

INTERNATIONAL STANDARD

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Determination of neptunium in nitric acid solutions by molecular absorption spectrophotometry

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*Détermination du neptunium dans les solutions d'acide nitrique par
spectrophotométrie d'absorption moléculaire*

ISO 13465:1997

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INTERNATIONAL

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

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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International Standard ISO 13465 was prepared by Technical Committee ISO/TC 85, *Nuclear energy*, Subcommittee SC 5, *Nuclear fuel technology*.

Annex A of this International Standard is for information only.

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Determination of neptunium in nitric acid solutions by molecular absorption spectrophotometry

1 Scope

This International Standard specifies an analytical method for determining the neptunium concentration in nitric acid solutions 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 mass of neptunium equal to at least 50 µg when the spectrophotometer used has an expanded scale reading (0,1 in optical density for the entire scale) or 500 µg of neptunium otherwise.

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2 Principle

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

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3 Interferences

3.1 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 its concentrations in the sample and standard do not differ by more than 0,2 mol/l during the analyses.

3.2 Acidity influences the formation of neptunium(V), and its concentration shall be kept between 2,5 mol/l and 4 mol/l in a 5 ml volume prior to the addition of the vanadium(V)/vanadium(IV) buffer mixture, and to $(1 \pm 0,2)$ mol/l at the final measurement.

3.3 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).

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

3.5 Nitrate ions at a concentration up to 0,1 mol/l in the sample have no effect when the initial vanadium(V)/vanadium(IV) ratio is 0,5.

4 Reagents

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

4.1 Hydrofluoric acid solution, $c(\text{HF}) = 0,1 \text{ mol/l}$.

4.2 Nitric acid solution, $c(\text{HNO}_3) = 16 \text{ mol/l}$ ($d_4^{20} = 1,42$).

4.3 Nitric acid solution, $c(\text{HNO}_3) = 3 \text{ mol/l}$.

4.4 Nitric acid solution, $c(\text{HNO}_3) = 0,5 \text{ mol/l}$.

4.5 Nitric acid solution, $c(\text{HNO}_3) \approx 0,1 \text{ mol/l}$.

4.6 Vanadium(IV) oxide sulfate solution, $c(\text{VOSO}_4 \cdot 5\text{H}_2\text{O}) = 0,75 \text{ mol/l}$

Weigh 18,98 g of vanadium(IV) oxide sulfate ($\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$) and dissolve it in 80 ml of the nitric acid solution (4.5). Pour into a 100 ml flask and bring to volume with nitric acid solution (4.5). Homogenize. This solution shall not be used more than one month after the date of preparation.

4.7 Cerium(IV) nitrate solution, $c[\text{Ce}(\text{NO}_3)_4] = 0,25 \text{ mol/l}$

Weigh 13,7 g of ammonium cerium hexanitrate $[(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6]$ and dissolve it in 80 ml of the nitric acid solution (4.5). Pour into a 100 ml flask and bring to volume with nitric acid solution (4.5). Homogenize.

4.8 Vanadium(V)/vanadium(IV) redox buffer mixture

Add 40 ml of vanadium(IV) oxide sulfate solution (4.6) and 40 ml of cerium nitrate solution (4.7) into a 100 ml flask. Shake and bring to 100 ml with distilled water. Homogenize. This solution shall not be used more than one month after the date of preparation.

4.9 Uranyl nitrate solution

Prepare a uranyl nitrate solution in nitric acid (4.3) with a concentration equal to that of the sample to be analyzed.

4.10 Reference neptunium solution

Weigh accurately about 1,15 g of pure neptunium oxide (NpO_2) and dissolve it in 10 ml of nitric acid (4.2) and 1 ml hydrofluoric acid (4.1). Bring to boiling under reflux. After cooling, pour into a 500 ml flask, add 400 ml of nitric acid (4.4) and make up to the mark with distilled water.

Calibrate the solution obtained using one of the following methods (or better, using both):

- controlled potential coulometry: each aliquot will preferably be evaporated until nearly dry and then diluted with 0,5 mol/l sulfuric acid before analysis;

- b) volumetric analysis: oxidation with silver oxide (AgO), reduction by Fe(II) in excess in 2,5 mol/l sulfuric acid medium and titration of excess of Fe(II) by cerium(IV) or potassium dichromate.

One ml of the reference neptunium solution contains approximately 2 mg of neptunium.

5 Apparatus

Usual nuclear laboratory equipment and, in particular, a high quality, double-beam grating spectrophotometer designed for measurements on fully contained high alpha solutions and having, as far as possible, the following features:

- bandpass lower than 0,7 nm at 981 nm, corresponding to a low background of the detector (fluctuation approximately 0,001 in optical density);
- spectrum scanning speed equal to the bandpass width-to-period ratio (the period corresponds to the time taken by the pen to perform 98,6 % of the total displacement requested by a signal);
- stable baseline;
- scale expansion in order to obtain 0,1 in optical density for the entire scale;
- 1 cm optical pathlength cuvettes.

6 Calibration

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6.1 Sample preparation

- Take six 25 ml volumetric flasks and add to each of them:
 - one volume of uranyl nitrate solution (4.9) (less than 5 ml) containing a mass of uranyl nitrate equivalent to the uranium content of the sample to be analysed,
 - enough nitric acid solution (4.3) to give a total volume of 5 ml.
- Add respectively 1 ml, 2 ml, 3 ml, 4 ml, 5 ml and 6 ml of the reference solution (4.10).
- Add to each flask 5 ml of the buffer mixture (4.8).
- Rinse the walls of the flasks with 1 ml to 2 ml of nitric acid (4.4) and leave to react for 5 min.
- Make up each flask to volume with nitric acid (4.4).

The neptunium concentration in the six flasks is respectively equal to 40a mg/l, 80a mg/l, 120a mg/l, 160a mg/l, 200a mg/l and 240a mg/l, where a is the quantity, in milligrams, of neptunium contained in 1 ml of the reference neptunium solution (4.10).

6.2 Measurement

- Adjust the spectrophotometer baseline between 1020 nm and 940 nm by filling the reference cuvette and the sample cuvette with nitric acid (4.4) and scanning the spectrum.
- Rinse and fill the test sample cuvette with one of the neptunium solutions.
- Record the spectrum between 1020 nm and 940 nm.
- Successively proceed in the same way with the six solutions.

The adjustments of the spectrophotometer (slit width and height, spectrum scanning speed, pen damping) shall be previously chosen to obtain the neptunium(V) peak under optimum conditions and shall be strictly the same for all measurements.

6.3 Spectral evaluation

- a) Draw the tangent at the wavelength axis at the basis of the neptunium(V) peak and the perpendicular line from the peak maximum to the wavelength axis of the spectrophotometer.
- b) Measure the optical density between the peak maximum and the intersection of the perpendicular line with the tangent at the wavelength axis of the neptunium(V) peak. A typical neptunium(V) spectrum in 1 mol/l nitric acid medium is shown in annex A.
- c) Calculate the regression curve giving the optical density measured against the neptunium concentration. If the adjustments of the spectrophotometer enable the true absorbance to be measured, this curve is a straight line passing through the origin. In a 1 mol/l nitric acid medium, the molar extinction coefficient varies between $350 \text{ mol}^{-1} \cdot \text{cm}^{-1} \cdot \text{l}$ and $405 \text{ mol}^{-1} \cdot \text{cm}^{-1} \cdot \text{l}$, depending on the uranium concentration.

If the spectrophotometer used provides scale expansion to obtain 0,1 in optical density for the entire scale, complete the calibration curve by performing the same operations (6.2 and 6.3) again, using the neptunium reference solution (4.10) diluted by a factor of 10 in nitric acid (4.4). If necessary, the other measuring scales shall be calibrated in the same way.

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7 Operating procedure

7.1 Perform duplicate analyses. The volumes of the two aliquots may be identical or not. Each aliquot shall contain at least:

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- 50 µg of neptunium in a volume less than 5 ml, when the spectrophotometer provides an expanded scale reading 0,1 optical density for the whole scale,
- 500 µg of neptunium in a volume less than 5 ml if the spectrophotometer has no scale expansion capabilities.

In the two 25 ml volumetric flasks numbered (1) and (2), add first the test samples, then an additional quantity of nitric acid (4.3) to obtain a volume of 5 ml and an acidity between 2,5 mol/l and 4 mol/l.

Add in flask (2) only a measured volume of the reference neptunium solution (4.10) or of this reference solution diluted by a factor of 10, depending on whether the spectrophotometer used has scale expansion capabilities or not. The volume added shall contain a mass of neptunium close to that of the sample aliquot.

Add to both flasks:

- a) 5 ml of the vanadium(V)/vanadium(IV) redox buffer mixture (4.8);
- b) 1 ml to 2 ml of nitric acid (4.4) in order to rinse the walls of the volumetric flasks;
- c) shake and leave to react for 5 min [10 min if plutonium(VI) is present in the sample aliquot];
- d) dilute to volume with nitric acid (4.4) and homogenize.

7.2 Record the spectrum of the solutions contained in flasks (1) and (2) under conditions strictly identical to those described in 6.2.

7.3 Measure the absorbances as described in 6.3 and calculate the neptunium concentration from the regression equation.

8 Expression of the results

The neptunium mass concentration c , expressed in milligrams per litre, is calculated from

- a) for the solution without addition of neptunium:

$$c = c_1 V_3 / V_1$$

- b) for the solution with addition of neptunium:

$$c = (c_2 V_4 - c_0 V_0) / V_2$$

where

c_0 is the concentration of neptunium in the added reference solution;

c_1 is the concentration obtained for the solution without neptunium addition;

c_2 is the concentration obtained for the solution with neptunium addition;

V_0 is the volume of neptunium reference solution added to flask (2);

V_1 is the volume of the sample aliquot without addition in flask (1);

V_2 is the volume of the sample aliquot with addition in flask (2);

V_3 is the make-up volume of the solution without addition in flask (1), normally 25 ml;

V_4 is the make-up volume of the solution with addition in flask (2), normally 25 ml.

These two values of c shall be equal within the reproducibility range of the results if the operating conditions are satisfactory (medium, adjustment of the equipment). Otherwise, the reason for the disparity shall be determined.

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9 Reproducibility <https://standards.iteh.ai/catalog/standards/sist/c1c662a3-15ea-4256-9e67-8693c3be7147/iso-13465-1997>

For pure neptunium solutions and for a single determination, the 95 % confidence interval is approximately

- $\pm 3,5$ mg/l for a neptunium concentration of 50 mg/l to 600 mg/l in the dilution flask. This was derived from a regression straight line obtained with 54 measurements at nine different concentrations.
- $\pm 2,6$ mg/l for a neptunium concentration of 15 mg/l to 55 mg/l in the dilution flask. This was derived from a regression straight line obtained with 15 measurements at five different concentrations.

10 Sensitivity

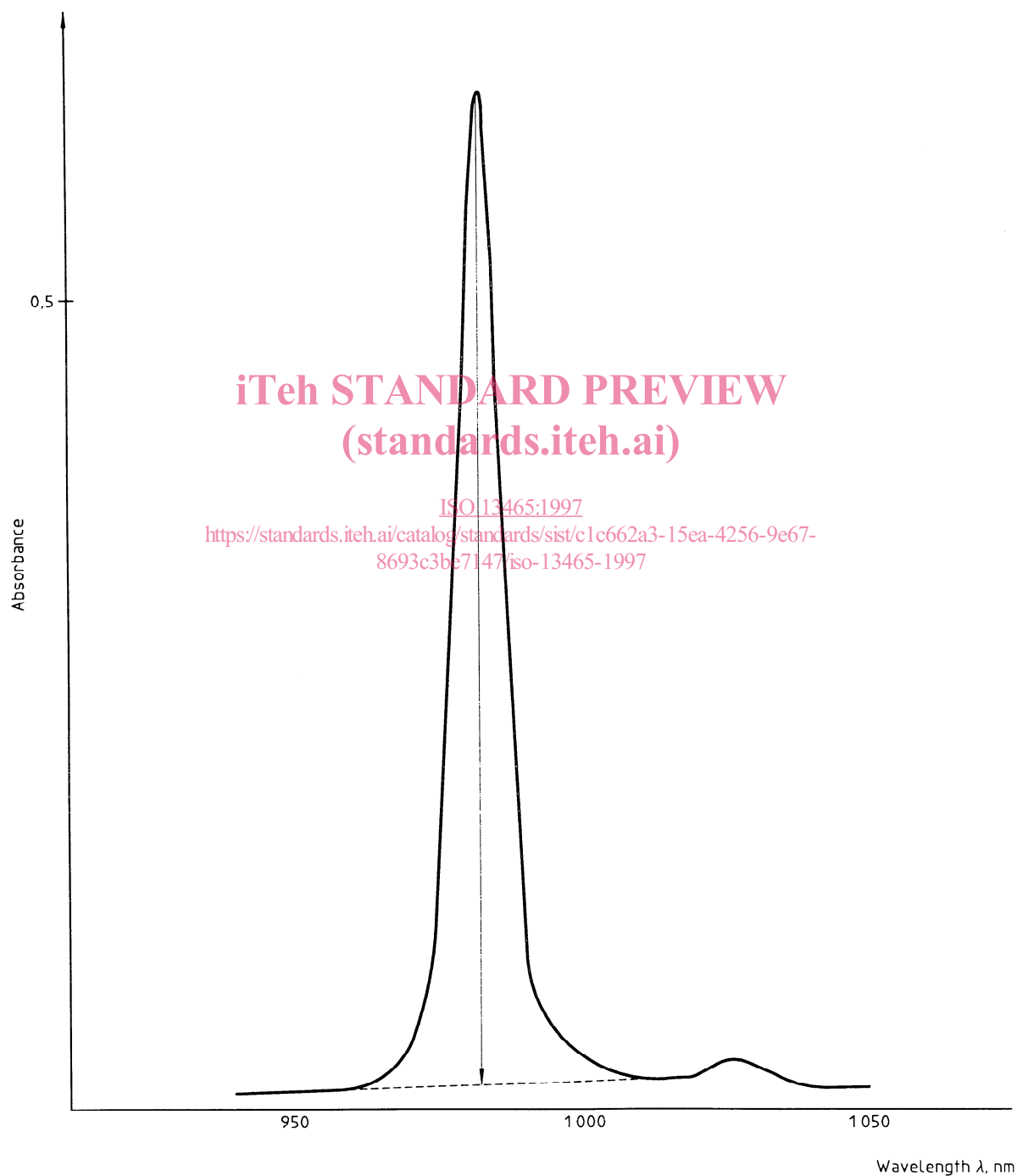
Under routine operating conditions, a variation of approximately 0,6 mg/l in the neptunium concentration during measurements induces a variation of approximately 0,001 in the optical density.

11 Detection limit

The detection limit equals 2 mg/l of neptunium in the dilution flask, using a path length of 1 cm.

Annex A
(informative)

Typical spectrum of neptunium(V) in 1 mol/l nitric acid medium



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