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Nuclear fuel technology — Preparation of plutonium sources and determination of ^{238}Pu/^{239}Pu isotope ratio by alpha spectrometry

Technologie du combustible nucléaire — Préparation des sources de plutonium et détermination du rapport isotopique ^{238}Pu/^{239}Pu par spectrométrie alpha

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Foreword

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ISO 11483 was prepared by Technical Committee ISO/TC 85, *Refrigeration and air-conditioning*, Subcommittee SC 5, *Nuclear fuel technology*.

This second edition cancels and replaces the first edition (ISO 11483:1994), of which it constitutes a technical revision.

Nuclear fuel technology — Preparation of plutonium sources and determination of ^{238}Pu/^{239}Pu isotope ratio by alpha spectrometry

1   Scope

This International Standard describes three simple and fast procedures to prepare plutonium sources and a procedure to measure the activity ratio of ^{238}Pu to (^{239}Pu + ^{240}Pu) by α spectrometry. The α spectrometry method is used for the determination of isotopic abundance of ^{238}Pu in combination with mass spectrometry and eliminates the possible interferences of ^{238}U in the latter method. It applies to the analysis of purified solutions of plutonium in 2 mol/l to 4 mol/l nitric acid containing 50 µg to 200 µg of plutonium per millilitre, as may result from the chemical treatment and purification preceding plutonium isotopic analysis by mass spectrometry.

This International Standard applies to plutonium solutions free from ^{241}Am and those containing less than 10 % of other non-volatile impurities relative to the plutonium content. Anion exchange chromatography in accordance with ISO 8299:1993 [12], Subclauses 7.2 and 7.3, or solvent extraction chromatography in ISO 15366 [13] are suitable purification methods.

The methods given in this International Standard are intended for use in conjunction or in parallel with mass spectrometry for the isotopic analysis of plutonium in spent-fuel solutions or nuclear-grade plutonium products.

2   Principle

There are two major methods to prepare plutonium sources: drop deposition and electrodeposition. Two types of drop-deposition methods are given: a drop of sample solution is mixed with wetting agent and deposited on a electrochemically polished stainless-steel disc or porcelain disc and dried. The dried residue is ignited in a flame or muffle furnace depending upon the selected types of disc to produce a thin and carrier-free source.

In the case of the electrodeposition method, the plutonium is deposited as hydrous oxide from a buffered, slightly acidic aqueous solution onto a stainless-steel disc.

The source is measured by α spectrometry with a semiconductor detector.

The spectrum is processed to obtain the activity ratio of ^{238}Pu to (^{239}Pu + ^{240}Pu). The tailing of the ^{238}Pu peak is corrected by the "Geometric-Progression Decrease" method or exponential extrapolation method.

The isotope ratio ^{238}Pu/^{239}Pu is calculated using the isotope ratio ^{240}Pu/^{239}Pu determined by mass spectrometry.

3   Source preparation

The source should be very thin. Its thickness should not significantly limit the α peak resolution.

Different procedures can be used to prepare α sources, such as

—   sublimation in vacuum,

—   electrodeposition,

—   solution evaporation with a wetting agent and subsequent ignition, or

—   coprecipitation of Pu(III)F$_3$ with lanthanide fluoride, such as NdF$_3$ or CeF$_3$

Sublimation is the preferred procedure when the aim is to study the fine structure of the plutonium α spectrum and an energy resolution of 9 keV is needed [1]. It is possible, but more difficult, to reach such a resolution with sources prepared by electrodeposition [2]. Coprecipitation is well suited to determine trace contents of plutonium in environmental or biological samples by α spectrometry [3]. However, sources prepared by coprecipitation exhibit α peaks with greater tailing.

Depositing and drying a small drop of solution of the purified sample onto an inert support produce satisfactory sources for the purpose of plutonium accountancy measurements. Two examples of the procedure of drop-deposition are described below. These alternatives were selected because they are convenient and in common use when the sample is measured in parallel by α and mass spectrometry. It is also easy, with these procedures, to prepare five to twenty sources simultaneously. Drop deposition yields sources of appropriate properties when using semiconductor detectors with an intrinsic energy resolution of 20 keV or less for 5,50 MeV alpha-particle energy of ^{238}Pu.

The source support shall have a clean and perfectly smooth surface, which shall remain physically and chemically inert during the preparation of the sources. In particular, the material of the support shall not melt and shall be resistant against nitric acid, plutonium nitrate, the wetting agent and their decomposition products, as well as against atmospheric corrosion.

3.1   Source preparation on electrochemically polished stainless-steel disc [4]

In the following procedure, the sources shall be prepared in a fume cupboard or a glove box designed for work with α-emitting radioisotopes where the use of a gas burner is authorized.

3.1.1   Apparatus

3.1.1.1   Electrochemically polished discs, of heat-resistant stainless steel, about 25 mm in diameter and 0,5 mm thick; stainless steels of the following composition would be suitable: Cr 17 % to 20 %; Ni 8 % to 15 %; Mo 2,5 % to 4 %; C 0,12 % max.; Si 1,0 % max.; Mn 2,0 % max.; S 0,030 % to 0,045 %; P 0,045 %.

3.1.1.2   Burner

3.1.1.3   Piston pipette, of capacity 10 µl, with disposable tip.

3.1.1.4   Sample holder, made of a 50 mm diameter and 5 mm thick stainless-steel plate with a 25 cm long insulated handle. A 0,2 mm to 0,3 mm deep recess shall be provided in the centre of the plate with a diameter 1 mm greater than the diameter of the disc.

3.1.2   Reagents

3.1.2.1   Ethanol, analytical grade.

3.1.2.2   Colourless varnish

3.1.2.3 **Tetraethylene glycol**, analytical grade.

3.1.3 Procedure

3.1.3.1 Clean the disc with the ethanol (3.1.2.1).

3.1.3.2 Draw a circular rim, of about 12 mm diameter, on the polished surface of the disc with a varnish (3.1.2.2) and let it dry.

NOTE   An artist's brush can be useful for this operation.

3.1.3.3 Place the disc in the recess of the sample holder.

3.1.3.4 Pipette 10 µl of the tetraethylene glycol (3.1.2.3) inside the circular rim.

3.1.3.5 Change the pipette tip and pipette 10 µl of the sample solution inside the circular rim.

3.1.3.6 Gently heat the holder and the disc with a gas burner, swirling slowly over the flame to mix the sample well with the tetraethylene glycol. The solution should be evaporated slowly, without boiling.

3.1.3.7 When the disc is dry, heat more strongly to burn off the rim of varnish.

3.1.3.8 Finally, introduce the disc into the reducing zone of the flame and bring the source to a dull red heat for approximately 30 s.

3.1.3.9 Let the holder and the disc cool to ambient temperature. The source is ready for measurement.

3.2   Source preparation on porcelain disc [5]

3.2.1   Apparatus

3.2.1.1 **Glazed porcelain disc**, of about 29 mm diameter and 5,5 mm thickness. A circular recess of 8,5 mm diameter and 1 mm depth shall be provided in the centre of the disc to receive the sample solution, which defines the source area. The glazing shall not melt below 1 000 °C.

3.2.1.2 **Hotplate**, with a maximum temperature of 250 °C.

NOTE   A surface thermometer may be used to monitor the temperature of the plate.

3.2.1.3 **Muffle furnace**, controllable to 1 000 °C and equipped with a removable quartz boat or tube, about 100 mm to 200 mm long and 30 mm in diameter. The boat shall be wide enough to accept the porcelain discs.

3.2.1.4 **Piston pipette**, of capacity 10 µl, with disposable tip.

3.2.1.5 **Pencil**, to mark the porcelain disc. The marking shall still be readable after ignition at 850 °C.

3.2.2   Reagents

3.2.2.1 **Ethanol**, analytical grade.

3.2.2.2 **Tetraethylene glycol**, analytical grade.

3.2.3   Procedure

3.2.3.1 Clean the surface of the porcelain disc using a tissue paper moistened with ethanol (3.2.2.1). Write the identification of the sample with a pencil (3.2.1.5) on the reverse side of the disc.

3.2.3.2   Pipette 10 µl, of tetraethylene glycol (3.2.2.2) into the recess in the centre of the porcelain disc and spread it, with the pipette tip, over the entire surface of the recess.

3.2.3.3   Change the pipette tip and pipette 10 µl of the sample solution into the recess in the centre of the disc, previously moistened with tetraethylene glycol; mix both solutions well with the tip of the pipette.

3.2.3.4   Place the porcelain disc on the hotplate (3.2.1.2), set the temperature to 100 °C and warm it up for 1 h; then increase the temperature to 150 °C for another hour; after 2 h, the disc should be dry.

3.2.3.5   Introduce the porcelain disc into the quartz tube or boat of the muffle furnace (3.2.1.3), set the temperature control to 850 °C and ignite at this temperature for 20 min; the furnace reaches 850 °C in about 20 min.

3.2.3.6   Switch off the furnace and let it cool for about 20 min before removing the source.

The source is ready for measurement.

3.3   Source preparation by electrodeposition [2]

3.3.1   Apparatus

3.3.1.1   **Stainless-steel discs**, as described in 3.1.1.1. The diameter has to fit the electroplating cell.

3.3.1.2   **Device for electroplating**, with adjustable voltage of up to 12 V and adjustable current of up to 200 mA/cm^2 of area of deposition. The anode must be rotating to serve as a stirrer.

3.3.1.3   **Disposable electroplating cell**, of 10 ml capacity and diameter compatible with the diameter of the stainless-steel discs (3.1.1.1).

3.3.1.4   **Pt-anode**

3.3.2   Reagents

3.3.2.1   **Nitric acid**, analytical grade, concentrated, 3 mol/l, 0,1 mol/l, 0,001 mol/l.

3.3.2.2   **H_2O_2**, analytical grade, 30 %.

3.3.2.3   **Ammonium nitrate**, analytical grade, saturated solution in distilled water.

3.3.2.4   **Ammonia solution**, analytical grade, 5 % in distilled water.

3.3.2.5   **Acetone**, analytical grade.

3.3.3   Procedure

3.3.3.1   A redox treatment is necessary to ensure isotopic homogenization if the Pu was mixed from different origins. This can be done by first treating the mixture twice with concentrated nitric acid (HNO_3) to break the polymer and then adding H_2O_2 in 3 mol/l HNO_3 medium. Then evaporate to dryness and redissolve in 0,1 mol/l HNO_3 to adjust the concentration to about 1 µg Pu/10 µl.

3.3.3.2   Add 5 ml of 0,001 mol/l HNO_3 to the electrodeposition cell. Transfer 10 µl of the Pu solution to the cell.

3.3.3.3   Connect the mirror-polished stainless-steel disc and the platinum stirrer to act as cathode and anode, respectively. It is important to stir the solution during electrodeposition, since there is gas evolution during the process.

3.3.3.4 Now start the electrodeposition by maintaining a voltage of 10 V to 12 V and adjusting the current density to about 200 mA/cm^2 by the addition of saturated solution of ammonium nitrate.

3.3.3.5 Run the deposition for about 1 h.

3.3.3.6 Before stopping the electrodeposition, add a few drops of diluted ammonia solution.

3.3.3.7 Remove the electrical connections and wash the electrodeposited source with water and acetone and keep for drying.

3.3.3.8 Wash the Pt electrode thoroughly with concentrated nitric acid (HNO_3). Always use a fresh cell for a new source.

4 Alpha spectrometry

4.1 Apparatus

4.1.1 Vacuum chamber, equipped with a vacuum gauge and a pump providing pressures of 5 Pa or less.

4.1.2 Si detector, surface barrier passivated or ion-implanted, energy resolution (FWHM) 20 keV or better, active area about 100 mm^2.

Passivated ion-implanted detectors have a resolution of 9 keV to 10 keV, but are not required unless the source is prepared by vacuum sublimation or electrodeposition and the aim is to reach a much better accuracy or to study the fine structure of the plutonium α spectrum.

The detector shall be mounted in the vacuum chamber at a distance of about 15 mm from the α source, i.e. about 1,5 times the diameter of the source.

4.1.3 Electronic modules

Bias voltage supply, adjustable up to 200 V, preamplifier and spectrometry amplifier, 1 024 or more memory multichannel analyser. The amplifier gain is adjusted in such a way that the peaks of ^{238}Pu and ^{239}Pu + ^{240}Pu are displayed on the upper energy side of the screen; the energy scale should be about 1,5 keV/channel for the 1 024 multichannel analyser.

4.1.4 Small computing device, separate or incorporated in the multichannel analyser.

4.2 Measurement

4.2.1 Place the source in the vacuum chamber and pump until a vacuum of about 5 Pa (5×10^{-2} mbar) is obtained. Then set the detector voltage to the value recommended by the manufacturer.

4.2.2 Record the spectrum of α particle radiation, collecting whenever practical at least 500 000 counts in the smaller of the two peak groups [corresponding to ^{238}Pu or (^{239}Pu + ^{240}Pu) peaks]. The spectrum recorded in the semi-logarithmic scale shall be similar to the one presented in Figure 1. The upper energy sides of the two peak groups shall be smooth, while the lower energy sides shall decrease monotonically, except for the two small peaks indicated in Figure 1. At mid-height, the 5,5 MeV peak of ^{238}Pu shall have a width of 20 keV or less. The counts per channel in the valley between the two groups shall be no greater than 1 % of the counts at the ^{238}Pu peak top.

4.3 Spectra evaluation

A number of computer software have been developed to perform elaborate evaluations of α spectra [6, 7, 8]. Some can be used on personal computers. However, sources with very high resolution are needed to draw a

significant advantage out of such sophisticated evaluations, compared to the simple empirical procedure described in 4.3.2.

4.3.1 Principle

Very simple models are very efficient for accurately correcting the tailing of the ^{238}Pu peak, as long as the spectrum is well resolved and the tailing is small.

The following assumptions are then generally applicable:

a)   single α peaks all have the same shape;

b)   the tails are the sum of the tailings of all single peaks of higher energies;

c)   in the flat portion of the tail, peak tailing contributions are proportional to the corresponding peak areas.

The above assumptions form the basis of the procedures which are described below.

4.3.2 Geometric-progression decrease method [9]

The method involves two assumptions:

⸺   the self absorption of the alpha particles of ^{238}Pu, ^{239}Pu and ^{240}Pu is the same;

⸺   the counts in the tail of a peak decrease in geometric progression.

Its main features are as follows:

a)   equal intervals of integration are selected for the ^{238}Pu and (^{239}Pu + ^{240}Pu) peaks;

b)   each interval is selected to include all the relevant single peaks which contribute at least 0,05 % of the total activity of the group of interest;

c)   the intervals of integration of the ^{238}Pu peaks include only contributions from ^{238}Pu (and ^{241}Am) isotopes;

d)   the interval of integration of the (^{239}Pu + ^{240}Pu) peaks excludes all the major ^{242}Pu and ^{241}Pu peaks;

e)   tail-contribution estimates also exclude the contributions of the major ^{242}Pu and ^{241}Pu peaks and the minor ^{238}Pu peak at 5,357 9 MeV.

4.3.2.1   Divide the plutonium α-spectrum into four regions: A, B, C and D, each region having an equal number of channels (see Figure 1).

4.3.2.2   Select the high-energy end of region A: $E^{A}_{max} = 5{,}499\ 0$ MeV + FWHM, where FWHM(MeV) is the full width at half-maximum of the ^{238}Pu peak at the energy 5,499 0 MeV.

4.3.2.3   Fix the low-energy end of the region A: $E^{A}_{min} = E^{A}_{max} - 0{,}267\ 7$ MeV.

4.3.2.4   Select the high-energy and the low energy ends of region B: $E^{B}_{max} = 5{,}168\ 2$ MeV + FWHM and $E^{B}_{min} = E^{B}_{max} - 0{,}267\ 7$ MeV.

4.3.2.5   Select the high-energy and low-energy ends of the region C: $E^{C}_{max} = 4{,}856\ 2$ MeV $-$ FWHM and $E^{C}_{min} = E^{C}_{max} - 0{,}267\ 7$ MeV.

4.3.2.6   Select the high-energy and low-energy ends of the region D:

$$E^{D}_{max} = E^{B}_{max} - (E^{A}_{max} - E^{C}_{max})\ \text{and}\ E^{D}_{min} = E^{D}_{max} - 0{,}267\ 7\ \text{MeV}.$$
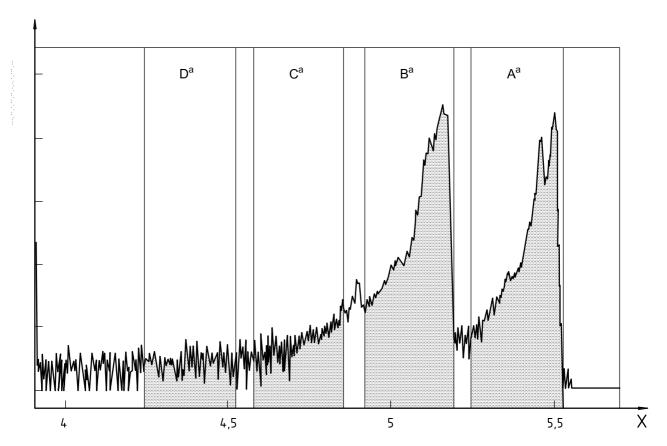
4.3.2.7 The interval width 0,267 7 MeV is the energy interval between the ^{240}Pu peak at 5,168 2 MeV and the ^{242}Pu peak at 4,900 5 MeV (see Table 1).

4.3.2.8 Obtain the sums of the counts in the channels of regions A, B, C and D. Call the corresponding counts a, b, c and d respectively.

4.3.2.9 The ^{238}Pu/(^{239}Pu + ^{240}Pu) alpha activity ratio, $R(\alpha)$, is calculated from

$$R(\alpha) = \cfrac{a}{b - \cfrac{ac}{b + \cfrac{ad}{c}}} \tag{1}$$

See reference [9] for more details.

4.3.3 Exponential decrease method

4.3.3.1 Divide the plutonium α spectrum into two regions: A and B as described in 4.3.2 (see Figure 1).

X   Energy, MeV

ª   Region.

Figure 1 — Example of α spectrum

4.3.3.2 Use the 96 keV interval above region B for fitting an exponential function

$$Y_i = A_0 \cdot e^{a_1 X_i} \tag{2}$$

or a straight line:

$$\ln Y_i = \ln A_0 + a_1 X_i \tag{3}$$

where

Y_i is the number of counts in the channel X_i;

A_0 and a_1 are the fitting parameters.

4.3.3.3   Calculate the area $T = \Sigma\ Y_i$ under this line in the region B and subtract this number from the sum of counts in region B.

T is a number of counts in the extrapolated tail under ^{239}Pu + ^{240}Pu peaks.

4.3.3.4   Calculate the activity ratio from

$$R(\alpha) = \frac{A}{B - T} \tag{4}$$

where A and B are the number of counts in respective regions.

5   Expression of results

The isotope ratio ^{238}Pu/^{239}Pu, $\overline{R}_{8/9}$ is calculated from

$$\overline{R}_{8/9} = R(\alpha)T_8\left(\frac{1}{T_9} + \frac{\overline{R}_{0/9}}{T_0}\right) \tag{5}$$

where

$R(\alpha)$ is the activity ratio calculated in Equation (1);

$\overline{R}_{0/9}$ is the isotope ratio ^{240}Pu/^{239}Pu measured by mass spectrometry;

T_8 is the half-life of isotope ^{238}Pu ($87,7 \pm 0,3$ years);

T_9 is the half-life of isotope ^{239}Pu ($24\ 110 \pm 30$ years);

T_0 is the half-life of isotope ^{240}Pu ($6\ 563 \pm 7$ years).

6   Interference of americium

The isotope ^{241}Am emits alpha particles of energies very close to the energies of the radiation emitted by isotope ^{238}Pu (see Table 1). Its presence yields positive biases.

Since plutonium always contains some isotope ^{241}Am, resulting from the decay of isotope ^{241}Pu, it is necessary to purify the sample by removing americium just before α spectrometry is done. The purification should be verified by gamma spectrometry.

The α spectrometry should be done within one week after the separation is completed. If the spectrometry is not done immediately after purification of the plutonium, the analysis will have a positive bias. The resulting

relative bias δ is given by the following equation, where the delay t and the half-lives, T_1 to T_8 and T_A, are expressed in the same units:

$$\delta = \frac{T_8}{T_A \overline{R}_{8/9}} \ln 2 \frac{\overline{R}_{1/9} \cdot t}{T_1} \tag{6}$$

where

T_A is the half-life of isotope ^{241}Am ($432{,}7 \pm 0{,}5$ years);

$\overline{R}_{8/9}$ is the isotope ratio ^{238}Pu/^{239}Pu at the time of the separation;

$\overline{R}_{1/9}$ is the isotope ratio ^{241}Pu/^{239}Pu at the time of the separation;

T_1 is the half-life of isotope ^{241}Pu ($14{,}35 \pm 0{,}1$ years).

Isotopic ratio ^{241}Pu/^{239}Pu $\overline{R}_{1/9}$ should be measured by gamma spectrometry [10] or mass spectrometry.

In the case of plutonium containing 1 % of ^{238}Pu isotope and 10 % of ^{241}Pu isotope, a bias of 0,027 % accumulates every day following the separation.

7 Resolution of the α spectra

When starting with pure plutonium compounds, the present method should yield sources which display a full width at half-maximum (FWHM) of 20 keV to 10 keV for the ^{238}Pu peak.

8 Repeatability

For a complete measurement, involving the preparation of one source and its spectrometry, the coefficient of variation of the repeatability on $R(\alpha)$ is of the order of 0,2 % and corresponds to the value expected from counting statistics.

9 Reproducibility

A measure of performance is that the measurement system gives reproducible results. A check source is counted n times according to the measurement procedure described above. The measured spectra are evaluated by both geometrical progression and exponential decrease methods. Finally, $\overline{R}_{8/9}$ and its combined standard uncertainty are calculated according to Annex A. It contains details of the evaluation and error propagation scheme. Both random and systematic terms are taken into account.

10 Interferences

In addition to the interference of isotope ^{241}Am, which is discussed above, the method can be subject to two other kinds of interferences.

Firstly, the isotopes emitting α particles of energies between 4,9 MeV and 5,6 MeV can interfere if they are not separated during the purification of plutonium. If emitters of α particles of energies above 5,5 MeV are present, an additional tailing correction shall be made to avoid a positive bias.

Secondly, any chemical compound, which is not completely eliminated during the chemical separation or during the preparation of the source, decreases the quality of the source and the resolution of the α spectra.

Even if these compounds are not radioactive, the errors in the processing of the spectra become significant when the half-height width of the peaks become greater than 25 keV. When the width of the peaks is 40 keV, these errors can be as large as ± 2 % or more.

Table 1 — Nuclear data relevant for the alpha spectrometry of plutonium [11]

Isotope	Half-life years	I %	E keV
^{238}Pu	87,7 ± 0,3	70,91	5 499,03
		28,98	5 456,3
		0,105	5 357,91
		0,003	5 207,76
^{239}Pu	24110 ± 30	73,3	5 156,59
		0,03	5 156,50
		15,1	5 144,3
		0,015	5 111,2
		11,5	5 105,5
		0,036	5 076,13
		0,03	5 055,19
^{240}Pu	6563 ± 7	72,8	5 168,17
		27,1	5 123,68
		0,085 2	5 021,23
		0,001 08	4 863,6
^{241}Pu	14,35 ± 0,1	2,5E-6	5 054,0
		2,5E-5	5 042,0
		1,0E-5	4 998,0
		3,1E-5	4 972,0
		2,01E-3	4 896,4
		2,92E-4	4 853,4
		2,9E-5	4 798,0
		5,0E-6	4 784,0
^{242}Pu	$(3,735 ± 0,011) \times 10^{5}$	78,0	4 900,5
		22,4	4 856,2
		0,098	4 754,6
		0,001 30	4 598,5
^{241}Am	432,7 + 0,5	0,34	5 544,5
		0,22	5 511,47
		84,5	5 485,56
		13,0	5 442,80
		1,6	5 388,23
		0,015	5 322,0

Annex A
(informative)

Combined standard uncertainty evaluation

A.1 Standard uncertainty $R(\alpha)$

A.1.1 Geometrical progression decrease method

Equation for the $R(\alpha)$ evaluation is as follows (see 4.3.2):

$$R(\alpha) = \frac{a}{b - \dfrac{ac}{b + \dfrac{ad}{c}}} \tag{A.1}$$

The combined standard uncertainty of the $R(\alpha)$, $u_c[R(\alpha)]$ is evaluated from the following equation:

$$u_c^2[R(\alpha)] = \left[R'_a(\alpha)u_c(a)\right]^2 + \left[R'_b(\alpha)u_c(b)\right]^2 + \left[R'_c(\alpha)u_c(c)\right]^2 + \left[R'_d(\alpha)u_c(d)\right]^2 +$$

$$+2s(a,b)R'_a(\alpha)R'_b(\alpha) + 2s(a,c)R'_a(\alpha)R'_c(\alpha) + 2s(a,d)R'_a(\alpha)R'_d(\alpha) +$$

$$+2s(b,c)R'_b(\alpha)R'_c(\alpha) + 2s(b,d)R'_b(\alpha)R'_d(\alpha) + 2s(c,d)R'_c(\alpha)R'_d(\alpha) \tag{A.2}$$

where $u_c(a)$, $u_c(b)$, $u_c(c)$, $u_c(d)$ are the standard uncertainties of a, b, c, d

$$R'_a(\alpha) = \frac{1}{b - \dfrac{ac}{b + \dfrac{ad}{c}}} + \frac{a}{\left(b - \dfrac{ac}{b + \dfrac{ad}{c}}\right)^2}\left[\frac{c}{b + \dfrac{ad}{c}} - \frac{ad}{(b + \dfrac{ad}{c})^2}\right] \tag{A.3}$$

$$R'_b(\alpha) = \frac{a}{\left[b - \dfrac{ac}{b + \dfrac{ad}{c}}\right]^2}\left[1 - \frac{ac}{(b + \dfrac{ad}{c})^2}\right] \tag{A.4}$$

$$R'_c(\alpha) = \frac{a}{\left[b - \dfrac{ac}{b + \dfrac{ad}{c}}\right]^2}\left[\frac{a}{b + \dfrac{ad}{c}} + \frac{ad^2}{c}\frac{1}{(b + \dfrac{ad}{c})^2}\right] \tag{A.5}$$

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$$R'_d(\alpha) = \frac{a^3}{\left[b - \dfrac{ac}{b + \dfrac{ad}{c}}\right]^2 \left(b + \dfrac{ad}{c}\right)^2} \tag{A.6}$$

$s(a,b)$ is the covariance between a and b, etc. The covariances are calculated from the results of n repeated measurements of one sample:

$$s(a,b) = \frac{1}{n}\sum(a_i - \bar{a})(b_i - \bar{b}) , \text{ etc.} \tag{A.7}$$

The correlation coefficients $q(a,b)$

$$q(a,b) = s(a,b)/(\overline{ab}) \tag{A.8}$$

are used often instead of covariances, because they reflect correlation between a and b in relative units.

A.1.2 Exponential decrease method

The activity ratio $R(\alpha)$ is obtained through the following equation [see [1] and Equation(4)]:

$$R(\alpha) = \frac{A}{B - T} \tag{A.9}$$

where

A is the area of the ^{238}Pu peak region in the measured α spectrum;

B is the area of the ^{239}Pu + ^{240}Pu peaks region;

T is the extrapolated tail area under region B.

The combined standard uncertainty of the $R(\alpha)$, $u_c[R(\alpha)]$ is evaluated from the following equation:

$$u_c^2\left[R(\alpha)\right] = \left[R'_A(\alpha)u_c(A)\right]^2 + \left[R'_B(\alpha)u_c(B)\right]^2 + \left[R'_T(\alpha)u_c(T)\right]^2 +$$

$$+ 2s(A,B)R'_A(\alpha)R'_B(\alpha) + 2s(A,T)R'_A(\alpha)R'_T(\alpha) + 2s(B,T)R'_B(\alpha)R'_T(\alpha) \tag{A.10}$$

where

$u_c(A)$, $u_c(B)$, $u_c(T)$ sont les incertitudes standards de A, B, T;

$$R'_A(\alpha) = \frac{1}{B - T} \tag{A.11}$$

$$R'_B(\alpha) = \frac{-A}{(B - T)^2} \tag{A.12}$$

$$R'_T(\alpha) = \frac{A}{(B - T)^2} \tag{A.13}$$

$s(A, B)$, $s(A, T)$, $s(B, T)$ are the covariances between A and B, A and T, B and T, respectively.

T is calculated by integration of the tail exponential function $t(i)$ over the region B:

$$T = \int_{N_1}^{N_2} t(i)\,di$$

(A.14)

where

    i is the channel number;

    N_1 and N_2 are the first and the last channel numbers of the region B;

$$t(i) = e^{a_0 - a_1 i}$$

(A.15)

where parameters a_0 and a_1 are calculated by fitting of an exponential function to the part of the α spectrum between regions A and B.

Equations for a_0 and a_1 are as follows:

$$a_0 = \frac{\sum i^2 \sum \ln Y_i - \sum i \sum i \ln Y_i}{\Delta}$$

(A.16)

$$a_1 = \frac{\sum i \sum \ln Y_i - n \sum i \ln Y_i}{\Delta}$$

(A.17)

$$\Delta = n \sum i^2 - \left(\sum i\right)^2$$

(A.18)

where

    sums (Σ) are taken over the part of the spectrum chosen for the tail approximation function;

    i is the channel number;

    Y_i is the number of counts in the channel i;

    n is the number of channels.

One can get, from equations (A.14) and (A.15), the following expression for T:

$$T = \frac{1}{a_1} \left[e^{a_0 - a_1 N_1} - e^{a_0 - a_1 N_2} \right]$$

(A.19)

The combined standard deviation of T is evaluated as follows:

$$u_c^2(T) = \left[T'_{a_0} u_c(a_0) \right]^2 + \left[T'_{a_1} u_c(a_1) \right]^2 + 2s(a_0, a_1) T'_{a_0} T'_{a_1}$$

(A.20)

where

$$T'_{a_0} = \frac{1}{a_1} \left[e^{a_0 - a_1 N_1} - e^{a_0 - a_1 N_2} \right]$$

(A.21)

$$T'_{a_1} = -\frac{1}{a_1^2} \left[e^{a_0 - a_1 N_1} - e^{a_0 - a_1 N_2} \right] - \frac{1}{a_1} \left[N_1 e^{a_0 - a_1 N_1} - N_2 e^{a_0 - a_1 N_2} \right]$$

(A.22)

$$u_c^2(a_0) = \frac{\chi^2 \sum i^2}{\Delta} \qquad (A.23)$$

$$u_c^2(a_1) = \frac{\chi^2 n}{\Delta} \qquad (A.24)$$

$$s(a_0, a_1) = -\frac{\sum i}{n} u_c^2(a_1) \qquad (A.25)$$

$$\chi^2 = \frac{\sum(\ln Y_i - a_0 - a_1 i)^2}{n-2} \qquad (A.26)$$

A.2 Combined standard uncertainty $\overline{R}_{8/9}$

The isotope ratio ^{238}Pu/^{239}Pu, $\overline{R}_{8/9}$ is derived from the following equation [see also Equation (2)]:

$$\overline{R}_{8/9} = R(\alpha)T_8 \left\{ \frac{1}{T_9} + \frac{\overline{R}_{0/9}}{T_0} \right\} \qquad (A.27)$$

where

$\overline{R}_{0/9}$ is the isotope ratio ^{240}Pu/^{239}Pu measured by mass spectrometry;

T_8, T_9, T_0 are the half-lives of isotopes ^{238}Pu, ^{239}Pu and ^{240}Pu, respectively.

The combined standard uncertainty of $\overline{R}_{8/9}$, $u_c(\overline{R}_{8/9})$ includes random and systematic terms:

$$u_c^2\left(\overline{R}_{8/9}\right) = \left\{ u_c\left[R(\alpha)\right]T_8\left[\frac{1}{T_9} + \frac{\overline{R}_{0/9}}{T_0}\right] \right\}^2 + \left[u_c\left(\overline{R}_{0/9}\right)R(\alpha)\frac{T_8}{T_0} \right]^2 + \left\{ u_c(T_8)R(\alpha)\left[\frac{1}{T_9} + \frac{\overline{R}_{0/9}}{T_0}\right] \right\}^2 +$$

$$+ \left[u_c(T_9)R(\alpha)\frac{T_8}{T_9^2} \right]^2 + \left[u_c(T_0)R(\alpha)T_8\frac{\overline{R}_{0/9}}{T_0^2} \right]^2 \qquad (A.28)$$

The standard uncertainties of $\overline{R}_{8/9}$ and $\overline{R}_{0/9}$ express the magnitude of random measurement uncertainties. Systematic terms include half-life uncertainties: $u_c(T_8)$, $u_c(T_9)$, $u_c(T_0)$.

When interference of americium is taken into account (see Clause 6), the equation for the corrected value of $\overline{R}_{8/9}$ is as follows:

$$\overline{R}_{8/9}^{\text{corr}} = R(\alpha)T_8 \left\{ \frac{1}{T_9} + \frac{\overline{R}_{0/9}}{T_0} \right\} + \frac{T_8}{T_A} \left\{ \frac{\overline{R}_{A/9}}{F} + \ln 2 \frac{\overline{R}_{1/9} \cdot t}{T_1} \right\} \qquad (A.29)$$

where

$\overline{R}_{A/9}$ is the isotope ratio ^{241}Am/^{239}Pu before purification of plutonium;

$\overline{R}_{1/9}$ is the isotope ratio ^{241}Pu/^{239}Pu at the time of separation;

T_A, T_1 are the half-lives of isotopes ^{241}Am and ^{241}Pu;

F is the decontamination factor of americium.

The combined standard uncertainty of $\overline{R}_{8/9}^{\,\text{corr}}$ is calculated from the following equation:

$$\left[u_\text{c}^{\text{corr}}(\overline{R}_{8/9})\right]^2 = \left\{u_\text{c}R(\alpha)T_8\left[\frac{1}{T_9}+\frac{\overline{R}_{0/9}}{T_0}\right]\right\}^2 + \left[u_\text{c}(\overline{R}_{0/9})R(\alpha)\frac{T_8}{T_9}\right]^2 + \left[u_\text{c}(\overline{R}_{A/9})\frac{T_8}{T_AF}\right]^2 +$$

$$+ \left[u_\text{c}(\overline{R}_{1/9})\frac{T_8\cdot t\cdot\ln2}{T_AT_1}\right]^2 + \left[u_\text{c}(F)\frac{T_8\overline{R}_{A/9}}{T_AF^2}\right]^2 + \left\{u_\text{c}(T_8)\left[R(\alpha)\left(\frac{1}{T_9}+\frac{\overline{R}_{0/9}}{T_0}\right)+\frac{1}{T_A}\left(\frac{\overline{R}_{A/9}}{F}+\ln2\frac{\overline{R}_{1/9}\cdot t}{T_1}\right)\right]\right\}^2 +$$

$$+ \left[u_\text{c}(T_9)R(\alpha)\frac{T_8}{T_9^2}\right]^2 + \left[u_\text{c}(T_0)R(\alpha)T_8\frac{\overline{R}_{0/9}}{T_0^2}\right]^2 + \left[u_\text{c}(T_A)\frac{\overline{R}_{A/9}T_8}{T_A^2F}\right]^2 + \left[u_\text{c}(T_1)\frac{\overline{R}_{1/9}T_8\cdot t\cdot\ln2}{T_1^2T_A}\right]^2 \qquad \text{(A.30)}$$

where additional random $u_\text{c}(\overline{R}_{A/9})$, $u_\text{c}(\overline{R}_{1/9})$ and systematic terms [$u_\text{c}(T_A)$, $u_\text{c}(T_1)$] are included.

A.3   Evaluation of $\overline{R}_{8/9}$

A.3.1   General

One hundred repeated measurements of Pu α-source prepared on the porcelain disk by the drop deposition method (3.2) were done using parameters specified in 4.1. The ^{238}Pu/^{239}Pu isotopic ratio in the measured sample was about 1 %. Measurement time was automatically adjusted to reach 500 000 counts in the ^{239}Pu + ^{240}Pu peak (the smaller one, 4.2). Parameters a, b, c, d were determined for every measured spectrum and used in evaluations of $R(\alpha)$, $\overline{R}_{8/9}$ and corresponding uncertainties for both geometrical progression and exponential decrease methods.

A.3.2   Calculation of $R(\alpha)$ and $u_\text{c}[(R(\alpha)]$

A.3.2.1   Geometrical progression decrease method

Table A.1 lists correlation coefficients between parameters a, b, c, d calculated from the measurements.

Table A.1 — Correlation coefficients between a, b, c, and d

$q(a,b)$	$q(a,c)$	$q(a,d)$	$q(b,c)$	$q(b,d)$	$q(c,d)$
−0,029	0,018	−0,013	0,020	−0,074	0,591

Only the correlation between c and d appears to be significant.

Fixed counting statistics in the area B (500 000 counts) leads to significant differences of the standard deviations of the actual results of repeated measurements and the values of square roots of the measured counts which would be expected from Poisson statistics (see Table A.2).

Table A.2 — Average values and standard deviations of the measured parameters

Parameter	a	b	c	d
Average	499 706,8	213 779,7	894,2	357,6
Measured standard deviation	38,4	575,8	47,5	30,0
Standard deviation for Poisson distribution	706,9	462,4	29,9	18,9

Three estimations of standard uncertainty $u_c[(R(\alpha)]$ were made. They are based on

— the calculation of standard deviation of replicate measurements,

— calculation of $u_c[R(\alpha)]$ from equations (A.1) to (A.6) using measured standard deviations,

— calculation of $u_c[R(\alpha)]$ from equations (A.1) to (A.6) using standard deviations for the Poisson distribution.

Table A.3 lists $R(\alpha)$ and estimations of $u_c[R(\alpha)]$ for the geometrical progression decrease method.

Table A.3 — $R(\alpha)$ and standard uncertainty $u_c[R(\alpha)]$ for geometrical-progression decrease method

$R(\alpha)$	$u_c[R(\alpha)]$, Direct measurement	$u_c[R(\alpha)]$, Equations (A.1) to (A.6), measured standard deviations	$u_c[R(\alpha)]$, Equations (A.1) to (A.6), standard deviations for Poisson distribution
2,349 4	0,272 %	0,272 %	0,256 %

Assuming that raw data obey Poisson statistics leads to a slight underestimate of standard uncertainty.

A.3.2.2 Exponential decrease method

Table A.4 lists correlation coefficients between parameters a, b, T [Equation (A.10)] and a_0, a_1 [Equation (A.20)].

Table A.4 — Correlation coefficients between a, b, T and a_0, a_1

$Q(a,b)$	$q(a,T)$	$q(b,T)$	$q(a_0,a_1)$
−0,029	0,093	0,127	−0,999 7

There is a strong correlation between parameters of the exponential function used for the evaluation of the tail parameter T [Equation (A.9)].

Standard uncertainty $u_c(T)$ calculated from the measured data is 15,2 %, and this value is in good agreement with that obtained according to Equation (A.20): $u_c(T) - 15,1$ %.

Table A.5 gives $R(\alpha)$ and estimations of $u_c[R(\alpha)]$ for the exponential decrease method for three different modes of the $u_c[R(\alpha)]$ calculation (A.3.2).

Table A.5 — $R(\alpha)$ and standard uncertainty $u_c[R(\alpha)]$ for exponential decrease method

$R(\alpha)$	$u_c[R(\alpha)]$, Direct measurement	$u_c[R(\alpha)]$, Equations (A.10) to (A.26), measured standard deviations	$u_c[R(\alpha)]$, Equations (A.10) to (A.26) standard deviations for Poisson distribution
2,346 1	0,270 %	0,269 %	0,253 %

Comparison of data from Tables A.3 and A.5 shows that both geometrical progression and exponential decrease methods give actually the same results for $R(\alpha)$ and $u_c[R(\alpha)]$. The simplified method of uncertainty calculation, based on the use of the Poisson distribution model for the measured values, gives underestimated uncertainties.

A.3.3 $\overline{R}_{8/9}$ Evaluation

Table A.6 lists $\overline{R}_{8/9}$, $u_c(\overline{R}_{8/9})$ and uncertainty components according to the exponential decrease method using nuclear data from Table 1, measured by mass spectrometry, $\overline{R}_{0/9} = 0,009\ 842$ and $u_c(\overline{R}_{0/9}) = 1,74E\text{-}5$.

Table A.6 — $\overline{R}_{8/9}$ and standard uncertainty components for exponential decrease method

$\overline{R}_{8/9}$	$u_c(\overline{R}_{8/9})$	$u_c[R(\alpha)]$	$u_c(\overline{R}_{0/9})$	$u_c(T_8)$	$u_c(T_9)$	$u_c(T_0)$
0,008 534	0,453 %	0,270 %	0,180 %	0,342 %	0,124 %	0,004 %

The conclusion can be drawn that systematic uncertainty components coming from nuclear data uncertainties overcome statistical components in the combined standard uncertainty value.

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