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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.

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.

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), $c(Ce^{4+})$ = 0,4 mol·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 $[(NH_4)_2Ce(NO_3)_6]$ (6.4.2) in 600 ml of 1 mol·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.

— Add a few ml of 3 mol·l^{-1} nitric acid (6.2.1) to clean the inner surface of the flask.

Then proceed in the same way as for the preparation of the calibration solution, from the addition of silver oxide step (see preparation in 8.1.1.1).

V_1 is chosen so that the plutonium concentration in the solution at the end of the preparation is lower than that in the calibration solution.

If needed, the nitrate concentration should be adjusted to 3 mol·l^{-1}, by the addition of nitric acid, of appropriate concentration. The effect of the sample and standard matrices can be significant. It is essential to match the matrix of both samples and standards to minimize the uncertainty of the method. If no effort is made to match matrices, then the analyst shall carefully characterize the effect or consequence of the mismatch between matrices. For this reason, it is recommended that the nitrate concentration be adjusted to 3 mol·l^{-1}.

8.1.2.2 Oxidation by Ce(IV)

The solution to analyse can be prepared as follows.

In a 50 ml volumetric flask, (7.3),

— introduce with a pipette (7.4) the desire 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 8.1.1.2), 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.

— Add a few ml of 3 mol·l^{-1} nitric acid (6.2.1) to clean the inner surface of the flask.

Then proceed in the same way as for the preparation of the calibration solution, from the addition of Ce(IV) solution step (see preparation in 8.1.1.2).

V_1 is chosen so that the plutonium concentration in the solution at the end of the preparation is lower than that in the calibration solution.

If needed, the nitrate concentration should be adjusted to 3 mol·.l^{-1}, by the addition of nitric acid, of appropriate concentration. The effect of the sample and standard matrices can be significant. It is essential to match the matrix of both samples and standards to minimize the uncertainty of the method. If no effort is made to match matrices, then the analyst shall carefully characterize the effect or consequence of the mismatch between matrices. For this reason, it is recommended that the nitrate concentration be adjusted to 3 mol·l^{-1}.

8.2 Spectrophotometer setup

Adjust the spectrophotometer baseline between 800 nm and 860 nm after filling the reference vial and the sample vial with nitric acid 3 mol·l^{-1} (6.2.1) and scanning the spectrum.

Other adjustments of the spectrophotometer (e.g. slit width and height) shall be previously chosen to obtain the Pu(VI) peak under optimum conditions and shall be strictly the same for all measurements.

8.3 Measurements

8.3.1 Background measurement

— Fill the reference vial or flow cell with nitric acid 3 mol·l^{-1} (6.2.1).

— Record the spectrum between 800 nm and 860 nm.

Typically it is recommended that background stay below 1×10^{-3} with variation around 1×10^{-4}.

8.3.2 Measurements on the calibration solution

— Fill the test sample vial or flow cell with the plutonium calibration solution prepared according to 8.1.1.

— Record the spectrum between 800 nm and 860 nm.

— Measure the absorbance of the Pu(VI) peak at 830 nm.

— In case of flow cell, rinse it with nitric acid 3 mol·l^{-1} (6.2.1).

The measurement of the absorbance can be done with the trapezoid method using at least three wavelengths to determine the height of the peak (maximum absorbance) or with other statistical methods that are equally valid. The chosen points on both sides of the peak should be representative of the background.

To improve the result with the trapezoid method, using a range of 3 to 5 wavelengths can be required to determine the height or area of the peak.

In case of a flow cell, proceed the same way after filling the cell, first with nitric acid solution (background), secondly with the plutonium calibration solution. The volume of solution needed depends on the measurement loop volume.

In both cases, check that the ratio of absorbance to Pu concentration for the calibration solution for which the plutonium concentration is known is in accordance with the expected one i.e. the ones that were measured earlier. For example, for a measurement cell with a 3 cm optical path, for plutonium calibration solution concentration about 20 mg·l^{-1}, the absorbance can be around 1×10^{-2} (the ratio of absorbance to Pu concentration is around 5×10^{-4}).

If the spectrophotometer is permanently in operation, these controls (background and absorbance of calibration solution) can be performed regularly for instance once per shift.

The ratio of absorbance to plutonium concentration for the calibration solution can be followed by using a control card with alarm and alert thresholds.

8.3.3 Measurements on the sample solution

— Fill the test sample vial with the sample solution prepared according to 8.1.2.

— Fill the reference vial with nitric acid 3 mol·l^{-1} (6.2.1).

— Record the spectrum between 800 nm and 860 nm.

— Measure the absorbance of the Pu(VI) peak at 830 nm.

The spectrum analysis by the trapezoid method or with other statistical methods that are equally valid should be carried out in the same way as for the calibration solution.

9 Expression of the result

9.1 Calculation of the concentration of plutonium in the sample

The concentration of plutonium in the sample to analyse is obtained using Formula (1):

$$[\mathrm{Pu}]_x = [\mathrm{Pu}]_\mathrm{e} \times \frac{D_x}{D_\mathrm{e}} \times \frac{V_{10}}{V_1} \times \frac{V_2}{V_{20}} \quad (1)$$

where

$[Pu]_e$ is the plutonium concentration in the reference solution;

$[Pu]_x$ is the plutonium concentration in the sample solution;

V_{10} is the volume of the reference solution added to flask;

V_1 is the volume of the sample solution added to flask;

V_{20} is the make-up volume of the calibration solution without addition in flask (50 ml in the example of 8.1.1);

V_2 is the make-up volume of the sample solution without addition in flask (50 ml in the example of 8.1.2);

D_e is the absorbance on the plutonium peak in the calibration solution;

D_x is the absorbance on the plutonium peak in the sample solution.

9.2 Reproducibility

The reproducibility of this method depends on the apparatus used and the arrangement of the working place. It shall be determined for each installation.

As an example, in hot cell or gloves box, for Pu concentration under 0,5 mg·l^{-1}, the reproducibility of the method described in this document can be lower than 10 % (with coverage factor k = 2).

If needed, improved reproducibility can be achieved with specific care.

9.3 Detection limit

The detection limit, i.e. the minimum absorbance that can be detected, depends mainly on:

— the optical path in the measurement cell;

— the resolution of the spectrophotometer;

— the matrix to be analysed.

For a 3 cm optical path measurement cell (7.2), a spectral slit width 2 nm spectrophotometer (7.1), absorbance around 1 × 10^{-4} can be achieved for pure plutonium in 3 mol·l^{-1} nitric acid solution.

In the conditions described in this document (dilution 10 of the sample prior to the analysis according to 8.1.2), the detection limit of the method can be around 0,2 mg·l^{-1} for pure plutonium in nitric acid 3 mol·l^{-1} solution.

For sample from the process, depending on the matrix, the detection limit can be increased to a value between 0,5 mg·l^{-1} and 1 mg·l^{-1}.

10 Interferences

10.1 Anions

Any anions likely to form complexes with the $(PuO_2)^{2+}$ ion can interfere by changing the molar extinction coefficient i.e. the molar attenuation coefficient. Anions forming complexes with Pu(IV) or Ce(IV) can interfere with the oxidation by cerium. Tests have been made leading to the following conclusions:

— Perchlorate ions (ClO_4^-) do not interfere even at a concentration of 0,1 mol·l^{-1}.

— The concentration of nitrate ions (NO_3^-) has a major influence on the molar extinction coefficient (see 5.4).

— Fluoride ions (F^-) have a very large effect in the absence of complexing cations with the AgO oxidation method: fluoride ions should be complexed by replacing some of the 3 mol·l^{-1} nitric acid in the method by the mixture 0,1 mol·l^{-1} Al $(NO_3)_3$ – 2,7 mol·l^{-1} HNO_3, in order to obtain an aluminium/fluoride ratio of at least 3. Under these conditions there is no interference.

— Chloride ions (Cl^-) can form a complex with Pu(VI) and precipitate silver, but they are not present in process solutions.

— The concentration of sulfate ions (SO_4^{2-}) should be established and the calibration should be made in the same medium, since sulfates influence the molar extinction coefficient. For example, this is about 298 m^2·mol^{-1} in 0,5 mol·l^{-1} of H_2SO_4 and 4 mol·l^{-1} of HNO_3 compared with 455 m^2·mol^{-1} in 4 mol·l^{-1} of HNO_3 (the peak develops a shoulder at 834 nm). Moreover, sulfates can impede the quantitative oxidation of plutonium by Ce(IV).

— Tests have shown that the presence of 2 × 10^{-4} mol of phosphate (PO_4^{3-}) in the sample aliquot does not impede the quantitative oxidation of 4 mg of plutonium by Ce(IV) and does not affect the molar extinction coefficient of Pu(VI). Only a very slow precipitation of cerium has been observed. At the levels normally present in plant inlet solutions (about 10^{-5} mol·l^{-1}), there is no effect.

10.2 Cations

The Pu(VI) peak is very specific. The presence of a cation which absorbs at 831 nm is generally revealed by absorption between 800 nm and 810 nm or 850 nm and 860 nm; in this case it is possible to estimate the additional contribution to the 831 nm peak from the absorption measured at 800 nm or 860 nm.

If the concentration of interfering cations is large, it is necessary to take into account the nitrate ions associated with these cations when adjusting the final nitrate ion concentration. For example: two NO_3^- ions for one UO_2^{2+}ion.

Tests have been made leading to the following conclusions:

— Protons (H^+) have a very small influence on the molar extinction coefficient. It is however not recommended to operate with a concentration of free protons below 1 mol·l^{-1} because the plutonium species become less stable.

— The molar extinction coefficient of Fe^{3+} is constant between 800 nm and 860 nm.

— Chromium ions (Cr) do not interfere even at a chromium/plutonium ratio of 10.

— The concentrations of Mn, Ni, and Cu ions in reprocessing solutions are usually sufficiently low not to cause any problems.

— Molybdenum ions (Mo) do not interfere even at a molybdenum/plutonium ratio of 5.

— Sodium ions (Na) do not interfere even at a sodium/plutonium ratio of 2 × 10^4.

— It is possible to measure 25 µg·g^{-1}[2)] of plutonium in uranium (U), taking into account the associated nitrate.

— Aluminium ions (Al) do not interfere, even at an aluminium/plutonium ratio greater than 100.

— Neptunium ions (Np) do not interfere, even at a neptunium/plutonium ratio of 1 000.

2) The unit µg g^{-1} is a quantity of dimension 1 (dimensionless), and is equivalent to the deprecated unit “ppm”.

— For an americium (Am)/plutonium ratio of about 10, there is 5 % interference (if no precautions are taken in the chart measurements). The americium content of reprocessing solutions is sufficiently low not to cause interference.

— Fission neodymium (Nd) does not cause any interference with reprocessing plant feed solutions provided that it is not used as an internal standard.

Reducing agents in very large amounts consume Ce(IV); the volume of ceric nitrate solution in the oxidation step should then be increased.