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Nuclear fuel technology — Determination of uranium in uranyl nitrate solutions of nuclear grade quality — Gravimetric method

Technologie du combustible nucléaire — Détermination de l'uranium dans les solutions de nitrate d'uranyle de qualité nucléaire — Méthode gravimétrique

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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.

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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 7476 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 7476:1990), which has been technically revised.

Nuclear fuel technology — Determination of uranium in uranyl nitrate solutions of nuclear grade quality — Gravimetric method

1 Scope

This International Standard specifies a precise and accurate gravimetric method for determining the mass fraction of uranium in uranyl nitrate solutions of nuclear grade quality containing more than 100 g/kg of uranium.

Non-volatile impurities influence the accuracy of the method.

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 10980:1995, *Validation of the strength of reference solutions used for measuring concentrations*

3 Principle

Conversion of uranyl nitrate to uranium octoxide (U_3O_8) by ignition in air to constant mass at 900 °C ± 10 °C.

Calculation of the mass fraction of uranium in the sample using a gravimetric conversion factor which depends on the isotopic composition of the uranium. Determination of the isotopic composition by mass spectrometry.

NOTE Conversion to U_3O_8 can also be performed at 875 °C ± 25 °C but, in any case, the temperature must not exceed 910 °C.

4 Interferences

Non-volatile impurities interfere; they shall be determined by an appropriate technique, such as emission spectroscopy, atomic absorption spectroscopy or mass spectrometry, the appropriate correction being applied. If the total mass fraction of non-volatile impurities is greater than 0,1 %, the overall uncertainty of the method depends on the accuracy of the measurements of impurities.

Uranium octoxide (U_3O_8) ignited to 900 °C is not normally hygroscopic. However, after a lengthy exposure to moist air, a mass increase of about 0,1 % to 0,2 % can be observed.

The experimental conditions specified assume ignition in air at standard atmospheric pressure. For any laboratory at a high altitude, the oxide formed may differ slightly from the stoichiometric state, unless the air pressure is controlled or the temperature is adjusted.

5 Reagents

Use only reagents of recognized analytical grade and distilled or de-ionized water.

5.1 Ashless filter-paper powder or **ashless tablets** or **alternatively sulfuric acid**, concentrated, diluted to a volume fraction of 50 %.

5.2 Concentrated nitric acid, $c(\text{HNO}_3) \approx 16$ mol/l $(\rho = 1{,}42$ g/ml$)$.

5.3 Nitric acid solution, $c(\text{HNO}_3) = 3$ mol/l.

5.4 Standard uranyl nitrate solution

A uranium standard solution containing about 100 g/kg is prepared by dissolving accurately known amounts of a certified reference material such as NBL-CRM-112-A, or CETAMA-MU2 metal with a uranium concentration certified with an accuracy of 0,05 % or better in accordance with ISO 10980:1995, Annex A.

6 Apparatus

Normal laboratory equipment and the following.

6.1 Platinum crucibles, of capacity between 15 ml and 30 ml.

6.2 Weighing burette.

6.3 Infrared heating lamp.

6.4 Hotplate.

6.5 Muffle furnace, able to be controlled at 900 °C ± 10 °C, with a calibrated thermocouple.

NOTE A muffle furnace able to be controlled at 875 °C ± 25 °C may also be used in accordance with the Note in Clause 3. In this case, the temperature of the furnace is easier to control.

6.6 Desiccator.

6.7 Analytical balance, sensitive to 0,05 mg.

7 Procedure

7.1 Ignite a platinum crucible (6.1) for 10 min at 900 °C. Cool in the desiccator (6.6) until ambient temperature is reached (1 h is recommended) and then weigh the crucible to ± 0,1 mg.

Repeat the ignition and cooling cycle until the mass remains constant to within ± 0,1 mg; record this mass as m_1.

7.2 Weigh out between 3 g and 15 g of sample solution containing about 1 g of uranium from the weighing burette (6.2) into the crucible. Record the masses (before sample delivery m_2; after sample delivery m_3) to within ± 0,1 mg.

7.3 Evaporate carefully to a volume of between about 1 ml and 2 ml on the hotplate (6.4) or under the infrared lamp (6.3) to avoid spattering of the sample.

7.4 Add sufficient ashless filter-paper powder (5.1) to absorb the liquid. Continue the evaporation to dryness.

NOTE The powder helps to avoid spattering when the uranyl nitrate decomposes. As an alternative, for use if the sample contains much free nitric acid, 2 ml of the sulfuric acid solution (5.1) may be added in place of the filter-paper powder, as uranyl sulfate decomposes without spattering.

WARNING — Do not use both filter-paper powder and sulfuric acid, to avoid the possible formation of nitro-cellulose.

7.5 Place the crucible and dried contents in the muffle furnace (6.5) at about 100 °C and raise the temperature to 900 °C over a period of 30 min.

7.6 Heat the sample in air with the muffle furnace (6.5) and keep it steadily for 1 h within the temperature range 890 °C to 910 °C. Cool the crucible in the desiccator (6.6) until ambient temperature is reached (1 h is recommended) and then weigh the crucible to ± 0,1 mg.

Repeat the ignition and cooling cycle in the same condition as above until the mass remains constant to within ± 0,1 mg and record this mass as m_4.

NOTE Alternatively, a temperature of 875 °C ± 25 °C may be substituted for 900 °C in this procedure.

7.7 Determine the non-volatile impurities which may be present in the ignited uranium octoxide (U_3O_8), using an appropriate technique.

7.8 Empty the platinum crucible and clean by boiling in the nitric acid solution (5.3). Clean the weighing burette with concentrated nitric acid (5.2) before re-use.

8 Expression of results

8.1 Calculate the mass, m_s, in grams, of sample solution taken using the formula

$$m_\text{s} = m_2 - m_3$$

where

m_2	is the mass, in grams, of the weighing burette before sample delivery;
m_3	is the mass, in grams, of the weighing burette after sample delivery.

8.2 Calculate the mass, m_o, in grams, of oxide formed using the formula

$$m_\text{o} = m_4 - m_1$$

where

m_1	is the mass, in grams, of the empty crucible (clean and ignited to constant mass);
m_4	is the mass, in grams, of the crucible plus oxide.

NOTE Depending on the context in which the results are to be used, masses m_s and m_4 may require standard corrections for air buoyancy effects.

8.3 Calculate the total mass of impurities (in the ignited state), m_i, in the sample using the formula

$$m_\text{i} = 10^{-6} \times m_\text{s} \sum_n w_n C_n$$

where

m_s	is the mass, in grams, of the sample solution taken (see 8.1);
w_n	is the mass fraction of impurity element n, in micrograms per gram of sample solution (see 7.7);
C_n	is the gravimetric conversion factor for element n. Gravimetric conversion factors for common impurities are given in Annex A.

8.4 Calculate the corrected mass of U_3O_8, m_c, in grams, using the formula

$$m_\text{c} = m_\text{o} - m_\text{i}$$

where

m_o is the original mass, in grams, of U_3O_8;

m_i is the total mass, in grams, of impurities (see 8.3).

8.5 Calculate the gravimetric conversion factor for uranium, C_U, using the formula

$$C_\text{U} = \frac{3A_\text{r}(\text{U})}{3A_\text{r}(\text{U}) + 8A_\text{r}(\text{O})}$$

where

$A_\text{r}(\text{O}) = 15{,}999\,4$ is the relative atomic mass of oxygen;

$A_\text{r}(\text{U})$ is the mean relative atomic mass of uranium calculated using the expression

$$A_\text{r}(\text{U}) = \sum a_i A_i$$

where

a_i is the atom fraction of isotope i given by mass spectrometry measurements;

A_i is the relative atomic mass of isotope i (see Table 1).

Table 1

Isotope i	A_i
234	234,040 9
235	235,043 9
236	236,045 6
238	238,050 8

NOTE $A_\text{r}(\text{U})$ can also be calculated using the following expression:

$$A_\text{r}(\text{U}) = \frac{1}{\sum \left(\frac{w_i}{A_i}\right)}$$

where w_i is the mass fraction of the uranium isotopes ${}^{i}\text{U}$ in the sample, determined by mass spectrometry.

Mass fractions, w_i, can be derived from atom fractions:

$$w_i = \frac{a_i A_i}{\sum \left(\frac{w_i}{A_i}\right)}$$

8.6 Calculate the mass fraction of uranium in the sample, w_U, in grams per kilogram of sample solution, using the formula

$$w_\text{U} = \frac{10^3 \times m_\text{c} C_\text{U}}{m_\text{s}}$$

9 Procedure validation and quality control

The accuracy of the procedure should be verified regularly by analysing accurately weighed aliquots of about 10 g of the standard uranyl nitrate solution (5.4). If the bias of the average results of at least four replicate analyses exceeds 0,1 %, the conditions of the ignition must be adjusted to eliminate this bias.

The repeatability of the procedure is checked by performing at least two independent analyses of each sample. The results of duplicate analyses should not differ by more than 0,15 %.

10 Repeatability

The coefficient of variation for single determinations is about 0,05 % under optimum conditions.

Given a coefficient of variation of 0,05 % for repeatability in optimum conditions (no impurities), the overall coefficient of variation (including correction for impurities) remains less than 0,1 % if a maximum impurity amount of

- 0,10 % is determined with a coefficient of variation of about 50 % (detection limits);
- 0,25 % is determined with a coefficient of variation of about 25 % (semi-quantitative analysis);
- 0,65 % is determined with a coefficient of variation of about 10 % (quantitative trace analysis).

11 Accuracy and bias

The bias of the method is normally, with air-thrust correction on the mass of sample solution, less than 0,1 % when the uranium contains less than 0,1 % of total non-volatile impurities and less than 0,05 % of any one impurity.

NOTE If air-thrust correction is not applied to the mass of the sample solution, the bias is about 0,1 %.

12 Test report

The test report shall include the following information:

a) identification of the sample;

b) the reference of the method used;

c) the results and method of expression used (unit of the result);

d) any unusual features noted during the test;

e) any operations not included in this International Standard;

f) a note of whether or not buoyancy corrections have been applied (see Note to 8.2).

Annex A

(normative)

Gravimetric conversion factors for non-volatile impurities

Impurity	Probable form of impurity	Conversion factor, C_n
Ag	Ag	1,00
Al	Al_2O_3	1,89
Am	AmO_2	1,13
B	B_2O_3	3,22
Ba	BaO	1,12
Be	BeO	2,78
Bi	Bi_2O_3	1,11
Ca	CaO	1,40
Cd	Cd	1,00
Co	CoO	1,27
Cr	Cr_2O_3	1,46
Cu	Cu	1,00
Fe	Fe_3O_4	1,38
K	K_2O	1,21
Mg	MgO	1,66
Mn	Mn_3O_4	1,39
Na	Na_2O	1,35
Ni	Ni_2O_3	1,40
P	P_2O_5	2,29
Pb	PbO	1,07
Rare earth elements	M_2O_3	1,16
Sb	Sb_2O_3	1,20
Si	SiO_2	2,14
Sn	SnO	1,13
Ta	Ta_2O_5	1,22
Th	ThO_2	1,14
Ti	TiO_2	1,67
V	V_2O_5	1,78
W	WO_3	1,26
Zn	ZnO	1,24
Zr	ZrO_2	1,35

NOTE These values are based on the best information available, with account being taken of the ignition and cooling conditions, and the effects of the uranium oxide matrix. The final chemical form is not well established; the total mass fraction of non-volatile impurities is therefore limited to 0,1 % in order to maintain the precision of the method.

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