INTERNATIONAL STANDARD

ISO 8425

Second edition
2013-12-01

Nuclear fuel technology — Determination of plutonium in pure plutonium nitrate solutions — Gravimetric method

Technologie du combustible nucléaire — Détermination du plutonium dans les solutions de nitrate de plutonium pur — Méthode gravimétrique

Reference number
ISO 8425:2013(E)

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Published in Switzerland

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Foreword

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The committee responsible for this document is ISO/TC 85, *Nuclear energy, nuclear technologies, and radiological protection*, Subcommittee SC 5, *Nuclear fuel cycle*.

This second edition cancels and replaces the first edition (ISO 8425:1987).

Introduction

This International Standard specifies a precise and accurate method for determining the concentration of plutonium in pure plutonium nitrate solutions and reference solutions.

This method is based on an oxidation of the plutonium followed by weighing.

Respecting certain conditions, the overall standard deviation on a single determination (gravimetric determination and impurities correction) can be below 0,1 %.

Nuclear fuel technology — Determination of plutonium in pure plutonium nitrate solutions — Gravimetric method

1 Scope

This International Standard specifies a precise and accurate gravimetric method for determining the concentration of plutonium in pure plutonium nitrate solutions and reference solutions, containing between 100 g and 300 g of plutonium per litre, in a nitric acid medium.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. 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*

3 Principle

The principle is as follows:

a) treatment of a weighed portion of the plutonium nitrate solution with sulphuric acid and evaporation to dryness;

b) decomposition of the plutonium sulfate which is converted to oxide by heating in air;

c) heating in air of the oxide at 1 200 °C to 1250 °C and weighing as stoichiometric plutonium dioxide, which is stable and non-hygroscopic;

d) calculation of the plutonium content using a gravimetric conversion factor which depends slightly on the isotopic composition of the plutonium.

If the latter is not known, it shall be measured, usually by mass spectrometry.

4 Interferences

All non-volatile impurities interfere. If the mass fraction of the impurities is greater than 0,05 %, a correction shall be applied. If the mass fraction of the total non-volatile impurities is up to 0,1 %, the overall uncertainty of the measurement will depend on the precision of the impurities determination. There is no interference from up to at least 1 000 $\mu g \cdot g^{-1}$ of phosphorus (present as phosphate) which is lost during the sulphuric acid treatment. The chloride and fluoride contents of the sample should not exceed 25 $\mu g \cdot g^{-1}$.

5 Reagents

5.1 Deionised water, with at least grade 1, in accordance with ISO 3696.

5.2 Sulphuric acid, solution with volume fraction of 50 %.

While stirring, cautiously add 500 ml of the analytical reagent quality sulphuric acid (ρ = 1,84 $g \cdot ml^{-1}$) to 500 ml of cold distilled or deionised water (5.1). Allow to cool.

6 Apparatus

Normal laboratory equipment for a plutonium laboratory.

6.1 Platinum crucibles, approximately 8 ml in capacity.

6.2 Polythene weighing burettes.

6.3 Furnace, in an air atmosphere glove box, with a temperature range from 300 °C to 1 250 °C.

6.4 Semi-micro balance, in an air atmosphere glove box, to weigh 25 g with an accuracy of ±0,1 mg; the balance and weights should be certified or calibrated to ±0,05 mg.

6.5 Radiant heater, in a glove box.

6.6 Desiccators.

7 Procedure

7.1 Heat a clean crucible (6.1) for 1 h at 1 200 °C to 1 250 °C. Cool in a desiccator for 20 min and then in the balance (6.4) for 5 min. Weigh to within ±0,1 mg, repeating the heating until the mass remains constant to within ±0,1 mg.

7.2 Weigh out 1 g to 2 g of the sample solution containing 0,2 g to 0,4 g of plutonium from a polythene weighing burette (6.2) into the crucible. Record the masses (before the sample delivery, m_2, and after the sample delivery, m_3) to within ±0,1 mg.

In order to avoid errors due to thermal effects, the weighing burette shall be allowed to adjust to the balance temperature before each weighing.

7.3 Add 1,0 ml of the sulphuric acid solution (5.2) to the crucible and swirl gently to mix.

7.4 Evaporate the solution under a radiant heater (6.5), by heating gently until sulphuric acid fumes evolve and then more strongly until a dry residue has been obtained and the fuming has practically ceased.

NOTE Plutonium nitrate is converted to plutonium sulphate as the nitrate compound spatters during the evaporation to dryness.

7.5 Without delay, transfer the crucible and dried plutonium sulfate to the furnace (6.3) set at about 300 °C. Maintain this temperature for about 15 min. Then raise the temperature by 5 °C to 10 °C per minute to about 850 °C at which temperature the plutonium sulfate will have decomposed.

7.6 Increase the temperature to 1 200 °C to 1 250 °C and ignite at this temperature for 1 h.

NOTE Alternatively, the operations in 7.4, 7.5, and 7.6 can be done in a temperature-programmed furnace with controlled air flow.

7.7 Cool the crucible and oxide in a desiccator (6.6) for 15 min and then in the balance for 5 min. Weigh to within ±0,1 mg.

7.8 Heat again at 1 200 °C to 1 250 °C for periods of 1 h (7.6), cool and weigh as in 7.7 until the mass remains constant to within ±0,05 mg. Record this mass as m_4.

7.9 Perform an isotopic analysis of the plutonium in a separate portion of the sample to calculate its mean relative atomic mass, A_r(Pu).

7.10 Perform an analysis of the impurities that are not volatile at 1 200 °C, usually by an emission spectrometric method or a mass spectrometric method, calculating the results for each impurity element as micrograms per gram of the sample solution.

8 Expression of results

8.1 Method of calculation

8.1.1 Calculate the mass of the sample solution taken, m_s, in grams, using Formula (1):

$$m_s = m_2 - m_3 \quad (1)$$

where

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

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

8.1.2 Calculate the mass of the oxide formed, m_0, in grams, using Formula (2).

$$m_0 = m_4 - m_1 \quad (2)$$

where

m_4 is the mass, in grams, of the crucible plus oxide;

m_1 is the mass, in grams, of the empty crucible.

Depending on the context in which the results are to be used, masses m_s and m_0 can require standard corrections for air buoyancy effects.

8.1.3 Calculate the total mass of impurities (in the heated state), I_0, in grams, in the sample using Formula (3).

$$I_0 = 10^{-6} \times m_s \times \sum_n (I_n C_n) \quad (3)$$

where

m_s is the mass of the sample solution taken, in grams (see 8.1.1);

I_n is the quantity of the impurity element, n, in micrograms per gram of the sample solution (see 7.10);

C_n is the gravimetric conversion factor for the element n on heating at 1 200 °C (see Annex A for the gravimetric conversion factors for common impurities).

8.1.4 Calculate the mass of pure PuO_2 in the oxide, m_c, in grams, using Formula (4).

$$m_c = m_0 - I_0 \quad (4)$$

where

I_0 is the total mass of impurities, in grams (see 8.1.3).

8.1.5 Calculate the gravimetric conversion factor for this batch of plutonium, C_{Pu}, using Formula (5).

$$C_{Pu} = \frac{A_r(Pu)}{A_r(Pu)+2A_r(O)} \quad (5)$$

where

$A_r(0)$ (= 15,999 4) is the relative atomic mass of oxygen;

$A_r(Pu)$ is the mean relative atomic mass of plutonium calculated using Formula (6).

$$A_r(Pu) = \frac{1}{\frac{m_{238}}{238{,}050}+\frac{m_{239}}{239{,}052}+\frac{m_{240}}{240{,}054}+\frac{m_{241}}{241{,}057}+\frac{m_{242}}{242{,}059}+\frac{m_{244}}{244{,}064}} \quad (6)$$

where m_{238}, m_{239}, etc. are the mass fractions of the plutonium isotopes ^{238}Pu, ^{239}Pu, etc. in the sample, determined by mass spectrometry (see 7.9).

8.1.6 Calculate the plutonium content of the sample, Pu, in grams per kilogram of the sample solution, using Formula (7).

$$Pu = \frac{10^3 \times m_c \times C_{Pu}}{m_s} \quad (7)$$

8.2 Repeatability

The standard deviation for a single gravimetric determination is about 0,05 %.

In order that the standard deviation of the impurity correction factor stands below 0,1 %, the impurities shall be measured to the following:

— with a standard deviation of 50 % (detection limit), up to 1 000 $\mu g \cdot g^{-1}$ of impurities;

— with a standard deviation of 25 % (semiquantitative analysis), up to 2 500 $\mu g \cdot g^{-1}$ of impurities;

— with a standard deviation of 10 % (quantitative analysis), up to 6 500 $\mu g \cdot g^{-1}$ of impurities.

In these conditions, the overall standard deviation on a single determination (gravimetric determination and impurities correction) is below 0,1 %.

8.3 Systematic errors

The systematic errors due to weighing have a coefficient of variation not greater than 0,014 %.

Non-stoichiometry of the plutonium oxide is a potential source of bias. The coefficient of variation of this factor is expected to be less than 0,1 %.

Non-volatile impurities are responsible for three further possible sources of bias:

a) calibration errors in the impurity analysis;

b) uncertainties in the impurity conversion factors;

c) impurities that are not corrected for because they are neither measured nor detected (sources of positive bias).

These sources can cause a systematic error of up to 20 % of the total impurity concentration.

9 Test report

The test report shall include the following information:

a) the identification of the sample;

b) a reference to the method used;

c) the results of the measurement and the associated overall uncertainties, impurities percentage, and method of expression used;

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 8.1.2).