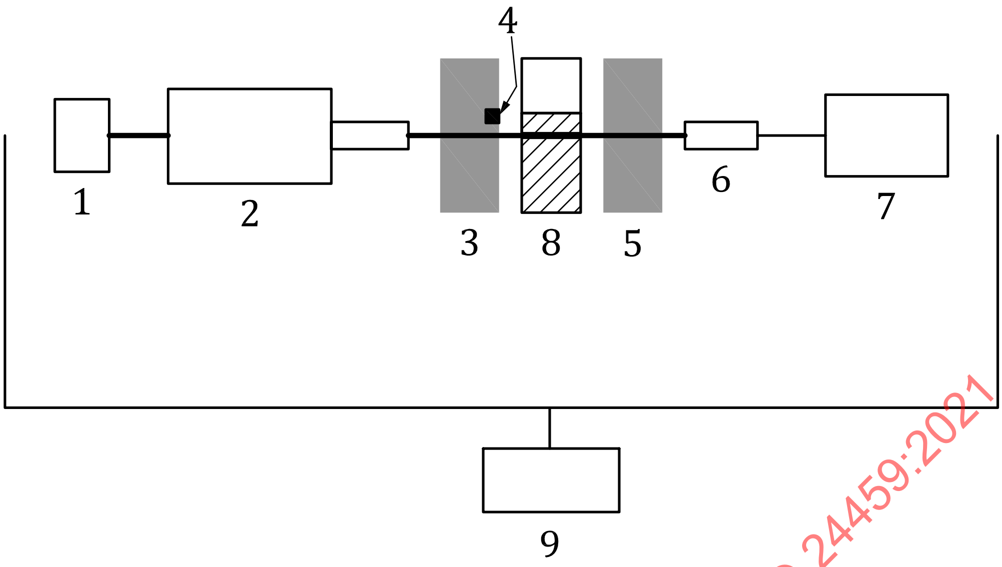
### 5.1 **Nitric acid solutions**, $c(HNO_3) \approx 3$ mol/l, prepared from $w(HNO_3)$ 65 %, $\rho = 1{,}42$ g/cm$^3$.

### 5.2 Uranium reference solutions.

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 with its HV control unit, an X-ray detector, a multichannel analyser (MCA), 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 control unit |
| 2 | X-ray tube |
| 3 | collimator |
| 4 | temperature sensor |
| 5 | collimator |
| 6 | detector |
| 7 | MCA |
| 8 | sample cell |
| 9 | computer |

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

### 6.1 X-ray tube.

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 µA) 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 shielding 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 µl.

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

The X-ray detector should have an energy resolution better than 135 eV (for the $^{55}$Fe peak at 5,9 keV). For example, a Peltier-cooled, high-resolution 10 mm$^2$ × 0,5 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 $L_{III}$ 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 $HNO_3$, 3 mol/l using the reagents described in 5.1. For process control, 3 mol/l $HNO_3$ 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.

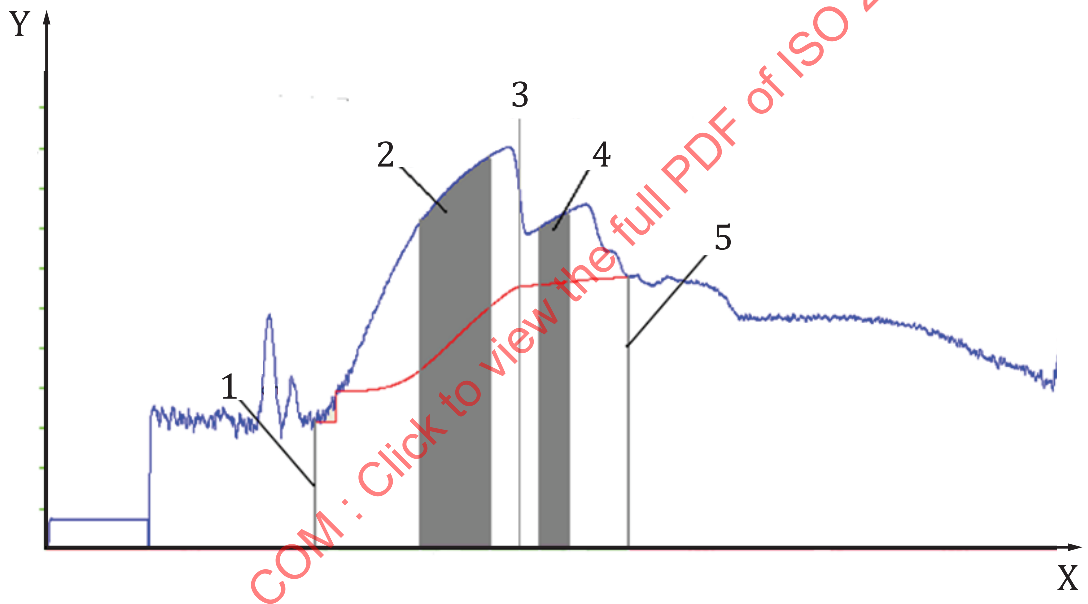
Dissolution and dilutions shall be performed gravimetrically on a calibrated analytical balance.

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):

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

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):

$$\mathrm{Y}_{\mathrm{i},b} = Y_l + (Y_r - Y_l)\left[\sum_{j=l}^{i} Y_j \Big/ \sum_{j=l}^{r} Y_j\right] \tag{2}$$

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.

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

$$Y_{i,n} = Y_i - Y_{i,b} \tag{3}$$

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):

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

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).

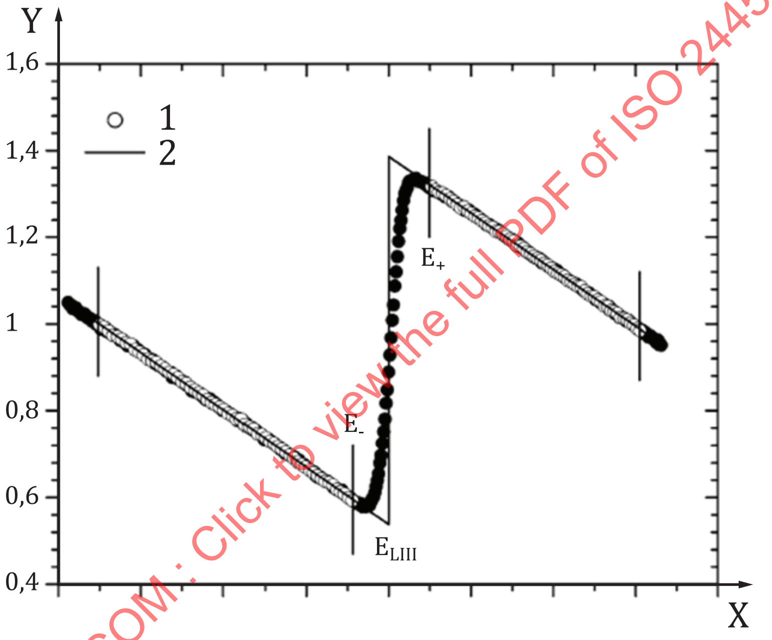
$$\ln\left[\ln\left(\frac{1}{T_i}\right)\right] = c\ln(E_i) + d \tag{5}$$

where

$E_i$ is the energy corresponding to channel $i$;

$c$, $d$ are the fitting factors.

The two lines, which are obtained from the fitting intervals below and above the L-absorption edge, are extrapolated to the edge energy $E_- = E_+ = E_{\mathrm{LIII}}$, and the transmission $T_{E\_}$ and $T_{E+}$ are calculated. Figure 3 shows the processing of the X-ray spectrum near $\mathrm{L_{III}}$ edge.



**Key**

X In($E$)

Y $\ln\left[\ln\left(\frac{1}{T}\right)\right]$

1 fitted intervals

2 linear fits

**Figure 3 — Processing of the X-ray spectrum near $L_{\mathrm{III}}$ edge**

## 7.6 Calculation of the concentration of uranium

For process control, the concentration of uranium is calculated according to Formula (6), which is obtained by measuring the reference solution with known uranium concentration.

$$C_{\mathrm{U}} = a\ln\left(\frac{T_{E\_}}{T_{E_+}}\right) + b \tag{6}$$

where

| | |
|---|---|
| $C_U$ | is the concentration of uranium in solution, g/l; |
| $a$, $b$ | are the fitting factors. |

For high accuracy purposes, the concentration of uranium is calculated according to Formula (7):

$$C_U = F_{AW} \cdot F_t \cdot \frac{\ln[T_{E\_} / T_{E_+}]}{\Delta\mu_U \cdot d} \tag{7}$$

where

| | |
|---|---|
| $C_U$ | is the uranium concentration in g/l; |
| $\Delta\mu_U$ | is the difference of uranium mass attenuation coefficients at photon energies $E_+$ and $E\_$, cm$^2$/g. It is determined from calibration on reference solution with known uranium concentration; |
| $d$ | is the sample cell length, in cm; |
| $F_{AW}$ | is the enrichment-dependent correction factor that accounts for the deviation of the atomic weight of enriched uranium from that of natural uranium; |
| $F_t$ | is the temperature correction factor that converts the measured concentration to the reference temperature. |

The calculation method for calibration factors of $F_{AW}$ and $F_t$ is detailed in Annex A.

## 7.7 Quality control

An independent reference solution with a concentration representative of the sample, and prepared as described in 7.3, is measured under the same condition as the sample (7.4). Alternatively, a solid reference sample prepared as described in Annex B can be used for quality control,

— if the difference between the measured and the reference value is higher than the targeted accuracy, and/or

— if the standard deviation between the replicates is too high for the targeted precision.

Investigation should be carried out to determine the root cause of the bias or of the scatter. The parameters that are tracked may include (but not limited to) the HV cut-off, count-rate, detector resolution, energy shift, electromagnetic interference, etc.

Typically for high accuracy measurement, the relative standard deviation stays below 0,16 %.

## 7.8 Uncertainty evaluation

### 7.8.1 Standard uncertainty of the calibration factor

The standard uncertainty for the calibration factor, $\sigma_{cal}$, is calculated according to Formula (8):

$$\sigma_{cal} = \sqrt{\sigma_{ref}^2 + \sigma_t^2 + \sigma_{cell}^2 + \sigma_{count}^2 + \sigma_{repro}^2} \tag{8}$$

where

$\sigma_{\mathrm{ref}}$ is the relative uncertainty contribution from the reference value of the reference solution (including among others, the contributions from certified value, preparation steps (if required));

$\sigma_t$ is the relative uncertainty contribution from the temperature correction;

$\sigma_{\mathrm{cell}}$ is the relative uncertainty contribution from the length of cell ($\sigma_{\mathrm{cell}} = 0$ if unique cell is used);

$\sigma_{\mathrm{count}}$ is the relative uncertainty contribution from the counting precision;

$\sigma_{\mathrm{repro}}$ is the relative uncertainty contribution from the reproducibility.

Under the conditions for high accuracy measurements described in this document, the individual contribution of each factor does not exceed 0,06 % for a standard uncertainty of less than 0,11 %.

### 7.8.2 Standard uncertainty of the uranium concentration

The standard uncertainty for the uranium concentration, $\sigma_{\mathrm{U}}$ is calculated according to Formula (9):

$$\sigma_{\mathrm{U}} = \sqrt{\sigma_{\mathrm{cal}}{}^2 + \sigma_{\mathrm{prep}}{}^2 + \sigma_{\mathrm{lin}}{}^2 + \sigma_{\mathrm{mat}}{}^2 + \sigma_{\mathrm{AW}}{}^2 + \sigma_t{}^2 + \sigma_{\mathrm{cell}}{}^2 + \sigma_{\mathrm{count}}{}^2 + \sigma_{\mathrm{repro}}{}^2} \qquad (9)$$

where

$\sigma_{\mathrm{cal}}$ is the relative uncertainty contribution from the calibration factor;

$\sigma_{\mathrm{prep}}$ is the relative uncertainty contribution from the preparation step(s) of the sample (weighing);

$\sigma_{\mathrm{lin}}$ is the relative uncertainty contribution from the non-linearity

$\sigma_{\mathrm{mat}}$ is the relative uncertainty contribution from the matrix effects;

$\sigma_{\mathrm{AW}}$ is the relative uncertainty contribution from the atomic weight correction;

$\sigma_t$ is the relative uncertainty contribution from the temperature correction;

$\sigma_{\mathrm{cell}}$ is the relative uncertainty contribution from the length of cell ($\sigma_{\mathrm{cell}} = 0$ if unique cell is used);

$\sigma_{\mathrm{count}}$ is the relative uncertainty contribution from the counting precision;

$\sigma_{\mathrm{repro}}$ is the relative uncertainty contribution from the reproducibility.

Under the conditions for high accuracy measurements described in this document, the individual contribution of each factor typically does not exceed 0,07 % except for the contribution of the calibration factor described in 7.8.1. Typically, the standard uncertainty of uranium concentration is not higher than 0,2 %.

# Annex A

(informative)

# Calculation method for correction factors of atomic mass and temperature

There are two factors applied to the uranium concentration calculation according to Formula (7). One accounts for the atomic mass of uranium, $F_{AW}$, and one for the sample temperature, $F_t$.

## A.1 Calculation of $F_{AW}$

The L-absorption edge spectrometry method, which is based on non-isotope specific interactions with atomic electrons, measures the number of uranium atoms. In order to obtain the result expressed in mass units, the isotopic composition of uranium must be known to calculate the effective atomic mass. The correction factor of atomic mass, $F_{AW}$, is calculated according to Formula (A.1):

$$F_{\mathrm{AW}} = \frac{\varepsilon \cdot 235{,}043\,9 + (100 - \varepsilon) \cdot 238{,}050\,8}{238{,}028\,8 \cdot 100} \tag{A.1}$$

where $\varepsilon$ is the $^{235}$U enrichment expressed in atom%.

## A.2 Calculation of $F_t$

The volume concentration measured depends on the temperature of the sample. So the concentration measured at ambient room temperature $t$(°C) shall be normalized to a reference temperature (usually chosen to be 20 °C) by multiplying a temperature correction factor, $F_t$, which is calculated as (A.2).

$$F_t = 1 + 0{,}000\,5(t - t_{\mathrm{ref}}) \tag{A.2}$$

where $t_{\mathrm{ref}}$ is the reference temperature.