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Nuclear energy — Nuclear fuel technology — Determination of plutonium in nitric acid solutions by spectrophotometry

Énergie nucléaire — Technologie du combustible nucléaire — Détermination du plutonium dans les solutions d'acide nitrique par spectrophotométrie

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 85, *Nuclear energy, nuclear technologies, and radiological protection*, Subcommittee SC 5, *Nuclear installations, processes and technologies*.

This third edition cancels and replaces the second edition (ISO 9463:2009), which has been technically revised. The main change compared to the previous edition is the use of silver (II) oxide powder for the plutonium valence adjustment.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

INTERNATIONAL STANDARD **ISO 9463:2019(E)**

Nuclear energy — Nuclear fuel technology — Determination of plutonium in nitric acid solutions by spectrophotometry

1 Scope

This document specifies an analytical method by spectrophotometry, for determining the plutonium concentration in nitric acid solutions, with spectrophotometer implemented in hot cell and glove box allowing the analysis of high activity solutions. Commonly, the method is applicable, without interference, even in the presence of numerous cations, for a plutonium concentration higher than 0,5 mg·l^{-1} in the original sample with a standard uncertainty, with coverage factor $k = 1$, less than 5 %.

The method is intended for process controls at the different steps of the process in a nuclear fuel reprocessing plant or in other nuclear facilities.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements 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 1042, *Laboratory glassware — One-mark volumetric flasks*

3 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at http://www.electropedia.org/

4 Principle

Plutonium is quantitatively oxidized to the hexavalent state either with cerium (IV) or with silver oxide. The excess of silver oxide is destroyed by the addition of sulfamic acid. The optical density of the plutonium (VI) (PuO_2^{2+}) absorption peak at the wavelength of 831 nm is then measured on a spectrophotometer. The result is obtained by comparison to a calibration performed under similar conditions (with the same nitrate content).

5 Chemical conditions

5.1 Stability of Pu(VI)

Pu(VI) is very stable under the operating conditions of the method over the range 2 mol·l^{-1} < $c(H^+)$ < 5 mol·l^{-1}.

5.2 Rate of oxidation of Pu(IV) to Pu(VI)

The rate of oxidation by Ce(IV) decreases as the acidity increases. With the reagent quantities stated in the method, the oxidation is complete in 2 min or more in 2 mol·l^{-1} or 3 mol·l^{-1} nitric acid.

As an example, the oxidation of Pu(IV) in 4 mol·l^{-1} nitric acid is complete in between 10 min and 15 min when the Ce/Pu initial ratio is higher than 20[2].

With silver oxide, the oxidation is very fast, much faster than with Ce(IV).

In addition, the Ag^{2+}/Ag^{+} redox potential is higher than that of Ce^{4+}/Ce^{3+} and is better adapted to cope with the presence of organic traces in solution.

On the other hand, cerium presents the advantage to be stable in sulfuric acid so that it can be added as a precise quantity in solution.

5.3 Destruction of the excess oxidant

With cerium the excess reagent and product Ce(III), does not interfere (no absorption above 450 nm) and does not need to be destroyed[2].

With silver oxide as oxidant, the excess reagent shall be destroyed by reaction with a small excess of sulfamic acid or rise of temperature[2].

5.4 Comparison of Ce(IV) and Ag(II)

As regards Pu(IV) oxidation into Pu(VI), the reactivity and use of Ce(IV) and Ag(II) are compared in Table 1, in order to guide the analyst in the selection of the best reactant for oxidation.

Table 1 — Comparison of Ce(IV) and Ag(II)

Oxidizer	Ag(II)	Ce(IV)
Introduction of reactants	–	+
Spectral interferences	–	+
Oxidizing power	++	+
Oxidation kinetics	++	–
Oxidizer excess destruction	Sulfamic acid or rise of temperature	Not necessary
Operating temperature	Room temperature	

5.5 Molar extinction coefficient of Pu(VI)

The nominal molar extinction coefficient[1] i.e. the molar attenuation coefficient of Pu(VI) in nitric acid solution varies between 400 l·mol^{-1}·cm^{-1} and 500 l·mol^{-1}·cm^{-1}[3], with a very narrow full width at half maximum (FWHM) of about 4 nm.

The molar extinction coefficient and therefore absorbance depends upon a number of parameters, for example:

- **The nitrate ion concentration**. The decrease in molar extinction coefficient becomes more pronounced at higher nitrate levels. At about 3 mol·l^{-1} nitrate, an increase of 0,1 mol·l^{-1} in the total nitrate content causes a decrease of about 0,7 % in the molar extinction coefficient.
- **The acidity**. This change is generally less than 0,1 % for a free acid change of 0,1 mol·l^{-1}. Thus the influence of free acidity is an order of magnitude less than that of the nitrate content.

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[1] The molar extinction coefficient is the absorbance of light by a chemical species at a given wavelength and for a 1 cm light path. It is an intrinsic property of the species. The SI unit of molar attenuation coefficient is the square metre per mole (m^{2}·mol^{-1}), but in practice, it is usually taken as the mol^{-1}·cm^{-2} or the l.mol^{-1}·cm^{-1}.

- **The temperature**. The decrease in molar extinction coefficient is about 0,5 % per degree Celsius.

6 Reagents

6.1 General

All reagents shall be of analytical grade.

This procedure requires that measurements are made in nitric acid medium as this permits either Ce(IV) or silver oxide to be used as oxidant and is convenient for most applications. Commonly the sample is diluted into 3 mol·l^{-1} nitric acid. It is acceptable to use Ce(IV) as oxidant at low acidities and silver oxide as oxidant at high acidities provided that the concentration of the nitric acid used for calibration is similarly adjusted.

6.2 Common reagents for methods using silver oxide or cerium as oxidant

6.2.1 Nitric acid, $c(HNO_3)$ = (3 ± 0,05) mol·l^{-1}. It can be prepared by dilution of concentrated nitric acid in water (6.2.2).

6.2.2 Water, complying with grade 3 of ISO 3696.

6.2.3 Reference solution, plutonium in solution in nitric acid with a nitrate concentration close to that of the sample to analyse.

The recommended minimum plutonium concentration is 5 mg·l^{-1}. For instance the plutonium concentration can be about 20 mg·l^{-1}.

The plutonium reference solution used for the analysis can be prepared by dilution of a concentrated reference mother plutonium solution.

6.3 Reagents for method using silver oxide as oxidant

6.3.1 Sulfamic acid $c(NH_2SO_3H)$ = 0,5 mol·l^{-1} solution in water.

It can be prepared by dissolution of 48,5 g NH_2SO_3H in 1 l of water:

- in a beaker, weigh 48,5 g of NH_2SO_3H;
- add 800 ml of water (6.2.2);
- homogenize;
- transfer the solution into a 1 l volumetric flask;
- adjust the volume with water (6.2.2).

6.3.2 Silver (II) oxide (AgO) powder, fine black powder commercially available.

The protocol to prepare AgO, if AgO powder is not available, is given in Annex A.

6.4 Reagents for method using Ce(IV) as oxidant

6.4.1 Nitric acid, $c(HNO_3)$ = 1 mol·l^{-1}.

6.4.2 Ceric ammonium nitrate, $(NH_4)_2Ce(NO_3)_6$, orange-red, water-soluble cerium salt.

6.4.3 Ce(IV), $c(\mathrm{Ce}^{4+}) = 0{,}4\ \mathrm{mol{\cdot}l^{-1}}$.

This reagent can be prepared in a number of ways. One procedure can be as follows.

Dissolve 219,3 g of ceric ammonium nitrate $[(\mathrm{NH_4})_2\mathrm{Ce}(\mathrm{NO_3})_6]$ (6.4.2) in 600 ml of 1 $\mathrm{mol{\cdot}l^{-1}}$ nitric acid (6.4.1) and dilute to 1 l with water (6.2.2).

Other preparation procedures can be acceptable. Depending on the needed volume of solution, the mass and volume can be reduced or increased, e.g. both can be reduced by a factor of 10 for a 100 ml volume preparation.

7 Apparatus

Usual nuclear laboratory equipment.

7.1 Spectrophotometer, with spectral slit width of 2 nm or better, double-beam grating spectrophotometer, or equivalent, designed for measurements on fully contained high beta-gamma solutions and having, as far as possible, the following features.

a) Capable of performing absorbance measurements from 0,001 to 1,5.

b) Stable baseline.

c) A measurement spectral range of 800 nm to 860 nm shall be included. Usually, spectrometers with a minimum capability of 190 nm and a maximum capability of 1 100 nm, or greater which allow the analysis of other element or the study of potential method interferences are convenient.

7.2 Measurement cell, a static or a flow cell. Main characteristic is the optical path in the cell. Common cell have an optical path of 1 cm but it can be greater to enhance sensitivity (e.g. 3 cm or 4 cm).

7.3 Volumetric flasks, volume 50 ml, complying with the requirements of ISO 1042.

7.4 Pipette, volume 5 ml or less, with a sampling uncertainty of ± 1 % or less.

8 Test procedure

The following test procedure is given as an example. The varying concentrations or/and volumes, in particular concentration and/or volume of reference solution, flask volume and other equipment or conditions, may be modified if needed.

The spectrophotometer shall be calibrated with a plutonium calibration solution to determine the relationship between plutonium concentration and absorbance.

The frequency of the calibration is chosen in accordance with the required accuracy of the analysis.

8.1 Preparation of the different solutions

8.1.1 Plutonium calibration solution

8.1.1.1 Oxidation by silver oxide

The plutonium calibration solution can be prepared as follows.

In a 50 ml volumetric flask (7.3),

— introduce with a pipette (7.4) the desired volume, V_{10}, of the plutonium reference solution (6.2.3), commonly V_{10} is 5 ml,

- add a few ml of the 3 mol·l^{-1} nitric acid solution (6.2.1) to clean the inner surface of the flask,
- add the minimum amount (a few grain) of silver oxide powder (6.3.2) to give a persistent dark colour,
- stir,
- keep reacting for 5 min while stirring,
- check that the solution is still a dark colour,
- add, with a burette, 2 drops of sulfamic acid (6.3.1),

  NOTE The addition of an excess of sulfamic acid will significantly reduce the molar extinction coefficient therefore the absorbance (as an example, the addition of 12 drops of sulfamic acid reduces the absorbance by approximately 0,8 %).

- homogenize until the solution becomes colourless, which shows that the excess of AgO has been consumed; if the excess of AgO is too high, the fading of the colour of the solution from dark to colourless will go through a brown colour. In this case, wait 2 min or 3 min more,
- adjust the volume of the flask with 3 mol·l^{-1} nitric acid (6.2.1).

In order to keep the plutonium at the hexavalent state, it is mandatory to perform the analysis within a few hours following the addition of the silver oxide powder. Otherwise, repeat the valence adjustment by adding a few grains of silver oxide powder (6.3.2).

8.1.1.2 Oxidation by Ce(IV)

The plutonium calibration solution can be prepared as follows.

In a 50 ml volumetric flask (7.3),

- introduce with a pipette (7.4) the desired volume, V_{10}, of the plutonium reference solution (6.2.3), commonly V_{10} is 5 ml,
- add a few ml of the 3 mol·l^{-1} nitric acid solution (6.2.1) to clean the inner surface of the flask,
- add 5 ml of the cerium (IV) solution (6.4.3),
- stir,
- keep reacting 5 min while stirring,
- adjust the volume of the flask with 3 mol·l^{-1} nitric acid (6.2.1).

8.1.2 Sample solutions

8.1.2.1 Oxidation by silver oxide

The solution to analyse can be prepared as follows.

In a 50 ml volumetric flask (7.3),

- introduce with a pipette (7.4) the desired volume, V_1, of solution to analyse.

  The analyst shall use available information to estimate the concentration of the sample and adjust the volume V_1, of sample (solution to analyse) so that the final concentration is likely to be less than the calibration solution. If the result of the measurement shows that the sample concentration is higher than expected and is above the concentration of the calibration solution (prepared in 8.1.1.1), a new sample dilution shall be made to ensure that the concentration of the injected solution is less than the concentration of the calibration solution.