INTERNATIONAL STANDARD

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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

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 2.

The main task of technical committees is to prepare International Standards. 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.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 7097-2 was prepared by Technical Committee ISO/TC 85, *Nuclear energy*, Subcommittee SC 5, *Nuclear fuel technology*.

This first edition of ISO 7097-2, together with ISO 7097-1:2004, cancels and replaces ISO 7097:1983, which has been technically revised, and ISO 9989:1996.

ISO 7097 consists of the following parts, under the general title: *Nuclear fuel technology — Determination of uranium in solutions, uranium hexafluoride and solids*:

Part 1: Iron(II) reduction/potassium dichromate oxidation titrimetric method

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

Introduction

This part of ISO 7097 describes procedures for determination of uranium in solutions, uranium hexafluoride and solids. The procedures described in the two independent parts of this International Standard are similar: this part 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 part of ISO 7097 describes an analytical method for the determination of uranium in pure product material samples such as U metal, UO_2, UO_3, uranyl nitrate hexahydrate, uranium hexafluoride and U_3O_8 from the nuclear fuel cycle. This procedure is sufficiently accurate and precise to be used for nuclear materials accountability.

This method does not generate a toxic mixed waste as does the potassium dichromate titration. The method may not be applied to scrap or waste samples until such time as it is qualified by obtaining results statistically equivalent to those obtained by the potassium dichromate method on the same sample types.

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 any alternative techniques which could give equivalent performance. As the performance of some steps of the method is critical, the use of some automatic device has some advantages, mainly in the case of routine analysis.

2 Normative references

The following referenced documents are indispensable for the application 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 9894, *Subsampling of uranium hexafluoride in the liquid phase*

ISO 10980, *Validation of the strength of reference solutions used for measuring concentrations*

3 Principle

An aliquot of the sample containing about 40 mg to 60 mg of uranium in sulfuric acid solution is taken for the titration. Amidosulfuric acid is added to eliminate nitrites or nitrogen oxides (NO_x) formed in subsequent stages. An excess of iron(II) sulfate solution is then added to reduce all the uranium to the quadrivalent state in concentrated phosphoric acid solution. The excess of iron(II) is oxidized by nitric acid, catalyzed by molybdenum, in a time- and temperature-controlled operation. The uranium(IV) is determined by mass titration with standardized cerium(IV) sulfate solution to a potentiometric end point; see References[1, 2, 3, 4]. To improve precision, the titration is performed in the presence of vanadium(IV), which increases the kinetic reaction. The addition of the V(IV) solution also 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 an internationally recognized uranium reference material, as described in 5.15.

4 Reactions and interferences

4.1 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 may 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:

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

4.2 Interferences

Preliminary results indicate that the chemical interference using the ceric titrant is similar to those listed below for the dichromate procedure.

The oxidation/reduction titration procedure is less subject to interference from foreign ions than most other methods of determining uranium. 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 by current data. Nitrate and peroxide will not interfere unless present in higher than normal concentration.

More precisely:

a) Al, Zr and NO_2^- do not interfere in the range 0 mg to 10 mg in the aliquot.

b) As(V) and Th do not interfere in the range 0 mg to 2 mg in the aliquot.

c) Mo and Mn do not interfere in the range 0 mg to 1 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 slightly.

e) Interference from iodine, iodate, Ag, V and Tc is more severe.

f) As(III) and Sb(III) interfere proportionally to the amount present. These interferences are eliminated if sufficient Ce(IV) is added to the concentrated phosphoric acid reagent.

Since the types of material to be analyzed cover a very wide range, the user of the method should consider the possibility of interference for each specific case, considering the detailed published information and the results of any additional experiments which may be necessary.

5 Reagents

Use only reagents of recognized analytical grade and distilled or de-ionized water (resistivity better than 10 MΩ.cm).

5.1 Hydrofluoric acid (HF), $c \approx 29$ mol/l ($d_4^{20} = 1{,}18$).

5.2 Nitric acid (HNO_3), $c \approx 16$ mol/l ($d_4^{20} = 1{,}42$).

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

Dilute the 16 mol/L nitric acid (5.2) 4 to 1 with water.

5.4 Orthophosphoric acid (H_3PO_4), $c \approx 15$ mol/l ($d_4^{20} = 1{,}71$), test each lot number purchased for the presence of excessive amounts of reducing agents such as Sb(III) as follows: Mix together 10 ml orthophosphoric acid (5.4), 10 ml distilled water, and 0,2 ml 0,02 mol/l $KMnO_4$ (5.13). Heat to boiling on a hot plate, transfer to a steam bath, and allow to stand for 10 min. Reject the preparation lot if the pink colour disappears. (This step may be eliminated if the user is certain that the amount of reducing agents is low.)

5.5 Phosphoric acid reagent. Add 1 ml 0,4 mol/l ceric sulfate solution (5.12) to a 2,5 l reagent bottle of orthophosphoric acid and mix.

5.6 Sulfuric acid (H_2SO_4), $c \approx 18$ mol/l ($d_4^{20} = 1{,}84$).

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

Add 56 ml of sulfuric acid (5.6) slowly and carefully to 900 ml of water, whilst stirring. Allow to cool and adjust the solution to 1 000 ml with water.

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

Add 10 ml of concentrated sulfuric acid (5.6) slowly and carefully to 75 ml of water in a 500 ml beaker with constant stirring. Add 28 g ± 1 g of iron(II) sulfate ($FeSO_4\ 7H_2O$) and stir until it is dissolved. Dilute to 100 ml and mix. This solution is not stable under all conditions nor for extended periods of time; its use must be verified on a regular basis determined by laboratory experience using an appropriate quality control test.

5.9 Amidosulfuric acid (NH_2SO_3H), $c \approx 1{,}55$ mol/l.

Dissolve 150 g of amidosulfuric acid in less than 1 l of water at room temperature and dilute final solution to 1 l. As this solution is almost saturated, heating would tend to decompose the amidosulfuric acid. This solution is not stable and its use must be verified, as appropriate, on a regular basis using an appropriate quality control test.

5.10 Oxidizing reagent.

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

Add 10 ml of amidosulfuric acid (5.9) to 50 ml of nitric acid (5.2), mix well, add 10 ml of the hexaammonium heptamolybdate solution and add 30 ml of pure water. This solution may be unstable in some environments and its use must be verified, as appropriate, on a regular basis using an appropriate quality control test.

5.11 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 sulfuric acid solution (5.7). Adjust to 1 000 ml with pure water and mix well. This solution is not stable and its use must be verified, as appropriate, on a regular basis using an appropriate quality control test.

New lots of vanadyl sulfate dihydrate may be verified by titrating uranium samples, as described in 8.1 to 8.10, using both the new vanadium(IV) oxide sulfate solution and a solution of vanadyl sulfate from a previously verified lot.

5.12 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 (5.7), and dilute to 100 ml with additional H_2SO_4 (5.7). (The solution may be boiled to increase its stability, if desired.) Store in the dark.

5.13 Potassium permanganate, 0,02 mol/l.

Dissolve 0,33 g $KMnO_4$ in 100 ml distilled water. Boil gently for 15 min, cool and filter through a plug of glass wool. Store in a brown glass bottle.

5.14 Preparation of 0,027 mol/l cerium(IV) titrant solution.

This procedure will prepare 5 l of 0,027 mol/l Ce(IV) titrant solution. Other volumes may be prepared as desired.

NOTE The procedure must be started at least one month prior to expected use.

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 (5.7). Dilute to volume with 1,0 mol/l H_2SO_4 (5.7) and mix well.

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. (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.) Dispose of the remaining residue in accordance with approved laboratory procedures.

5.15 Standardization of ceric titrant.

A titrant equivalency factor for the ceric titrant must be experimentally derived. A protocol is given below. Other statistically equivalent standardization protocols may be substituted. (However, fewer titrations may result in decreased precision and lead to a bias in the final results.)

Using the newly-prepared cerium(IV) solution (5.14), titrate at least ten aliquots of (a) certified uranium standard solution(s) prepared according to the instructions for this reference material; alternate titration of aliquots from each of two independently prepared and verified solutions is recommended; see ISO 10980. Using the titration method described in Clause 8, perform initial and final quality-control titrations with previously standardized titrant. 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 ten titrations where aliquots of standard uranium were over-titrated or otherwise improperly assayed.

Calculate the certified value for each aliquot of standard uranium solution.

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

a) 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

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

   2) the standard deviations of the factors for each solution, individually and combined as a set excluding outliers, are less than 0,07 %, or

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

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

6 Apparatus

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

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

6.2 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 end-point begins to deteriorate, the electrode shall be cleaned by immersion in boiling nitric acid (5.2) containing a little ceric sulfate, 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).

6.3 Reference electrode: commercially available saturated calomel or a mercurous sulfate reference electrode in saturated potassium sulfate.

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.

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

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

6.6 Mass titration device, equipped with a micro-dispenser, capable of delivering the titrating solution by equal increments of 20 mg or less.

Volumetric titration is acceptable if the volumetric titration device is calibrated with a reference material: applying the procedure of 5.14 provides an apparent concentration of the cerium(IV) titrant solution (including possible bias of the volumetric burette). Temperature effects on solutions shall be corrected for. The related uncertainties shall be estimated.

6.7 Magnetic stirrer and **plastic-coated stirring bars**: the coating on the stir bar must be inert to acids and strong oxidizing agents.

6.8 Heating furnace, with inert atmosphere.

6.9 Sampling and hydrolysis devices for UF_6.

Suitable devices are described in Annex A.

7 Sample preparation

7.1 General

It is recommended that a buoyancy correction be applied to the masses obtained for the solid uranium samples (metal, oxide, etc.) although 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.

7.2 Uranium metal

Remove surface oxides, if required, by treatment of the sample with HNO_3 (5.3) at room temperature until a bright surface is obtained. Flush the sample with copious amounts of water and then with alcohol. Dry at 80 °C for 30 min under an inert atmosphere.

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

Add 10 ml of nitric acid (5.2) and one drop of hydrofluoric acid (5.1). (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 (5.7). Cool and quantitatively transfer the solution with the aid of sulfuric acid (5.7) to a tared polyethylene bottle. Dilute with sulfuric acid (5.7) to 30 g, weigh to the nearest 0,1 mg, and record this mass as m_2; close the bottle and mix well. This solution is the test solution. Proceed as in Clause 8.

7.3 Uranium dioxide pellets

Lightly crush the laboratory sample in a percussion mortar.

Weigh to the nearest 0,1 mg 1,2 g to 1,3 g of uranium dioxide into a tall-form 100 ml beaker. Record the mass of the test sample as m_1.

Follow the dissolution procedure of uranium metal (7.2), starting at “Add 10 ml of nitric acid ... ”.

7.4 Uranium oxide powder (UO_2, UO_3, U_3O_8)

Powder sample may contain some adsorbed and partially bound water. To remove adsorbed water heat for 1 h at 200 °C under an inert atmosphere (6.8). To remove adsorbed and bound water heat for 1 h at 600 °C under an inert atmosphere. Cool under an inert atmosphere and keep the sample in a desiccator until used. 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 to the nearest 0,1 mg 1,2 g to 1,3 g of uranium oxide into a tall-form 100 ml beaker. Record this mass as m_1. Add 10 ml of water and follow the dissolution procedure of uranium metal (7.2), starting at “Add 10 ml of nitric acid ...”.

7.5 Uranium hexafluoride

See A.2.

7.6 Uranyl nitrate hexahydrate

A suitable sampling device must 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 8.

8 Procedure

8.1 Fill the mass titration device with ceric sulfate solution (5.14), 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 are not corrected for buoyancy.

8.2 Fill the clean, dry, sample weighing bottle (6.4) 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 40 mg to 60 mg of uranium to a 100 ml tall-form beaker, and re-weigh the sample weighing bottle to the nearest 0,1 mg. Record this mass as m_6. (See Clause 7 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 $\pm$ 0,05 %. The sample aliquot shall not exceed 2 ml, otherwise the reduction step might not reach completion in the stated time.

8.3 Stir the solution and add the following reagents in the order stated, allowing mixing between each addition: 8 ml of phosphoric acid reagent (5.5), 1 ml of amidosulfuric acid solution (5.9) and 1 ml of iron(II) sulfate solution (5.8).

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 (5.1) can be added in some cases to improve the electrode response.

8.4 Continue stirring the solution for a minimum of 1 min, and heat it briefly on a hot plate if necessary to adjust the temperature within the range 35 °C to 40 °C. Add by pipette 2 ml of oxidizing reagent (5.10), 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.

8.5 Stir for an additional 2,5 min, and stop the stirrer. Allow the solution to stand unstirred for 30 s, and then add 20 ml of the vanadium(IV) solution (5.11). To avoid significant error, the titration shall be completed within 7 min after the addition of the vanadium(IV) oxide sulfate solution.

8.6 Insert the platinum and the reference electrodes into the solution, and start rapid stirring without splashing. For the mercurous sulfate reference electrode, the initial potential reading is normally – 60 mV to – 10 mV. Continuously add ceric sulfate solution (5.14) 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.

8.7 Add ceric sulfate solution (5.14) 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 20 mg.

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

8.8 Continue the addition of ceric sulfate solution (5.14) 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 ceric sulfate solution (5.14) at this stage.

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

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

9 Expression of the results

9.1 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.

9.2 Method of calculation

a) Calculate the mass m_9 of ceric sulfate solution (5.14) used to reach the equivalent point of the titration.

Table 1 — Table of differentials for the calculation

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

A linear interpolation is performed on the second differentials and yields Equation (1):

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

where

m_4 is the mass, in grams, of the micro-dispenser before the start of the titration (see 8.1);

m_7 is the mass, in grams, of the micro-dispenser after the first ceric solution addition (see 8.6);

m_8 is the mass, in grams, of the micro-dispenser after the end of the titration (see 8.9);

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

The Fortuin method[3], modified by Wolf[4], based also on the second differentials, can be used to calculate the mass m_9 with a better accuracy; see Reference[2].

b) Calculate the uranium content, $B_{U,1}$, in milligrams of uranium per gram of the test solution using Equation (2):

$$B_{U,1} = \frac{m_9 \cdot B_n \cdot \frac{A_{t2}}{A_{t1}}}{m_3} \quad (2)$$

where

m_9 is the mass, in grams, of ceric solution used to reach the equivalent point, as calculated from Equation (1);

B_n is the concentration, in milligrams of U per gram of titrant (5.15);

A_{t1} is the atomic mass of uranium of the uranium standard used to standardize the ceric solution (5.15);

A_{t2} is the average atomic mass of uranium; as calculated from Equation (3);

m_3 $(= m_5 - m_6)$ is the measured mass, in grams, of the aliquot.

NOTE 1 For uranium metal or oxide samples, instead of applying 9.2 b), see A.1.

NOTE 2 For uranium hexafluoride sample, instead of applying 9.2 b), see A.2.

NOTE 3 For uranium nitrate hexahydrate sample, instead of applying 9.2 b), see A.3.

The average atomic mass, A_{t2}, of the uranium may be calculated from the isotopic composition, in mass percent, using Equation (3):

$$A_{t2} = \frac{100}{\frac{F_{U,234}}{234{,}041\,0} + \frac{F_{U,235}}{235{,}043\,9} + \frac{F_{U,236}}{236{,}045\,6} + \frac{F_{U,238}}{238{,}050\,8}} \quad (3)$$

where

$F_{U,234}$ is the mass in percent of ^{234}U;

$F_{U,235}$ is the mass in percent of ^{235}U;

$F_{U,236}$ is the mass in percent of ^{236}U;

$F_{U,238}$ is the mass in percent of ^{238}U.

9.3 Repeatability

The coefficient of variation for a single determination is better than 0,1 % when the method is applied to a pure uranium solution analysed on 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 glove-box or in a heavily shielded cell equipped with telemanipulators.

9.4 Bias

Comparison between the dichromate and the ceric titrations are available from the New Brunswick Laboratory's Measurement Evaluation Program data. The results given in the table below show that the dichromate and the ceric titration give comparable results on uranyl nitrate solutions. The relative difference, Δ, expressed in percent, is defined as in Equation (4):

$$\Delta = \frac{\left(X_{obs} - X_{ref}\right)}{X_{ref}} \cdot 100 \quad (4)$$

where

X_{obs} is the observed value;

X_{ref} is the reference value.

Table 2 — Calculated results

Facility/Titrant	N	Mean of the Δs	Standard deviation of the Δs
F/Dichromate	55	–0,016 2	0,024
G/Ceric	32	–0,038 6	0,056

10 Test report

The test report shall include the following information:

— identification of the sample;

— reference to this part of ISO 7097:2004;

— 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 International Standard or regarded as optional.

Annex A
(informative)

Information about sampling and calculations of results

A.1 Uranium metal or dioxide

Instead of applying the procedure described in 9.2 b), calculate the uranium content in the sample in accordance with Equation (A.1):

$$B_{\mathrm{U}} = \frac{m_9 B_{\mathrm{n}} \left(\frac{A_{t2}}{A_{t1}} \right) m_2}{m_3 \cdot 1\,000 \cdot m_1} \cdot 100 \qquad \text{(A.1)}$$

where

B_{U} is the uranium content, in mass percent, in the laboratory sample;

m_9 is the mass, in grams, of ceric solution used to reach the equivalent point, as calculated from Equation (1);

B_{n} is the concentration of U, in milligrams, per gram of titrant (see 5.15);

A_{t1} is the atomic mass of uranium of the uranium standard used to standardize the ceric solution (see 5.15);

A_{t2} is the average atomic mass of uranium, as calculated from Equation (3);

m_1 is the mass, in grams, of the test sample;

m_2 is the mass, in grams, of the test solution;

m_3 $(= m_5 - m_6)$ is the mass, in grams, of the aliquot.

A.2 Uranium hexafluoride

A.2.1 Sampling

A.2.1.1 A suitably equipped sub-sampling facility, in accordance with ISO 9894 or equivalent, must 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.2.1.2 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.2.1.3 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.2.1.4 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_{10}.

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

A.2.2 Preparation of the test solution

A.2.2.1 Weigh a dry, wide mouthed, screw-capped 500 ml polyethylene bottle to the nearest 0,001 g. Record this mass as m_{12}.

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.2.2.2 Add about 150 ml of water to the bottle and stand the open bottle in a beaker containing ice and water.

A.2.2.3 Attach a piece of wire to the closed tube containing the test sample and immerse the tube into liquid nitrogen so that the contents of the tube are fully immersed. Leave the tube in this position for 10 min.

A.2.2.4 Remove the tube from liquid nitrogen and detach the wire.

A.2.2.5 Immediately remove the flare nut, plug and centering ring. Immerse the gasket and tube mouth-down into the polyethylene bottle. Keep the mouth of the tube immersed in water and replace the screwcap tightly on the polyethylene bottle.

Care shall be taken to avoid any loss of contents from the polyethylene bottle through splashing.

A.2.2.6 Remove the polyethylene bottle from the ice water and stand it in a carriage so that the tube is submerged at all times. Leave the sample to hydrolyse slowly, occasionally swirling the contents of the bottle carefully.

NOTE Several hours will be necessary to attain complete hydrolysis; overnight standing is preferable.

A.2.2.7 When hydrolysis is complete, remove the tube and gasket, washing carefully with water and add the washing to the bottle. Dry the bottle, close with the screw cap and weigh the bottle and contents to the nearest 0,001 g. Record this mass as m_{13}. Shake the bottle to homogenize the contents. Calculate the mass of the test solution (m_2) from Equation (A.2):

$$m_2 = (m_{13} - m_{12}) \quad \text{(A.2)}$$

Wash the tube, gasket, centering ring, flare nut and plug with water and then with alcohol, dry at 110°C for 2 h, and determine the total mass to the nearest 0,1 mg. Record this mass as m_{11}. Calculate the mass of test sample (m_1) from Equation (A.3):

$$m_1 = (m_{10} - m_{11}) \quad \text{(A.3)}$$

A.2.2.8 Weigh to the nearest 0,1 mg an aliquot of the test solution containing 0,05 g to 0,06 g of uranium into a 100 ml tall form beaker. Record this mass as m_3. Adjust the volume of the liquid in the beaker to about 2 ml by the addition of sulfuric acid (5.7). Continue with 8.3

A.2.3 Expression of results

Instead of applying the procedure described in 9.2 b), calculate the uranium hexafluoride content in the sample from Equation (A.4):

$$B_{\mathrm{UF6}} = \frac{m_9 \cdot B_{\mathrm{n}} \cdot \left[\left(\frac{A_{t2}}{A_{t1}} \right) + 113{,}99 \right] \cdot m_2}{m_3 \cdot 1\,000 \cdot m_1} \cdot 100 \qquad \text{(A.4)}$$

where

B_{UF6} is the uranium hexafluoride content, in mass percent, in the laboratory sample and the other parameters are as defined for Equation (A.1).

A.3 Uranyl nitrate hexahydrate

Calculate the uranium hexahydrate content in the sample from Equation (A.5):

$$B_{\mathrm{NUH}} = \frac{m_9 \cdot B_{\mathrm{n}} \cdot \left[\left(\frac{A_{\mathrm{t2}}}{A_{\mathrm{t1}}} \right) + 264 \right] \cdot m_2}{m_3 \cdot 1\,000 \cdot m_1} \cdot 100 \qquad \text{(A.5)}$$

where

B_{NUH} is the uranium hexahydrate content, in mass percent, in the laboratory sample and the other parameters are as defined for Equation (A.1).

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