INTERNATIONAL STANDARD

ISO 13464

First edition
1998-04-01

Simultaneous determination of uranium and plutonium in dissolver solutions from reprocessing plants — Combined method using K-absorption edge and X-ray fluorescence spectrometry

Dosage simultané de l'uranium et du plutonium dans les solutions de dissolution des usines de retraitement — Méthode combinée de spectrométrie d'absorptiométrie K et de fluorescence X

Reference number
ISO 13464:1998(E)

Contents

1 Scope 1

2 Principle 1

3 Apparatus 1

4 Operating procedure 5

5 Method of calculation 6

6 Calibration 8

7 Bias correction factors 10

8 Measurement uncertainty 11

Annex A (informative) **Bibliography** 13

International Organization for Standardization
Case postale 56 • CH-1211 Genève 20 • Switzerland
Internet central@iso.ch
X.400 c=ch; a=400net; p=iso; o=isocs; s=central

Printed in Switzerland

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.

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 13464 was prepared by Technical Committee ISO/TC 85, *Nuclear energy,* Subcommittee 5, *Nuclear fuel technology*.

Annex A of this International Standard is for information only.

Simultaneous determination of uranium and plutonium in dissolver solutions from reprocessing plants — Combined method using K-absorption edge and X-ray fluorescence spectrometry

1 Scope

This International Standard specifies a nondestructive method for the simultaneous determination of volumetric uranium and plutonium concentrations in nitric acid feed solutions from reprocessing plants. The method is directly applicable, without interference, to the original feed solution, which typically contains about 150 $g \cdot l^{-1}$ to 300 $g \cdot l^{-1}$ uranium and 1 $g \cdot l^{-1}$ to 2,5 $g \cdot l^{-1}$ plutonium in the presence of fission products with a total ß,γ-activity of up to 10 $TBq \cdot l^{-1}$.

2 Principle

A sample vial containing about 3 ml to 5 ml of the feed solution is irradiated with a suitably filtered X-ray continuum from an X-ray tube. The X-ray continuum must include X-ray energies up to about 150 keV, and the maximum of its intensity distribution should occur at an energy above 100 keV.

The attenuation of a highly collimated X-ray beam, crossing a well-defined pathlength of solution in the vial, is measured with a HPGe detector below and above the K-absorption edge energy of uranium (E_K = 115,6 keV). The underlying K-edge densitometry (KED) method determines the uranium concentration from the abrupt change of the photon attenuation across the K-absorption edge.

At the same time a second HPGe detector, viewing a larger portion of the sample, measures the intensity ratio of fluoresced $K\alpha_1$ X-rays from uranium and plutonium. This X-ray fluorescence (XRF) measurement determines the U/Pu element ratio. The plutonium concentration is calculated from the measured values for the uranium concentration and the U/Pu ratio. The advantage of this XRF method arises from the fact that it is totally based on intensity ratio measurements. Further details on the measurement principle can be found in [1].

3 Apparatus

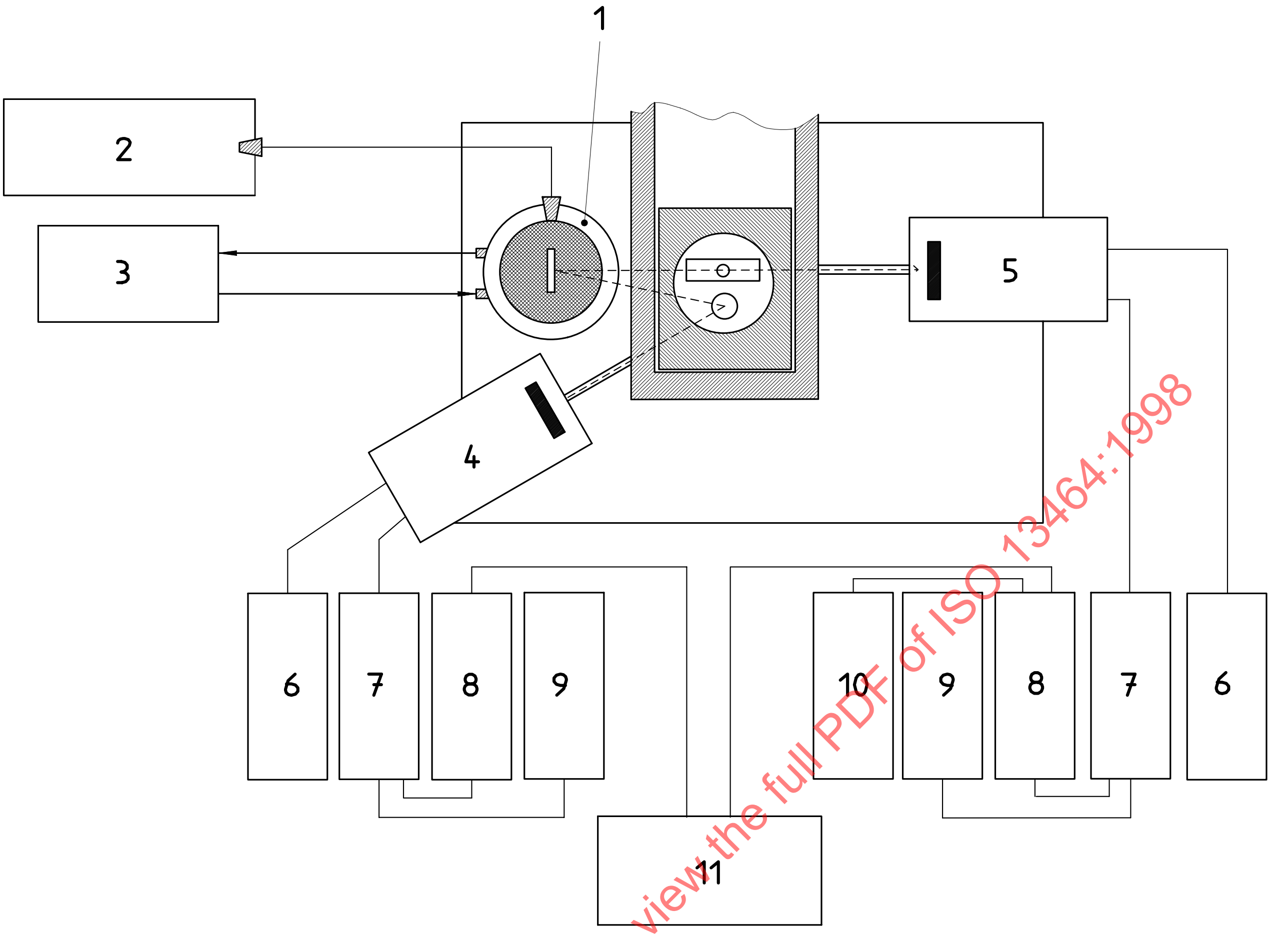
3.1 Components

3.1.1 Advanced standard spectroscopy equipment for high-resolution gamma spectroscopy including two HPGe detectors, electronics for fast pulse processing, and a computer-based multichannel analyzer for spectrum acquisition and evaluation.

3.1.2 X-ray equipment with X-ray tube, high voltage power supply, operating console and a circuit for water cooling.

3.1.3 Mechanics including beam collimators, shielding materials, adjustment device for the X-ray tube, and a system for transferring the sample into a defined position in the spectrometer.

A block diagram of the instrument components is shown in figure 1.



Key:

1	X-ray tube	7	Main amplifier
2	H.V. generator	8	ADC
3	Water cooling	9	Ratemeter
4	HPGe detecto XRF	10	Stabilizer
5	HPGe detector K-edge	11	MCA and PC system
6	H.V.		

Figure 1 — Block diagram of the instrument components

3.2 Geometric arrangement

The geometric arrangement (see figure 2) shall satisfy three basic requirements:

a) The distance *D* between X-ray tube and sample shall be kept as short as technically feasible ($D \approx 6,5$ cm) in order to achieve the highest possible flux of X-rays from the tube at the sample position (integrated flux of X-rays with energies from 115 keV to 150 keV $\approx 5 \times 10^{10}$ photons·cm^{-2}·s^{-1}).

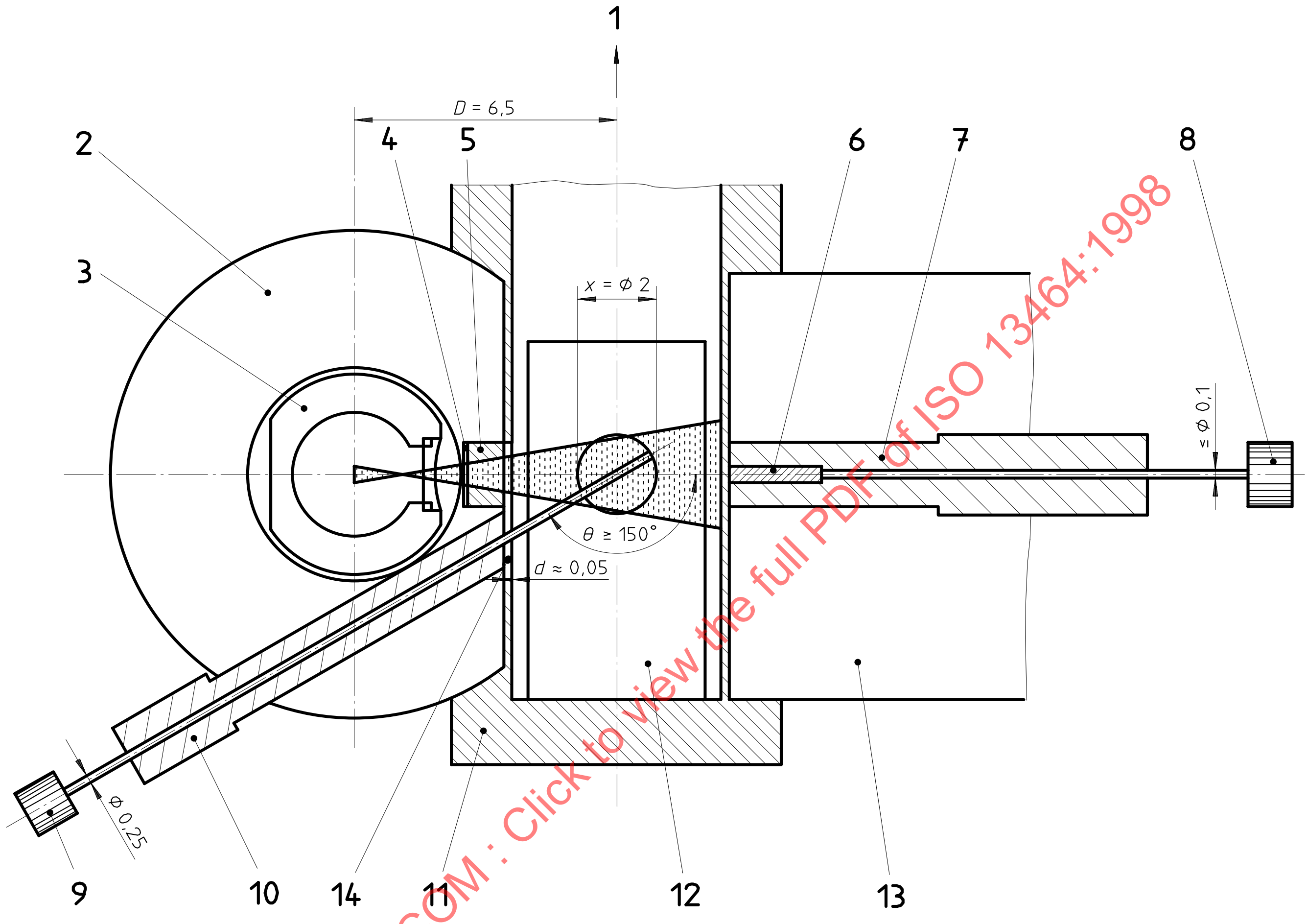
b) The angle Θ between primary X-ray beam and collimator axis directed towards the XRF detector shall take values $\Theta \geq 150°$ in order to shift inelastically scattered radiation out of the energy region of analysis in the XRF spectrum.

c) The solid angle subtended by the collimator between sample and K-edge detector shall be limited to values $\Omega \leq 10^{-4}$ sr in order to minimize elastic scattering towards the detector.

The transfer of the sample into the spectrometer can be accomplished either horizontally by means of a suitably designed sample conveyor system coupled to a shielded glovebox or hot cell facility (as indicated in figure 2), or vertically through a pneumatic sample transfer system.

The material thickness of the containment of the sample transfer system in the area of the incoming and outgoing X-ray beams shall be properly adapted to ensure an optimum signal rate for the XRF measurement. For a containment made of stainless steel, the window thickness, d, should be reduced to about 0,05 cm. If aluminium is used as containment, a window thickness, d, of up 0,4 cm is acceptable.

Dimensions in centimetres



Key:

1	Access to shielded glovebox
2	Shielding
3	X-ray tube, $\varnothing \leqslant 5$
4	Filter (Cd), $d \simeq 0,1$
5	Collimator (W)
6	Filter (Fe), $d \simeq 2$
7	Collimator (W) $L \geqslant 10$
8	HPGe detector for KED
9	HPGe detector for XRF
10	Collimator (W) $L \geqslant 10$
11	Containment of sample transfer system
12	Sample conveyor
13	Shielding
14	Window of containment of sample transfer system; for XRF measurements $d \approx 0,05$ (stainless steel) or $d \leqslant 0,4$ (aluminium)

Figure 2 — Principle geometric arrangement.

3.3 Specifications

3.3.1 X-ray system

A 3 kW X-ray unit providing maximum ratings of 160 kV/19 mA, preferably equipped with a metal-ceramic X-ray tube of smallest possible diameter (≤ 5 cm) along the radiation window section to allow a shortest possible distance between focus and sample, thus minimizing interferences from fission products. Stability of the high-voltage supply ≤ 0,1 %. High-voltage and tube current continuously adjustable. Water cooling at a minimum flowrate of 4 l·min^{-1} is required.

3.3.2 Detectors

True planar or pseudoplanar-type HPGe detectors in standard horizontal dipstick cryostate. Active detector area 100 mm^2 to 200 mm^2, depletion depth 10 mm to 13 mm. Detector coupled to an RC feedback preamplifier with an energy rate limit of about 20 GeV·s^{-1}. Energy resolution ≤ 0,6 keV FWHM at 122 keV at an input pulse rate of 5 × 10^4 counts·s^{-1}.

3.3.3 Pulse processing chain

Fast-pulse processing equipment with a typical processing time of about 5 µs, ensuring throughput rates ≥ 60 % at input rates of 5 × 10^4 counts·s^{-1}. Pulse processor equipped with an effective pulse pile-up rejection circuit. Conventional amplifiers with near-Gaussian filter shaping should be operated at a shaping time constant of 1 µs.

NOTE It is recommended to include into the electronic chain of the K-edge detector a dual-point digital stabilizer for zero and gain stabilization in order to simplify the data evaluation procedure. The reference lines for stabilization may be obtained from a suitable radioactive source such as ^{109}Cd (E = 22 keV and 88 keV). A source activity of about 0,5 MBq to 1 MBq will be sufficient when the source is located near the detector.

3.3.4 Data acquisition system

Advanced computer-based multichannel analyzer system providing two independent input channels with direct memory access for digitized data. Memory size ≥ 16 MB.

3.3.5 Sample container

Both cylindrical vials and rectangular cuvettes are suitable. The optimum inner diameter or cell length is in the range of 1,5 cm to 2,5 cm. The wall thickness of the sample container should be kept as thin as possible at the level of the incident X-ray beam in order to minimize the intensity of scattered radiation for the XRF measurement. The vertical sample position and the filling height shall ensure a solution layer extending at minimum from about 0,5 cm below to 0,5 cm above the level of the incident X-ray beam.

The K-edge measurement critically depends on the effective pathlength of solution crossed by the X-ray beam. This geometrical parameter shall be carefully controlled, because its uncertainty propagates directly into the measurement result. The preferred types of sample vial are standard spectroscopy glass cells with exactly known cell length. If cylindrical samples are used, the tolerances for lateral displacements relative to the X-ray beam axis shall be limited to meet a certain degree of measurement accuracy. For guidance refer to figure 3. Further, cylindrical sample containers should be perfectly circular to make the measurement result independent of the azimuthal position of the sample.

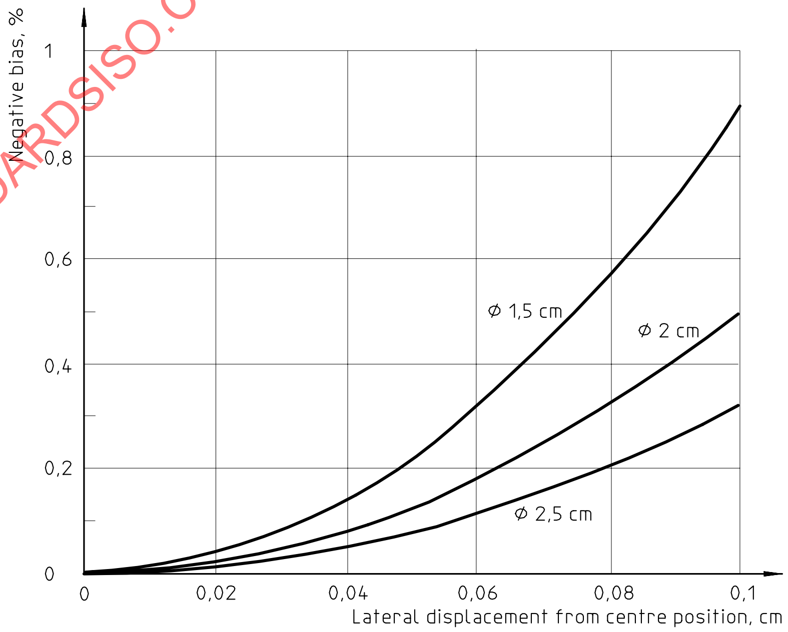


Figure 3 — Effect of lateral displacements on the KED result for cylindrical samples with different inner diameter $\varnothing_i$

3.3.6 Collimators and beam filters

Collimators should be made from high-density heavy metal (for example tungsten). The aperture of the primary collimator next to the X-ray tube shall allow the irradiation of the full sample section seen by the XRF detector (see figure 2). Use a primary beam filter of about 0,1 cm Cd (or equivalent material) to reduce the intensity of low-energy X-rays.

Choose the length L of the collimators in front of the K-edge and XRF detector to be ≥ 10 cm to provide sufficient shielding against self-radiation from the feed solution. The condition $\Omega \leq 10^{-4}$ sr for the K-edge collimator (see 3.2) will be met with collimator hole diameters ≤ 0,1 cm.

Adjust the length of the beam filter in the K-edge collimator (≈ 2 cm of stainless steel or equivalent, see figure 2) to yield, with a sample containing about 250 g $\text{U}\cdot\text{l}^{-1}$, a total counting rate of $\approx 2 \times 10^4$ $\text{counts}\cdot\text{s}^{-1}$ in the K-edge detector at the nominal X-ray tube rating of 150 kV/15 mA.

Adjust likewise, under the same conditions, the collimator diameter for XRF to yield a total counting rate of $\approx (3{,}5 \text{ to } 4) \times 10^4$ $\text{counts}\cdot\text{s}^{-1}$ in the XRF detector. Typical collimator diameters are about 0,25 cm.

3.4 Instrument settings

Accumulate both the K-edge and XRF spectra into two K channels.

Adjust the amplifier gain to cover energy ranges in both spectra from zero up to about 170 keV, corresponding to a conversion gain of approximately 80 eV to 85 eV per channel.

Adjust the vertical position of the X-ray tube to yield maximum counting rate in the K-edge detector.

Operate the X-ray tube at a high voltage of about 150 kV, and set the tube current to about 15 mA.

The actual value of the high voltage supplied to the X-ray tube shall be not exactly equal to 150 kV. Deviations of about ± 2 kV from this value are acceptable for the voltage setting. However, once selected, the high voltage setting shall be kept constant within about 0,1 % for all measurements. The high voltage can be monitored from the endpoint energy of the X-ray continuum measured with the K-edge detector. Small changes in the tube current will not affect the measurement, because both the K-edge and XRF method are based on intensity ratio measurements.

4 Operating procedure

Perform an initial instrument calibration as described in clause 6.

Introduce by means of the adopted system for sample transfer the feed solution sample in its appropriate sample container (see 3.3.5) into a defined measurement position in the spectrometer.

Run the X-ray tube at the adopted ratings (150 kV/10 mA to 15 mA).

Initiate the simultaneous acquisition of spectra from the K-edge and XRF detector. Make sure that the digital stabilizer for the K-edge electronics is properly stabilizing on the selected reference lines.

Choose the counting time according to the desired uncertainty level for repeatability. The expected standard deviations (s) of results from repeated measurements with counting time t (t = live time, in seconds) are for representative feed solutions (250 g $\text{U}\cdot\text{l}^{-1}$ and 2 g $\text{Pu}\cdot\text{l}^{-1}$) as follows :

$$s(\%) \approx 0{,}25 \cdot \sqrt{\frac{1000}{t}}$$ for [U] from KED, and

$$s(\%) \approx 0{,}8 \cdot \sqrt{\frac{1000}{t}}$$ for the U/Pu-ratio from XRF

At the end of the spectrum acquisition, programs for spectrum evaluation (see clause 5) are run to calculate the U and Pu concentrations.

5 Method of calculation

5.1 K-edge densitometry

5.1.1 Spectrum evaluation

Deduce from the sample measurement the photon transmission below and above the K-absorption edge of uranium at energies $E_- \cong E_k$ - 4 FWHM and $E_+ \cong E_k$ + 3 FWHM (E_k = absorption edge energy, FWHM = energy resolution of the detector measured at 122 keV).

Determine the transmission as the ratio of background-corrected counts accumulated at the respective energies in the K-edge spectra from the sample and from a blank nitrate solution. Estimate the background in both spectra from a calculated smoothed transition between background levels in front and behind the X-ray continuum as indicated in figure 4.

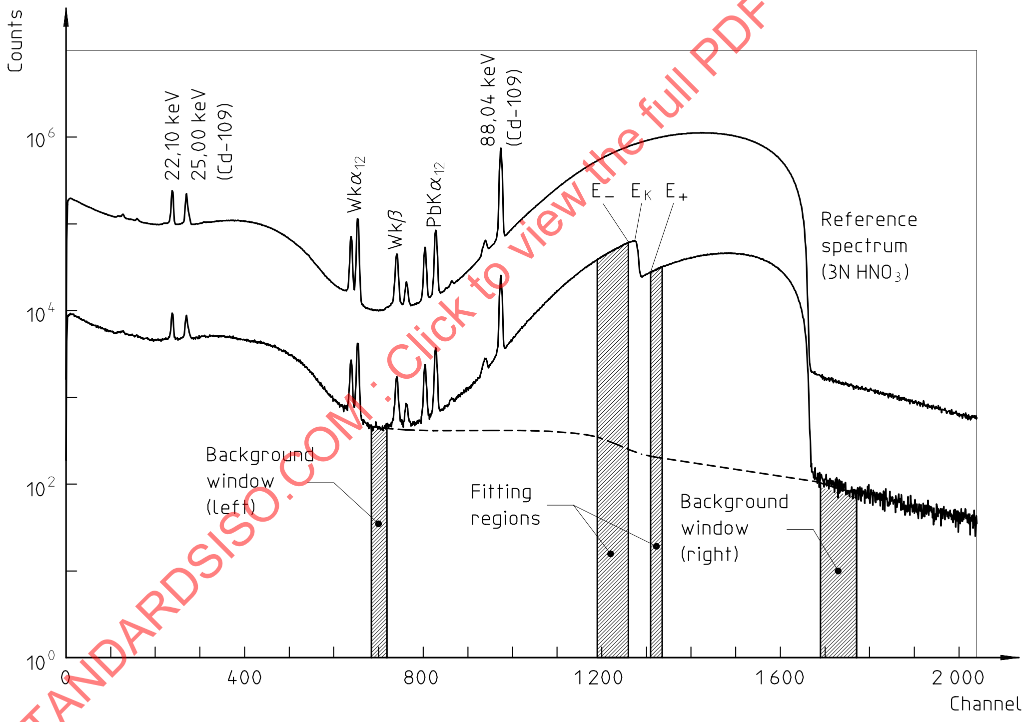


Figure 4 — Typical K-edge spectra from a blank nitrate solution (top) and from a feed solution (bottom).

NOTE A proven method for the determination of the transmission values $T(E_-)$ and $T(E_+)$ is based on linear least-squares fits of the form ln ln $1/T(E)$ versus ln E in fitting intervals covering energy ranges of about 5 keV to 6 keV below and about 2,5 keV above the edge, with the window limits next to the edge set at E_- and E_+ (see figure 4). The interval above the edge should exclude the K-absorption edge of plutonium at 121,8 keV. This method of analysis also allows determination of the change of the transmission across the K-edge directly at the absorption edge energy E_k by extrapolating the linear fits on both sides to the edge.

5.1.2 Expression of results

Calculate the uranium concentration from the relation

$$[U] = \frac{1}{\Delta\mu \cdot x} \cdot \frac{A(S)}{A(R)} \cdot \ln \frac{T(E_-)}{T(E_+)} \cdot 1000$$

where

$[U]$ is the uranium concentration, in $g \cdot l^{-1}$,

x is the effective pathlength of the sample vial, in cm,

$\Delta\mu$ is the difference $\mu(E_+) - \mu(E_-)$ of the total photon mass attenuation coefficient (in $cm^2 \cdot g^{-1}$) of uranium at the respective energies (to be determined from a calibration),

A is the atomic mass of uranium in the sample (S) and in the reference solutions (R) used for calibration,

T is the photon transmission measured at E_- and E_+.

5.2 X-Ray fluorescence measurement

5.2.1 Spectrum evaluation

Determine from the XRF spectrum the net peak counts for the X-rays U $K\alpha_2$, U $K\alpha_1$, Pu $K\alpha_2$, Pu $K\alpha_1$, Am $K\alpha_1$, and U $Kß_{1,3}$ using peak and background window settings as indicated in figure 5. Note that the net peak counts of the Pu $K\alpha_2$ line, which is not resolved from the U $K\alpha_1$ line, are best determined relative to the net peak counts of the Pu $K\alpha_1$ line.

Subtract first the number of counts due to the sample self-radiation from the integrated counts in the selected peak windows $P_1 - P_5$, and in the background windows $B_1 - B_4$.

NOTE The correction for self-radiation is best accomplished by measuring a separate passive spectrum. However, the contributions from self-radiation can also be estimated from the actual XRF spectrum. Use the fraction of counts due to fission products in the background window B_5 (≅ 125 keV to 131 keV) as reference and put the contribution of the self-radiation to the remaining energy windows in proportion to these counts. The necessary relations can be established from some passive spectra taken from representative feed solutions, and from XRF spectra taken from samples without fission products.

Correct the U$K\alpha_1$ peak counts for contributions from the Pu $K\alpha_2$ line, and the counts in the background window B_2 for contributions from the Am $K\alpha_2$ line.

Evaluate the net peak counts by using the following windows for background assessment: $B_1 - B_2$ for U $K\alpha_2$ and U α_1, $B_2 - B_3$ for Pu $K\alpha_1$, B_3 for Am $K\alpha_1$, and $B_3 - B_4$ for U $Kß_{1,3}$.

Establish the relative detection efficiency for the X-ray energies of U $K\alpha_1$ and Pu $K\alpha_1$ from the evaluated net peak counts of U $K\alpha_2$, U $K\alpha_1$ and U $Kß_{1,3}$ together with their known relative emission rates.

5.2.2 Expression of results

Calculate the U/Pu mass ratio from the expression

$$\frac{U}{Pu} = \frac{A(U)}{A(Pu)} \cdot \frac{P(UK\alpha_1)}{P(PuK\alpha_1)} \cdot \frac{ORE(PuK\alpha_1)}{ORE(UK\alpha_1)} \cdot \frac{1}{R}$$

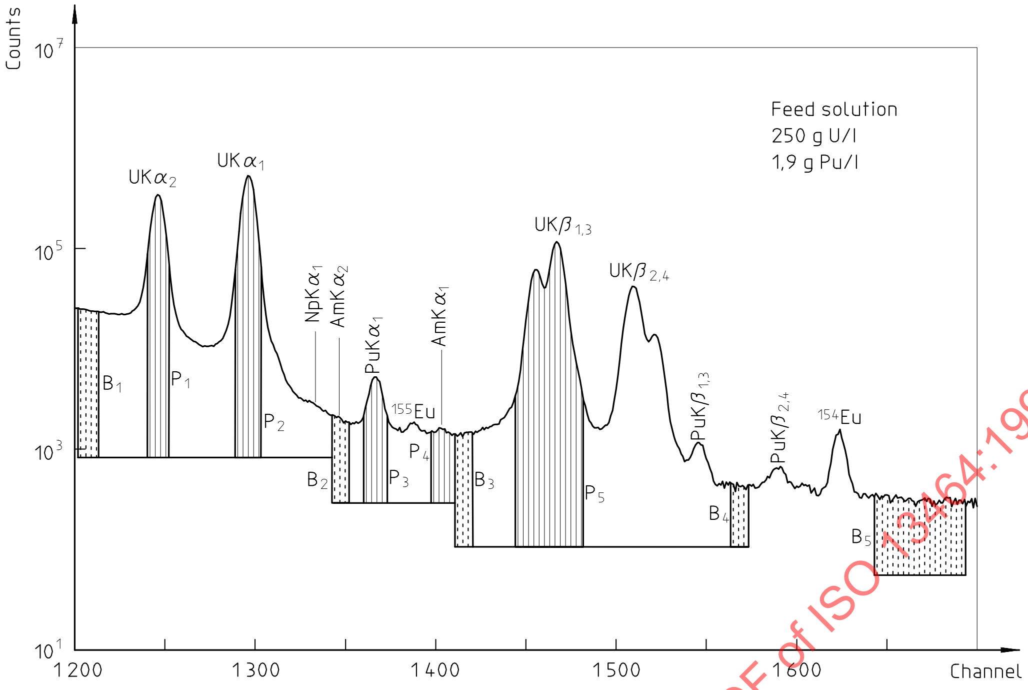


Figure 5 — Proposed window settings in the XRF spectrum for net peak count evaluation.

where

A	is the atomic mass for uranium and plutonium, respectively,
P	is the number of net peak counts in the Kα$_1$ X-rays,
ORE	is the overall relative detection efficiency for the Kα$_1$ X-rays,
R	is the calibration factor describing the ratio of excitation probabilities for emission of U Kα$_1$ and Pu Kα$_1$ X-rays in the primary X-ray beam.

Calculate from the uranium concentration [U] measured by K-edge densitometry, and from the U/Pu ratio measured by XRF, the plutonium concentration [Pu] in grams per litre as

$$[Pu] = [U] \cdot \left(\frac{U}{Pu} \right)^{-1}$$

6 Calibration

6.1 Reference solutions

The calibration requires three types of solution:

a) a blank nitrate solution with a nitrate concentration similar to that of the feed solution (≅ 2 mol·l^{-1} to 3 mol·l^{-1}).

b) a set of three to four synthetic U-Pu nitrate solutions simulating the sample characteristics of feed solutions with respect to uranium concentration (≅ 100 g·l^{-1} to 300 g·l^{-1}), U/Pu-ratio (≅ 100 to 150), and nitrate concentration

(≅ 2 mol·l^{-1} to 3 mol·l^{-1}). The samples shall be characterized for the volumetric concentrations of U, Pu and Am, and for the atomic masses of U and Pu.

c) a set of two to three representative feed solutions with typical values for the uranium concentration and the ß, γ-activity from fission products. These solutions do not need to be specifically characterized.

6.2 Calibration measurements

Measure with the K-edge detector a reference spectrum from a blank nitrate solution. Accumulate ≥ 10^6 counts/channel in the energy interval between 110 keV and 120 keV (counting time ≅ 2 h to 3 h). Reduce the tube current to about 5 mA for this measurement. Save the reference spectrum, because it is needed for all subsequent evaluations of K-edge spectra.

Acquire simultaneous K-edge and XRF spectra from the synthetic U-Pu reference solutions under the same measurement conditions as used for feed solutions. Perform several repeat measurements on each sample to reduce the uncertainty for the calibration factors to be determined.

NOTE The expected relative standard uncertainty of the calibration factor associated with counting statistics is approximately estimated to s (%) ≅ 0,2·(Σ t_i)$^{-1/2}$ for KED, and to s (%) ≅0,6·(Σ t_i)$^{-1/2}$ for XRF, where Σ t_i is the sum of the counting times (in hours) for all measurements on the reference solutions.

Switch off the X-ray tube and acquire with the XRF detector passive spectra of the self-radiation from the feed solution samples. Choose a counting time of about 1 h for each sample.

6.3 Evaluation of calibration factors

6.3.1 K-edge densitometry

Determine from the individual calibration runs the calibration factors

$$\Delta\mu_{i,k} = \frac{1}{[U]_i \cdot x_i} \cdot \ln \frac{T_{i,k}(E_-)}{T_{i,k}(E_+)}$$

where the index k denotes the number of the repeat measurement on the reference solution i with known uranium concentration [U]$_i$ (for other notations see 5.1.2).

Calculate from the individual Δμi,k-values a weighted mean value as final calibration factor Δμ. The obtained Δμ-values should be in close agreement with the theoretical value derived from tabulations of photon cross-sections.

EXAMPLE: for transmission energies E- = 113,2 keV and E+ = 117,2 keV, one expects a value of $\Delta\mu$ = 3,30 ± 0,03 cm^2·g^{-1}.

If the pathlength x is not accurately known, determine as calibration factor the product of $\Delta\mu \cdot x$.

6.3.2 X-ray fluorescence

Determine from the quantities evaluated from the individual XRF spectra and from the reference values the calibration factors

$$R_{i,k} = \left(\frac{U}{Pu}\right)_i^{-1} \cdot \frac{A_i(U)}{A_i(Pu)} \cdot \frac{P_{i,k}(UK\alpha_1)}{P_{i,k}(PuK\alpha_1)} \cdot \frac{ORE_{i,k}(PuK\alpha_1)}{ORE_{i,k}(UK\alpha_1)}$$

where k denotes the number of the repeat measurement on the reference solution i with known U/Pu mass ratio (U/Pu)$_i$ (for other notations see 5.2.2).

The values $R_{i,k}$ will slightly decrease with increasing concentration of U and Pu. This dependence can be reasonably approximated by a linear relationship of the form

$$R_{i,k} = R_0 \cdot (1 + \alpha [U]_i)$$

Determine the coefficients R_0 and α from a linear least-squares fit.

NOTE 1 The coefficient α, describing the dependence of the calibration, R, on the uranium concentration can also be calculated from physical data, taking into account the attenuation of the incoming X-ray beam in the sample and its photoelectric interactions with U and Pu, and the attenuation of the outgoing Kα_1 X-rays.

NOTE 2 Alternatively, it is also possible to form for the evaluation of calibration factors a set of linear equations, and to solve them for the unknowns by a multiple linear regression analysis. For example, combining the two equations given above in this clause with the relation

$$PuK\alpha_1 = P_3 - k \cdot (B_2 + B_3)$$

used for the evaluation of the net peak counts PuKα1 from the total counts P3, B2 and B3 in the respective windows (see figure 5) yields the following linear calibration :

$$Y \cdot UK\alpha_1 = R_0 \cdot P_3 - k \cdot R_0 \cdot (B_2 + B_3)$$

where

$$Y = \frac{A(U)}{A(Pu)} \cdot \frac{Pu}{U} \cdot \frac{ORE\left(PuK\alpha_1\right)}{ORE\left(UK\alpha_1\right)} \cdot \exp\ \left(-\alpha \cdot U\right)$$

(for notations see 5.2.2). The set of calibration equations thus formed with data from the calibration measurements on reference solutions with different U/Pu ratios is solved for the unknowns R_0 and $k \cdot R_0$. The coefficient, α, is taken as input parameter from the separate X-ray beam attenuation calculations, carried out for the given geometry.

Determine from the XRF spectra a functional relationship between the total counts in the background window B_5 (125 keV to 131 keV, see figure 5) and the uranium concentration.

Establish from the passive spectra average values for the ratios of total counts B_5/B_i (i = 1..., 4) and B_5/P_i (i = 1..., 5).

The information obtained from the two preceding steps are required if the user wants to correct the XRF spectra from feed solutions for self-radiation without measuring a separate passive spectrum for each sample (see 5.2.1).

7 Bias correction factors

7.1 Uranium concentration

The difference in chemical composition between the actual feed solution sample and the synthetic U-Pu reference solutions used for calibration will lead to a small bias for the uranium concentration determined from the K-edge measurement.

The bias introduced by any matrix element M can be calculated from physical data by

$$Bias\ (\%) = \frac{\Delta\mu_M}{\Delta\mu_U} \cdot \frac{\Delta C_M}{C_U} \cdot 100$$