



Nuclear fuel technology — Chemical separation and purification of uranium and plutonium in nitric acid solutions for isotopic and isotopic dilution analysis by solvent extraction chromatography —

Part 1:

Samples containing plutonium in the microgram range and uranium in the milligram range

Technologie du combustible nucléaire — Séparation et purification chimiques de l'uranium et du plutonium dans les solutions d'acide nitrique par extraction chromatographique par solvant pour les mesures isotopiques et les analyses par dilution isotopique —

Partie 1: Échantillons ayant des teneurs en plutonium de l'ordre du microgramme et en uranium de l'ordre du milligramme

[Revision of first edition (ISO 15366:1999)]

ICS 27.120.30

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ISO 15366 was prepared by Technical Committee ISO/TC 85, *Nuclear Energy*, Subcommittee SC 5, *Nuclear Fuel Technology*.

This first edition cancels and replaces the first edition of ISO 15366:1999.

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Part 1:

Samples containing plutonium in the microgram range and uranium in the milligram range

1 SCOPE

This International Standard describes procedures to **chemically** separate and purify uranium and plutonium in dissolved solutions of irradiated light water reactor fuels and in samples of High Active Liquid Waste of spent fuel reprocessing plants, prior to their isotopic analysis by e.g. mass spectrometric method (ISO 8299) or alpha spectrometry (ISO 11483).

This Part 1, describes a technique for the separation of uranium and plutonium in spent fuel type samples based on chromatographic method. The procedure applies to samples containing 1 µg to 150 µg Pu (IV) and (VI) and 0,1 mg to 2 mg U (IV) and (VI) in up to 2 ml of 3 mol.l⁻¹ nitric acid solution. It is applicable to mixtures of uranium and plutonium in which the U/Pu-ratio may range from 0 up to 200.

2 PRINCIPLE OF THE METHOD

The chemical separation is based on a column extraction chromatography using tri-n-octylphosphine-oxide (TOPO) as extractant [1,2]. The necessary valency adjustment prior to the separation is done with iron(II) sulphate and sodium nitrite. The extraction process is performed in disposable columns loaded with a silica gel powder coated with the TOPO [3]. Plutonium (IV) and uranium (VI) in 3 mol.l⁻¹ nitric acid medium are selectively extracted into the TOPO while americium, the fission products and other interfering elements are not retained. Plutonium is eluted after reduction to the trivalent state with ascorbic acid [4]; uranium is eluted by an ammonium carbamate solution. Besides the measurement by mass spectrometry the plutonium fractions are also measured by alpha spectrometry for the determination of the isotopic abundance of ²³⁸Pu (mass spectrometry might be biased by residual amounts of uranium in the plutonium fraction) and for checking the recovery of plutonium.

In order to ensure favourable kinetics of the chemical reactions the (gravity) column flow rates should not exceed 0,1 ml.min⁻¹.

Parallel measurement of blank and/or control sample is recommended to verify the analysis.

Blanks are run in parallel with the samples to verify the absence of significant external cross contamination and cross contamination between samples.

Control samples prepared from certified or analysed materials are also prepared and separated along with the sample to verify that suitable valency adjustment, isotopic equilibration and separation efficiency are achieved.

3 APPARATUS

3.1 Biological shielding, e.g. shielded glove box or fume cupboard.

3.2 Disposable polypropylene or glass columns, length 90 mm, funnel reservoir 9,5 ml, support bed volume 1,4 ml, height of bed 26 mm, inner diameter of bed reservoir 8,4 mm. Frits of polyethylene or glass 20 µm resp. 70 µm porosity (See Figure A-1 in annex). Suitable polypropylene columns with polyethylene frits are available commercially and well adapted to robotised operation. The packing and conditioning of the columns are described in the Annex. The chromatographic columns are to be disposed of in the radioactive waste after use.

3.3 Two hot plates.

3.4 Standard laboratory equipment (flasks and beakers, pipettes, glassware, stands and supports for columns, sample vials, fraction tubes, etc.).

3.5 Glass vials

4 REAGENTS

Use only reagents of recognised analytical grade. All aqueous solutions shall be prepared with distilled or de-ionised water (resistivity 1 MΩ.m to 10 MΩ.m).

4.1 Concentrated nitric acid and nitric acid solutions, $c(\text{HNO}_3) = 6 \text{ mol.l}^{-1}$ and 3 mol.l^{-1} .

4.2 Formic acid solution, $c(\text{HCOOH}) = 1 \text{ mol.l}^{-1}$.

4.3 Ammonium carbamate [CAS No. 1111-78-0] solution, $c(\text{NH}_4\text{CO}_2\text{NH}_2) = 0,7 \text{ mol.l}^{-1}$.

4.4 Silicagel 100, 63 – 200 µm, prewashed with 3 mol.l^{-1} nitric acid solution (4.1) and distilled or de-ionised water (see Annex A.3.1).

4.5 L(+)-Ascorbic acid solution $c(\text{C}_6\text{H}_8\text{O}_6) = 1 \times 10^{-5} \text{ mol.l}^{-1}$ or $c(\text{C}_6\text{H}_8\text{O}_6) = 1 \times 10^{-3} \text{ mol.l}^{-1}$ in formic acid solution (4.2)

4.6 Tri-n-octylphosphine-oxide, $c(\text{TOPO}) = 0,2 \text{ mol.l}^{-1}$ solution in cyclohexane.

Warning: this reagent is flammable and should always be handled in a well ventilated place and never in the vicinity of a naked flame.

4.7 Iron(II) sulphate solution, $c(\text{FeSO}_4) = 0,1 \text{ mol.l}^{-1}$ or $c(\text{FeSO}_4) = 0,8 \text{ mol.l}^{-1}$ in water. To be prepared freshly for each working session.

4.8 Sodium nitrite solution, $c(\text{NaNO}_2) = 1 \text{ mol.l}^{-1}$ or $c(\text{NaNO}_2) = 5 \text{ mol.l}^{-1}$ in water. To be prepared freshly for each working session.

5 PROCEDURE ¹⁾(Figure 5.1)

5.1 The sample should contain 1 µg to 150 µg plutonium and 0,1 mg to 2 mg uranium in a volume of 0,5 ml of 3 mol.l^{-1} nitric acid solution (4.1). Whenever starting with dried samples apply the following dissolution procedure:

(a) Add 0,5 ml of 6 mol.l^{-1} nitric acid solution (4.1) to the dried samples and evaporate slowly on the hot plate, keeping the temperature slightly below the boiling point to avoid any splashing and bubbling until nitrate salts crystallise.

1) This procedure is an example. If equivalent results could be expected, other conditions than these described in clause 5, can be applied for sample preparation.

(b) Remove the sample vessels from the hot plate and redissolve the salts by adding 0,5 ml of 3 mol.l⁻¹ nitric acid solution (4.1), while still warm (40 °C to 60 °C). Shake the vessels for a few seconds.

5.2 Perform a redox valency cycle to ensure that all plutonium isotopes are in the tetravalent state before starting the separation, as follows:

(a) Add 50 µl of iron(II)-sulphate solution (4.7) to the sample.

(b) Mix and wait for **five** minutes for a complete reduction of plutonium (VI) or plutonium (IV) to plutonium (III).

(c) Add 50 µl sodium nitrite solution (4.8) to reoxidize plutonium to the tetravalent state and add further 100 µl of 6 mol.l⁻¹ nitric acid solution (4.1) to reach an acid concentration of 3 mol.l⁻¹. Mix again and wait for at least five minutes.

5.3 Transfer half of the pre-treated sample onto the column, wait approximately one minute, add the rest of the sample and let it flow through. This favours the retention of plutonium and uranium in the very upper layers of the column.

5.4 Wash out the fission products, together with americium, from the column using 3 mol.l⁻¹ nitric acid solution (4.1) in 3 successive aliquots of 2, 3 and 4 ml.

5.5 Condition the column for the plutonium elution by adding 2 ml of 1 mol.l⁻¹ formic acid solution (4.2). Discard waste collected up to this point.

5.6 Elute the plutonium from the column with the ascorbic acid solution (4.5) with two successive aliquots of 3 ml. Place the vials containing the collected plutonium fractions on one of the hot plates.

5.7 Wash out the 'tail' of the plutonium with 4 ml of the ascorbic acid solution (4.5) in one aliquot and discard the plutonium 'tail' washings to the waste.

5.8 Condition the column for the elution of the uranium fraction by adding two aliquots each of 1 ml distilled water. Discard the water washings to the waste.

5.9 Elute the uranium with 4 ml ammonium carbamate solution (4.3). Place the vials containing the collected uranium fractions on the other hot plate.

5.10 Let the plutonium and uranium fractions evaporate gently to dryness on the hot plates at 90 °C.

5.11 Remove the fractions from the hot plates, add 0,25 ml of concentrated nitric acid (4.1) and evaporate again to dryness. Repeat this step once.

5.12 Redissolve the plutonium fractions, while the vials are still warm (40 °C to 60 °C), with a volume $V(\text{Pu})$ of nitric acid solution 3 mol.l⁻¹ (4.1) to obtain a Pu concentration of about 50 ng.µl⁻¹.

$V(\text{Pu}) = 0,018 m(\text{Pu})$ in ml, where $m(\text{Pu})$ is the mass of plutonium (in µg).

Gently swirl the vial to facilitate the dissolution.

5.13 Redissolve the uranium fractions, while the vials are still warm (40 °C to 60 °C), with a volume $V(\text{U})$ of nitric acid solution 3 mol.l⁻¹ (4.1) to obtain a U concentration of about 400 µg.ml⁻¹.

$V(\text{U}) = 0,9 m(\text{U})$ in ml, where $m(\text{U})$ is the mass of uranium (in mg).

Gently swirl the vial to facilitate the dissolution.

5.14 Stopper the vials containing the plutonium and uranium fractions. Before submitting the plutonium fractions for mass spectrometric measurement ensure the proper plutonium concentration and the successful decontamination from americium by a rough check using gamma-spectrometry.

5.15 Forward all fractions for measurement by mass spectrometry and by alpha spectrometry.

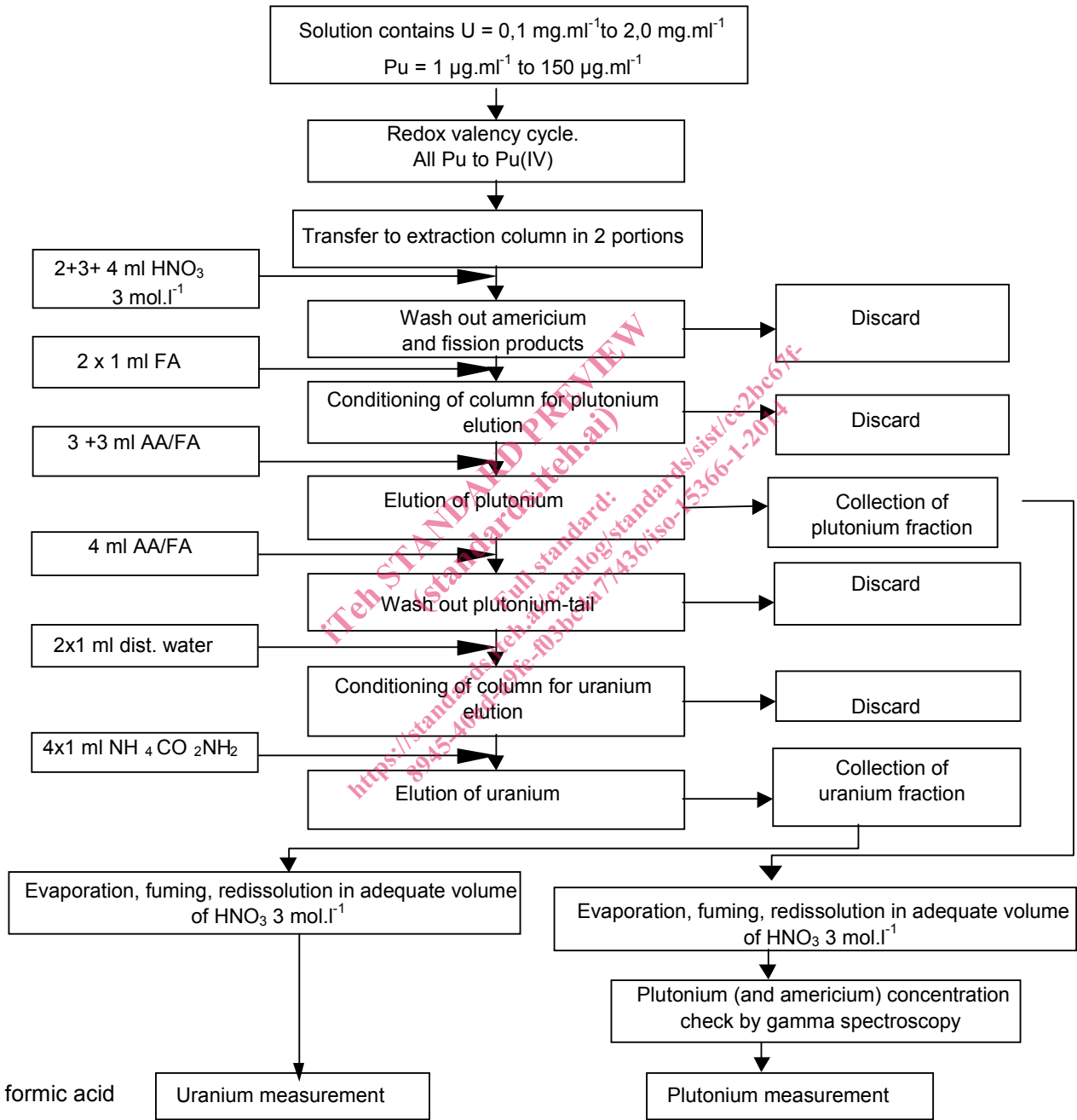


Fig. 5.1 – U and Pu separation scheme

6 CHARACTERISTICS OF THE SEPARATION

- 6.1 The element recovery varies between 80 % and 90 % for both uranium and plutonium in the range of 1 µg to 150 µg Pu and 0,1 mg to 2 mg U.
- 6.2 The separation procedure has no significant effect on the mass spectrometric measurement when compared to the measurement of pure unseparated uranium and plutonium reference materials, provided that the working environment (blanks – see 6.1) is adequately controlled.
- 6.3 The column has the capacity to retain up to about 15 mg of uranium.
- 6.4 The plutonium fractions contain less than a mass fraction of 0,001 % americium compared to total plutonium (a typical sample contains 0,3 µg to 0,4 µg ²⁴¹Am and 6 µg to 8 µg total plutonium).
- 6.5 The plutonium fraction can be separated from uranium with a decontamination factor of the order of 10⁵ or better.
- 6.6 The uranium fraction can be separated from plutonium with a decontamination factor of the order of 10³ or better.
- 6.7 This method differs essentially from other U/Pu separation procedures (in particular ion exchange) in its robustness – the procedure may be interrupted and continued (e.g. over night) at almost any step.

7 QUALITY CONTROL

- 7.1 Blanks: Blank samples are spiked with known amounts of highly enriched tracers, such as ²⁴²Pu and ²³³U and processed in the same way as, and in parallel with the actual samples. The amounts of plutonium and uranium coming from the blank are determined by isotope dilution mass spectrometry following ISO 8299. The amounts of blank U and Pu should be monitored (in QC charts) and should usually remain well below 0,1 % relative to the amounts of the respective element in a typical sample.
- 7.2 Control samples: Solutions of plutonium and uranium nitrate of known isotopic and elemental composition, similar to the composition of the actual samples, are used to monitor the accuracy of the isotopic and elemental assays by alpha and mass spectrometry following the separation. Samples of such solutions are processed and measured in the same way as, and in parallel with the actual samples. The results of such control measurements are preferably followed with statistical control charts.

8 INTERFERENCES

- 8.1 Extractable elements: According to reference [1], only Ti(IV), Zr(IV), Hf(IV), Ge(IV), Sn(IV), Tc(VIII), Eu(III), Ce(IV), Th(IV), Np(IV) and Np(V) may be extracted from nitric acid, 3 mol.l⁻¹, along with uranium and plutonium.
- 8.2 Interferences in mass spectrometry measurements according to ISO 8299: Elements yielding ions with mass 233, 234, 235, 236 and 238 cause interference in the mass spectrometric analysis of uranium if they have not been removed, or if they have been introduced as impurities during the chemical treatment; potassium for example will emit hexa-atomic ions of mass 234 and 236.

Elements yielding ions with mass 238 (particularly ²³⁸U), 239, 240, 241 and 242 cause interference in the mass spectrometric analysis of plutonium if they have not been completely removed during chemical treatment.

In addition to the isobaric interferences, another class of interfering elements can alter the fractionation patterns in mass spectrometric analyses. For example, thorium, zirconium, hafnium, rare earth metals, aluminium, and titanium can increase the temperature required to volatilise and ionise uranium and