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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

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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Contents

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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.

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 $< 70\ nS \cdot cm^{-1}$, or resistivity $R > 15\ M\Omega \cdot cm$).

5.1 Concentrated nitric acid and nitric acid solutions, $c(HNO_3)$ = 6 mol/l, 3 mol/l and 1,7 mol/l.

5.2 Hydroiodic acid solution, $c(HI)$ = 0,1 mol/l, **in nitric acid**, $c(HNO_3)$ = 1,7 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**, $c(NH_4CO_2NH_2)$ = 0,7 mol/l.

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

5.5 Tri-*n*-octylphosphine oxide, $c(TOPO)$ = 0,2 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, $c(FeSO_4)$ = 0,1 mol/l. To be prepared freshly for each working session.

5.7 Sodium nitrite solution, $c(NaNO_2)$ = 1 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.

a) 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.

b) 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:

a) 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(Pu) of 3 mol/l nitric acid solution (5.1) to obtain a plutonium concentration of about 50 ng/µl. V(Pu) = 0,018 m(Pu) in millilitres, where m(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(U) of 1,7 mol/l nitric acid solution (5.1) to obtain a uranium concentration of about 1mg/ml. V(U) = 0,9 m(U) in millilitres, where m(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.

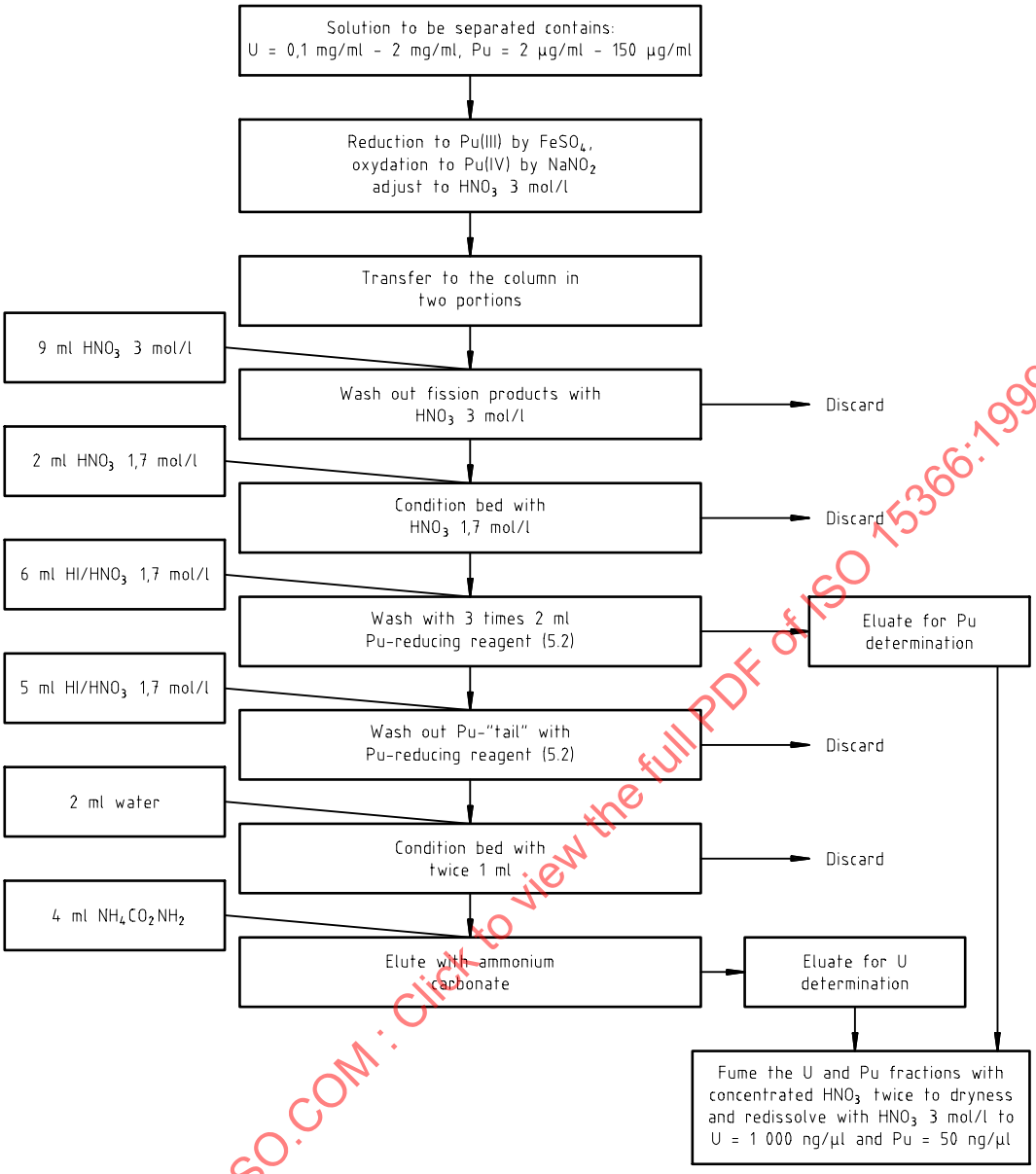

Figure 1 — U and Pu separation scheme

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 ^{241}Am and 6 µg-8 µg total plutonium).

The plutonium fraction can be separated from uranium with a decontamination factor of the order of 10^5 or better.

The uranium fraction can be separated from plutonium with a decontamination factor of the order of 10^3 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 radio or concentration	Typical value	Coefficients of variation	
			repeatability [a] %	reproductibility [a] %
Mass spectrometry	$^{233}U/^{238}U$	1	0,25	0,25
	$^{234}U/^{238}U$	1×10^{-4}	1,0	1,5
	$^{235}U/^{238}U$	2×10^{-2}	0,10	0,15
		2×10^{-1}	0,05	0,10
	$^{236}U/^{238}U$	1×10^{-4}	2,0	4,0
	U concentration	150 g/kg	0,15	0,20
Alpha spectrometry	$^{238}Pu/^{239}Pu$	3×10^{-3}	0,20	0,30
	$^{238}Pu/^{239}Pu$	3×10^{-3}	0,50	0,50
Mass spectrometry	$^{240}Pu/^{239}Pu$	0,24	0,02	0,05
	$^{241}Pu/^{239}Pu$	0,020	0,10	0,15
	$^{242}Pu/^{239}Pu$	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.

9.3 Interferences in alpha spectrometry measurements according to ISO 11483

The nuclide ^{241}Am emits alpha particles of energies very close to the energies of the radiation emitted by the nuclide ^{238}Pu. Its presence yields positive biases in the determination of the ^{238}Pu abundance by alpha spectrometry. In the case of a five year old plutonium sample, containing 1 % of the ^{238}Pu isotope, 10 % of the ^{241}Pu isotope and 2,7 % of the ^{241}Am isotope, the relative bias is equal to 0,06 % immediately after separation, if the americium decontamination factor is 10^3. An additional bias of 0,027 % accumulates every day following the separation.

The efficiency of the ^{241}Am-decontamination should be checked regularly by gamma spectrometry or by repeating the alpha spectrometry after submitting the plutonium fraction to a second separation. The alpha spectrometry should be done within one week after the separation is completed.

Nuclides emitting alpha particles of energies between 4,9 MeV and 5,6 MeV can interfere in the alpha spectrometric analysis if they are not separated during the purification of plutonium.

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 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 becomes greater than 25 keV. Silicon compounds which may leach out of the column shall be removed by prewashing the column just before use in accordance with A.3 and A.5 of annex A.

10 Quality control

10.1 Blanks

Reagent blanks are spiked with known amounts of highly enriched ^{242}Pu and ^{233}U tracers 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 in accordance with ISO 8299. These amounts should not exceed 0,1 % of the amounts of plutonium and uranium present in the actual sample ([4], in the Bibliography).

10.2 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 measure the rate of recovery of plutonium and uranium after the separation, and to measure the accuracy of the isotopic or/and elemental assays by alpha or/and mass spectrometry following the separation ([4], in the Bibliography).

Samples of such solutions are processed and measured in the same way as, and in parallel with, the actual samples.

The recovery of uranium and plutonium following the separation of a control sample should not be less than 80 %. The bias of the alpha or mass spectrometric assays should not exceed the prescribed control limits ([4], in the Bibliography).

Annex A
(normative)

The packing and conditioning of the chromatographic columns loaded with an inert silica support coated with tri-*n*-octylphosphine oxide (TOPO)

A.1 Scope

This annex describes the procedure for the preparation of the chromatographic columns.

The aim is to obtain an inert support uniformly coated with tri-*n*-octylphosphine oxide and its homogeneous packing into the column, ensuring that the flow of the effluents is reproducible and uniform during the separation process.

A.2 Apparatus

The column shall be prepared in a clean area where contamination by actinides can be excluded.

A.2.1 Columns and frits (see Figure A.1).

A.2.2 Dispensing spoon, PVC custom-made, to measure 0,25 g of the TOPO/silicagel powder.

A.2.3 Rubber bulb.

A.2.4 Shaker with column holder. A custom-built plastic rack is mounted on a commercial “Vortex“-mixer.

A.2.5 Sieve, stainless steel, approximately 600 mm diameter, 0,25 mm pores.

A.2.6 PVC-rod, 6 mm diameter, 150 mm length, to push the frit into the column.

A.3 Coating the silicagel support with TOPO

The silicagel powder is coated with TOPO as follows to obtain a dry and loose powder.

A.3.1 First wash the silicagel 100 in the following manner.

Weigh 40 g of silicagel 100 (5.4) into a beaker and wash with about 100 ml of nitric acid solution 3 mol/l (5.1), swirling and mixing the slurry each 10 min for at least 0,5 h. Allow the slurry to set and discard the acid solution. Wash the silicagel 100 in a similar way with distilled water at least 10 times in order to obtain an acid-free support. Dry the wet silicagel 100 on a big watch-glass overnight at 120 °C. Allow the powder to cool before further use.

A.3.2 Weigh 30 g of the washed and dried silicagel into a 250 ml beaker.

A.3.3 Place the beaker on the balance in a well ventilated area and swiftly add 45 g of 0,2 mol/l solution of TOPO in cyclohexane.

Using a volumetric cylinder to measure the required amount of TOPO solution is not recommended, as the cyclohexane would evaporate so fast during its transfer that an uncontrolled amount of TOPO would crystallize on the inner walls of the cylinder.

A.3.4 Stir steadily and quickly with a plastic spoon, taking care that the silicagel is uniformly wetted and coated with the TOPO solution.

A.3.5 Transfer the mixture to a large watch-glass or Petri dish, spread it evenly with the spoon and allow the material to dry. The cyclohexane evaporates rapidly leaving a dry silicagel coated with TOPO. Leave uncovered in a well ventilated room for 48 h at room temperature to reach complete dryness.

Never dry above room temperature. Drying at higher temperatures will produce crusty clumps and the TOPO will tend to flake away from the surface of the silicagel particles.

A.3.6 Store the powder in plastic bottles until it is used.

A.4 Packing the columns

The chromatographic columns shall be prepared, as follows, only for a single use and they shall discarded to the radioactive waste after the performance of the separation.

A.4.1 Sieve the TOPO/silicagel powder through a stainless-steel sieve with 0,25 mm pores to assure that no bulk TOPO is added to the column.

A.4.2 Take a 20 µm frit and place it in the column reservoir. Push the frit gently with the PVC rod down the column until it rests on the flat bottom of the column, without damaging or twisting the frit (Figure A.1).

A.4.3 Bring the column onto the column holder of the shaker and introduce a glass funnel into its upper reservoir.

A.4.4 Fill the special dispensing plastic spoon with sieved TOPO/silicagel powder up to the rim and pour it through the funnel into the column. Remove the funnel from the column.

A.4.5 Fill as many columns as needed, following steps A.4.2 to A.4.4.

A.4.6 Set the shaker to 1 200 rpm and let the columns vibrate for about 5 s. This has the purpose of distributing homogeneously the TOPO/silicagel beads in the column. Half of the support material has now been packed in the column.

A.4.7 The second half is added by repeating steps A.4.4 to A.4.6; 0,5 g of TOPO/silicagel have now been added to each column.

A.4.8 Take a 70 µm frit and place it in the column reservoir on top of the bed of TOPO/silicagel. Push the frit carefully with the PVC rod until it presses gently on the TOPO/silicagel filling. Take care that the frit sits horizontally on the TOPO/silicagel (Figure A.1).

A.4.9 Store the column in a sealed plastic bag for later use, and condition it as described in A.5 before use.

A.5 Conditioning the columns

Condition the columns immediately before use in a clean area, excluding contamination by actinides, and outside of the analytical glove box to avoid unnecessary production of radioactive waste, as described in A.5.1 to A.5.4.

A.5.1 Take the necessary number of columns.

A.5.2 Remove the columns from their storage bags and place them on a stand above a waste-collection vessel.

A.5.3 Add 8 ml of 3 mol/l nitric acid solution to the column and press the solution gently with a rubber bulb through the TOPO/silicagel until liquid drops appear at the column tip. The diluted acid will now flow unattended by gravity until the reservoir is empty.

A.5.4 When the reagent stops flowing and the reservoir is empty, transfer the column into the glove box and proceed with the separation.