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

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

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

Partie 1: Méthode titrimétrique par réduction au fer(II) et oxydation au bichromate de potassium

Reference number
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Foreword

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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 7097-1 was prepared by Technical Committee ISO/TC 85, *Nuclear energy*, Subcommittee SC 5, *Nuclear fuel technology*.

This first edition of ISO 7097-1 together with ISO 7097-2:2004 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 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 part uses a titration with potassium dichromate and ISO 7097-2 uses a titration with cerium(IV).

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

Part 1: Iron(II) reduction/potassium dichromate 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 can be used directly for the analysis of most uranium and uranium oxide nuclear reactor fuels, either irradiated or unirradiated, 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 any alternative technique 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

Uranium(VI) is reduced to uranium(IV) in concentrated phosphoric acid solution, in the presence of amidosulfuric 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 potassium dichromate solution to a potentiometric end point; see References [1], [2], [3], [4].

An aliquot of the sample containing about 40 mg to 60 mg of uranium in nitric acid solution is taken for the titration. An excess of iron(II) sulfate solution is then added to reduce all the uranium to the quadrivalent state. Amidosulfuric acid is added to eliminate nitrite ions present at this stage. The excess of iron(II) is oxidized by nitric acid, catalysed by molybdenum, in a time- and temperature-controlled operation. The uranium is determined by mass titration with standardized potassium dichromate solution to a potentiometric end point. To improve precision, the titration is performed in the presence of vanadium(IV), which increases the kinetic 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 potassium dichromate solution is calibrated either with an internationally recognized uranium reference material or using a standard solution of potassium dichromate SRM 136 from NIST (National Institute of Standards and Technology); see ISO 10980.

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 potassium dichromate solution:

$$Cr_2O_7^{2-} + 6V^{3+} + 2H^+ \rightarrow 2Cr^{3+} + 6VO^{2+} + H_2O$$

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

$$Cr_2O_7^{2-} + 3U^{4+} + 2H^+ \rightarrow 2Cr^{3+} + 3UO_2^{2+} + H_2O$$

4.2 Interferences

This 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, Np, Am, the rare earths and the alkaline earth metals do not interfere. Nitrate and peroxide will not interfere unless present in higher than normal concentrations.

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(V) and Tc is more severe.

f) As(III) and Sb(III) yield a bias which is proportional to the amount added.

In such conditions, the cumulative interference will not be significant, i.e. less than 0,2 %.

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. 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 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), $c \approx 22$ 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 $KMnO_4$ (5.12). 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 Sulfuric acid (H_2SO_4), $c \approx 18$ mol/l ($d_4^{20} = 1{,}84$).

5.6 Sulfuric acid (H_2SO_4), $c \approx 0{,}5$ mol/l.

Add 28 ml of sulfuric acid (5.5) slowly and carefully to 900 ml of water, whilst stirring. Allow to cool and adjust the solution to 1 000 ml with water.

5.7 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 $\pm$ 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.

5.8 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.

5.9 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 (5.8) 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.

5.10 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 (5.6). 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.

5.11 Potassium dichromate solution ($K_2Cr_2O_7$), $c \approx 0{,}008\ 5$ mol/l.

Weigh to the nearest 10 mg a clean, dry, 500 ml volumetric flask and record this mass as m_1. Weigh out to the nearest 0,1 mg about 1,25 g of dried potassium dichromate, record this mass as m_2 and dissolve it in water.

NOTE Potassium dichromate may contain some adsorbed water. Follow the instruction of the NIST certificate to dry the NIST SRM 136 potassium dichromate.

Quantitatively transfer the potassium dichromate solution to the tared flask, dilute to 500 ml with water. Weigh the flask plus contents to the nearest 10 mg; record this mass as m_3 and mix well. Calculate, in accordance with Equation (1), the concentration, B_1, in moles per kilogram, of dichromate in the solution, correcting for the purity and applying a buoyancy correction to the mass, m_2, in moles per kilogram, of solid dichromate:

$$B_1 = \frac{m_2}{0{,}294\ 18\ (m_3 - m_1)} \qquad (1)$$

5.12 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.

5.13 Verification of the concentration of the potassium dichromate solution

The concentration of the potassium dichromate solution shall be verified by comparison with an internationally recognized uranium reference material certified to ± 0,05 % or better, such as pure uranium metal (for example NBL CRM 112A or CETAMA-MU2) or pure U_3O_8 (for example, NBL CRM 129). The comparison shall be made by taking at least five separate portions of the selected reference material through the following procedure.

Weigh to the nearest 0,1 mg 1,0 g to 1,2 g of the uranium reference material into a 100 ml tall-form beaker. Record this mass as m_4. Add 10 ml of water, 30 ml of nitric acid (5.2) and 1 drop of hydrofluoric acid (5.1) and place the beaker, covered with a watch glass, on a boiling water bath 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_5. Dilute to 50 ml with water and weigh the flask plus contents to the nearest 0,1 mg. Record this mass as m_6. Take a weighed aliquot of the solution through the procedure described in 7.2 to 7.5 as if the solution were a sample, calculating the uranium concentration ($B_{U,1}$) of the solution in accordance with Equation (5) of 9.2 b).

Apply a buoyancy correction to m_4 only, in accordance with Equation (2):

$$m_{ref} = \left[1 + \rho_a \left(1/\rho - 1/\rho'\right)\right] m_4 \quad (2)$$

where

m_{ref} is the mass of reference material;

m_4 is the apparent mass read on the balance;

ρ_a is the density of the air;

ρ is the density of the sample;

ρ' is the density of the balance reference weight.

Calculate the measured uranium content, $B_{U,2}$, in milligrams per gram of the reference material, from Equation (3):

$$B_{U,2} = B_{U,1} \frac{m_6 - m_5}{m_{ref}} \quad (3)$$

where

$B_{U,1}$ is the uranium concentration, in milligrams, per gram of the reference solution;

m_5 is the mass, in grams, of the 50 ml volumetric flask;

m_6 is the mass, in grams, of the 50 ml volumetric flask plus content.

The dichromate concentration (B_1) is accepted if the relative difference between the measurement and the certified uranium content does not exceed 0,05 %. If not, repeat the procedure.

Alternatively, the potassium dichromate solution may be verified by comparison with a standard solution of NIST potassium dichromate SRM 136; see ISO 10980.

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 5.13 provides an apparent concentration of the potassium dichromate 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 (5.6). Cool and quantitatively transfer the solution with the aid of sulfuric acid (5.6) to a tared polyethylene bottle. Dilute with sulfuric acid (5.6) 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 this mass 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 samples 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 potassium dichromate solution (5.11), and weigh it to the nearest 0,1 mg. Record this mass as m_7.

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_8. Transfer a portion of sample containing about 40 mg to 60 mg of uranium to a 100 ml tall-form beaker and reweigh the sample weighing bottle to the nearest 0,1 mg. Record this mass as m_9. 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 orthophosphoric acid (5.4), 0,04 ml of potassium dichromate solution (5.11), 1 ml of amidosulfuric acid solution (5.8) and 1 ml of iron(II) sulfate solution (5.7).

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 (5.9), 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 immediately add 20 ml of the vanadium(IV) solution (5.10). 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. The potential reading is normally –60 mV to –10 mV versus the Hg/Hg_2SO_4 reference electrode. Continuously add potassium dichromate solution (5.11) 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_{10}.

8.7 Add potassium dichromate solution (5.11) 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 potassium dichromate solution (5.11) until the equivalence point of titration, indicated by a sharp inflection in potential at about 170 mV versus the Hg/Hg_2SO_4 reference electrode, is reached. Make one further addition and record the number (n) of additions of potassium dichromate solution at this stage.

8.9 Weigh the micro-dispenser to the nearest 0,1 mg and record this mass as m_{11}.

8.10 At the end of titration, the 100 ml beaker shall be thoroughly washed to remove all 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_{12} of potassium dichromate solution (5.11) used to reach the equivalent point of titration.

Table 1 — Table of differentials for the calculation

$K_2Cr_2O_7$ 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 Equation (4):

$$m_{12} = m_7 - m_{10} + \frac{m_{10} - m_{11}}{n}\left(n - 2 + \frac{\Delta_{n-1}}{\Delta_n + \Delta_{n-1}}\right) \quad (4)$$

where

m_7 is the mass, in grams, of the micro-dispenser before the start of the titration (see 8.1);

m_{10} is the mass, in grams, of the micro-dispenser after the first dichromate solution addition (see 8.6);

m_{11} 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 dichromate 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_{12} 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 (5):

$$B_{U,1} = \frac{m_{12} \cdot 6B_1 \cdot A_t}{2m'_3} \quad (5)$$

where

m_{12} is the mass, in grams, of dichromate solution used to reached the equivalent point, as calculated from Equation (4);

B_1 is the concentration, in moles per kilogram, of the dichromate solution;

A_t is the average atomic mass of uranium; see Equation (6);

m'_3 $(= m_8 - m_9)$, 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 uranyl nitrate hexahydrate sample, instead of applying 9.2 b), see A.3.

c) The average atomic mass, A_t, of the uranium may be calculated from the isotopic composition, in mass percent, using Equation (6):

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

where

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

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

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

$F_{U,238}$ is the mass 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

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.

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):

$$B_U = \frac{m_{12} \cdot 6B_1 \cdot A_t}{2 \cdot m'_3 \cdot 1000} \cdot \frac{m'_2}{m'_1} \cdot 100 \qquad \text{(A.1)}$$

where

B_U is the uranium content, in mass percent, in the laboratory sample;

m_{12} is the mass, in grams, of the dichromate solution used to reached the equivalent point, as calculated in Equation (4);

B_1 is the concentration, in moles per kilogram, of the dichromate solution;

A_t is the average atomic mass of uranium, as calculated in Equation (6);

m'_1 is the mass, in grams, of the test sample;

m'_2 is the mass, in grams, of the test solution;

m'_3 $(= m_8 - m_9)$, 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 into a polytrifluorochloroethylene (PTFCE) tube, where it can be solidified by immersion in liquid nitrogen.

A.2.1.2 Dry a suitable 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.