INTERNATIONAL STANDARD

ISO
8425

First edition
1987-03-01

INTERNATIONAL ORGANIZATION FOR STANDARDIZATION
ORGANISATION INTERNATIONALE DE NORMALISATION
МЕЖДУНАРОДНАЯ ОРГАНИЗАЦИЯ ПО СТАНДАРТИЗАЦИИ

Determination of plutonium in pure plutonium nitrate solutions — Gravimetric method

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

Reference number
ISO 8425 : 1987 (E)

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.

Draft International Standards adopted by the technical committees are circulated to the member bodies for approval before their acceptance as International Standards by the ISO Council. They are approved in accordance with ISO procedures requiring at least 75 % approval by the member bodies voting.

International Standard ISO 8425 was prepared by Technical Committee ISO/TC 85, *Nuclear energy*.

Users should note that all International Standards undergo revision from time to time and that any reference made herein to any other International Standard implies its latest edition, unless otherwise stated.

Printed in Switzerland

Determination of plutonium in pure plutonium nitrate solutions — Gravimetric method

1 Scope and field of application

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 and 300 g of plutonium per litre, in a nitric acid medium.

2 Principle

Treatment of a weighed portion of the plutonium nitrate solution with sulfuric acid and evaporation to dryness. Decomposition of the plutonium sulfate which is formed to oxide by heating in air. Ignition in air of the oxide at 1 200 to 1 250 °C and weighing as stoichiometric plutonium dioxide, which is stable and non-hygroscopic.

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.

3 Interferences

All non-volatile impurities interfere. If the impurity content is greater than 0,05 %, a correction shall be applied. If this correction exceeds about 0,5 %, the accuracy of the impurity measurements may limit the overall performance of the method. There is no interference from up to at least 1 000 ppm of phosphorus (present as phosphate) which is lost during the sulfuric acid treatment. The chloride and fluoride contents of the sample should not exceed 25 ppm.

4 Reagents

4.1 Sulfuric acid, solution at 50 % (V/V).

While stirring, cautiously add 500 ml of analytical reagent quality sulfuric acid (ϱ = 1,84 g/ml) to 500 ml of cold distilled or deionized water. Allow to cool.

5 Apparatus

Normal laboratory equipment for a plutonium laboratory, and

5.1 Platinum crucibles, approximately 8 ml in capacity.

5.2 Polythene weighing burettes.

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

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

5.5 Radiant heater, in a glove box.

6 Procedure

6.1 Ignite a clean crucible (5.1) for 1 h at 1 200 to 1 250 °C. Cool in a desiccator for 20 min and then in the balance (5.4) for 5 min; weigh to within ± 0,1 mg, repeating the ignition until the mass remains constant to within 0,1 mg.

6.2 Weigh out 1 to 2 g of sample solution containing 0,2 to 0,4 g plutonium from a polythene weighing burette (5.2) into the crucible. Record the masses (before sample delivery m_2, after sample delivery m_3) to within ± 0,1 mg.

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

6.3 Add 1,0 ml of the sulfuric acid solution (4.1) to the crucible and swirl gently to mix.

6.4 Evaporate the solution under a radiant heater (5.5), by heating gently until sulfuric acid fumes are evolved and then more strongly until a dry residue has been obtained and fuming has practically ceased.

NOTE — Plutonium nitrate is converted to plutonium sulfate as the nitrate compound spatters on evaporation to dryness.

6.5 Without delay, transfer the crucible and dried plutonium sulfate to the furnace (5.3) set at about 300 °C. Maintain this temperature for about 15 min. Then raise the temperature by 5 to 10 °C per minute to about 850 °C at which temperature the plutonium sulfate will have decomposed.

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

NOTE — Alternatively, the operations in 6.4, 6.5 and 6.6 can be done in a temperature-programmed furnace with controlled air flow.

6.7 Cool the crucible and oxide in a desiccator for 15 min and then in the balance for 5 min; weigh to within ± 0,1 mg.

6.8 Reignite at 1 200 to 1 250 °C for periods of 1 h, cool and weigh as in 6.7 until the mass remains constant to within 0,05 mg. Record this mass as m_4.

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

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

7 Expression of results

7.1 Method of calculation

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

$$m_s = m_2 - m_3$$

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.

7.1.2 Calculate the mass of oxide formed, m_0, in grams, using the formula

$$m_0 = m_4 - m_1$$

where

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

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

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

7.1.3 Calculate the total mass of impurities (in the ignited state), I_0, in the sample using the formula

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

where

m_s is the mass of the sample solution taken (see 7.1.1);

I_n is the quantity of impurity element, n, in micrograms per gram of sample solution (see 6.10);

C_n is the gravimetric conversion factor for element n on ignition at 1 200 °C. Gravimetric conversion factors for common impurities are given in the annex.

7.1.4 Calculate the mass of pure PuO_2 in the oxide, m_c, using the formula

$$m_c = m_0 - I_0$$

where I_0 is the total mass of impurities (see 7.1.3).

7.1.5 Calculate the gravimetric conversion factor for this batch of plutonium, C_{Pu}, using the formula

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

where

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

$A_r(Pu)$ is the mean relative atomic mass of plutonium calculated using the expression

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

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 6.9.)

7.1.6 Calculate the plutonium content of the sample, Pu, in grams per kilogram of sample solution, using the formula

$$Pu = \frac{10^3 \times m_c \times C_{Pu}}{m_s}$$

7.2 Repeatability

The coefficient of variation for a single determination on a typical plutonium product solution (total impurities less than 0,05 %) is about 0,05 %. If the total impurity concentration is less than 0,5 %, measured with 20 % relative precision, the coefficient of variation of the total random error of a single determination is expected to lie in the range from 0,05 to 0,15 %, depending on the purity.

7.3 Systematic errors

7.3.1 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 %.

7.3.2 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) the impurities that are not corrected for, because they are neither measured nor detected, are a source of positive bias.

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

8 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;

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 7.1.2).

Annex

Gravimetric conversion factors for non-volatile impurities

(This annex forms an integral part of the standard.)

Impurity	Probable form of impurity	Conversion factor, C_n
Ag	Ag	1,00
Al	Al_2O_3	1,89
Am	AmO_2	1,13
Ba	$BaSO_4$	1,70
B	B_2O_3	3,22
Be	BeO	2,78
Bi	Bi_2O_3	1,11
Ca	$CaSO_4$	3,40
Cd	Cd	1,00
Co	CoO	1,27
Cr	Cr_2O_3	1,46
Cu	Cu	1,25
Fe	Fe_3O_4	1,38
K	K_2SO_4	2,23
Mg	MgO	1,66
Mn	Mn_3O_4	1,39
Rare earth elements	M_2O_3	1,16
Na	Na_2SO_4	3,09
Ni	NiO_3	1,40
Np	NpO_2	1,13
P	P_2O_5	2,29
Pb	PbO	1,07
Sb	Sb_2O_3	1,26
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
U	U_3O_8	1,18
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 conversion to sulfate, the ignition and cooling conditions, and the effects of the plutonium oxide matrix.

This page intentionally left blank

UDC 661.879.94 : 621.039 : 543.21 : 546.799.4

Descriptors : nuclear energy, nuclear fuels, plutonium inorganic compounds, chemical analysis, determination of content, plutonium, gravimetric analysis.

Price based on 4 pages