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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)*

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CP 401 • Ch. de Blandonnet 8  
CH-1214 Vernier, Geneva  
Phone: +41 22 749 01 11  
Email: [copyright@iso.org](mailto:copyright@iso.org)  
Website: [www.iso.org](http://www.iso.org)

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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.

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](http://www.iso.org/directives)).

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. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see [www.iso.org/patents](http://www.iso.org/patents)).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

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](http://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](http://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.

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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 document describes an analytical method for the determination of uranium in samples from pure product materials such as U metal,  $\text{UO}_2$ ,  $\text{UO}_3$ ,  $\text{U}_3\text{O}_8$ , 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.

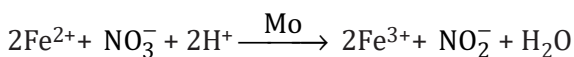
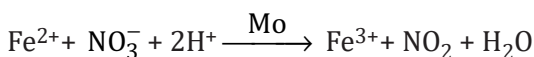
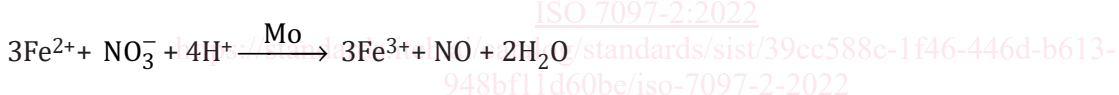
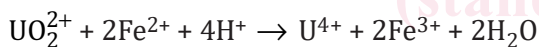
The ceric sulfate solution is calibrated with a certified uranium reference material, as described in 6.16; see ISO 10980<sup>[1]</sup>.

## 5 Reactions and interferences

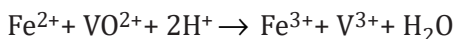
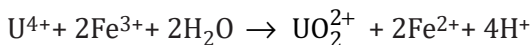
### 5.1 Reactions

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

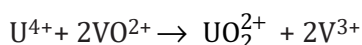
- a) In concentrated phosphoric acid solution:



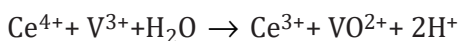
- b) In diluted phosphoric acid solution:



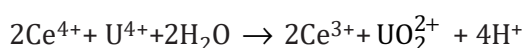
The overall reaction can be represented as follows:



- c) On titration with ceric sulfate solution:



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





## 5.2 Interferences

This procedure is less subject to interference from foreign ions than most other methods of determining uranium<sup>[7]</sup>. 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  $\text{NO}_2^-$  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  $\beta$  and  $\gamma$  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 M $\Omega$ ·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 M $\Omega$ ·m (usually expressed by manufacturers of water purification systems as 18 M $\Omega$ ·cm).

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

**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<sub>3</sub>),**  $c \approx 16 \text{ mol/l} \approx \text{mass fraction of } 69 \% \left(d_4^{20} = 1,42\right)$ .

**6.4 Nitric acid (HNO<sub>3</sub>),**  $c \approx 8 \text{ mol/l}$ .

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

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

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

**6.6 Orthophosphoric acid (H<sub>3</sub>PO<sub>4</sub>),**  $c \approx 15 \text{ mol/l} \approx \text{mass fraction of } 85 \% \left(d_4^{20} = 1,71\right)$ .

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<sub>2</sub>SO<sub>4</sub>),**  $c \approx 18 \text{ mol/l} \approx \text{mass fraction of } 96 \% \left(d_4^{20} = 1,84\right)$ .

**6.9 Sulfuric acid (H<sub>2</sub>SO<sub>4</sub>),**  $c \approx 1,0 \text{ mol/l}$ .

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<sub>4</sub>·7H<sub>2</sub>O),**  $c \approx 1 \text{ mol/l}$ .

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<sub>4</sub>·7H<sub>2</sub>O) 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<sub>2</sub>SO<sub>3</sub>H),**  $c \approx 1,55 \text{ mol/l}$ .

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<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O] 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 ( $\text{VOSO}_4 \cdot 2\text{H}_2\text{O}$ ) 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,  $\text{Ce}(\text{SO}_4)_2$ ,  $c = 0,4$  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  $\text{H}_2\text{SO}_4$  (6.9), and dilute to 100 ml with additional  $\text{H}_2\text{SO}_4$  (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  $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$  or 45 g of  $\text{Ce}(\text{SO}_4)_2$  into a weighing boat, scoop, or paper. Any equivalent source of Ce(IV) is acceptable. Transfer to a 5 l volumetric flask, and dissolve in about 4 l of 1,0 mol/l  $\text{H}_2\text{SO}_4$  (6.9). Dilute to volume with 1,0 mol/l  $\text{H}_2\text{SO}_4$  (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<sup>[1]</sup>. Using