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

*Énergie nucléaire — Séparation et purification chimique 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 isotopiques*

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International Organization for Standardization
Case postale 56 • CH-1211 Genève 20 • Switzerland
Internet iso@iso.ch

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.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 3.

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 15366 was prepared by Technical Committee ISO /TC 85, *Nuclear energy*, Subcommittee SC 5, *Nuclear fuel technology*.

Annex A forms a normative part of this International Standard. Annex B is for information only.

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

1 Scope

This International Standard specifies a procedure to separate and purify uranium and plutonium contained in input solutions of irradiated nuclear fuels and final products handled at spent-fuel reprocessing plants, before their isotopic analysis by a mass spectrometric method as described ISO 8299 or alpha spectrometry as described in ISO 11483. The procedure applies to samples containing 2 µg to 150 µg Pu and 0,1 mg to 2 mg U in up to 2 ml of 3 mol/l nitric acid solution. The U/Pu-ratio may range from 0 up to 200.

2 Normative references

The following normative documents contain provisions which, through reference in this text, constitute provisions of this International Standard. For dated references, subsequent amendments to, or revisions of, any of these publications do not apply. However, parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the normative documents indicated below. For undated references, the latest edition of the normative document referred to applies. Members of ISO and IEC maintain registers of currently valid International Standards.

ISO 5725-2:1994, *Accuracy (trueness and precision) of measurement methods and results — Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method*.

ISO 8299:1993, *Determination of isotopic content and concentration of uranium and plutonium in nitric acid solution — Mass spectrometric method*.

ISO 11483:1994, *Preparation of plutonium sources and determination of ²³⁸Pu/²³⁹Pu isotope ratio by alpha spectrometry*.

3 Principle

The chemical separation is performed on a chromatography column of silicagel impregnated with tri-*n*-octylphosphine oxide (TOPO). Plutonium(IV) and uranium(VI) in 3 mol/l nitric acid are selectively fixed on the column. Americium, the fission products and other interfering elements are not retained. Plutonium is eluted after reduction to the trivalent state with a mixture of hydroiodic and nitric acids; uranium is eluted by an ammonium carbamate solution.

Reagent blanks are treated and measured in parallel with the samples to verify the absence of significant cross-contamination between samples.

Control samples prepared from reference materials are also treated according to the same procedure, with the same reagents and columns of the same batch, and measured along with the samples to verify the whole procedure of separation and purification.

4 Apparatus

4.1 Shielded glove box or fume cupboard.

4.2 Disposable polypropylene or glass columns, with a length of 90 mm, a funnel reservoir of 9,5 ml, a support bed volume of 1,4 ml, a bed height of 26 mm, an inner diameter of bed reservoir of 8,4 mm, and fitted with frits of polyethylene or glass of 20 μm , respectively 70 μm porosity (see Figure A.1). Suitable polypropylene columns with polyethylene frits are available commercially and well adapted to robotized operation. The packing and conditioning of the columns are described in normative annex A. The chromatographic columns shall be disposed of in the radioactive waste after use.

4.3 Three hotplates, reserved respectively for the treatment of the samples preceding their separation, and the treatment of the separated fractions of plutonium and uranium.

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

5 Reagents

Use only reagents of recognized analytical grade or better. All aqueous solutions shall be prepared with distilled or deionized water (conductivity $< 70 \text{ nS} \cdot \text{cm}^{-1}$, or resistivity $R > 15 \text{ M}\Omega \cdot \text{cm}$).

5.1 Concentrated nitric acid and nitric acid solutions, $c(\text{HNO}_3) = 6 \text{ mol/l}$, 3 mol/l and $1,7 \text{ mol/l}$.

5.2 Hydroiodic acid solution, $c(\text{HI}) = 0,1 \text{ mol/l}$, **in nitric acid**, $c(\text{HNO}_3) = 1,7 \text{ mol/l}$ (5.1). The acid mixture shall be prepared freshly for each working session. The acid mixture is stable for about 8 h. The concentrated hydroiodic acid (suprapure, mass fraction of 56 %) is commercially available as suprapure reagent in sealed glass ampoules. It is kept in a refrigerator at about 6 °C. If more than 7 days elapsed since cutting the ampoule, open a new one.

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

5.4 Silicagel 100, 63 μm – 200 μm (see A.3.1).

5.5 Tri-*n*-octylphosphine oxide, $c(\text{TOPO}) = 0,2 \text{ mol/l}$ 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 flame.

5.6 Ferrous sulfate solution, $c(\text{FeSO}_4) = 0,1 \text{ mol/l}$. To be prepared freshly for each working session.

5.7 Sodium nitrite solution, $c(\text{NaNO}_2) = 1 \text{ mol/l}$. To be prepared freshly for each working session.

6 Procedure (see Figure 1)

6.1 The sample should contain 2 μg to 150 μg of plutonium and 0,1 mg to 2 mg of uranium in a volume of 0,5 ml of 3 mol/l nitric acid solution (5.1). When starting with dried nitrate samples, apply the following dissolution procedure.

- Add 0,5 ml of 6 mol/l nitric acid solution (5.1) to the dry samples and evaporate slowly on the first hotplate, keeping the temperature slightly below the boiling point to avoid any splashing and bubbling until nitrate salts crystallize.
- Remove the sample vessels from the hotplate and redissolve the salts by adding 0,5 ml of 3 mol/l nitric acid solution (5.1) while still warm (40 °C to 60 °C). Shake the vessels for a few seconds.

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

- Add 50 μl of ferrous sulfate solution (5.6) to the sample.

- b) Mix and wait for 5 min for a complete reduction of plutonium(VI) or plutonium(IV) to plutonium(III).
- c) Add 50 µl of sodium nitrite solution (5.7) to reoxidize plutonium to the tetravalent state and add a further 100 µl of 6 mol/l nitric acid solution (5.1) to reach an acid concentration of 3 mol/l. Mix again and wait for at least 5 min.
- 6.3** Transfer half of the pretreated sample onto the column, wait approximately 1 min, 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.
- 6.4** Wash out the fission products, together with americium, from the column using 3 mol/l nitric acid solution (5.1) in 3 successive aliquots of 2 ml, 3 ml and 4 ml.
- 6.5** Condition the column for the plutonium elution by adding 2 ml of 1,7 mol/l nitric acid solution (5.1). Discard all the wastes collected until now.
- 6.6** Elute the plutonium from the column with the hydroiodic acid solution in nitric acid solution (5.2) with three successive aliquots of 2 ml. Place the vials containing the collected plutonium fractions on the second hotplate.
- 6.7** Wash out the "tail" of the plutonium with 5 ml of the hydroiodic acid solution in nitric acid solution (5.2) in one aliquot and discard the plutonium "tail" washings to the waste.
- 6.8** Condition the column for the elution of the uranium fraction by adding successively two aliquots of 1 ml distilled water. Discard the water washings to the waste.
- 6.9** Elute the uranium with 4 ml of ammonium carbamate solution (5.3). Place the vials containing the collected uranium fractions on the third hotplate.
- 6.10** Let the plutonium and uranium fractions evaporate gently to dryness on the hotplates at 90 °C.
- 6.11** Remove the fractions from the hotplates, add 0,25 ml of concentrated nitric acid (5.1) and evaporate again to dryness. Repeat this step once again.
- 6.12** Redissolve the plutonium fraction, while the vial is still warm (40 °C to 60 °C), with a volume $V(\text{Pu})$ of 3 mol/l nitric acid solution (5.1) to obtain a plutonium concentration of about 50 ng/µl. $V(\text{Pu}) = 0,018 m(\text{Pu})$ in millilitres, where $m(\text{Pu})$ is the mass of plutonium in micrograms, in the initial sample. Swirl the vial to facilitate the dissolution.
- 6.13** Redissolve the uranium fraction, while the vial is still warm (40 °C to 60 °C), with a volume $V(\text{U})$ of 1,7 mol/l nitric acid solution (5.1) to obtain a uranium concentration of about 1 mg/ml. $V(\text{U}) = 0,9 m(\text{U})$ in millilitres, where $m(\text{U})$ is the mass of uranium, in micrograms. Swirl the vial to facilitate the dissolution.
- 6.14** Stopper the vials containing the plutonium and uranium fractions and transfer them for measurement by mass spectrometry and by alpha spectrometry.

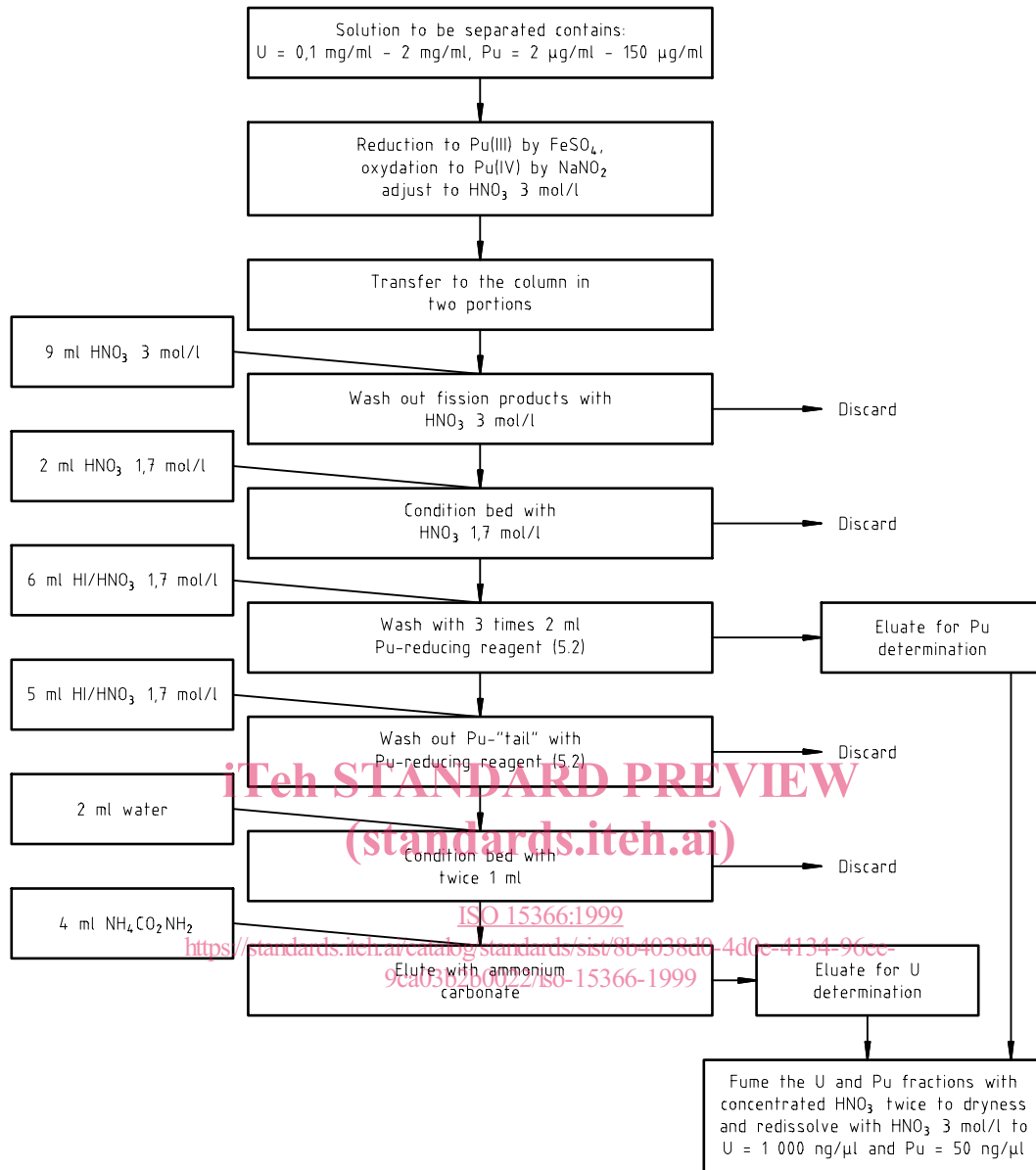


Figure 1 — U and Pu separation scheme

7 Characteristics of the separation

The element recovery varies between 80 % and 90 % for both uranium and plutonium.

The column has the capacity to retain up to about 15 mg of uranium.

The plutonium fractions contain a mass fraction of less than 0,001 % americium compared to total plutonium (A typical sample contains 0,3 µg-0,4 µg ²⁴¹Am and 6 µg-8 µg total plutonium).

The plutonium fraction can be separated from uranium with a decontamination factor of the order of 10⁵ or better.

The uranium fraction can be separated from plutonium with a decontamination factor of the order of 10³ or better.

8 Repeatability and reproducibility of the results

Table 1 lists the coefficients of variation of the repeatabilities and reproducibilities achievable in isotopic ratio measurements of uranium and plutonium separated according to the present procedure for the purpose of isotopic and/or isotopic dilution analyses.

Table 1

Measurement method	Isotope ratio or concentration	Typical value	Coefficients of variation	
			repeatability ^a %	reproducibility ^a %
Mass spectrometry	$^{233}\text{U}/^{238}\text{U}$	1	0,25	0,25
	$^{234}\text{U}/^{238}\text{U}$	1×10^{-4}	1,0	1,5
	$^{235}\text{U}/^{238}\text{U}$	2×10^{-2}	0,10	0,15
		2×10^{-1}	0,05	0,10
	$^{236}\text{U}/^{238}\text{U}$	1×10^{-4}	2,0	4,0
	U concentration	150 g/kg	0,15	0,20
Alpha spectrometry	$^{238}\text{Pu}/^{239}\text{Pu}$	3×10^{-3}	0,20	0,30
Mass spectrometry	$^{238}\text{Pu}/^{239}\text{Pu}$	3×10^{-3}	0,50	0,50
	$^{240}\text{Pu}/^{239}\text{Pu}$	0,24	0,02	0,05
	$^{241}\text{Pu}/^{239}\text{Pu}$	0,020	0,10	0,15
	$^{242}\text{Pu}/^{239}\text{Pu}$	0,015	0,10	0,10
	Pu concentration	2 g/kg	0,10	0,15

^a According to ISO 5725.

9 Interferences

9.1 Extractable elements

According to reference [1] in the Bibliography, 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, along with uranium and plutonium.

9.2 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 ^{238}U), 239, 240, 241 and 242 cause interference in the mass spectrometric analysis of plutonium if they have not been completely removed during chemical treatment or if they have been introduced during the 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, the rare earth metals, aluminum, and titanium can increase the temperature required to volatilize and ionize uranium and plutonium. Iron, vanadium, copper and alkali metals can lower the temperature at which volatilization of uranium and plutonium occurs. Among these, only Th, Zr, Hf and Ti may be retained by TOPO from 3 mol/l nitric acid.