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Nuclear energy — Uranium dioxide powder and sintered pellets — Determination of oxygen/uranium atomic ratio by the amperometric method

Énergie nucléaire — Poudre et pastilles frittées de dioxyde d'uranium — Détermination du rapport atomique oxygène/uranium par la méthode ampérométrique

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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.

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ISO 9005 was prepared by Technical Committee ISO/TC 85, *Nuclear energy*, Subcommittee SC 5, *Nuclear fuel technology*.

This second edition cancels and replaces the first edition (ISO 9005:1994), which has been technically revised.

Nuclear energy — Uranium dioxide powder and sintered pellets — Determination of oxygen/uranium atomic ratio by the amperometric method

1 Scope

This International Standard specifies an analytical method for the determination of the oxygen/uranium atomic ratio in uranium dioxide powder and sintered pellets.

The method is applicable to reactor grade samples of hyper-stoichiometric uranium dioxide powder and pellets. The presence of reducing agents or residual organic additives invalidates the procedure.

2 Principle

2.1 The test sample is dissolved in orthophosphoric acid, which does not oxidize the uranium(IV) from UO_2 molecules. Thus, the uranium(VI) that is present in the dissolved solution is from UO_3 and/or U_3O_8 molecules only, and is proportional to the excess oxygen in these molecules. The uranium(VI) content of the solution is determined by titration with a previously standardized solution of ammonium iron(II) sulfate hexahydrate in orthophosphoric acid. The end-point of the titration is determined amperometrically using a pair of polarized platinum electrodes. The oxygen/uranium ratio is calculated from the uranium(VI) content.

2.2 A portion, weighing about 1 g, of the test sample is dissolved in orthophosphoric acid. The dissolution is performed in an atmosphere of nitrogen or carbon dioxide when sintered material is being analysed. When highly sintered material is being analysed, the dissolution is performed at a higher temperature in purified phosphoric acid from which the water has been partly removed.

The cooled solution is titrated with an orthophosphoric acid solution of ammonium iron(II) sulfate, which has previously been standardized against potassium dichromate. The end-point of the titration is detected by the sudden increase of current between a pair of polarized platinum electrodes on the addition of an excess of ammonium iron(II) sulfate solution.

3 Reactions

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

4 Reagents

Use only reagents of recognised analytical grade and demineralised water.

4.1 Orthophosphoric acid, $\rho(H_3PO_4) = 1{,}75$ g/ml.

4.2 Concentrated nitric acid, $c(HNO_3) = 14$ mol/l; $\rho(HNO_3) = 1{,}4$ g/ml.

4.3 Orthophosphoric acid, purified.

Add 1 500 ml of orthophosphoric acid (4.1) to 40 ml of nitric acid (4.2) to a cylinder quartz vessel and raise the temperature gradually to 275 °C. Maintain this temperature for 45 min while a gentle stream of nitrogen or carbon dioxide is passed through the solution. After cooling to room temperature, store the liquid in a glass bottle.

4.4 Ammonium iron(II) sulfate, approximately $c[(NH_4)_2Fe(SO_4)_2] = 0{,}05$ mol/l or $\rho[(NH_4)_2Fe(SO_4)_2] = 14{,}5$ g/l.

Heat 1 000 ml of orthophosphoric acid (4.1) to a temperature of 60 °C to 70 °C in a glass vessel. Add 20 g of ammonium iron(II) sulfate hexahydrate $[(NH_4)_2Fe(SO_4)_2{\cdot}6H_2O]$ and stir until dissolved. Cool and store the solution in a nitrogen or carbon dioxide atmosphere.

Standardize this solution against potassium dichromate in the conventional way with each run of samples. Calculate the molarity of the iron(II) solution.

4.5 Naturally occurring U_3O_8 **standard solution**, $c(U_3O_8) = 0{,}01$ mol/l or $\rho(U_3O_8) = 0{,}084\ 21$ g/l.

Dissolve 0,842 1 g of pure U_3O_8 in purified orthophosphoric acid (4.3), warming if necessary. Cool and dilute to 100 ml with purified orthophosphoric acid (4.3).

NOTE The concentration of UO_2^{2+} in this solution is 0,02 mol/l. Upon dissolution, one mole of U_3O_8 forms one mole of U^{4+} ions (non-reactive) and two moles of UO_2^{2+} ions, which is equivalent to dissolving one mole of UO_2 (non-reactive) and two moles of UO_3. Thus, this solution contains 0,02 moles of UO_2^{2+} per litre.

To ensure stoichiometric U_3O_8, ignition just prior to use is recommended.

4.6 Nitrogen or **carbon dioxide**, containing less oxygen than a volume fraction of 20×10^{-6}.

5 Apparatus

Use laboratory apparatus and

5.1 Inert dissolution apparatus, type A; see Figure 1.

5.2 Inert dissolution apparatus, type B; see Figure 2.

5.3 Electrode assembly; see Figure 3.

When not in use, the electrodes shall be stored in a completed titration solution; see 7.4.2.

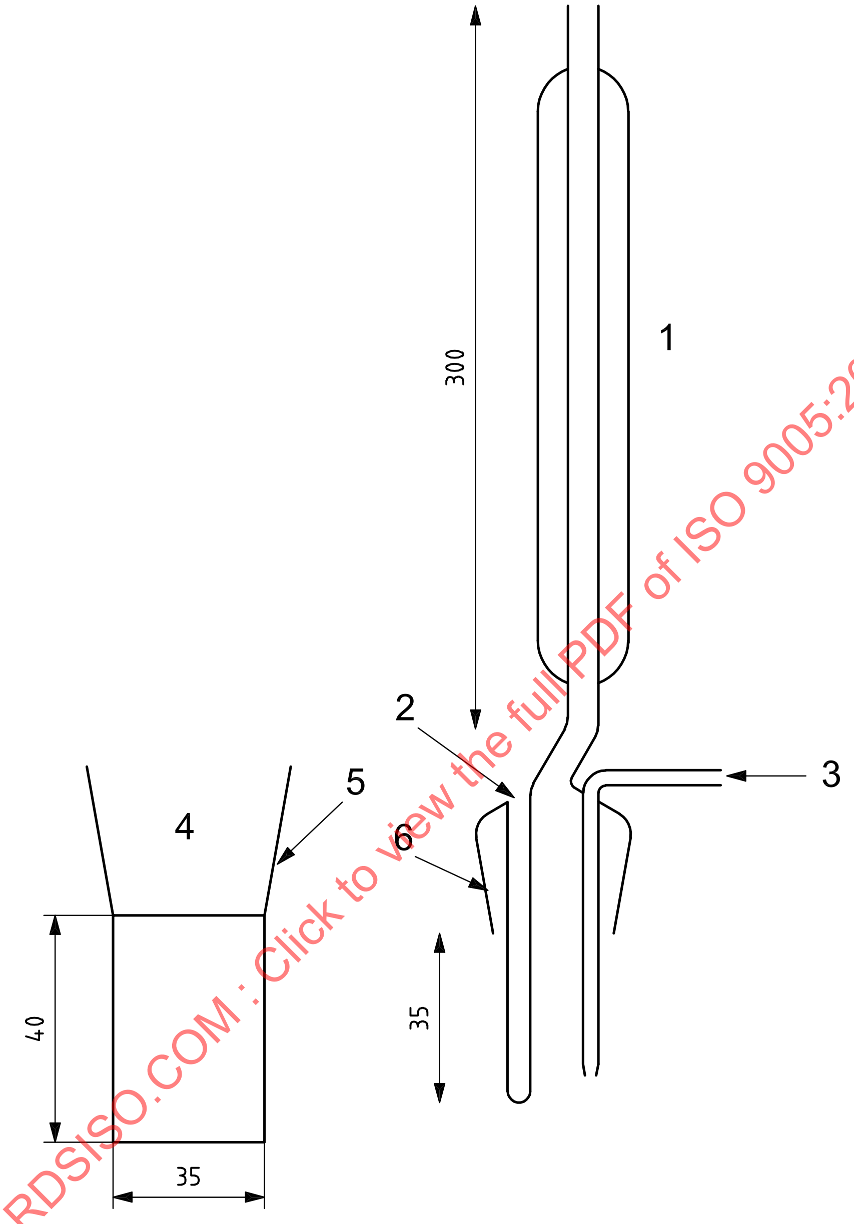
The electrodes should be cleaned when needed as follows. Immerse the platinum electrodes in boiling concentrated nitric acid (4.2) containing 10 g/l to 20 g/l of potassium dichromate for about 5 min. Rinse with demineralized water, then immerse in 1 mol/l iron(II) sulfate solution for 30 s to 60 s and then rinse with demineralized water.

5.4 Bi-amperometric endpoint-detection circuit; see Figure 4.

5.5 Piston burette, 5 ml or 1 ml capacity, capable of reading to 0,001 ml, fitted with a capillary end to dip into the titration solution.

5.6 Thermostatically controlled heating block or **isomantle**.

Dimensions in millimetres

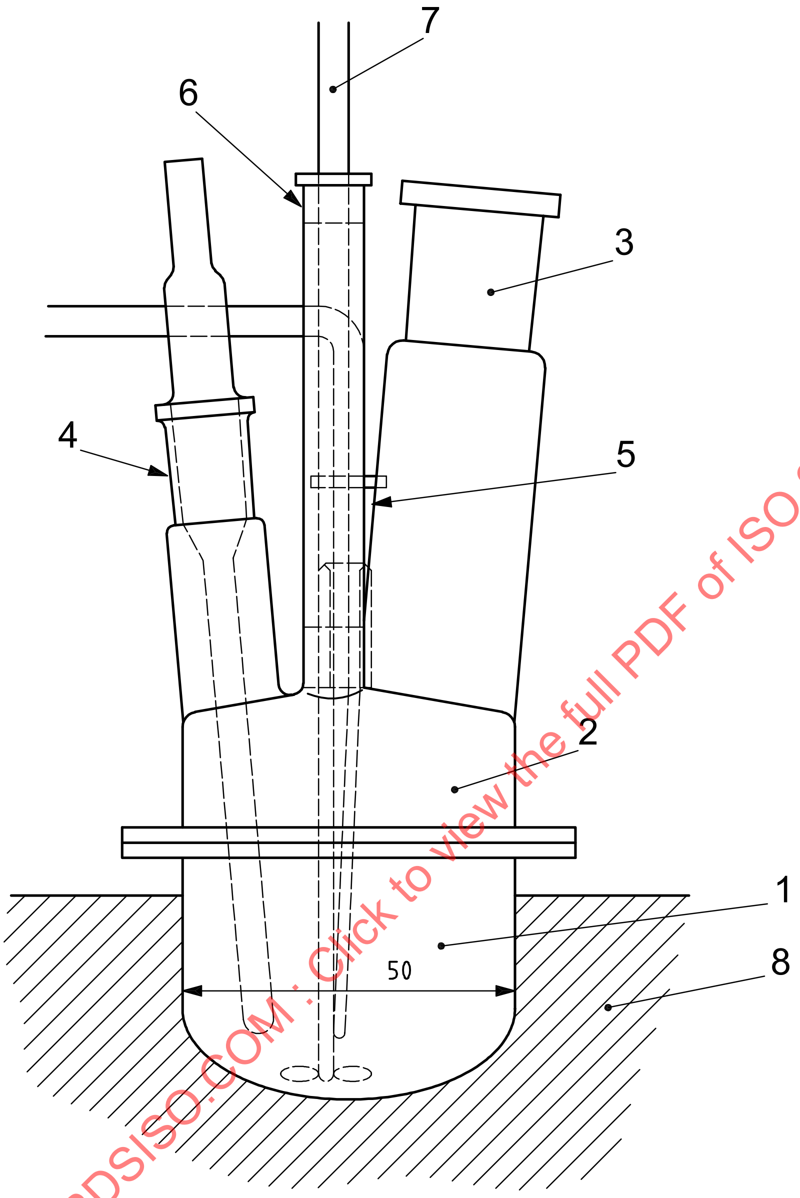


Key

1	condenser
2	thermometer well
3	nitrogen purge
4	flask
5	ISO 383-34/35 tapered, ground socket
6	ISO 383-34/35 tapered, ground cone

Figure 1 — Dissolution apparatus —Type A

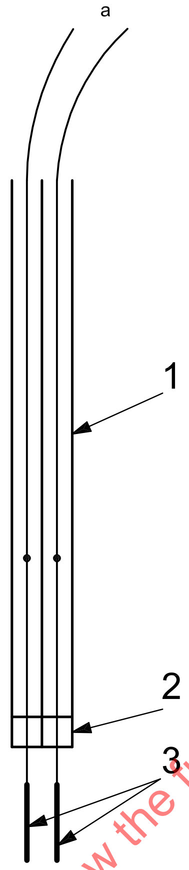
Dimensions in millimetres



Key

1	quartz dissolution vessel with ground rim
2	pyrex or equivalent cover with ground rim, equipped with four (items 3 to 6) joints
3	ISO 383-24/29 tapered ground joint for adding the test portion
4	ISO 383-14/23 tapered ground joint for inserting the thermometer
5	ISO 383-7/16 tapered groundjoint for inserting the nitrogen-purge tube
6	central tube for inserting the stirrer, equipped with two polytetrafluoroethylene (PTFE) bearings
7	quartz stirrer, with the total length of the stirring blades equal to 25 mm, rotating at a constant angular velocity of 900 r/min
8	electric heating mantle powered by a temperature regulator in combination with the thermocouple in the joint number 4

Figure 2 — Dissolution apparatus —Type B

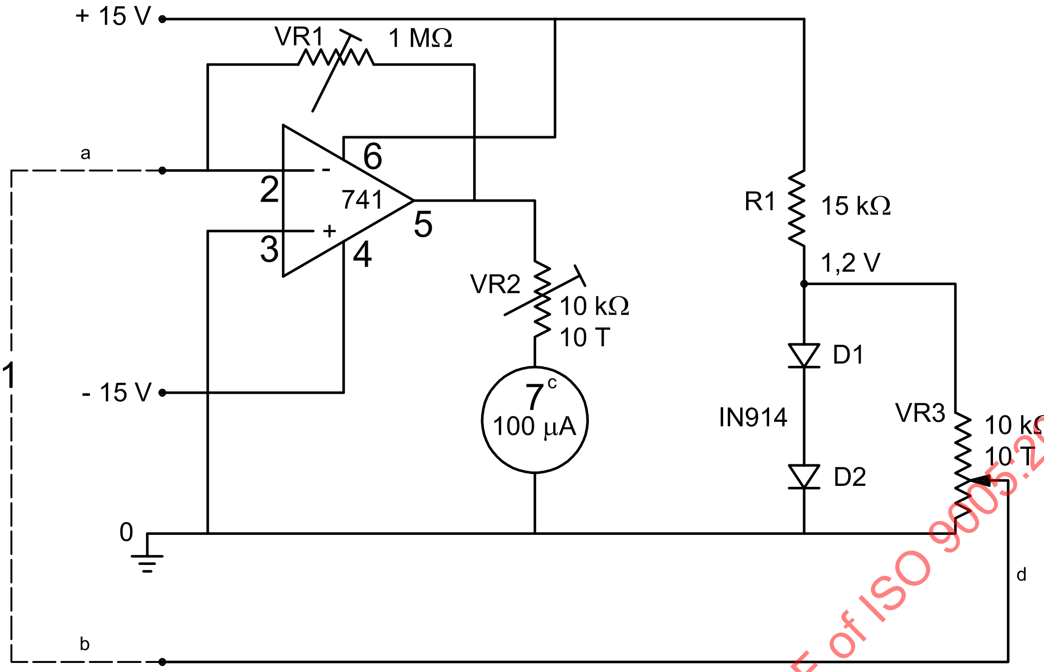


Key

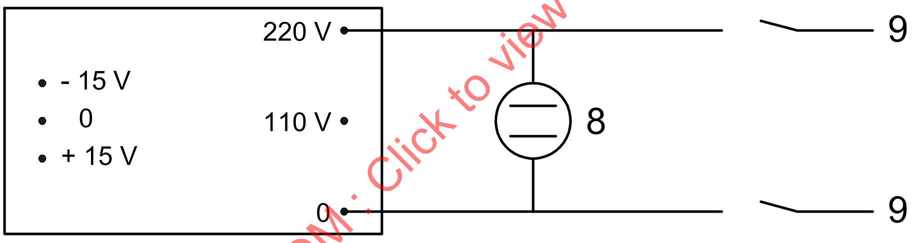
1	glass tubes, ID 3 mm, taped together
2	glass seal
3	platinum electrodes (10 × 10)

[a] To the bi-amperometric endpoint-detection circuit.

Figure 3 — Electrode assembly



a) **Circuit**



b) **Underside** (pin view)

Key

1	electrode assembly
2–6	pin numbers
7	multimeter, 100 µA
8	neon
9	mains switch

[a] Red.

[b] Black.

[c] To adjust multimeter for full scale, remove 741, or equivalent, feed 1 V in at pin 6 and adjust VR2 for full-scale deflection.

[d] Adjust for 300 mV.

Power supply: Ancom DPS or equivalent.

Figure 4 — Bi-amperometric endpoint-detection circuit

6 Preparation of the test sample

6.1 Uranium dioxide powder

The laboratory sample is analysed without further preparation.

6.2 Uranium dioxide sintered pellets

Crush the laboratory sample in a percussion mortar and pass it through 250 µm and 150 µm aperture sieves until about 2 g of sample has passed through the 250 µm sieve and has been retained in the 150 µm sieve. Retain this 150 µm to 250 µm portion for use as the test sample.

The test sample should not be in a finely ground form; otherwise significant oxidation can occur.

Whole pellets or large pieces may be used but dissolution times are prolonged.

The crushing of sintered pellets implies an important risk of re-oxidation. The crushing should be carried out in an inert atmosphere to minimize measurement uncertainty.

7 Procedure

7.1 Uranium dioxide powder

7.1.1 Weigh, to the nearest 0,001 g, approximately 1 g of the test sample and record this value as m. Transfer the test portion to a 50 ml squat-form beaker and add 30 ml ± 0,5 ml of orthophosphoric acid (4.1). Cover the beaker with a watch-glass.

7.1.2 Prepare the blank test solution using normal dissolution, by adding 30 ml ± 0,5 ml of orthophosphoric acid (4.1) to a 50 ml squat-form beaker. Cover the beaker with a watch-glass.

7.1.3 Heat the test portion and blank-test solution to a temperature of 160 °C to 180 °C until dissolution is complete. Cool to room temperature.

7.1.4 To correct for humidity, the sample may be dried before the weighing or the uranium content determined independently.

7.1.5 If greater accuracy is required, the dissolution should be performed in an inert dissolution apparatus, type A (5.1).

7.2 Sintered pellets of uranium dioxide

7.2.1 Weigh, to the nearest 0,001 g, approximately 1 g of the test sample and record this value as m. Transfer the test portion to the flask of an inert dissolution apparatus, type A (5.1), and add 30 ml ± 0,5 ml of orthophosphoric acid (4.1).

7.2.2 Prepare the blank-test solution, using inert dissolution by adding 30 ml ± 0,5 ml of orthophosphoric acid (4.1) to the flask of an inert solution apparatus, type A (5.1).

7.2.3 Assemble the inert-dissolution apparatus. Pass a stream of nitrogen or carbon dioxide (4.6) through the solution and heat the test portion and blank to a temperature of 160 °C to 180 °C until dissolution is complete. Cool at room temperature.

NOTE 1 Some batches of orthophosphoric acid can contain reducing impurities. The procedure in 7.3 is more accurate.

NOTE 2 It can be necessary to heat certain highly sintered samples at a higher temperature to achieve dissolution. The procedure can continue as described in 7.3.

7.3 Highly sintered pellets of uranium dioxide

7.3.1 Weigh, to the nearest 0,001 g, approximately 1 g of the test sample and record this value as m. Transfer the test portion to the quartz vessel of an inert dissolution apparatus, type B (5.2) and add 50 ml ± 1 ml of purified orthophosphoric acid (4.3).

7.3.2 Prepare the blank-test solution, using inert dissolution of highly sintered pellets, as follows. Add 50 ml ± 1 ml of purified orthophosphoric acid (4.3) to the quartz vessel of an inert-dissolution apparatus, type B (5.2). Add 0,5 ml of standard U_3O_8 solution (4.5) measured to the nearest 0,001 ml.

7.3.3 Assemble the inert dissolution apparatus. Start stirring the test portion and blank with the quartz stirrer and pass a stream of nitrogen or carbon dioxide through the solution.

Heat to a maximum temperature of 275 °C and maintain the temperature for 1 h. Cool to about 70 °C and add 5 ml of demineralized water to the test portion and blank solution.

7.4 Determination

7.4.1 Stir the test and blank solutions at high speed to create a vortex of about 5 mm depth. Insert the electrode assembly (5.3) into the solution and switch on the bi-amperometric endpoint-detection circuit (5.4).

7.4.2 Titrate with ammonium iron(II) sulfate solution (4.4) from the piston burette (5.5) until a small permanent current reading is obtained. Record the volume of the titrant used for the test solution as V_1 and for the blank solution as V_2.

NOTE 1 To minimize measurement uncertainty, it is possible pass a stream of nitrogen or carbon dioxide through the solution during the titration.

NOTE 2 It is preferable to use a more concentrated titrant when analysing samples with an oxygen/uranium ratio of more than 2,1.

NOTE 3 The aim should be to obtain the same small permanent current at the end-point for both test solution and blank solution.

8 Expression of results

8.1 Method of calculation

8.1.1 Uranium dioxide powder and uranium dioxide sintered pellets

Calculate the corrected mass, m_1, expressed in milligrams, of uranium(VI) reduced in the titration of the test solution using Equation (1):

$$m_1 = \frac{\rho_{\text{AIS}} \times A_{\text{U}}}{2}\left(V_1 - V_2\right) \tag{1}$$

where

ρ_{AIS}	is the concentration of the ammonium iron(II) sulfate solution (4.4), expressed in grams per litre;
V_1	is the volume of titrant used for the test solution, expressed in millilitres;
V_2	is the volume of titrant used for the blank solution, expressed in millilitres;
A_{U}	is the relative atomic mass of the uranium in the test sample.

The mass of uranium(VI) in the test portion is equal to m_1.

NOTE In material where the uranium-235 level is less than 10 %, a value of A_{U} of 238 is sufficiently accurate.