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

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

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Foreword

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International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

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.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 13465 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 13465:1997), which has been technically revised.

Introduction

This International Standard specifies an analytical method for determining the neptunium concentration in nitric acid solutions after the 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 neptunium in nitric acid solutions by spectrophotometry

1 Scope

This International Standard specifies an analytical method for determining the neptunium concentration by spectrophotometry, with a standard deviation of about 5 %, in nitric acid solutions after the dissolution of nuclear reactor irradiated fuels, at different steps of the process in a nuclear fuel reprocessing plant. The method is applicable to aliquots containing a concentration of neptunium between 10 $mg{\cdot}l^{-1}$ and 200 $mg{\cdot}l^{-1}$.

2 Normative references

The following referenced documents are indispensable for the application 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 3696, *Water for analytical laboratory use — Specification and test methods*

3 Principle

Neptunium is quantitatively transformed to neptunium(V) using a vanadium(V)/vanadium(IV) redox buffer. The neptunium content is determined by spectrophotometry by measuring the height of the absorbance peak at a wavelength of 981 nm.

4 Interferences

4.1 Uranium(VI) forms an intercationic complex with neptunium(V). The complex has a maximum absorption at 992 nm. The presence of uranium(VI), therefore, reduces the sensitivity of the determination. However, the formation constant of this complex is low, and up to 1,5 g of uranium can be present in the aliquot, provided that the calibration be carried out with the same quantities of uranium(VI) or that the technique of standard addition be used.

Nitrate ions influence the formation of the uranium(VI)/neptunium(V) complex. In the presence of uranium(VI), the nitrate concentration shall be controlled so that the concentrations in the sample and standard do not differ by more than 0,2 $mol{\cdot}l^{-1}$ during the analyses.

4.2 Acidity contributes to the formation of neptunium(V), and its concentration shall be kept between 2,5 $mol{\cdot}l^{-1}$ and 4 $mol{\cdot}l^{-1}$ in a 5 ml volume prior to the addition of the vanadium(V)/vanadium(IV) buffer mixture, and to $(1 \pm 0{,}2)$ $mol{\cdot}l^{-1}$ at the final measurement. The apparent molar extinction coefficient decreases with an increasing acidity.

4.3 The redox buffer vanadium(V)/vanadium(IV) stabilizes plutonium at valency (IV). It is therefore not necessary to correct for the contribution of plutonium(VI) under the neptunium peak at 981 nm. The mass of plutonium shall be lower than 30 mg in the aliquot. Usually, most of the plutonium contained in the dissolution solutions is at valency (IV).

4.4 Redox species in the sample influence the redox buffer vanadium(V)/vanadium(IV) ratio. The quantity of redox species, including plutonium(VI), that can be present in the aliquot shall be such that the final vanadium(V)/vanadium(IV) ratio remains between 0,25 and 1.

4.5 Nitrite ions at a concentration smaller than 0,1 mol·l^{-1} in the sample have no effect when the initial vanadium(V)/vanadium(IV) ratio is 0,5.

5 Reagents

Use only reagents of recognized analytical grade and distilled or demineralized water with a resistivity greater than 10 MΩ·cm.

5.1 **Nitric acid** solution, $c(HNO_3) = 3$ mol·l^{-1}.

5.2 **Nitric acid** solution, $c(HNO_3) = 0{,}5$ mol·l^{-1}.

5.3 **Nitric acid** solution, $c(HNO_3) \approx 0{,}1$ mol·l^{-1}.

5.4 **Vanadium(IV) oxide sulfate** solution, $c(VOSO_4 \cdot 5H_2O)$ of about 1 mol·l^{-1}.

This reagent can be prepared in various ways.

For example, for a solution at 0,75 mol·l^{-1}, the procedure can be as follows:

- Weigh 18,98 g of vanadium(IV) oxide sulfate (5.10) and dissolve it in 80 ml of the nitric acid solution (5.3).
- Pour into a 100 ml flask and bring to volume with nitric acid solution (5.3).
- Homogenize.

This solution shall not be used more than one month after the date of preparation.

5.5 **Cerium(IV) nitrate** solution, $c[Ce(NO_3)_4]$ of about 0,25 mol·l^{-1}.

This reagent can be prepared in various ways.

For example, for a solution at 0,25 mol·l^{-1}, the procedure can be as follows:

- Weigh 13,7 g of ammonium hexanitratocerate (5.11) and dissolve it in 80 ml of the nitric acid solution (5.3).
- Pour into a 100 ml flask and bring to volume with nitric acid solution (5.3).
- Homogenize.

5.6 **Vanadium(V)/vanadium(IV)** redox buffer mixture.

The vanadium concentration in the solution is about 0,3 mol·l^{-1}. The ratio between vanadium(V) and vanadium(IV) is about 0,5.

This solution can be prepared in various ways.

For example, for a solution at 0,3 mol·l^{-1} of vanadium, the procedure can be as follows:

- Add 40 ml of vanadium(IV) oxide sulfate solution (5.4) and 40 ml of cerium(IV) nitrate solution (5.5) to a 100 ml flask.

- Shake and bring to 100 ml with distilled water (5.9).
- Homogenize.

This solution shall not be used more than one month after the date of preparation.

5.7 Uranyl nitrate solution.

Prepare a uranyl nitrate solution, with a concentration of uranium and nitrate close to those in the analyzed sample. For example, for a certain fuel dissolution solution, $[U] = 300\ g \cdot l^{-1}$ and $[NO_3] = 3\ mol \cdot l^{-1}$.

5.8 Neptunium calibration standard.

Neptunium reference solution in nitric acid $3\ mol \cdot l^{-1}$, with a concentration of about $100\ mg \cdot l^{-1}$. This concentration, as it impacts the precision of the desired method, shall be known with a specified precision and with negligible bias.

5.9 Water, complying with grade 3 of ISO 3696.

5.10 Vanadium(IV) oxide sulfate powder, ($VOSO_4 \cdot 5H_2O$).

5.11 Ammonium hexanitratocerate(IV) powder, $[(NH4)_2Ce(NO_3)_6]$.

6 Apparatus

Usual nuclear laboratory equipment, plus the following.

6.1 A high-quality, 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) fluctuation below 0,001 in absorbance;

b) stable baseline;

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

7 Measurements

7.1 Calibration

It is necessary to calibrate the spectrophotometer. The calibration frequency is determined according to the desired accuracy of the results.

7.2 Sample preparation

7.2.1 Neptunium calibration solution

The neptunium calibration solution can be prepared in various ways.

For example, in a 25 ml volumetric flask,

- add one volume of neptunium calibration standard (5.8) corresponding to a neptunium amount slightly over that in the aliquot of sample to analyze;

- add one volume of the uranyl nitrate solution (5.7), corresponding to a uranium amount close to that in the aliquot of sample to analyze;
- adjust the volume to 5 ml with nitric acid solution 3 mol·l^{-1} (5.1);
- add 5 ml of the vanadium(V)/vanadium(IV) redox buffer solution (5.6);
- adjust to a total volume of 25 ml with nitric acid solution 0,5 mol·l^{-1} (5.2).

The calibration is made within the linear concentration range of the spectrophotometer, which depends on the spectral bandwidth.

NOTE The narrower the bandwidth, the wider the linear concentration range.

7.2.2 Sample solution

The sample solution can be prepared in various ways.

For example, in a 25 ml volumetric flask,

- add a volume, V_1, of the sample, corresponding to a neptunium quantity close to that of the calibration solution prepared in 7.2.1;
- adjust to a volume of 5 ml with nitric acid solution 3 mol·l^{-1} (5.1);
- add 5 ml of the vanadium(V)/vanadium(IV) redox buffer solution (5.6);
- adjust to a total volume of 25 ml with nitric acid solution 0,5 mol·l^{-1} (5.2).

The volume, V_1, shall be less than the volume of the redox buffer solution. V_1 is also chosen so that the neptunium concentration in the final solution is less than that in the standardization solution.

7.3 Spectrophotometer setup

Set up the spectrophotometer baseline between 940 nm and 1 020 nm after filling both the reference cell and the measurement cell with nitric acid 0,5 mol·l^{-1} (5.2).

The other adjustments of the spectrometer (slit width and height) have already been chosen so as to obtain the neptunium line in the best way. These setups should be kept identical for all measurements.

7.4 Measurements

7.4.1 Measurement on the calibration solution

Wait at least 20 min after the preparation of the calibration solution (prepared according to 7.2.1), then proceed as follows.

- Fill up the measurement cell of the spectrophotometer with the calibration solution.
- Fill up the reference cell with nitric acid 0,5 mol·l^{-1} (5.2).
- Record the spectrum between 940 nm and 1 020 nm.
- Determine the absorbance of the neptunium(V) line at 981 nm.

The measurement of the absorbance may be made using the trapezoid method at three wavelengths. The chosen points on the two parts of both sides of the neptunium peak should be representative of the background.

NOTE The apparent molar extinction coefficient, ε, depends on the uranium and nitrate concentrations and on the spectral bandwidth. As an example, with a 3 cm cell, a uranium concentration of 300 g·l^{-1}, a nitrate concentration of 3 mol·l^{-1} and a bandwidth of 1.5 nm, ε is of the order of 300.

7.4.2 Measurement on the sample solution

Wait at least 20 minutes after the preparation of the sample solution (prepared according to 7.2.2), then proceed as follows.

- Fill up the measurement cell of the spectrophotometer with the sample solution.
- Fill up the reference cell with nitric acid 0,5 mol·l^{-1} (5.2).
- Record the spectrum between 940 and 1 020 nm.
- Determine the absorbance of the neptunium(V) line at 981 nm.

The sample spectra shall be evaluated in the same manner as that for the calibration.

8 Expression of the results

8.1 Calculation of the neptunium concentration in the sample

The neptunium concentration, $[\mathrm{Np}]_\mathrm{x}$, in the sample being analyzed is calculated as given in Equation (1):

$$[\mathrm{Np}]_\mathrm{x} = [\mathrm{Np}]_\mathrm{e} \times \frac{\alpha_\mathrm{x}}{\alpha_\mathrm{e}} \times \frac{V_{10}}{V_1} \times \frac{V_2}{V_{20}} \tag{1}$$

where

$[\mathrm{Np}]_\mathrm{e}$ is the neptunium concentration of the calibration standard (5.8);

V_{10} is the volume of the neptunium calibration standard (5.8);

V_1 is the volume of the sample solution;

V_{20} is the volume of the flask used to prepare the calibration solution (25 ml in the example quoted in 7.2.1);

V_2 is the volume of the flask used to prepare the sample solution (25 ml in the example quoted in 7.2.2);

α_e is the absorbance of the neptunium line in the calibration solution;

α_x is the absorbance of the neptunium line in the sample solution.

8.2 Reproducibility

The reproducibility of this method depends on the instrument and on the operating conditions of the high active cell.

It should be especially determined for each particular case.