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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 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.

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ISO 9463 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 9463:1990), which has been technically revised.

Introduction

This International Standard specifies an analytical method for determining the plutonium concentration in nitric acid solutions of dissolution of nuclear reactor irradiated fuels. The method is devoted to process controls at the different steps of the process in a nuclear fuel reprocessing plant.

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

1 Scope

This International Standard specifies an analytical method by spectrophotometry for determining the plutonium concentration of nitric acid solutions in reprocessing plants. The method is applicable, without interference, in the presence of numerous cations, with a standard deviation of about 5 %, where the concentration of plutonium in the solution is at least 0,5 mg·l^{-1}.

2 Normative references

ISO 3696:1987, *Water for analytical laboratory use — Specification and test methods*

3 Principle

Plutonium is quantitatively oxidized to the hexavalent state either with cerium(IV) or with silver oxide, the excess of which is destroyed by the addition of sulfamic acid.

The optical density of the 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).

4 Chemical conditions

4.1 Stability of plutonium(VI)

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

4.2 Rate of oxidation of plutonium(IV) to plutonium(VI)

The rate of oxidation by cerium(IV) decreases as the acidity increases. With the reagent quantities stated in the method, the oxidation is complete in 5 min in 2 mol·l^{-1} or 3 mol·l^{-1} nitric acid.

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

4.3 Destruction of the excess oxidant

With cerium(IV), the excess reagent does not interfere and it is not necessary to destroy it.

With silver oxide as oxidant, it is necessary to destroy the excess reagent by reaction with a small excess of sulfamic acid or by heating to about 80 °C.

4.4 Molar extinction coefficient of plutonium(VI)

The molar extinction coefficient and, therefore, absorbance can vary according to a number of parameters, for example:

- 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;
- 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;
- temperature: the decrease in molar extinction coefficient is about 0,5 % per degree Celsius.

5 Reagents

5.1 General

All reagents shall be of analytical grade.

This procedure uses 3 mol·l^{-1} nitric acid as this permits the use of either cerium(IV) or silver oxide as the oxidant and is convenient for most applications. It is acceptable to use cerium(IV) as oxidant at lower acidities and silver oxide as oxidant at higher acidities, provided that the concentration of the nitric acid used for calibration is similarly adjusted.

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

5.2.1 Nitric acid, $c(HNO_3) = (3 \pm 0,05\ mol \cdot l^{-1})$.

5.2.2 Water, complying with grade 3 of ISO 3696:1987.

5.2.3 Plutonium, plutonium reference solution in nitric acid with a plutonium concentration and a nitrate concentration close to that of the sample being analysed.

5.3 Method using silver oxide as oxidant

5.3.1 Sulfamic acid, $c(NH_2SO_3H) = 0,5\ mol \cdot l^{-1}$ solution in water $w(NH_2SO_3H) = 48,5\ g \cdot l^{-1}$.

5.3.2 Silver oxide (AgO).

This reagent can be prepared in a number of ways, such as the following.

- Dissolve 72 g of sodium hydroxide (5.3.3) in 1 l of water (5.2.2) in a very clean Pyrex conical flask or beaker and heat to 85 °C.
- Add, while stirring, 75 g of potassium persulfate ($K_2S_2O_8$) (5.3.4) to the hot solution.

WARNING 1 — Never use ammonium persulfate on account of explosion risks.

- Add, whilst still stirring, a solution of 51 g of silver nitrate (5.3.5) in a minimum of water (about 40 ml) (5.2.2). Heat the mixture to 90 °C and stir for 15 min.
- Allow to cool, and then filter with a No. 4 glass frit.

- Wash with 0,25 mol·l^{-1} sodium hydroxide solution (10 g·l^{-1}) until free from sulfate ions, as verified by testing the effluent solution for precipitation with barium; the volume necessary is generally between 0,5 l and 1 l.
- Wash with water until neutral.
- Dry with compressed air at room temperature, stirring occasionally with care to form a powder; use a sieve if necessary.

WARNING 2 — Never dry at a temperature above 35 °C as there is a risk of explosion.

- Dry in a desiccator at room temperature for one day and store in a stoppered, brown glass bottle.

5.3.3 Sodium hydroxide, (NaOH).

5.3.4 Potassium persulfate, ($K_2S_2O_8$).

5.3.5 Silver nitrate solution, [$Ag(NO_3)_2$].

5.4 Method using cerium(IV) as oxidant

5.4.1 Cerium(IV), $c(Ce^{4+}) = 0{,}4$ mol·l^{-1} in a nitrate medium.

This reagent can be prepared in a number of ways, such as the following:

- Dissolve 219,3 g of ceric ammonium nitrate [$(NH_4)_2Ce(NO_3)_6$] (5.4.2) in 600 ml of 1 mol·l^{-1} nitric acid (5.4.3) and dilute to 1 l with water (5.2.2).

5.4.2 Ceric ammonium nitrate, [$(NH_4)_2Ce(NO_3)_6$].

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

6 Apparatus

Usual nuclear laboratory equipment.

6.1 Spectrophotometer, high-quality, double-beam, grating, or equivalent, designed for measurements on fully contained high beta-gamma solutions and having, as far as possible, the following features:

a) fluctuation below 0,001 absorbance;

b) stable baseline;

c) useful spectral range at least up to 1 100 nm.

7 Measurements

To realize this operating mode, given as an example, the varying concentrations and/or volumes, in particular concentration and/or volume of reference solution, flask volume, etc., 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 this calibration is chosen in accordance with the required accuracy of the analysis.

7.1 Preparation of the different solutions

7.1.1 Plutonium calibration solution

7.1.1.1 Oxidation by silver oxide

The plutonium calibration solution may be prepared in the following way:

- Pour 5 ml of the plutonium reference solution (5.2.3) into a 50 ml flask.
- Add a few millilitres of the 3 mol·l^{-1} nitric acid solution (5.2.1) to clean the inner surface of the flask.
- Add the minimum amount (a few milligrams) of silver oxide (5.3.2) to give a persistent dark colour.
- Stir.
- Keep reacting for 5 min while stirring from time to time.
- Check that the solution is still a dark colour.
- Add, with a burette, 2 drops of sulfamic acid (5.3.1).

  NOTE The addition of an excess of sulfamic acid significantly reduces the molar extinction coefficient and, 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.

  NOTE If the excess of AgO was too high, the colour of the solution fades from dark to colourless by passing 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 (5.2.1).

7.1.1.2 Oxidation by cerium(IV)

The plutonium calibration solution may be prepared in the following way:

- Pour 5 ml of the plutonium reference solution (5.2.3) into a 50 ml flask.
- Add a few millilitres of the 3 mol·l^{-1} nitric acid solution (5.2.1) to clean the inner surface of the flask.
- Add 5 ml of the cerium(IV) solution (5.4.1).
- Stir the solution then let it rest for 5 min.
- Adjust the volume of the flask with 3 mol·l^{-1} nitric acid (5.2.1).

7.1.2 Sample solutions

7.1.2.1 Oxidation by silver oxide

The solution being analysed may be prepared in the following way:

- Pour into a 50 ml flask a volume, V_1, of the solution being analysed that corresponds to a mass of plutonium close to that in the calibration solution; see 7.1.1.1.

- Add a few millilitres of 3 mol·l^{-1} nitric acid (5.2.1) 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 the silver oxide step; see 7.1.1.1.

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 necessary, the nitrate concentration should be adjusted to 3 mol·l^{-1} by the addition of nitric acid of the appropriate concentration.

7.1.2.2 Oxidation by cerium(IV)

The solution being analysed may be prepared in the following way:

- Pour into a 50 ml flask a volume, V_1, of the solution being analysed corresponding to a mass of plutonium close to that in the calibration solution; see 7.1.1.2.

- Add a few millilitres of 3 mol·l^{-1} nitric acid (5.2.1) 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 cerium(IV) solution step; see 7.1.1.2.

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 the appropriate concentration.

7.2 Spectrophotometer setup

Adjust the spectrophotometer baseline between 800 nm and 860 nm after filling the reference vial and the sample vial with 3 mol·l^{-1} nitric acid (5.2.1) and scanning the spectrum.

The adjustments of the spectrophotometer (slit width, height, etc.) shall be previously chosen to obtain the plutonium(VI) peak under optimum conditions and shall be strictly the same for all measurements.

7.3 Measurements

7.3.1 Measurements on the calibration solution

Carry out the measurements as follows.

- Fill the test sample vial with the plutonium calibration solution prepared in accordance with 7.1.1.

- Fill the reference vial with 3 mol·l^{-1} nitric acid (5.2.1).

- Record the spectrum between 800 nm and 860 nm.

- Measure the absorbance of the plutonium(VI) peak at 830 nm.

The measurement of the absorbance may be done with the trapezoid method at three wavelengths. The chosen points on both sides of the peak should be representative of the background.

7.3.2 Measurements on the sample solution

Carry out the measurements as follows.

- Fill the test sample vial with the sample solution prepared in accordance with 7.1.2.
- Fill the reference vial with 3 mol·l^{-1} nitric acid (5.2.1).
- Record the spectrum between 800 nm and 860 nm.
- Measure the absorbance of the plutonium (VI) peak at 830 nm.

The spectrum analysis by the trapezoid method should be done in the same way as for the calibration solution.

8 Expression of the results

8.1 Calculation of the concentration of plutonium in the sample

The concentration, $[\mathrm{Pu}]_\mathrm{x}$, of plutonium in the sample being analysed is obtained as given in Equation (1):

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

where

$[\mathrm{Pu}]_\mathrm{e}$ is the plutonium concentration in the reference 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 volume of the flask used to dilute the calibration solution (50 ml in the example of 7.1.1);

V_2 is the volume of the flask used to dilute the sample solution (50 ml in the example of 7.1.2);

D_e is the absorbance of the plutonium peak for the calibration solution;

D_x is the absorbance of the plutonium peak for the sample solution.

8.2 Reproducibility

Reproducibility of this method depends on the apparatus used and of the ergonomics of the working place.

It shall be determined for each installation.

As an example, the reproducibility of the method described here can be lower than 10 %.

8.3 Detection limit

The detection limit of this method can be around 0,5 mg·l^{-1}.