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Nuclear fuel technology — Determination of uranium in solutions, uranium hexafluoride and solids —

Part 2: Iron(II) reduction/cerium(IV) oxidation titrimetric method

Technologie du combustible nucléaire — Dosage de l'uranium dans des solutions, l'hexafluorure d'uranium et des solides —

Partie 2: Méthode titrimétrique par réduction au fer(II) et oxydation au cérium(IV)

Reference number
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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 85, *Nuclear energy, nuclear technologies, and radiological protection*, Subcommittee SC 5, *Nuclear installations, processes and technologies*.

This second edition cancels and replaces the first edition (ISO 7097-2:2004), which has been technically revised.

The main changes are as follows:

— the Scope was updated (see Clause 1);

— information on interferences was updated (see 5.2);

— requirements for standardisation of ceric titrant were updated (see 6.16);

— Annex A was divided into two annexes (Annex A and Annex B).

A list of all parts in the ISO 7097 series can be found on the ISO website.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

This document describes procedures for the determination of uranium in solutions, uranium hexafluoride, and solids. The procedures described in the two independent parts of this International Standard are similar: this document uses a titration with cerium(IV) and ISO 7097-1 uses a titration with potassium dichromate.

Nuclear fuel technology — Determination of uranium in solutions, uranium hexafluoride and solids —

Part 2: Iron(II) reduction/cerium(IV) oxidation titrimetric method

1 Scope

This document describes an analytical method for the determination of uranium in samples from pure product materials such as U metal, UO_2, UO_3, U_3O_8, uranyl nitrate hexahydrate and uranium hexafluoride from the nuclear fuel cycle. This procedure is sufficiently accurate and precise to be used for nuclear materials accountability. This method can be used directly for the analysis of most uranium and uranium oxide nuclear reactor fuels, either irradiated or un-irradiated, and of uranium nitrate product solutions. Fission products equivalent to up to 10 % burn-up of heavy atoms do not interfere, and other elements which could cause interference are not normally present in sufficient quantity to affect the result significantly. The method recommends that an aliquot of sample is weighed and that a mass titration is used, in order to obtain improved precision and accuracy. This does not preclude the use of alternative techniques which could give equivalent performance. The use of automatic device(s) in the performance of some critical steps of the method has some advantages, mainly in the case of routine analysis.

This method does not generate a toxic mixed waste as does the potassium dichromate titration in ISO 7097-1.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 3696, *Water for analytical laboratory use — Specification and test methods*

ISO 9894, *Subsampling of uranium hexafluoride in the liquid phase*

ISO 5725-1, *Accuracy (trueness and precision) of measurement methods and results — Part 1: General principles and definitions*

3 Terms and definitions

For purposes of this document, the terms and definitions given in ISO 5725-1 apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at https://www.electropedia.org/

4 Principle

Uranium(VI) is reduced to uranium(IV) in concentrated phosphoric acid, in the presence of sulfamic acid, by reaction with iron(II) sulfate. The excess of iron(II) sulfate is subsequently oxidized by nitric acid in the presence of molybdenum, and the uranium(IV) is determined by mass titration with standardized cerium sulfate solution to a potentiometric end point; see References [2][3][4][5][6].

An aliquot of the sample containing about 15 mg to 25 mg of uranium is taken for the titration. An excess of iron(II) sulfate solution is then added to reduce all the uranium to the quadrivalent state. Sulfamic acid is added to eliminate nitrite ions present at this stage. The excess of iron(II) is oxidized by nitric acid, catalysed by molybdenum. The uranium is determined by mass titration with standardized cerium sulfate solution to a potentiometric end point. To improve precision, the titration is performed in the presence of vanadium in dilute phosphoric acid, which increases the kinetics of the reaction. The addition of vanadium(IV) solution acts to dilute the sample solution and shift the redox potential so as to allow the titration to proceed.

The ceric sulfate solution is calibrated with a certified uranium reference material, as described in 6.16; see ISO 10980[1].

5 Reactions and interferences

5.1 Reactions

Under the given experimental conditions, the principal reactions are as follows:

a) In concentrated phosphoric acid solution:

$$UO_2^{2+} + 2Fe^{2+} + 4H^+ \rightarrow U^{4+} + 2Fe^{3+} + 2H_2O$$

$$3Fe^{2+} + NO_3^- + 4H^+ \xrightarrow{Mo} 3Fe^{3+} + NO + 2H_2O$$

$$Fe^{2+} + NO_3^- + 2H^+ \xrightarrow{Mo} Fe^{3+} + NO_2 + H_2O$$

$$2Fe^{2+} + NO_3^- + 2H^+ \xrightarrow{Mo} 2Fe^{3+} + NO_2^- + H_2O$$

b) In diluted phosphoric acid solution:

$$U^{4+} + 2Fe^{3+} + 2H_2O \rightarrow UO_2^{2+} + 2Fe^{2+} + 4H^+$$

$$Fe^{2+} + VO^{2+} + 2H^+ \rightarrow Fe^{3+} + V^{3+} + H_2O$$

The overall reaction can be represented as follows:

$$U^{4+} + 2VO^{2+} \rightarrow UO_2^{2+} + 2V^{3+}$$

c) On titration with ceric sulfate solution:

$$Ce^{4+} + V^{3+} + H_2O \rightarrow Ce^{3+} + VO^{2+} + 2H^+$$

which is equivalent to the titration of U^{4+} with cerium:

$$2Ce^{4+} + U^{4+} + 2H_2O \rightarrow 2Ce^{3+} + UO_2^{2+} + 4H^+$$

5.2 Interferences

This procedure is less subject to interference from foreign ions than most other methods of determining uranium[7]. In usual reprocessing solutions, fluoride, perchlorate, sulfate, Be, Si, Nb, Ti, Cr, Fe, Co, Ni, W, Cu, Sb(V), Pb, Pu, Am, the rare earths and the alkaline earth metals do not interfere. The extent of Np interference, if any, has not been verified.

For titrations involving uranium aliquots in the range of 15 mg to 25 mg:

a) Al, Zr, and NO_2^- do not interfere when present in the range 0 mg to 4 mg in the aliquot.

b) As(V) and Th do not interfere when present in the range 0 mg to 1 mg in the aliquot.

c) Mo and Mn do not interfere when present in the range 0 mg to 0,5 mg in the aliquot; Mo interferes only if large amounts of nitrate are also present and vice versa.

d) Bromide, oxalate, Au, Sn, and some platinum group elements interfere at 0,1 % when present at levels of 2 mg in the aliquot.

e) Interference from iodine, iodate, Ag, V (V), and Tc is more severe. Each of these impurity levels shall be kept below 1 mg in the aliquot (0,1 % interference at 1 mg level).

f) As(III) and Sb(III) yield a bias which is proportional to the amount added. When present at 0,5 mg levels, As(III) can cause a positive bias of 0,3 % and Sb(III) can cause a bias of ~4 %.

g) Nitrate and peroxide will not interfere unless present in higher than normal concentrations as described here. Nitrate levels shall be <3 ml of concentrated nitric acid. Excessive amounts of peroxide are indicated by failure to observe dark coloration during the oxidation step. Thus, it is likely that the titration results of a sample containing excessive amounts of peroxide would be biased.

h) A temperature range of 20 °C to 31 °C will have no influence on the titration results. Temperatures outside of this range can affect reaction rates and times.

The possible effect of intense β and γ radiation and of some radioactive species (for example ruthenium) on the electrode system remains to be established. Effects on the electrode by intense radiation have been observed during a single run. Since the types of material to be analysed cover a very wide range, the user of the method should consider the possibility of interference for each specific case, considering published information and the results of any additional experiments which might be necessary.

6 Reagents

Use only reagents of recognized analytical grade and water as specified in 6.1.

6.1 Water, meeting the requirements for ISO 3696 grade 2 water (electrical conductivity less than 0,1 mS/m and resistivity greater than 0,01 MΩ·m at 25 °C).

It is recommended that the water used be obtained from a water purification system that delivers ultrapure water having a resistivity greater than 0,18 MΩ·m (usually expressed by manufacturers of water purification systems as 18 MΩ·cm).

6.2 Hydrofluoric acid (HF), $c \approx 29$ mol/l ≈ mass fraction of 48 % ($d_4^{20} = 1{,}18$).

WARNING — Hydrofluoric acid is a highly corrosive and toxic acid that can severely burn skin, eyes, and mucous membranes. The burning sensation is not immediately apparent and might not be felt for several hours. The fluoride ion readily penetrates the skin, even with dilute concentrations, causing destruction of deep tissue layers. Unlike other acids that are rapidly neutralized, hydrofluoric acid reactions with tissue can continue for days if left untreated. Familiarization and compliance with the Safety Data Sheet is essential.

6.3 Nitric acid (HNO_3), $c \approx 16$ mol/l ≈ mass fraction of 69 % $\left(d_4^{20} = 1,42\right)$.

6.4 Nitric acid (HNO_3), $c \approx 8$ mol/l.

Dilute the 16 mol/l nitric acid (6.3) 2 to 1 with water (6.1).

6.5 Nitric acid (HNO_3), $c \approx 4$ mol/l.

Dilute the 16 mol/l nitric acid (6.3) 4 to 1 with water (6.1).

6.6 Orthophosphoric acid (H_3PO_4), $c \approx 15$ mol/l ≈ mass fraction of 85 % $\left(d_4^{20} = 1,71\right)$.

Historically, issues relating to the presence of excessive amounts of reducing agents such as Sb(III) had been reported for this reagent. The use of analytical grade reagents is, in general, a sufficient precautionary measure to avoid these issues.

6.7 Phosphoric acid reagent.

Add 1 ml of 0,4 mol/l ceric sulfate solution (6.14) to a 2,5 l reagent bottle of orthophosphoric acid (6.6) and mix.

A pale straw colour is expected. If the solution turns green, it has been contaminated with reducing agents and should be discarded.

6.8 Sulfuric acid (H_2SO_4), $c \approx 18$ mol/l ≈ mass fraction of 96 % $\left(d_4^{20} = 1,84\right)$.

6.9 Sulfuric acid (H_2SO_4), $c \approx 1,0$ mol/l.

Add 56 ml of sulfuric acid (6.8) slowly and carefully to 900 ml of water, while stirring. Allow to cool and adjust the solution to 1 000 ml with water (6.1).

6.10 Iron(II) sulfate ($FeSO_4 \cdot 7H_2O$), $c \approx 1$ mol/l.

Add 10 ml of concentrated sulfuric acid (6.8) carefully to 75 ml of water (6.1) in a 500 ml beaker with constant stirring. Add 28 g ± 1 g of iron(II) sulfate ($FeSO_4 \cdot 7H_2O$) and stir until it is dissolved. Dilute to 100 ml with water (6.1) and mix. This solution is not stable under all conditions for extended periods of time and its use shall be verified on a regular basis determined by laboratory experience using an appropriate quality control test or be prepared fresh once a week.

6.11 Sulfamic acid (NH_2SO_3H), $c \approx 1,55$ mol/l.

Dissolve 150 g of sulfamic acid in less than 1 l of water (6.1) at room temperature and dilute final solution to 1 l. Filter freshly prepared sulfamic acid through a suitable filter paper before storing in glass or low-density polyethylene (LDPE) bottle. As this solution is almost saturated, heating would tend to decompose the sulfamic acid. This solution is not stable, and its use shall be verified, as appropriate, on a regular basis using an appropriate quality control test or be prepared fresh once a week.

6.12 Oxidizing reagent.

Dissolve 10,0 g ± 0,1 g of hexaammonium heptamolybdate $[(NH_4)_6Mo_7O_{24} \cdot 4H_2O]$ in 250 ml of water (6.1).

Add 10 ml of sulfamic acid (6.10) to 50 ml of nitric acid (6.3), mix well, add 10 ml of the hexaammonium heptamolybdate solution and add 30 ml of water (6.1). This solution can be unstable in some environments and its use shall be verified, as appropriate, on a regular basis using an appropriate quality control test or prepared fresh weekly.

6.13 Vanadium (IV) oxide sulfate, $c \approx 10^{-2}$ mol/l.

Weigh approximately 2 g of vanadium(IV) oxide sulfate ($VOSO_4$ $2H_2O$) and dissolve it in 200 ml of the 1 mol/l sulfuric acid solution (6.9). Adjust to 2 000 ml with water (6.1) and mix well. This solution is not stable, and its use shall be verified, as appropriate, on a regular basis using an appropriate quality control test or prepare fresh weekly.

6.14 Ceric sulfate, $Ce(SO_4)_2$, c = 0,4 mol/l.

Dissolve 13,5 g anhydrous $Ce(SO_4)_2$ or 16,5 g $Ce(SO_4)_2$ $4H_2O$ or 21,9 g $(NH_4)_2Ce(NO_3)_6$ in about 70 ml of 1,0 mol/l H_2SO_4 (6.9), and dilute to 100 ml with additional H_2SO_4 (6.9). (The solution can be boiled to increase its stability, if desired.) Store in the dark. Alternatively, pre-made solutions can be procured commercially.

6.15 Cerium(IV) titrant solution, 0,027 mol/l.

6.15.1 This procedure will prepare 5 l of 0,027 mol/l Ce(IV) titrant solution. Other volumes can be prepared as desired. The procedure shall be started at least one month prior to expected use.

6.15.2 Weigh 74 g of ammonium ceric nitrate or 54,6 g of $Ce(SO_4)_2$ $4H_2O$ or 45 g of $Ce(SO_4)_2$ into a weighing boat, scoop, or paper. Any equivalent source of Ce(IV) is acceptable. Transfer to a 5 l volumetric flask, and dissolve in about 4 l of 1,0 mol/l H_2SO_4 (6.9). Dilute to volume with 1,0 mol/l H_2SO_4 (6.9) and mix well.

6.15.3 Stopper the flask, place the flask in the dark, and allow to sit for at least one month. Carefully filter the top 4 l of the solution into a second flask or bottle without disturbing the bottom portion which contains a fine sediment. Cap and mix well. Store the decanted solution in the dark in tightly capped glass bottles. Dispose of the remaining residue in accordance with approved laboratory procedures.

NOTE Storage in certain containers, especially plastic ones, can lead to the degradation of the titrant. However, any alternative storage method that maintains a stable solution is acceptable.

6.16 Standardisation of ceric titrant.

6.16.1 A titrant equivalency factor for the ceric sulfate titrant shall be experimentally derived. This can be done once per preparation if the solution will be used quickly (within a month) and evaporative effects and other degradation effects of the concentration are minimal. If the ceric titrant solution is expected to be consumed over several months or longer, a daily calibration of the ceric titrant solution should be calibrated each day of use. This approach negates the effect of evaporation and other effects of degradation on the equivalency factor over time.

6.16.2 Weigh 1,0 g to 1,2 g of certified uranium reference material to the nearest 0,1 mg into a 100 ml beaker. Record this mass as m_1. Add 10 ml of water, 30 ml of nitric acid (6.3) and 1 drop of hydrofluoric acid (6.2) and place the beaker, covered with a watch glass, on a boiling water bath or hotplate to maintain a steady reaction. When the dissolution is complete, allow to cool, and transfer the solution quantitatively to a clean, dry 50 ml volumetric flask weighed to the nearest 0,1 mg. The mass of the flask is recorded as m_2. Dilute to 50 ml with water and weigh the flask plus contents to the nearest 0,1 mg. Record this mass as m_3. Take a weighed aliquot of the solution through the procedure described in 8.2 to 8.5 as if the solution were a sample.

6.16.3 For a single calibration of the solution (see 6.16.1), titrate at least ten aliquots of (a) uranium standard solution(s) prepared according to the instructions in 6.16.2. Alternate titration of aliquots from two independently prepared and verified solutions is recommended; see ISO 10980[1]. Using

the titration method described in Clause 9, perform initial and final quality control titrations with previously standardized titrant.

Alternatively, for daily determination of a titrant equivalency factor, titrate a minimum of 3 aliquots of (a) certified uranium standard solution(s) prepared according to the instructions in 6.16.2. Alternate titration of aliquots from two independently prepared and verified solutions is recommended; see ISO 10980[1]. Using the titration method described in Clause 9, perform initial quality control titrations using the just determined daily titrant equivalency factor, B_n. Additional standard aliquots or quality control samples should be interspersed over the day's analyses to bracket sample analyses.

For single calibrations and daily determinations, the quality control titrations should be run on well characterized standard uranium aliquots and the results should be in control as determined by a quality control program in order for the titration results to be accepted. Repeat any of the titrations where aliquots of standard uranium were over-titrated or otherwise improperly assayed.

6.16.4 Calculate the value for each aliquot of standard uranium solution. Using the equation in 10.2.1, determine the grams of ceric sulfate solution used to reach the equivalence point for each uranium calibration standard aliquot. The average equivalency factor for use with samples and control samples is the average of the calibration replicates.

6.16.5 Calculate the titrant equivalency factor, B_n, using Formula (1):

$$B_n = m_1 / m_2 \quad (1)$$

where

B_n is the titrant equivalency factor, expressed as the mass fraction of the uranium titrant solution, in milligrams per gram;

m_1 is the mass, in milligrams, of uranium standard in aliquot;

m_2 is the mass, in grams, of cerium(IV) titrant solution (6.15) used to reach the equivalent point of the titration.

A titrant equivalency factor for each titration is calculated to evaluate the precision of the data.

6.16.6 A mean titrant equivalency factor for normal uranium, B_n, expressed in units of milligrams of U per gram of titrant, is calculated from the data, excluding outliers, if

a) there is no more than one statistical outlier from each standard solution preparation,

b) the standard deviations of the factors for each solution, individually and combined as a set excluding outliers, are less than 0,1 %, or as specified by programmatic needs, or

c) the mean factors for the two solutions are statistically equivalent.

If the data do not meet the acceptance criteria, it is recommended that the standardization be repeated.

7 Apparatus

Necessary apparatus includes the usual nuclear laboratory equipment and the following:

7.1 Millivoltmeter, a high impedance millivoltmeter (100 MΩ input resistance) with a digital read-out, most suitably capable of discriminating to 1 mV.

7.2 Platinum wire or spade electrode, 2 cm^2 surface area.

The performance of the electrode shall be checked regularly by titrating aliquots of a control solution. If the response of the electrode at the titration endpoint begins to deteriorate, the electrode shall be cleaned by immersion in boiling nitric acid (6.3) containing a little ceric sulfate (6.14) and rinsing it thoroughly with distilled water. It is also possible to heat the electrode to red heat in an open flame (free from sulfur). It is recommended to flame and quench the Pt electrode with concentrated nitric acid prior to each use and to store the Pt electrode in 8 mol/l nitric acid (6.4) when not in use.

7.3 Reference electrode: commercially available saturated calomel or a mercurous sulfate reference electrode in saturated potassium sulfate. The reference electrodes, available commercially, can be maintained in a saturated solution of potassium chloride.

If the use of mercury is not permitted, an Ag/AgCl reference electrode in 1 mol/l KCl can be used. The calomel or Ag/AgCl electrode shall, however, be placed in a salt bridge filled with saturated K_2SO_4 to slow down the diffusion of chloride ions into the titration cell. Subtract 20 mV from all potentials specified in the procedure given in Clause 8 if the Ag/AgCl electrode in 1 mol/l KCl is used; add 400 mV to all potentials specified if the calomel electrode is used.

7.4 Sample weighing bottle, 20 ml, with a stopper and a delivery spout.

7.5 Analytical balance, with a weighing range up to 200 g, weighing to 0,1 mg or better.

7.6 Mass titration device, equipped with a micro-dispenser, capable of delivering the titrating solution by equal increments of 20 mg or less. For this method it is suggested that increments of 5 mg or less be used when approaching the endpoint of the titration.

Volumetric titration is acceptable if the volumetric titration device is calibrated with a reference material: applying the procedure of 6.16 provides an apparent concentration of the cerium(IV) titrant solution (including possible bias of the volumetric burette). Correction shall be made for temperature effects on solutions. The related uncertainties shall be estimated.

7.7 Magnetic stirrer and plastic-coated stirring bars, the coating on the stir bar shall be inert to acids and strong oxidizing agents.

7.8 Heating furnace, with optional inert atmosphere.

7.9 Sampling and hydrolysis devices for UF_6.

Suitable devices are described in Annex A.

7.10 Vacuum desiccator, which can be used with or without the vacuum or desiccant depending on the purpose of use.

7.11 Percussion mortar.

8 Sample preparation

8.1 General

A buoyancy correction to the masses obtained for the solid uranium samples (metal, oxide, etc.) is not required, because this correction factor, under usual laboratory conditions, is less than 0,01 %. The mass of the resulting bulk uranium solution does not need to be corrected for buoyancy as long as the mass of aliquots taken from that solution also are not corrected. Replicate dissolutions for each sample are recommended with acceptance criteria set by the local quality assurance (QA) programs. For well

prepared and homogenous materials differences between replicate solutions larger than 0,14 % would have to be investigated (an expanded uncertainty representing the 95 % confidence limit of 0,14 % is obtained for the analytical method by combining the precision and bias targets according to the International Target Values 2010 for measurement uncertainties in safeguarding nuclear materials[8]).

8.2 Uranium metal

8.2.1 Remove surface oxides, if required, by treatment of the sample with 4 mol/l HNO_3 (6.5) at room temperature until a bright surface is obtained. Flush the sample with copious amounts of water and then with alcohol. Dry using one of the following 3 options:

a) dry at 80 °C for 30 min under an inert atmosphere, or

b) dry at room temperature in a vacuum desiccator under house vacuum for 60 min, or

c) place the metal on a filter paper and allow to dry 10 min to 15 min, rolling the metal several times to expose all surfaces to the air.

Weigh 300 mg to 1,1 g of the clean dry uranium metal to the nearest 0,1 mg into a 100 ml beaker. Record this mass as m_1'.

8.2.2 Add 10 ml of nitric acid (6.3) and one drop of hydrofluoric acid (6.2). (Alternatively, a previously prepared nitric-hydrofluoric acid dissolution solution can be used.) Cover the beaker with a watch glass and heat to maintain a steady reaction. When dissolution is complete, remove the watch glass and evaporate to near dryness. Redissolve in sulfuric acid (6.8). Cool and quantitatively transfer the solution with the aid of sulfuric acid (6.8) to a tared polyethylene bottle. Dilute with sulfuric acid (6.8), weigh to the nearest 0,1 mg, and record this mass as m_2'. The final dilution is determined by the starting sample mass. Final concentration should allow a 1 g to 3 g aliquot of solution to contain the desired 15 mg to 25 mg of uranium. Close the bottle and mix well. This solution is the test solution. Proceed as in Clause 9.

8.3 Uranium dioxide pellets

Lightly crush the laboratory sample in a percussion mortar if needed.

Weigh, to the nearest 0,1 mg, 0,3 g to 1,3 g of uranium dioxide into a 100 ml beaker. Record the mass of the test sample as m_1'.

Follow the dissolution procedure of uranium metal (8.2.2).

8.4 Uranium oxide powder (UO_2, UO_3, U_3O_8)

Powder samples can contain some adsorbed and partially bound water. To remove adsorbed water from UO_2 or UO_3 powders heat in a heating furnace (7.8) for 1 h at 200 °C. An inert atmosphere is not required for the heating. The material should be cooled in an inert atmosphere or desiccator to prevent any reabsorption of atmospheric moisture prior to analysis.

To remove adsorbed and bound water from U_3O_8 powders, heat in a heating furnace (7.8) for 1 h at 600 °C under an inert atmosphere. Heating oxides at this temperature should not be done in air unless it is a pure U_3O_8 material. Otherwise, there is a risk of changing the form of the material by changing the oxidation state of the uranium. Cool under an inert atmosphere or desiccator to prevent any reabsorption of atmospheric moisture or reformation of hydrated oxides prior to analysis. Whether or not moisture should be removed shall be decided on before application of this document. The drying procedure, if any, shall be stated in the test report.

Weigh 0,3 g to 1,3 g of uranium oxide to the nearest 0,1 mg into a 100 ml beaker. Record this mass as m_1'. Add 10 ml of water and follow the dissolution procedure of uranium metal (8.2.2).

8.5 Uranium hexafluoride

Follow the sample preparation steps in Annex A.

8.6 Uranyl nitrate hexahydrate

A suitable sampling device shall be available which is capable of taking a representative portion of the bulk material. Record this mass as m_1'.

Dilute the whole sample with water in order to get a homogeneous solution of uranyl nitrate. Record this mass as m_2'.

Follow the analytical procedure beginning with Clause 9.

9 Procedure

9.1 Fill the mass titration device with ceric sulfate solution (6.14), and weigh it to the nearest 0,1 mg. Record this mass as m_4.

NOTE A buoyancy correction to the mass of the ceric sulfate solution is not necessary as long as the mass of the aliquots taken from that solution also is not corrected for buoyancy.

9.2 Fill the clean, dry, sample weighing bottle (7.4) with about 5 g of the test solution and weigh it to the nearest 0,1 mg. Record this mass as m_5. Transfer a portion of sample containing about 15 mg to 25 mg of uranium to a 100 ml beaker, and re-weigh the sample weighing bottle to the nearest 0,1 mg. Record this mass as m_6. (See Clause 8 regarding buoyancy corrections.) Carefully insert a stirring bar into the beaker and place it on a magnetic stirrer. Any alternative method of measuring the sample aliquot shall be shown to be accurate to better than ±0,05 %. The sample aliquot shall not exceed 3 ml; otherwise, the reduction step might not reach completion in the stated time.

9.3 Stir the solution and add the following reagents in the order stated, allowing mixing between each addition: 8 ml of phosphoric acid reagent (6.7), 1 ml of Sulfamic acid solution (6.11) and 1 ml of iron(II) sulfate solution (6.10).

The iron(II) sulfate shall be added from a pipette directly into the sample solution, without splashing the walls of the beaker.

NOTE 0,2 ml of hydrofluoric acid (6.2) can be added in some cases to improve the electrode response (see 9.6).

9.4 Continue stirring the solution for a minimum of 1 min. Add by pipette 2 ml of oxidizing reagent (6.12), using it to wash down the inside walls of the beaker. The sample solution turns to a dark brown colour on addition of the oxidizing reagent, but this colour should disappear after about 30 s.

9.5 After the colour dissipates, turn off the stirrer and start a timer set for 3 min. At the end of the 3 min, add 20 ml of the vanadium(IV) oxide sulfate solution (6.13). To avoid significant error, the titration shall be completed within 7 min after the addition of the vanadium(IV) oxide sulfate solution.

9.6 Insert the platinum and the reference electrodes into the solution and start rapid stirring without splashing. For the mercurous sulfate (Hg/Hg_2SO_4) reference electrode, the initial potential reading is normally −60 mV to −10 mV. Continuously add cerium(IV) titrant solution (6.15) from the mass titration device until a potential difference of 40 mV versus the Hg/Hg_2SO_4 reference electrode is reached. Record the mass of the micro-dispenser as m_7.

Ensure the tip of the dispenser does not ever touch the solution in the beaker. A precipitation reaction between the phosphate and cerium can occur which will block the dispenser tip. Automated titrators with submerged tips are not appropriate for this method.

9.7 Add cerium(IV) titrant solution (6.15) in constant increments from the micro-dispenser, recording the mass, the increment number, and the millivoltmeter readings, after each addition, when they have stabilized. The increment should be no larger than 5 mg of solution.

NOTE The reading is regarded as being stable when it does not change by more than 1 mV in 5 s.

9.8 Continue the addition of cerium(IV) titrant solution (6.15) until the equivalence point of titration indicated by a sharp inflection in potential at about 170 mV versus the Hg/Hg_2SO_4 electrode is reached. Make one further addition and record the number, n, of additions of cerium(IV) titrant solution (6.15) at this stage.

NOTE Once a suitable potential endpoint has been established through repeat titrations that endpoint can be used as a target for future work. Future titrations do not need to be done using the interpolation method described in Clause 10. Instead, a simpler calculation based off the titrant equivalency factor can be used directly in 10.2.2.

9.9 Weigh the micro-dispenser to the nearest 0,1 mg and record this mass as m_8.

9.10 At the end of titration, the 100 ml beaker shall be thoroughly washed to remove any traces of uranium and vanadium before any other use.

10 Expression of the results

10.1 General

A manual calculation method is described. Any alternative internal method of calculation employed by a computerized titrator is acceptable, as long as the calculation bias is shown to be negligible compared to other errors.

10.2 Method of calculation

10.2.1 Linear interpolation

Calculate the mass m_9 of cerium(IV) titrant solution (6.15) used to reach the equivalent point of the titration (refer to Table 1).

Table 1 — Table of differentials for the calculation

Ce increments	Potential mV	First differential	Second differential
n-3	E_{n-3}	—	—
n-2	E_{n-2}	$E_{n-2} - E_{n-3}$	—
n-1	E_{n-1}	$E_{n-1} - E_{n-2}$	$\Delta_{n-1} = (E_{n-1} - E_{n-2}) - (E_{n-2} - E_{n-3})$
n	E_n	$E_n - E_{n-1}$	$\Delta_n = (E_n - E_{n-1}) - (E_{n-1} - E_{n-2})$

A linear interpolation is performed on the second differentials and yields Formula (2):

$$m_9 = m_4 - m_7 + \frac{m_7 - m_8}{n}\left(n - 2 + \frac{\Delta_{n-1}}{\Delta_n + \Delta_{n-1}}\right) \quad (2)$$

where

m_4 is the mass, in grams, of the micro-dispenser before the start of the titration (see 9.1);

m_7 is the mass, in grams, of the micro-dispenser after the first ceric solution addition (see 9.6);

m_8 is the mass, in grams, of the micro-dispenser after the end of the titration (see 9.9);

n is the number of increments of ceric solution addition used for the titration.

The Fortuin method[5], modified by Wolf[6], based also on the second differentials, can be used to calculate the mass m_8 with a better accuracy; see Reference [3].

10.2.2 Calculation for the test solution

NOTE The alternative calculations in Annex B can also be used.

Calculate the uranium content, $B_{U,1}$, in milligrams of uranium per gram of the test solution using Formula (3):

$$B_{U,1} = \frac{m_9 . B_n . \frac{A_{t2}}{A_{t1}}}{m_{10}} \quad (3)$$

where

m_8 is the mass, in grams, of ceric solution used to reach the equivalent point, as calculated from Formula (2) or as measured at the set endpoint;

B_n is the mass fraction of the uranium titrant solution, in milligrams per gram (6.16);

A_{t1} is the atomic mass of uranium of the uranium standard used to standardize the ceric solution (6.16);

A_{t2} is the average atomic mass of uranium, as calculated from Formula (4);

m_{10} $(m_5 - m_6)$ is the measured mass, in grams, of the aliquot.

10.2.3 Calculations for samples

For uranium metal or oxide samples, use B.1.

For uranium hexafluoride samples, use B.2.

For uranium nitrate hexahydrate samples, use B.3.

10.2.4 Average atomic mass

The average atomic mass, A_{t2}, of the uranium can be calculated from the isotopic composition, in mass percent, using Formula (4):

$$A_{t2} = \frac{1}{\frac{F_{U234}}{234{,}041\,0} + \frac{F_{U235}}{235{,}043\,9} + \frac{F_{U236}}{236{,}045\,6} + \frac{F_{U238}}{238{,}050\,8}} \quad (4)$$

where

F_{U234} is the isotope mass fraction of ^{234}U;

F_{U235} is the isotope mass fraction of ^{235}U;

F_{U236} is the isotope mass fraction of ^{236}U;

F_{U238} is the isotope mass fraction of ^{238}U.

10.3 Repeatability

For a single determination, the uncertainty in the uranium amount content using this method (as represented by the variability in the titration results of standards) is better than 0,1 % when the method is applied to pure uranium materials analysed in an open bench or in a fume hood.

The use of reliable automatic apparatus is needed to achieve a similar repeatability when titrating highly radioactive solutions in a glovebox or in a heavily shielded cell equipped with telemanipulators.

10.4 Bias

The bias of the method is less than 0,05 % when applied to pure uranium solutions and less than 0,1 % when applied to irradiated fuel solutions. These values are derived from the repeatability and accuracy obtained at production plant and accountability-verification laboratories.

Based on a compilation of safeguards and accountability data, a combined standard uncertainty of 0,07 % is estimated for uranium amount content determinations following this method. This combined uncertainty includes both random and systematic components of the International Target Values 2010 for measurement uncertainties in safeguarding nuclear materials[8].

11 Test report

The test report shall include the following information:

— identification of the sample;

— a reference to this document, i.e. ISO 7097-2:2022;

— reference to the method used;

— drying process, if used, for powdered uranium oxide samples;

— method used and the results;

— any unusual features noted during the test;

— any operations not included in this document or regarded as optional.

Annex A
(normative)

Uranium hexafluoride sampling and preparation of the test solution

A.1 Sampling

A.1.1 A suitably equipped sub-sampling facility, in accordance with ISO 9894 or equivalent, shall be available which is capable of dispensing approximately 10 g of liquid uranium hexafluoride from a typical sample cylinder into a polytrifluorochloroethylene (PTFCE) tube, where it can be solidified by immersion in liquid nitrogen.

A.1.2 Dry a sampling tube and gasket for about 2 h in an oven at 110 °C. Cool the tube and gasket in a desiccator for 1 h. Connect the sampling tube to the sub-sampling facility, following the procedure given in ISO 9894.

A.1.3 Dispense about 10 g of liquid uranium hexafluoride into the tube. Solidify the uranium hexafluoride by immersion in liquid nitrogen before removing the tube from the sub-sampling facility. When solidification is complete, remove the tube and close it immediately by placing the gasket, centering ring, flare nut and plug in place.

There shall be a gap of about 2 cm above the sample in the tube.

A.1.4 Place the assembled tube and contents in a desiccator for at least 3 h, or preferably overnight, to allow it to reach ambient temperature and to evaporate condensed water. Weigh the assembled tube and content to nearest 0,1 mg. Record this mass as m_{20}.

If there is any yellow-green deposit around the closure the sample shall be rejected and a new sample dispensed.

A.2 Preparation of the test solution

A.2.1 Weigh a dry, wide mouthed, screw-capped 500 ml polyethylene bottle to the nearest 1 mg. Record this mass as m_{30}.

The shape of the bottle shall enable the tube containing the test sample to be submerged in the water. The bottle screw cap shall provide an efficient seal for liquid.

A.2.2 Wearing Cryo-gloves and a face shield or goggles, fill a large Dewar with liquid nitrogen, cover the Dewar and place it in the hood.

A.2.3 Slip the P-10 tube into a loop of copper wire. Holding on to the end of the wire, lower the tube into the liquid nitrogen without submerging the Monel fittings. Secure the wire by bending it over the top edge of the Dewar flask. Cover the Dewar with aluminium foil.

A.2.4 Leave the tube suspended in liquid nitrogen for at least 10 min. Immediately before removing the tube, pour a minimum of 100 ml (or sufficient amount to cover the tube) of water (6.1) at approximately 4 °C into a graduated cylinder.