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Uranium metal and uranium dioxide powder and pellets — Determination of nitrogen content — Method using ammonia-sensing electrode

Uranium métal, et poudre et pastilles de dioxyde d'uranium — Dosage de l'azote — Méthode utilisant l'électrode sensible à l'ammoniac

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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 9006 was prepared by Technical Committee ISO/TC 85, *Nuclear energy,* Subcommittee SC 5, *Nuclear fuel technology.*

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Uranium metal and uranium dioxide powder and pellets — Determination of nitrogen content — Method using ammonia-sensing electrode

1 Scope

This International Standard specifies an analytical method for determining the nitrogen content in uranium metal and uranium dioxide powder and pellets.

It is applicable to the determination of nitrogen, present as nitride, in uranium metal and uranium dioxide powder and pellets. The concentration range within which the method can be used is between 9 µg and 600 µg of nitrogen per gram. Interference can occur from metals which form complex ammines, but these are not normally present in significant amounts.

2 Principle

2.1 The sample is dissolved in a mixture of hydrochloric acid and hydrogen peroxide, producing a solution of uranium(VI) and converting any nitrogen, present as nitride, to the ammonium ion. Potassium carbonate is added to convert the ammonium ion to ammonia and uranium(VI) is retained in solution as the carbonate complex anion. Ethylene diaminetetraacetic acid (EDTA) is present to complex metals which form ammines. The ammonia content is measured using an ammonia-sensing electrode and a standard addition procedure.

2.2 A portion of sample containing about 0,5 g of uranium is dissolved in hydrochloric acid and hydrogen peroxide. The quantity of hydrochloric acid is kept to a minimum to ensure a low acidity after dissolution and to minimize the reagent blank. Nitrogen, present as nitride, is converted to ammonium ion by the acid, and hydrogen peroxide converts the uranium to the hexavalent state. Initially, a solid pale-yellow peroxy-uranium complex is formed; further heating decomposes this complex resulting in a clear yellow solution of uranium(VI).

The acid solution is made alkaline by the addition of excess potassium carbonate solution, the low free acid after dissolution ensuring that the evolution of carbon dioxide is minimal. The excess carbonate converts ammonium ion to ammonia gas and maintains uranium(VI) in solution as a complex anion, $UO_2(CO_3)_3^{4-}$.

The quantity of ammonia present in the alkaline solution is determined by recording the potential indicated by the ammonia-sensing electrode when it is inserted in the solution, adding a known amount of ammonia and again recording the potential indicated by the electrode.

The difference between the two values enables the ammonia content of the solution, and hence the nitrogen content of the sample, to be determined. The ammonia is added in the form of a standard solution of ammonium chloride, the ammonium ion being instantly converted to ammonia when it is added to the alkaline solution.

A blank test is carried out using the amounts of hydrochloric acid, hydrogen peroxide and water that are used for dissolving the test portion, and following the same procedure for measuring the ammonia content.

3 Reactions

$U^{4+} + (OO)^{2-} \rightarrow UO_2^{2+}$

$UO_2^{2+} + 3CO_3^{2-} \rightarrow UO_2(CO_3)_3^{4-}$

$NH_4^+ + OH^- \rightarrow NH_3 + H_2O$

4 Reagents

Use only reagents of recognized analytical grade and distilled water.

4.1 Distilled water.

The ammonia concentration shall be less than 0,1 µg/ml; laboratory grade water usually conforms to this requirement.

This water shall be used to prepare all reagents and shall also be used in the procedure specified in clause 7.

4.2 Hydrochloric acid, ρ 1,18 g/ml.

4.3 Hydrogen peroxide, 290 g/l solution.

4.4 Complexing agent.

Dissolve 250 g of anhydrous potassium carbonate and 2,5 g of ethylenediaminetetraacetic acid (EDTA), disodium salt, in water and dilute to 1 l.

4.5 Nitrogen, 1 g/l standard solution.

Weigh approximately 5 g of ammonium chloride and dry it at 120 °C for 4 h. Dissolve 3,821 g of the dried material in water and dilute to 1 l.

4.6 Nitric acid, ρ 1,42 g/ml.

4.7 Acetone.

5 Apparatus

Usual laboratory apparatus, and

5.1 Millivoltmeter, with digital readout, capable of discriminating to 0,1 mV.

5.2 Ammonia-sensing electrode.

When not in use, the electrode shall be stored in a solution consisting of 10 ml of water, 2 ml of complexing agent (4.4) and 50 µl of nitrogen standard solution (4.5).

5.3 Magnetic stirrer and plastic-coated stirrer bars.

5.4 Micrometer syringe pipette, 500 µl capacity, capable of delivering increments of 0,2 µl.

6 Sampling

6.1 Preparation of the test sample

6.1.1 Uranium metal

Place about 2 g of the sample in a 100 ml beaker. Add 10 ml of water (4.1) followed by 10 ml of nitric acid (4.6) and swirl to mix.

Stand until all trace of tarnish has been removed and the sample is silver in appearance.

Pour off the excess acid and wash thoroughly with water.

Drain off the excess water, cover the sample with acetone (4.7) and swirl to mix. Pour off the acetone.

Dry the cleaned sample with a stream of air and use it as the test sample.

Commence the procedure (see clause 7) immediately.

6.1.2 Uranium dioxide pellets

Crush the sample in a percussion mortar and pass it through a 75 µm sieve. Repeat this procedure if necessary until a sieved portion of more than 1 g is available. Retain the sieved portion for use as the test sample.

6.1.3 Uranium dioxide powder

Powder samples shall be analysed without any further preparation.

7 Procedure

7.1 Preparation of test solution

7.1.1 Weigh, to the nearest 0,001 g, 0,56 g to 0,58 g of the uranium dioxide test sample (see 6.1.2 or 6.1.3) or 0,48 g to 0,52 g of the uranium metal test sample (see 6.1.1) and record this mass as m_0. Transfer the sample to a 25 ml beaker.

NOTE 1 Turnings of uranium metal are easily broken to give the sample mass. Solid pieces are dissolved in nitric acid and a suitable aliquot of the solution taken.

7.1.2 Add, by pipette, 1 ml of water (4.1), 1 ml of hydrochloric acid (4.2) and 0,5 ml of hydrogen peroxide solution (4.3). Swirl to mix and cover with a watch-glass. Boil gently until a clear yellow solution is obtained. Allow the solution to cool to ambient temperature.

NOTE 2 This dissolution is suitable for all nitrides of uranium.

7.1.3 Dilute to 15 ml with complexing agent (4.4) and swirl to mix. Add a stirrer bar (5.3) to the solution and cover the beaker with a watch-glass.

7.1.4 Ammonia is lost slowly from the solution and measurements shall be made within 30 min of making the solution alkaline.

7.2 Standard addition procedure

7.2.1 Remove the ammonia-sensing electrode (5.2) from the solution in which it is stored and rinse it with water.

7.2.2 Immerse the electrode in the sample solution, prepared in accordance with 7.1, stir and take the voltage reading when it is stable, in millivolts, to the nearest 0,1 mV, and record U_1.

NOTE 3 Stirring by magnetic stirrer should be carried out continuously and at a steady rate throughout the series of measurements. The stability of the reading will be influenced by the impedance of the millivoltmeter used. A criterion of 0,2 mV/min or less may be appropriate when a high grade meter is used.

7.2.3 Using the micrometer syringe (5.4), make an addition of nitrogen standard solution (4.5) until the change in the voltage reading is in the range between 17 mV and 33 mV. Record the volume, in microlitres, of nitrogen standard solution (4.5) added as V.

NOTE 4 A volume of V µl of nitrogen standard solution contains V µg of nitrogen.

7.2.4 Take the voltage reading, when it is stable, in millivolts, to the nearest, 0,1 mV, and record as U_2.

7.3 Blank test

7.3.1 Determine the blank level of the reagents (recorded as mass m_2) by pipetting 1 ml of water, 1 ml of hydrochloric acid (4.2) and 0,5 ml of hydrogen peroxide (4.3) into a 25 ml beaker. Boil gently to remove excess hydrogen peroxide and allow the solution to cool to ambient temperature.

7.3.2 Follow the procedure described in 7.1.3 and 7.2.

NOTE 5 The measured blank solution must contain more than 1 µg of NH_3 otherwise it cannot be determined by the probe. At ammonia levels below this value the method of calculation (8.1.1) is not valid because the relationship between the voltage reading and ammonia concentration is not defined by the Nernst equation. The usual blank level is between 2 µg and 5 µg of NH_3.

8 Expression of results

8.1 Method of calculation

8.1.1 Calculate the total nitrogen content, in micrograms, of the test sample solution, m_1, or the blank solution, m_2, using the following formula:

$$m_1 \text{ or } m_2 = \frac{m_3}{10^{(U_1 - U_2)/S} - 1}$$

where

m_3 is the mass of nitrogen, in micrograms, in the standard addition;

$(U_1 - U_2)$ is the change in the voltage reading produced on making the standard addition of V µl of nitrogen standard solution (see 7.2.3);

S is the electrode slope determined in accordance with annex A.

NOTE 6 For maximum accuracy the formula should be

$$m_1 \text{ or } m_2 = \frac{m_3 \times 15}{10^{(U_1 - U_2)/S} \times (15 + 0{,}001V) - 15}$$

However, within the stated concentration range of the method, i.e. between 9 µg and 600 µg of nitrogen per gram of sample, the result calculated using this formula will not be significantly different.

8.1.2 Calculate the corrected value of the total nitrogen content, in micrograms, of the sample solution, m_4, by subtracting the blank value, m_2, of the reagents, as determined in accordance with 7.3.1, from the total nitrogen content, m_1, calculated in accordance with 8.1.1, using the following formula:

$$m_4 = m_1 - m_2$$

8.1.3 Calculate the nitrogen content, W_N, of the sample, in micrograms per gram, using the following formula:

$$W_N = \frac{m_4}{m_0}$$

where m_0 is the mass of the test portion (see 7.1.1).

8.2 Reproducibility

8.2.1 Uranium metal

The reproducibility (twice the standard deviation) based on 58 determinations at a nitrogen content level of 40 µg/g is ± 12 µg/g.

8.2.2 Uranium dioxide powder

The reproducibility (twice the standard deviation) based on 160 determinations at a nitrogen content level of 63 µg/g is ± 14,4 µg/g.

8.2.3 Uranium dioxide pellets

The reproducibility (twice the standard deviation) based on 45 determinations at a nitrogen content level of 6 µg/g is ± 6 µg/g.

8.3 Bias

There are no standard reference materials available to enable the accuracy of the method to be verified.

Checks with uranium nitride additions indicate that there is no significant bias.

9 Test report

The test report shall include the following information:

a) identification of the sample;

b) reference of the method used;

c) any results and method of expression used;

d) any unusual features noted during the test;

e) any operations not included in this International Standard or regarded as optional.