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Uranium dioxide powder and sintered pellets — Determination of oxygen/uranium atomic ratio — Amperometric method

Poudre et pastilles frittées de dioxyde d'uranium — Détermination du rapport atomique oxygène/uranium — Méthode ampérométrique

Reference number
ISO 9005:1994(E)

Foreword

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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.

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

Annex A of this International Standard is for information only.

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Uranium dioxide powder and sintered pellets — Determination of oxygen/uranium atomic ratio — Amperometric method

1 Scope

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

The method is applicable to reactor grade samples of hyperstoichiometric uranium dioxide powder and pellets. The presence of reducing agents or undecomposed organic additives invalidates the procedure. The limit of detection for deviation from stoichiometric composition is 2,002 for uranium dioxide powder and 2,000 2 for sintered pellets.

2 Principle

2.1 The test sample is dissolved in orthophosphoric acid which yields uranium(VI) in proportion to the hyperstoichiometric oxygen present. 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 amperiometrically using a pair of polarized platinum electrodes. The oxygen/uranium ratio is calculated from the uranium(VI) content.

2.2 A portion of the test sample, weighing about 1 g, 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 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 recognized analytical grade and demineralized water.

4.1 Orthophosphoric acid, ρ 1,75 g/ml.

4.2 Orthophosphoric acid, purified.

Add 1 500 ml of orthophosphoric acid (4.1) to 40 ml of nitric acid (ρ 1,42 g/ml) to a cylindrical 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.

4.3 Ammonium iron(II) sulfate, approximately 0,05 mol/l solution.

Heat 1 000 ml of orthophosphoric acid (4.1) to 60 °C to 70 °C in a glass vessel. Add 20 g of ammonium iron(II) sulfate hexahydrate $[(NH_4)_2Fe(SO_4)_2.6H_2O]$ 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.

4.4 Naturally occurring U_3O_8, 0,01 mol/l standard solution.

Dissolve 0,842 1 g of pure U_3O_8 in purified orthophosphoric acid (4.2) in a nitrogen or carbon dioxide atmosphere, warming if necessary. Cool and dilute to 100 ml with purified orthophosphoric acid (4.2).

NOTES

1 This solution will contain 0,02 moles of UO_2^{2+} per litre.

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

4.5 Nitrogen or **carbon dioxide**, containing less than 20 ppm (V/V) oxygen.

5 Apparatus

Usual 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 occasionally as follows. Immerse the platinum in boiling concentrated nitric acid 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 Biamperometric titration 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**.

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 on the 150 µm sieve. Retain this 150 µm to 250 µm portion for use as the test sample.

NOTES

3 The test sample should not be in finely ground form otherwise significant oxidation may occur.

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

5 The crushing of sintered pellets implies an important risk of reoxidation. The crushing should be carried out in an inert atmosphere for maximum accuracy.

Dimensions in millimetres

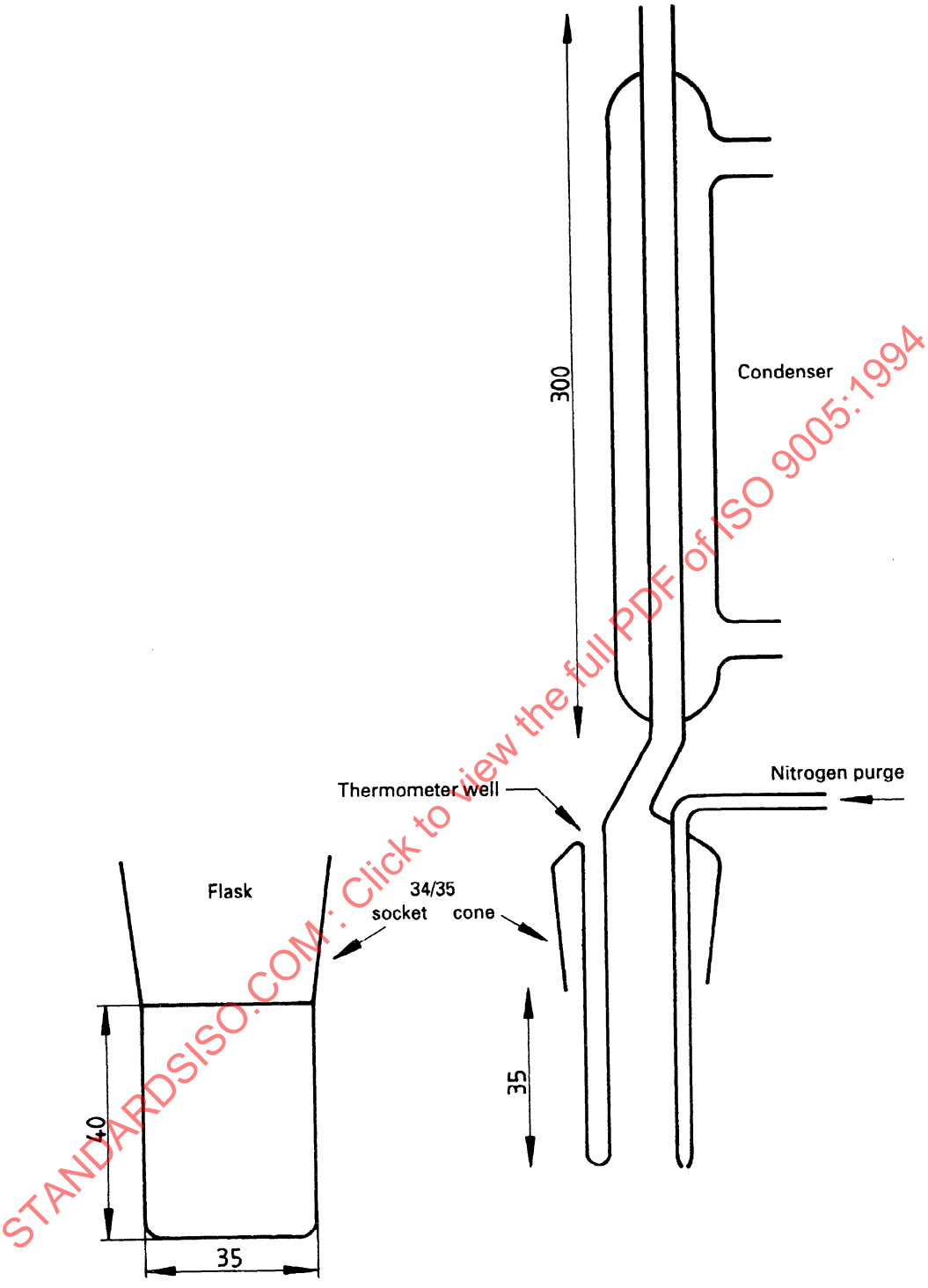
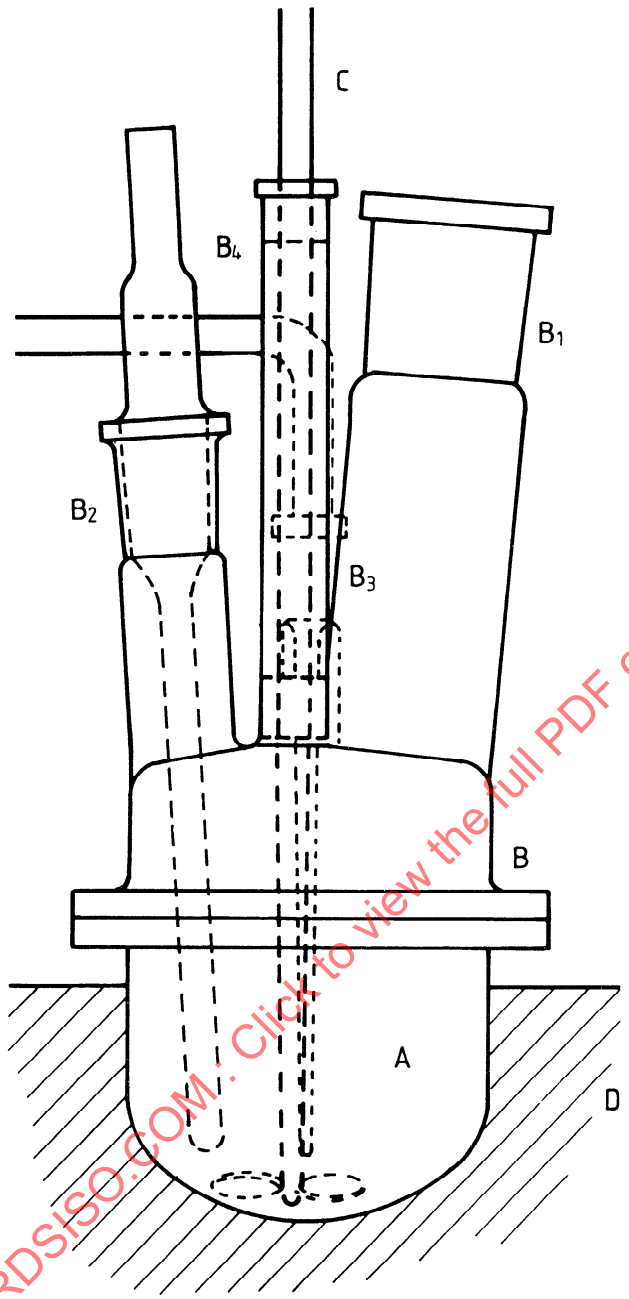


Figure 1 — Dissolution apparatus, type A



Key

A	Quartz dissolution vessel, ⌀ 50 mm, with ground rim	B_3	7/16 neck for insertion of nitrogen purge tube
B	Pyrex cover with ground rim equipped with four necks B_1 to B_4:	B_4	central tube, ⌀ internal 8 mm, for insertion of stirrer, equipped with two polytetrafluoroethylene (PTFE) bearings
B_1	24/29 neck for admittance of test portion	C	Quartz stirrer: total length of stirring blades 25 mm rotating at a constant rotational frequency of 900 r/min
B_2	14/23 neck for insertion of thermocouple	D	Electric heating mantle powered by a temperature regulator in combination with the thermocouple in neck B_2

Figure 2 — Dissolution apparatus, type B

Dimensions in millimetres

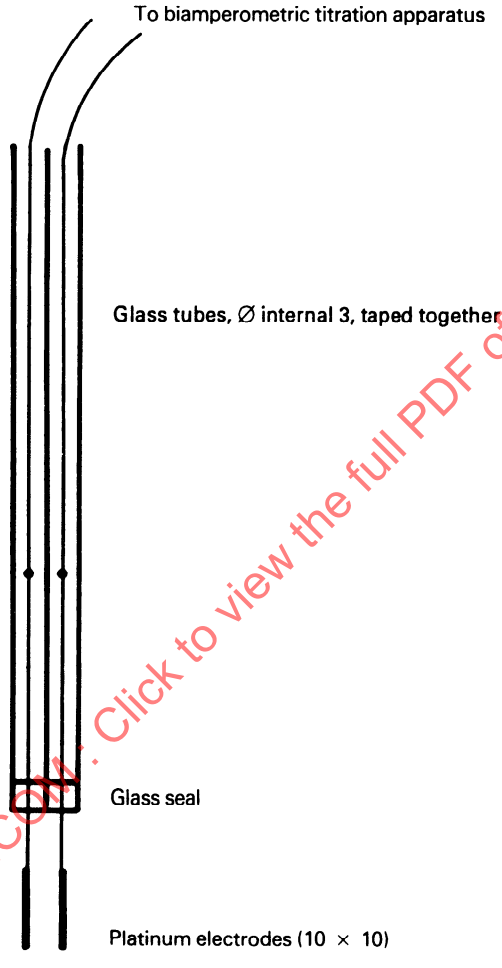
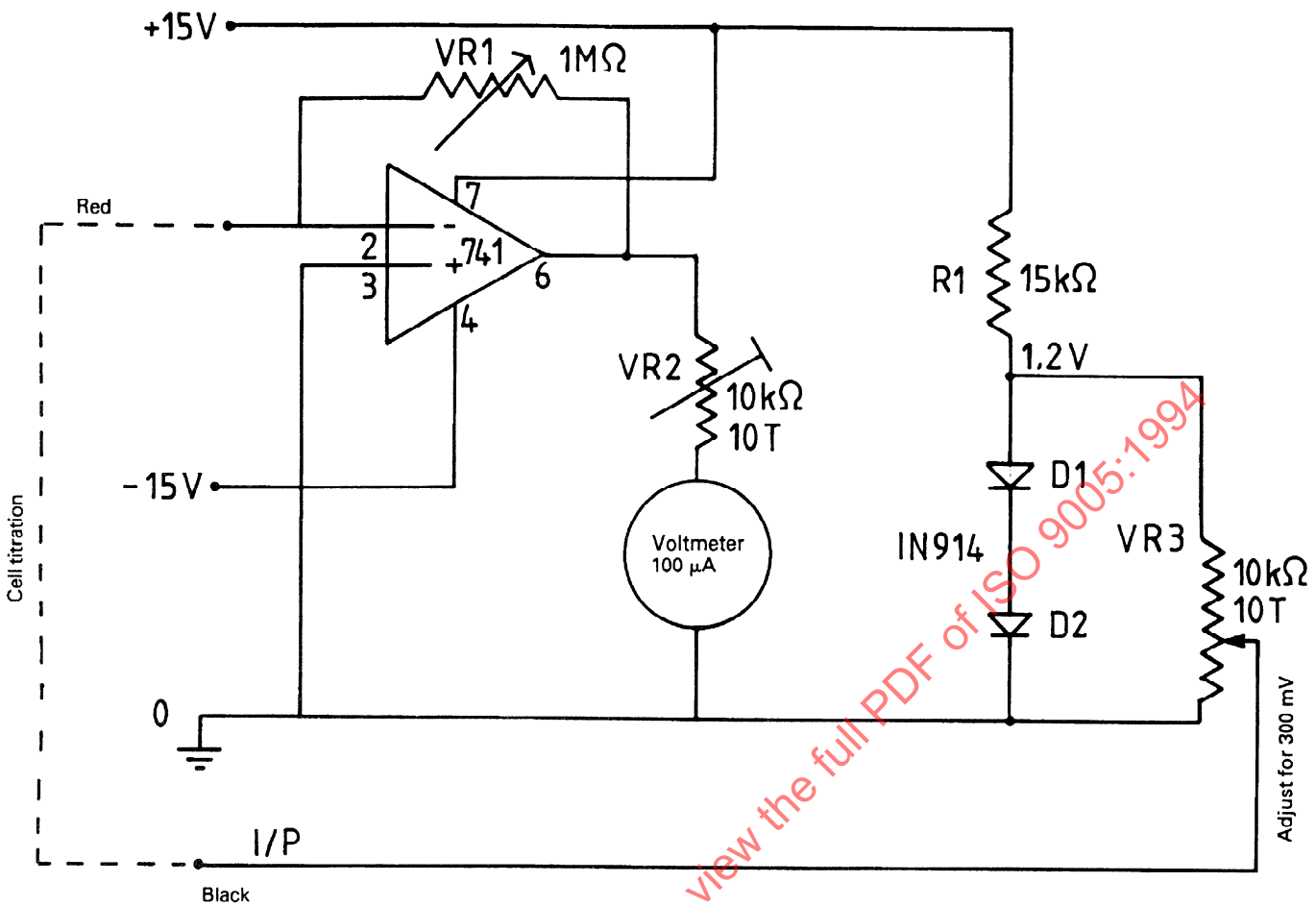
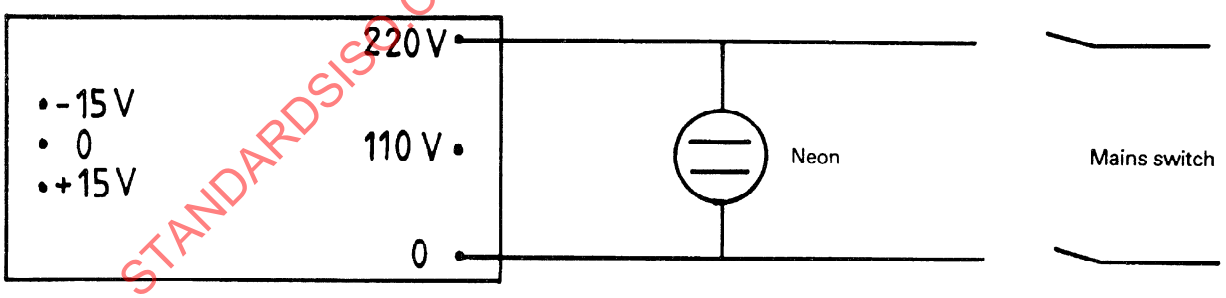


Figure 3 — Electrode assembly



To adjust voltmeter for full scale, remove 741, feed 1 V in at pin 6 and adjust VR2 for full-scale deflection.

Power supply: Ancom DPS 100



Underside (pin view)

Figure 4 — Biamperometric titration circuit

7 Procedure

7.1 Uranium dioxide powder

7.1.1 Weigh, to the nearest 0,001 g, approximately 1 g of the test sample (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, as follows. Add 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 at 160 °C to 180 °C until dissolution is complete. Cool to room temperature.

NOTE 6 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 (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, as follows. Add 30 ml ± 0,5 ml of orthophosphoric acid (4.1) to the flask of an inert dissolution apparatus, type A (5.1).

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

NOTES

7 Some batches of orthophosphoric acid can contain reducing impurities. For greater accuracy, the procedure of 7.3 should be followed.

8 It may be necessary to heat certain highly sintered samples at a higher temperature to achieve dissolution. Proceed 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 (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 (4.2).

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 (4.2) to the quartz vessel of an inert-dissolution apparatus, type B (5.2). Add 0,5 ml of standard U_3O_8 solution (4.4).

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 amperometric titration circuit (5.4).

7.4.2 Titrate with ammonium iron(II) sulfate solution (4.3) 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 (V_1) and for the blank solution (V_2).

NOTES

9 For maximum accuracy and precision, pass a stream of nitrogen or carbon dioxide through the solution during the titration.

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

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