INTERNATIONAL STANDARD

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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 2: Samples containing plutonium and uranium in the nanogram range and below

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 2: Échantillons ayant des teneurs en plutonium et en uranium de l'ordre du nanogramme et inférieures

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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.

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The committee responsible for this document is ISO/TC 85, *Nuclear Energy*, Subcommittee SC 5, *Nuclear Fuel Technology*.

This first edition, together with the first edition of ISO 15366-1, cancels and replaces the first edition of ISO 15366:1999, which has been technically revised.

ISO 15366 consists of the following parts, under the general title *Chemical separation and purification of uranium and plutonium in nitric acid solutions for isotopic and isotopic dilution analysis by solvent extraction chromatography* —

— *Part 1: Sample containing plutonium in the microgram range and uranium in the milligram range*

— *Part 2: Sample containing plutonium and uranium amounts in the nanogram range and below*

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 2: Samples containing plutonium and uranium in the nanogram range and below

1 Scope

This part of ISO 15366 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 (see ISO 8299[1]) or alpha spectrometry (see ISO 11483[2]). This part of ISO 15366 describes a slightly different separation technique from ISO 15366-1, based on the same chemistry, using smaller columns, different support material and special purification steps, applicable to samples containing plutonium and uranium amounts in the nanogram range and below. The detection limits were found to be 500 pg plutonium and 500 pg uranium. Annex A describes the preparation of the columns and the column support materials.

In comparison with ISO 15366-1, as uranium and plutonium amounts are lowest, additional purification on an anion exchange resin is performed.

2 Principle of the method

The chemical separation of small plutonium and uranium amounts (>500 pg) is also based on a column extraction chromatography using tri-*n*-octylphosphine-oxide (TOPO) as extractant.[3][4] The necessary valency adjustment prior to the separation is done with iron(II) sulfate and sodium nitrite. The extraction process is performed in disposable mini-columns loaded with a polyethylene or silica gel powder coated with the TOPO. 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[5]; uranium is eluted by an ammonium carbamate solution and finally purified from ammonium salts by an ion exchange separation[6] or fuming by 14 mol·l^{-1}nitric acid.

In order to ensure a favourable kinetics of chemical reactions the (gravity) column flow rates should not exceed 0,4 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 or 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.

The whole process is carried out under clean conditions preferably in a laminar flow fume hood.

3 Apparatus

3.1 Biological shielding, e.g. shielded glove box or fume cupboard, preferably a laminar flow fume cupboard.

3.2 Disposable polypropylene columns and frits (see Figure A.1). Type: micro-column. The packing and conditioning of the columns are described in Annex A. The chromatographic columns shall 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.). It is recommended to leach all equipment, which will be in contact with samples, eluates or eluents with nitric acid (4.1) and distilled water before use. After drying, store it in plastic bags in a clean area.

3.5 PTFE vials, of dimensions: volume 15 ml, diameter 28 mm, height 37 mm. With screw caps and metal jackets.

These vials may be used at least 10 times, after a careful cleaning with hot nitric acid, followed by a rinsing with demineralized or de-ionized water.

4 Reagents

Use only reagents of recognized suprapure grade or equivalent. All aqueous solutions shall be prepared with distilled water (resistivity 1 MΩ·m to 10 MΩ·m).

4.1 Concentrated nitric acid and nitric acid solutions, $c(HNO_3)$ = 6 mol·l^{-1} and 3 mol·l^{-1}.

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

4.3 Ammonium carbamate [CAS No. 1111-78-0] **solution**, $c(NH_4CO_2NH_2)$ = 0,7 mol·l^{-1}.

4.4 Polyethylene powder[1)] GUR X 117/PE-UHMW Ultra-high-molecular grain size 25 µm to 95 µm, pore size ≤5 µm (see A.2.5).

4.5 L(+)-Ascorbic acid solution $c(C_6H_8O_6)$ = 10^{-5} mol·l^{-1} or $c(C_6H_8O_6)$ = 10^{-3} mol·l^{-1} in formic acid solution (4.2)

4.6 Tri-*n*-octylphosphine-oxide, c(TOPO) = 0,2 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) sulfate solution, $c(FeSO_4)$ = 0,1 mol·l^{-1} or $c(FeSO_4)$ = 0,8 mol·l^{-1} in water. To be prepared freshly for each working session.

4.8 Sodium nitrite solution, $c(NaNO_2)$ = 1 mol·l^{-1} or $c(NaNO_2)$ = 5 mol·l^{-1} in water. To be prepared freshly for each working session.

4.9 Aqua regia, mixture 3:1 (per volume) of concentrated hydrochloric acid and concentrated nitric acid.

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1) Silica gel may also be used. See ISO 15366-1.

4.10 Concentrated hydrochloric acid and **hydrochloric acid solution** $c(HCl) = 6\ mol \cdot l^{-1}$

4.11 Anion exchange resin AG MP1, slurry in distilled water. Fill the mini-columns (3.2) with about 0,5 ml of the slurry. Condition the columns with two times 1 ml of distilled water and with three times 1 ml concentrated hydrochloric acid (4.10) immediately before use.

5 Procedure (see Figure 1)

NOTE 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.

5.1 The sample should contain 500 pg to 1 µg plutonium and 500 pg to 100 µg uranium in a volume of 0,5 ml of 3 $mol \cdot l^{-1}$ nitric acid solution (4.1). Whenever starting with dried samples, apply the following dissolution procedure.

a) Add 0,5 ml of 6 $mol \cdot l^{-1}$ nitric acid solution (4.1) to the dry 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 crystallize.

b) Remove the sample vessels from the hot plate and redissolve the salts by adding 0,5 ml of 3 $mol \cdot l^{-1}$ 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) sulfate solution (4.7) 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 sodium nitrite solution (4.8) to reoxidize plutonium to the tetravalent state and add further 100 µl of 6 $mol \cdot l^{-1}$ nitric acid solution (4.1) to reach an acid concentration of 3 $mol \cdot l^{-1}$. Mix again and wait for at least 5 min.

5.3 Transfer half of the pretreated sample on to 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.

5.4 Rinse the sample vial with 0,5 ml of 3 $mol \cdot l^{-1}$ nitric acid solution (4.1) and transfer the solution to the column.

5.5 Wash out the fission products, including americium, from the column using 3 $mol \cdot l^{-1}$ nitric acid solution (4.1) in four successive aliquots of 1 ml.

5.6 Condition the column for the plutonium elution by adding twice 0,5 ml of 1 $mol \cdot l^{-1}$ formic acid solution (4.2). Discard waste collected until this time.

5.7 Elute the plutonium from the column with the ascorbic acid solution (4.5) with five successive aliquots of 1 ml. Place the vials containing the collected plutonium fractions on one of the hot plates.

5.8 Wash out the "tail" of the plutonium with twice 1 ml of the ascorbic acid solution (4.5) in formic acid solution in one aliquot and discard the plutonium "tail" washings to the waste.

5.9 Condition the column for the elution of the uranium fraction by adding two aliquots each of 1 ml distilled or de-ionized water. Discard the water washings to the waste.

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

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

5.12 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. Proceed with the uranium fractions with 5.17 if necessary.

5.13 Redissolve the plutonium fractions in 0,5 ml of 3 mol·l^{-1} nitric acid solution (4.1) and transfer the solutions to the PTFE vials (3.5).

5.14 Rinse the vials of the plutonium fraction with 0,5 ml of 3 mol·l^{-1} nitric acid solution (4.1) and transfer the solutions to the corresponding PTFE vials.

5.15 Place all PTFE vials with the plutonium fractions on the hot plate, preferably in metal jackets for an even heating. Evaporate the solutions gently to dryness at 90 °C avoiding any bubbling and splashing.

5.16 After cooling down to room temperature, secure the cap of the PTFE vials with the plutonium fractions and forward them for mass spectrometric measurement. The mass spectrometer operator will redissolve the residues in a minimum (2 µl and less) of 3 mol·l^{-1} nitric acid solution immediately before loading the solutions on to the filaments of the mass spectrometer.. Performing this redissolution step by means of a microscope is recommended.

5.17 Redissolve all uranium fractions with 250 µl aqua regia (4.9) and evaporate to dryness.

5.18 Redissolve all uranium fractions with 250 µl concentrated hydrochloric acid (4.10) and evaporate to dryness.

5.19 Redissolve all uranium fractions with 1 ml concentrated hydrochloric acid (4.10) and transfer slowly all solutions to the conditioned anion exchange resin columns (4.11).

5.20 Rinse all uranium fraction vials with 1 ml concentrated hydrochloric acid (4.10) and transfer slowly all solutions to the corresponding columns.

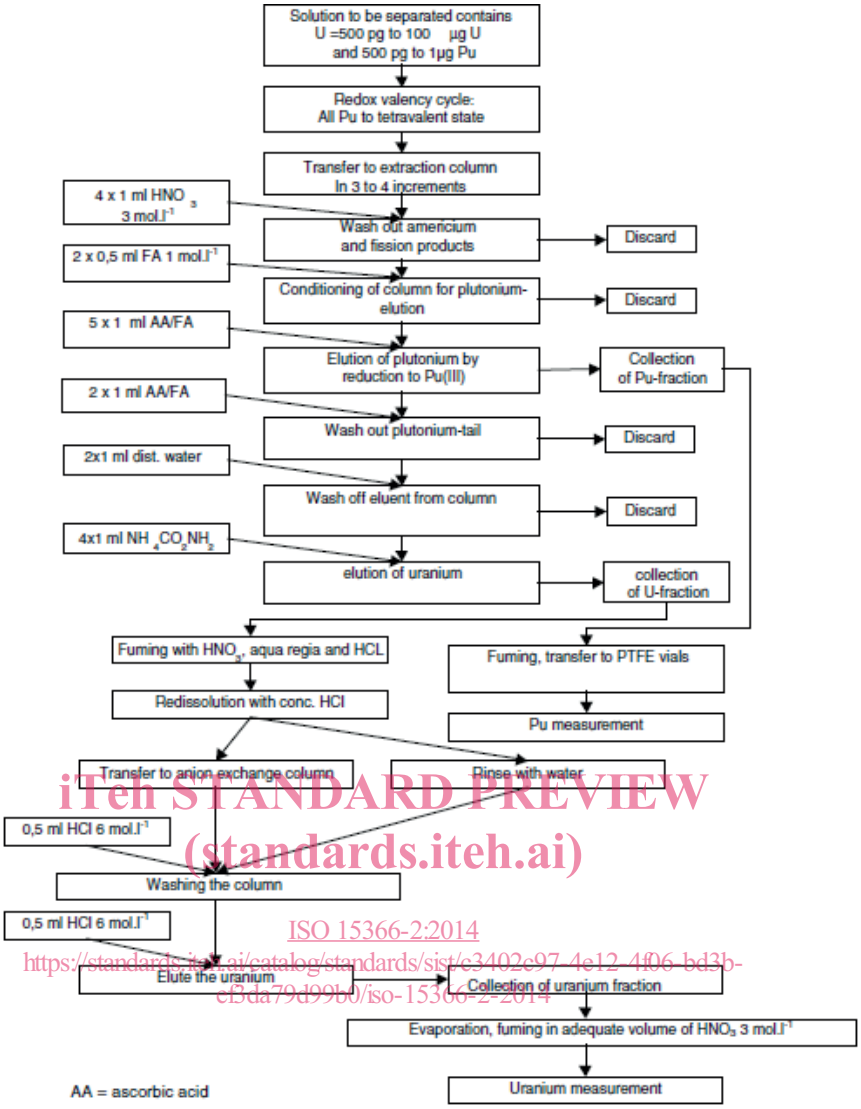
5.21 After the solutions (5.20) have completely passed the columns, wash each column with 0,5 ml of hydrochloride acid solution 6 mol·l^{-1} (4.1).

5.22 Elute the uranium into PTFE vials (3.5) with four successive aliquots of 1 ml distilled water.

5.23 Place all PTFE vials with the uranium fractions on the other hot plate, preferably in metal jackets for an even heating. Evaporate the solutions gently to dryness at 90 °C avoiding any bubbling and splashing.

5.24 Remove the uranium fractions from the hot plates, add 0,25 ml of concentrated nitric acid (4.1) and evaporate again to dryness in the same way as in 5.23. Repeat this step once.

5.25 After cooling down to room temperature secure the cap of the PTFE vials with the uranium fractions and forward them for mass spectrometric measurement. The mass spectrometer operator will redissolve the residues in a minimum (2 µl and less) of 3 mol·l^{-1} nitric acid solution immediately before loading the solutions on to the mass spectrometer filaments. Performing this redissolution step by means of a microscope is recommended.



Key

AA ascorbic acid

FA formic acid

Figure 1 — U and Pu separation scheme

6 Characteristics of the separation

The element recovery is 80 % for U and 60 % for Pu found after separations of the lowest element concentrations (500 pg). In higher concentrations, the Pu recovery reaches 80 % and more.

7 Quality control

7.1 Blanks: blank samples are spiked with known amounts of highly enriched tracers, such as ^{242}Pu and ^{233}U 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 according to ISO 8299.[1] The results of these blank level determinations should be checked for their actual value and their fluctuation (in terms of repeatability and mid-term reproducibility). The observed fluctuation should be commensurate with the assessment of the uncertainties of the method. Otherwise an uncontrolled source of contamination shall be suspected, which requires beforehand remedial environmental measures.