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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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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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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 13465:2009), which has been technically revised.

The main changes are as follows:

- Clause 3 and 5.3 added;
- 9.2 and 9.3 updated.

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.

Introduction

This document presents 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 document specifies an analytical method for determining the neptunium concentration by spectrophotometry, with spectrophotometer implemented in hot cell or glove box allowing the analysis of high activity solutions, with a standard uncertainty, with coverage factor $k = 1$ 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 or in other nuclear facilities. The method is applicable to sample from the process containing a concentration of neptunium between 10 mg·l^{-1} and 400 mg·l^{-1} and uranium concentrations of up to 300 g·l^{-1}.

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 terminology databases for use in standardization at the following addresses:

- ISO Online browsing platform: available at https://www.iso.org/obp
- IEC Electropedia: available at https://www.electropedia.org/

4 Principle

As neptunium(V) is naturally the most stable of the oxidation states of neptunium and because of the high molar extinction coefficient, for this valency, neptunium is quantitatively transformed to Np(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. The result is obtained by comparison to a calibration performed under similar conditions (with the same nitrate or uranium content).

5 Interferences

5.1 Uranium (VI)

Uramium(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 selectivity 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·l^{-1} during the analyses.

Other elements that may produce a spectral interference have very flat absorbance in this part of the spectrum making baseline corrections simple to use.

5.2 Acidity

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

5.3 Plutonium

Usually most of the plutonium contained in the dissolution solutions is at valency (IV). However small amounts of plutonium (VI) are found in solutions due to disproportionation reactions. For masses of plutonium lower than 30 mg in the aliquot the redox buffer vanadium (V)/vanadium(IV) will stabilize the plutonium at valency (IV). It is therefore not necessary to correct for the contribution of plutonium(VI) under the neptunium peak at 981 nm.

5.4 Redox species

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.

5.5 Nitrite ions

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.

6 Reagents

Use only reagents of recognized analytical grade.

6.1 Water, complying with grade 3 of ISO 3696.

6.2 Concentred nitric acid solution, $\rho(HNO_3)$ of about 1 420 g·l^{-1}.

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

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

6.5 Nitric acid solution, $c(HNO_3)$ = 3 mol·l^{-1}. It can be prepared by dilution of concentrated nitric acid (6.2) in water (6.1).

6.6 Nitric acid solution, $c(HNO_3)$ = 0,5 mol·l^{-1}. It can be prepared by dilution of concentrated nitric acid (6.2) in water (6.1).

6.7 Nitric acid solution, $c(HNO_3)$ = 0,1 mol·l^{-1}. It can be prepared by dilution of concentrated nitric acid (6.2) in water (6.1).

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

This reagent can be prepared in various ways.

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

- Weigh 18,98 g of vanadium(IV) oxide sulfate (6.3) and dissolve it in 80 ml of the 0,1 $\mathrm{mol \cdot l^{-1}}$nitric acid solution (6.7).
- Pour into a 100 ml flask and adjust the volume with 0,1 $\mathrm{mol \cdot l^{-1}}$nitric acid solution (6.7).
- Homogenize.

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

6.9 Cerium(IV) nitrate solution, $c[\mathrm{Ce(NO_3)_4}]$ of about 0,25 $\mathrm{mol \cdot l^{-1}}$.

This reagent can be prepared in various ways.

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

- Weigh 13,7 g of ammonium hexanitratocerate (6.4) and dissolve it in 80 ml of 0,1 $\mathrm{mol \cdot l^{-1}}$nitric acid solution (6.7).
- Pour into a 100 ml flask and adjust the volume with 0,1 $\mathrm{mol \cdot l^{-1}}$nitric acid solution (6.7).

Homogenize.

6.10 Vanadium(V)/vanadium(IV) redox buffer mixture.

The vanadium concentration in the solution is about 0,3 $\mathrm{mol \cdot l^{-1}}$. 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 $\mathrm{mol \cdot l^{-1}}$ of vanadium, the procedure can be as follows:

- Add 40 ml of freshly made vanadium(IV) oxide sulfate solution (6.8) and 40 ml of cerium(IV) nitrate solution (6.9) to a 100 ml flask.
- Shake and adjust the volume to 100 ml with distilled water (6.1).
- Homogenize.

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

6.11 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, $\rho(\mathrm{U}) = 300\ \mathrm{g \cdot l^{-1}}$ and $c(\mathrm{NO_3}) = 3\ \mathrm{mol \cdot l^{-1}}$.

6.12 Reference solution, neptunium in solution in nitric acid, $c(\mathrm{HNO_3}) = 3\ \mathrm{mol \cdot l^{-1}}$ with a nitrate concentration close to that of the sample to analyse.

For instance, the neptunium concentration can be about 100 $\mathrm{mg \cdot l^{-1}}$. This concentration, as it impacts the precision of the desired method, shall be known with accuracy.

The neptunium reference solution used for the analysis can be prepared by dilution of a concentrated reference mother neptunium solution prepared from certified reference material (such as the 1 $\mathrm{g \cdot l^{-1}}$ Np-237 standards from CETAMA or another one available).

7 Apparatus

Usual nuclear laboratory equipment, plus the following.

7.1 Spectrophotometer.

A high-quality, double-beam grating spectrophotometer, or equivalent, with spectral slit width of 2 nm or less, 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 measurement spectral range at least up to 1 100 nm. Usually, spectrophotometers with a minimum capability of 190 nm and a maximum capability of 1 100 nm, or greater which allow the analysis of other elements, or the study of potential interferences are convenient.

7.2 Measurement cell, a static or a flow cell, with the main characteristic being the optical path in the cell. Common cells 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, with a volume of 50 ml, complying with the requirements of ISO 1042. Volume can be less, for instance 25 ml, but in hot cell the recommended volume is 50 ml.

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

8 Measurement

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.

8.1 Calibration

It is necessary to calibrate the spectrophotometer with a neptunium reference solution to determine the relationship between neptunium concentration and absorbance.

The calibration frequency is determined according to the desired accuracy of the results.

8.2 Sample preparation

8.2.1 Neptunium calibration solution

The neptunium calibration solution can be prepared in various ways.

For example, in a 50 ml volumetric flask (7.3),

— introduce with a pipette (7.4) the desired volume, V_{10}, of neptunium reference solution (6.12) corresponding to a neptunium amount slightly over that in the aliquot of sample to analyse. If need, method validation experiments are required to determine an upper and lower limit based on expected neptunium content of samples;

— add with a pipette (7.4) one volume of the uranyl nitrate solution (6.11), corresponding to a uranium amount close to that in the aliquot of sample to analyse. If needed, method validation experiments are required to determine an upper and lower limit based on expected uranium content of samples;

— add 5 ml of nitric acid solution 3 mol·l^{-1} (6.5);

— add 5 ml of the vanadium(V)/vanadium(IV) redox buffer solution (6.10);

- stir,
- adjust to a total volume of 50 ml with nitric acid solution 0,5 mol·l^{-1} (6.6).

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.

8.2.2 Sample solution

The sample solution can be prepared in various ways.

For example, in a 50 ml volumetric flask,

- introduce with a pipette (7.4) a volume, V_1, of the sample, corresponding to a neptunium quantity close to that of the calibration solution prepared in 8.2.1;

  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 8.2.1), 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 5 ml of nitric acid solution 3 mol·l^{-1} (6.5);
- add 5 ml of the vanadium(V)/vanadium(IV) redox buffer solution (6.10);
- adjust to a total volume of 50 ml with nitric acid solution 0,5 mol·l^{-1} (6.6).

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 calibration solution.

8.3 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} (6.6) and scanning the spectrum.

The other adjustments of the spectrometer (slit width and height) shall be chosen so as to obtain the neptunium line in the best way. These setups shall be kept identical for all measurements (calibration solution and sample solution).

8.4 Measurement

8.4.1 Measurement on the calibration solution

Wait at least 20 min after the preparation of the calibration solution (prepared according to 8.2.1), then proceed as follows.

- Fill up the test sample vial or the measurement flow cell of the spectrophotometer with the calibration solution.
- Record the spectrum between 940 nm and 1 020 nm.
- Determine the absorbance of the neptunium(V) peak around 981 nm.
- In case of flow cell, rinse it with nitric acid nitric 0,5 mol·l^{-1} (6.6).

The measurement of the absorbance may be made using 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 the two parts of both sides of the neptunium 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 neptunium calibration solution. The volume of solution needed depends on the measurement loop volume.

In both cases, check that the ratio of absorbance to Np concentration for the calibration solution for which the Neptunium concentration is known is in accordance with the expected one i.e. the ones that were measured earlier.

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

NOTE The neptunium apparent molar extinction coefficient, ε[1], i.e. the molar attenuation coefficient 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 $\text{g}\cdot\text{l}^{-1}$, a nitrate concentration of 3 $\text{mol}\cdot\text{l}^{-1}$ and a bandwidth of 1,5 nm, ε is of the order of 300 $\text{l}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$.

8.4.2 Measurement on the sample solution

Wait at least 20 min after the preparation of the sample solution (prepared according to 8.2.2), then proceed as follows.

- Fill the measurement cell of the spectrophotometer with the sample solution.
- Fill the reference cell with nitric acid 0,5 $\text{mol}\cdot\text{l}^{-1}$ (6.6).
- Record the spectrum between 940 nm and 1 020 nm.
- Determine the absorbance of the neptunium(V) line at 981 nm.

The sample 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 results

9.1 Calculation of the neptunium concentration in the sample

The neptunium concentration in $\text{mg}\cdot\text{l}^{-1}$, $\rho(\text{Np})_x$, in the sample being analysed is calculated as given in Formula (1):

$$\rho(\text{Np})_x = \rho(\text{Np})_e \times \frac{\alpha_x}{\alpha_e} \times \frac{V_{10}}{V_1} \times \frac{V_2}{V_{20}} \quad (1)$$

where

$\rho(\text{Np})_e$ is the neptunium concentration ($\text{mg}\cdot\text{l}^{-1}$) of the calibration standard (6.12);

V_{10} is the volume of the neptunium calibration standard (6.12);

V_1 is the volume of the sample solution;

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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 ($\text{m}^2\cdot\text{mol}^{-1}$), but in practice, it is usually taken as the $\text{mol}^{-1}\cdot\text{cm}^{-2}$ or the $\text{l}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$.