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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**

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

ISO 7097-2:2004

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

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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.

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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

### 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,  $\text{UO}_2$ ,  $\text{UO}_3$ , uranyl nitrate hexahydrate, uranium hexafluoride and  $\text{U}_3\text{O}_8$  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.

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### 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 ( $\text{NO}_x$ ) 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<sup>[1, 2, 3, 4]</sup>. 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.

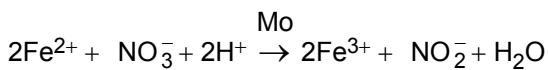
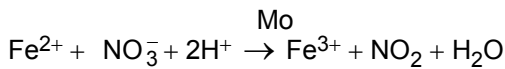
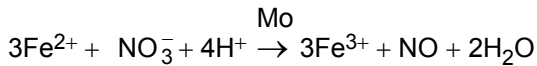
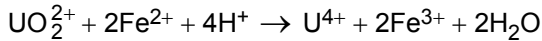
The ceric sulfate solution is calibrated with an internationally recognized uranium reference material, as described in 5.15.

## 4 Reactions and interferences

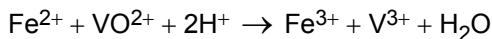
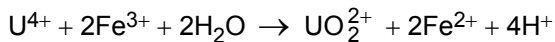
### 4.1 Reactions

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

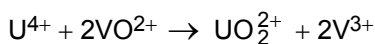
- a) In concentrated phosphoric acid solution:



- b) In diluted phosphoric acid solution:

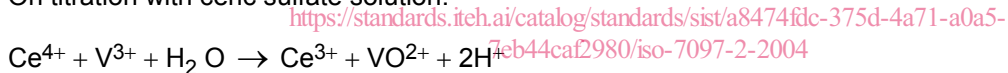


The overall reaction may be represented as follows:

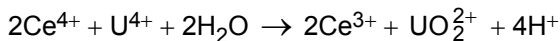


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- c) On titration with ceric sulfate solution:



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



### 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:

- Al, Zr and  $\text{NO}_2^-$  do not interfere in the range 0 mg to 10 mg in the aliquot.
- As(V) and Th do not interfere in the range 0 mg to 2 mg in the aliquot.
- 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.
- 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 M $\Omega$ .cm).

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

**5.2 Nitric acid** (HNO<sub>3</sub>),  $c \approx 16$  mol/l ( $d_4^{20} = 1,42$ ).

**5.3 Nitric acid** (HNO<sub>3</sub>),  $c \approx 4$  mol/l.

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

**5.4 Orthophosphoric acid** (H<sub>3</sub>PO<sub>4</sub>),  $c \approx 15$  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<sub>4</sub> (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<sub>2</sub>SO<sub>4</sub>),  $c \approx 18$  mol/l ( $d_4^{20} = 1,84$ ).

**5.7 Sulfuric acid** (H<sub>2</sub>SO<sub>4</sub>),  $c \approx 1,0$  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<sub>4</sub> 7H<sub>2</sub>O),  $c \approx 1$  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<sub>4</sub> 7H<sub>2</sub>O) 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<sub>2</sub>SO<sub>3</sub>H),  $c \approx 1,55$  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  $\pm$  0,1 g of hexaammonium heptamolybdate [(NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub> 4H<sub>2</sub>O] 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 ( $\text{VO}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ ), 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**,  $\text{Ce}(\text{SO}_4)_2$ ,  $c = 0,4$  mol/l.

Dissolve 13,5 g anhydrous  $\text{Ce}(\text{SO}_4)_2$  or 16,5 g  $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$  or 21,9 g  $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$  in about 70 ml of 1,0 mol/l  $\text{H}_2\text{SO}_4$  (5.7), and dilute to 100 ml with additional  $\text{H}_2\text{SO}_4$  (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  $\text{KMnO}_4$  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  $\text{Ce}(\text{IV})$  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  $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$  or 45 g of  $\text{Ce}(\text{SO}_4)_2$  into a weighing boat, scoop, or paper. Any equivalent source of  $\text{Ce}(\text{IV})$  is acceptable. Transfer to a 5 l volumetric flask, and dissolve in about 4 l of 1,0 mol/l  $\text{H}_2\text{SO}_4$  (5.7). Dilute to volume with 1,0 mol/l  $\text{H}_2\text{SO}_4$  (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 M $\Omega$  input resistance) with a digital read-out, most suitably capable of discriminating to 1 mV.

**6.2 Platinum wire or spade electrode,** 2 cm<sup>2</sup> 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<sub>2</sub>SO<sub>4</sub> 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<sub>6</sub>.

Suitable devices are described in Annex A.