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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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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 7097-1:2004), which has been technically revised.

The main changes are as follows:

- aliquot size has been reduced (see Clause 4);
- information on interferences has been updated (see 5.2);
- requirements for standardisation of potassium dichromate titrant were updated (see 6.16);
- previous 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.

Introduction

The ISO 7097 series documents describe two independent procedures for the determination of uranium in solutions, uranium hexafluoride and solids. The two procedures are similar: this document uses a titration with potassium dichromate while 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 document describes an analytical method for the determination of uranium in samples from pure product materials 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 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.

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 5725-1, *Accuracy (trueness and precision) of measurement methods and results — Part 1: General principles and definitions*

ISO 9894, *Subsampling of uranium hexafluoride in the liquid phase*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 5725-1 apply.

ISO and IEC maintain terminology 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 reagent, 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 potassium dichromate solution to a potentiometric end point[2][3][4][5].

An aliquot of the sample containing about 15 mg to 50 mg of uranium 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. 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 potassium dichromate solution to a potentiometric end point. To improve precision, the titration is performed in the presence of vanadium in dilute sulfuric 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 potassium dichromate solution is calibrated using an internationally recognized reference material, such as SRM 136e (or equivalent) from the U.S. National Institute of Standards and Technology (NIST), or one that is verified as described in 6.15; see ISO 10980[1].

5 Reactions and interferences

5.1 Reactions

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

a) In concentrated phosphoric acid solution:

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

$$3Fe^{2+} + NO_3^- + 4H^+ \xrightarrow{\text{Mo}} 3Fe^{3+} + NO + 2H_2O$$

$$Fe^{2+} + NO_3^- + 2H^+ \xrightarrow{\text{Mo}} Fe^{3+} + NO_2 + H_2O$$

$$2Fe^{2+} + NO_3^- + 2H^+ \xrightarrow{\text{Mo}} 2Fe^{3+} + NO_2^- + H_2O$$

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 can 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:

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

5.2 Interferences

This procedure is less subject to interference from foreign ions than most other methods of determining uranium.[6] 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. Titration shall be completed within five minutes of sample dilution with vanadyl solution to avoid negative assay errors due to air oxidation.

For titrations involving uranium aliquots in the range of 15 mg to 50 mg:

a) Al, Zr, and 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 proportional to the amount present. When present at 0,5 mg levels in the aliquot, 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 at high concentrations as described here. Nitrate levels shall be <3 ml of concentrated nitric acid. Excessive amounts of peroxide is 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 24 °C and at a fixed temperature will have no influence on the titration results. Temperatures outside of this range can affect reaction rates and times[6][7].

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. 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 only 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 MΩ·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 MΩ·m (usually expressed by manufacturers of water purification systems as 18 MΩ·cm).

6.2 Hydrofluoric acid (HF), $c \approx 29$ mol/l ≈ 48 % w/w ($d_4^{20} = 1{,}18$).

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 conformity with the safety data sheet is essential.

6.3 Nitric acid (HNO_3), $c \approx 16$ mol/l ≈ 69 % w/w ($d_4^{20} = 1{,}42$).

6.4 Nitric acid (HNO_3), $c \approx 8$ mol/l.

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

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

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

6.6 Orthophosphoric acid (H_3PO_4), $c \approx 15$ mol/l ≈ 85 % w/w ($d_4^{20} = 1{,}71$).

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 a few drops of 4 % potassium dichromate solution (6.14) to a 2,5 l reagent bottle of orthophosphoric acid 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_2SO_4), $c \approx 18$ mol/l ≈ 96 % in mass fraction ($d_4^{20} = 1{,}84$).

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

Add 56 ml of sulfuric acid (6.8) slowly and carefully to 900 ml of water (6.1), while stirring. Allow to cool and adjust the solution to 1 000 ml with water (6.1).

6.10 Iron(II) sulfate ($FeSO_4 \cdot 7H_2O$), $c \approx 1$ 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 ($FeSO_4 \cdot 7H_2O$) 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_2SO_3H), $c \approx 1{,}55$ 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 [$(NH_4)6Mo_7O_{24} \cdot 4H_2O$] in 250 ml of water (6.1).

Add 10 ml of sulfamic acid (6.11) 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 be prepared fresh weekly.