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

Part 1:

**Iron(II) reduction/potassium dichromate
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 7097-1:2004

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

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Contents

Page

Foreword	iv
Introduction	v
1 Scope	1
2 Normative references	1
3 Principle	1
4 Reactions and interferences	2
4.1 Reactions	2
4.2 Interferences	2
5 Reagents	3
6 Apparatus	5
7 Sample preparation	6
7.1 General	6
7.2 Uranium metal	6
7.3 Uranium dioxide pellets	7
7.4 Uranium oxide powder (UO_2 , UO_3 , U_3O_8)	7
7.5 Uranium hexafluoride	7
7.6 Uranyl nitrate hexahydrate	7
8 Procedure	7
9 Expression of the results	8
9.1 General	8
9.2 Method of calculation	8
9.3 Repeatability	10
9.4 Bias	10
10 Test report	10
Annex A (informative) Information about sampling and calculations of results	11
Bibliography	14

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 7097-1 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).

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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

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.

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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

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.

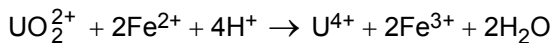
The potassium dichromate solution is calibrated either with an internationally recognized uranium reference material or using a standard solution of potassium dichromate SRM 136 from NIST (National Institute of Standards and Technology); see ISO 10980.

4 Reactions and interferences

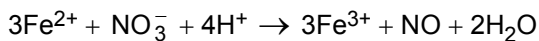
4.1 Reactions

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

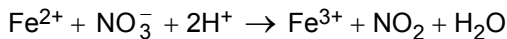
- a) In concentrated phosphoric acid solution:



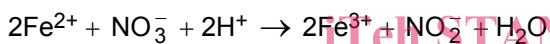
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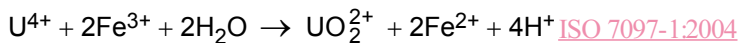
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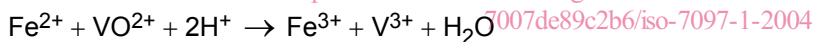
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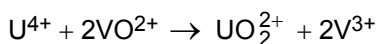
- b) In diluted phosphoric acid solution: standards.iteh.ai



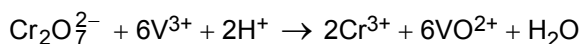
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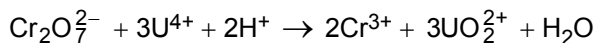
The overall reaction may be represented as follows:



- c) On titration with potassium dichromate solution:



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



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 M Ω .cm).

5.1 Hydrofluoric acid (HF), $c \approx 22$ mol/l ($d_4^{20} = 1,18$).

5.2 Nitric acid (HNO₃), $c \approx 16$ mol/l ($d_4^{20} = 1,42$).

5.3 Nitric acid (HNO₃), $c \approx 4$ mol/l.

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

5.4 Orthophosphoric acid (H₃PO₄), $c \approx 15$ 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 KMnO₄ (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 (H₂SO₄), $c \approx 18$ mol/l ($d_4^{20} = 1,84$).

5.6 Sulfuric acid (H₂SO₄), $c \approx 0,5$ 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 (FeSO₄ 7H₂O), $c \approx 1$ 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 (FeSO₄ 7H₂O) 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 ($\text{NH}_2\text{SO}_3\text{H}$), $c \approx 1,55 \text{ mol/l}$.

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 $10,0 \text{ g} \pm 0,1 \text{ g}$ of hexaammonium heptamolybdate $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}]$ 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, $c \approx 10^{-2} \text{ mol/l}$.

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 (5.6). 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 ($\text{K}_2\text{Cr}_2\text{O}_7$), $c \approx 0,008 5 \text{ mol/l}$

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:

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

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 $\pm 0,05 \%$ 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):

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

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):

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

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 M Ω input resistance) with a digital read-out, most suitably capable of discriminating to 1 mV.

6.2 Platinum wire or spade electrode, 2 cm² 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).