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

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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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 alpha particle spectrometry. The alpha 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.

It does not apply to purified plutonium solutions containing ^{241}Am nor to those containing more than 10 % of other nonvolatile impurities relative to the Pu content. Anion exchange chromatography in accordance with ISO 8299:1993, subclause 6.4 is a suitable purification method.

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

The source is prepared for alpha spectrometric measurement by solution evaporation with a wetting agent and subsequent ignition. The source is measured by alpha spectrometry with a semiconductor (surface barrier) detector. The spectrum is processed to obtain the activity ratio of ^{238}Pu to (^{239}Pu + ^{240}Pu).

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 alpha peak resolution. Intrinsic energy resolution of presently available detectors is generally better than 20 keV for 5,49 MeV alpha particle energy of ^{241}Am. Ion-implanted detectors have a resolution of 9 keV to 10 keV.

Sources of highest quality are prepared by vacuum sublimation or electrolysis. Excellent sources can also be prepared by depositing and drying a small drop of solution of the purified sample onto an inert support. Three examples of procedures of drop-deposition are described below. These alternatives were selected because they are in common use and well suited for use in parallel with mass spectrometry measurements.

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

In the following procedure, the sources shall be prepared in a fume cupboard 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 17/20; Ni 8/15; Mo 2,5/4; C 0,12 max.; Si 1,0 max.; Mn 2,0 max.; S 0,030/0,045; P 0,045.

3.1.1.2 Laboratory or **camping gas 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 heat 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 (see figure 1).

3.1.2 Reagents

3.1.2.1 Ethanol or **acetone**, analytical grade.

3.1.2.2 Colourless varnish (Zapon lacquer).

3.1.2.3 Tetraethylene glycol, analytical grade.

3.1.3 Procedure

3.1.3.1 Clean the disc with the ethanol or acetone (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 Zapon lacquer or an equivalent varnish (3.1.2.2).

NOTE 1 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 30 s only.

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

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 (see figure 2).

3.2.1.2 Hot plate, with maximum temperature of 250 °C.

NOTE 2 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 or **acetone**, 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 the ethanol or acetone (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 hot plate (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 on filaments for combined alpha and mass spectrometry

3.3.1 Apparatus

3.3.1.1 Filaments and filament assemblies, as used with the mass spectrometer.

3.3.1.2 Filament preheating and degassing device, for cleaning unloaded filaments.

3.3.1.3 Filament preparation device, for precise loading of the samples on to cleaned filaments and reproducible drying of the samples without cross contamination.

3.3.1.4 Pipette, of capacity 1 µl, with disposable tip.

3.3.2 Procedure

3.3.2.1 Purify the filaments by degassing in a vacuum chamber for 1 min to 30 min at approximately 2 000 °C.

3.3.2.2 With the pipette (3.3.1.4), deposit exactly in the centre of the previously degassed filament 1 µl of the sample solution, containing 0,05 µg to 0,5 µg of plutonium, depending upon the type of mass spectrometer to be used for the subsequent isotopic analysis. Heat the filament, e.g. by means of an electric current to an appropriate temperature in order to evaporate the solvent, to destroy the nitrate and to fix the oxides on the filament. The sample shall be dried to form a precise dot in the centre of the filament. Avoid temperatures higher than 600 °C. The temperature of the filament during the final stages of sample mounting is a critical factor and shall be carefully controlled.

For the subsequent analysis by mass spectrometry, it is important to reproduce closely all the following parameters, which control the quality of the deposit, from one analysis to another:

a) acidity;

b) element concentrations (± 30 %);

c) chemical purity especially with regard to the alkali elements;

d) amount (± 30 %);

e) position of deposit;

f) heating procedure.

4 Alpha spectrometry

4.1 Apparatus

4.1.1 Vacuum chamber, equipped with a vacuum gauge and a pump providing pressures of 0,5 Pa or less.

4.1.2 Si detector, surface barrier or ion-implanted, energy resolution (FWHM) 20 keV or better, active area about 100 mm^2. The detector shall be mounted in the vacuum chamber at a distance of about 15 mm from the alpha source, i.e. about 1,5 times the diameter of the source.

4.1.3 Bias voltage supply, adjustable up to 200 V, preamplifier and spectrometry amplifier, 1 K 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 sensitivity should be about 7 KeV/channel.

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

4.2 Measurement

4.2.1 Introduce the source in the vacuum chamber and pump until a vaccum of about 0,5 Pa $\left(5 \times 10^{-3}\ \text{mbar}\right)$ is obtained. Then set the detector voltage to the value recommended by the manufacturer.

4.2.2 Record the spectrum of alpha 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 semilogarithmic scale shall be similar to the one presented in figure 3. 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 3. At midheight, 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 2 groups shall be no greater than 1 % of the counts at the ^{238}Pu peak top.

4.3 Spectra evaluation

4.3.1 Principle

Very simple models are very efficient to accurately correct 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 alpha 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 areas.

The above assumptions form the basis of the two procedures which are described below, and which have the following features in common:

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 with energy below 4,96 MeV;

e) tail contribution estimates also exclude the contributions of the major ^{242}Pu and ^{241}Pu peaks between 4,96 MeV and 4,85 MeV and the minor ^{238}Pu peak at 5,36 MeV.

4.3.2 Geometric progression decrease method

4.3.2.1 The method involves two assumptions:

- the self-absorptions of the alpha particles of ^{238}Pu, ^{239}Pu, and ^{240}Pu are the same;
- the counts in the tail of a peak decrease in geometric progression.

4.3.2.2 Divide the plutonium alpha spectrum into four regions: A, B, C and D, each region having an equal number of channels (see figure 3).

4.3.2.3 Select the high energy end of region A from an examination of the alpha spectrum (typically 5,53 MeV).

4.3.2.4 Fix the low energy end of region B at 4,94 MeV so as to exclude the small alpha activity due to ^{241}Pu and ^{242}Pu isotopes (see table 1).

4.3.2.5 Obtain the high energy end of region B (typically 5,20 MeV) by subtracting the number of channels separating the ^{238}Pu and ^{239}Pu + ^{240}Pu peaks tops (corresponding to 0,33 MeV approximately) from the high energy end of region A.

4.3.2.6 The low energy end of the region A is thereby fixed automatically to be the channel of energy 5,27 MeV since the number of channels is the same as in region B (and usually corresponds to 0,26 MeV).

4.3.2.7 Fix regions C and D in a similar way.

4.3.2.8 Obtain the sums of the counts in the channels of regions A, B, C and D by selecting the regions of interest on the analyser. 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

$$R(\alpha) = \frac{a}{b - \dfrac{ac}{b + ad/c}} \qquad \dots (1)$$

5 Expression of results

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

$$\bar{R}'_{8/9} = R(\alpha) T_8 \left(\frac{1}{T_9} + \frac{\bar{R}'_{0/9}}{T_0} \right) \qquad \dots (2)$$

where

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

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

T_8 is the halflife of isotope ^{238}Pu (87,74 ± 0,10 years);

T_9 is the halflife of isotope ^{239}Pu (24 110 ± 30 years);

T_0 is the halflife of isotope ^{240}Pu (6 563 ± 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 quantitatively from americium just before alpha spectrometry is done.

If the purification is incomplete or if the spectrometry is not done immediately after purification of the plutonium, but after a delay, t, the analysis will still have a positive bias. The resulting relative bias Δ is given by the following equation, where the delay t and the halflives, T_1 to T_8 and T_A, are expressed in the same units:

$$\Delta = \frac{T_8}{T_A} \frac{\bar{R}'_{A/9}}{\bar{R}'_{8/9}} \times \frac{1}{F} + \ln 2 \times \frac{\bar{R}'_{1/9}}{\bar{R}'_{8/9}} \times \frac{t}{T_1} \qquad \ldots (3)$$

where

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

F is the americium decontamination factor;

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

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

T_1 is the halflife of isotope ^{241}Pu (14,4 ± 0,1 years);

T_A is the halflife of isotope ^{241}Am (432,7 ± 0,5 years).

In the case of a five year old plutonium, containing 1 % of ^{238}Pu isotope, 10 % of ^{241}Pu isotope and 2,7 % of ^{241}Am isotope, the relative bias is equal to 0,06 % immediately after separation, if the americium decontamination factor is 1 000. An additional bias of 0,027 % accumulates every day following the separation.

The efficiency of the ^{241}Am decontamination shall be checked regularly by repeating the alpha spectrometry of actual samples after submitting them to two successive separations.

The alpha spectrometry should be done within one week after the separation is completed.

7 Resolution of the alpha 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 or less for the ^{238}Pu peak.

^{241}Am sources prepared by the same method from pure americium compounds have a resolution of 9,2 keV (FWMH) or less.

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

The reproducibility of the method depends essentially upon the quality of the prior purification of plutonium.

40 samples of nonirradiated nuclear grade materials containing 0,1 % to 1,5 % of ^{238}Pu isotope and with U/Pu ratios ranging between 0 and 72 were analysed at one laboratory by the present procedure and mass spectrometry. The relative differences between the results of the two methods had a standard deviation of 0,34 % and a mean difference of – 0,32 %. For 20 samples of light-water-reactor spent fuel solutions, the standard deviation of the relative differences was equal to 1,0 % with a mean difference of – 0,9 %.

These values include the coefficient of variation of the errors due to the method of processing of the spectrum, and to the uncertainty in the halflives of isotopes ^{238}Pu, ^{239}Pu and ^{240}Pu which produce an uncertainty of 0,35 % on the result.

10 Accuracy

Over 150 replicate analyses of the certified isotopic reference material NBS947 had a coefficient of variation of 0,3 % and a mean relative difference of 0,12 % from the certified value.

11 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 alpha particles of energies between 4,9 MeV and 5,6 MeV can intefere if they are not separated during the purification of plutonium. If emitters of alpha particles of energies above 5,5 MeV are present, an additional tailing correction must be made to avoid a positive bias.

Secondly, any chemical compound, which is not completely eliminated during the chemical separation or during the ignition of the source, decreases the quality of the source and the resolution of the alpha 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

Isotope	Halflife years	*I* %	*E* keV
^{238}Pu	87,7 ± 0,1	71,6 28,3 0,10 0,003	5 499,21 5 456,5 5 357,7 5 205,6
^{239}Pu	24 110 ± 30	73,3 15,1 < 0,03 11,5 0,036 0,025	5 155,4 5 142,9 5 112,0 5 104,6 5 076,0 5 054,0
^{240}Pu	6 563 ± 7	73,4 26,5 0,091 0,002	5 168,3 5 123,8 5 014,0 4 851,0
^{241}Pu	14,4 ± 0,1	0,35 1,02 0,41 1,3 83,2 12,1 1,2 0,2	5 054,0 5 042,0 4 998,0 4 972,0 4 896,5 4 853,5 4 799,0 4 784,0
^{242}Pu	$(3{,}735 \pm 0{,}011) \times 10^5$	77 23	4 900,9 4 856,6
^{241}Am	(432,7 ± 0,5)	0,34 0,20 85,2 < 0,04 12,8 0,01 1,4	5 544,3 5 512,0 5 485,74 5 469,0 5 442,98 5 417,0 5 388,0