

# INTERNATIONAL STANDARD

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## Nitric acid feed solutions from reprocessing plants — Spectrophotometric determination of plutonium after oxidation to plutonium(VI)

### iTeh STANDARD PREVIEW

*Solutions nitriques d'entrée des usines de retraitement —  
Dosage spectrophotométrique du plutonium après oxydation en  
plutonium(VI)*

ISO 9463:1990

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INTERNATIONAL

ISO



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## Foreword

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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.

International Standard ISO 9463 was prepared by Technical Committee ISO/TC 85, *Nuclear energy*.

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# Nitric acid feed solutions from reprocessing plants — Spectrophotometric determination of plutonium after oxidation to plutonium(VI)

## 1 Scope

This International Standard specifies an analytical method for determining the plutonium concentration of nitric acid feed solutions from reprocessing plants. The method is applicable, without interference, in the presence of numerous cations, it is applicable to test portions containing between 0,5 mg and 2,5 mg of plutonium.

## 2 Principle

The nitrate concentration is adjusted to 3 mol/l with nitric acid.<sup>1)</sup>

Plutonium is oxidized to the hexavalent state either with cerium(IV) or with argentic oxide, in which case the excess is destroyed by adding sulfamic acid.

The volume is adjusted with 3 mol/l nitric acid.

The optical density of the  $\text{PuO}_2^{2+}$  absorption peak at 831 nm is measured on a spectrophotometer. The result is based on a calibration established under the same conditions.

The procedure uses 3 mol/l nitric acid as this permits either cerium(IV) or argentic oxide to be used as oxidant and is convenient for most applications. It is acceptable to use cerium(IV) as oxidant at lower acidities and argentic oxide as oxidant at higher acidities provided that the concentration of the nitric acid used for calibration is similarly adjusted.

## 3 Chemical conditions

### 3.1 Stability of Pu(VI)

Plutonium(VI) is very stable under the operating conditions of the method over the range 2 mol/l  $< c(\text{H}^+) < 5$  mol/l.

### 3.2 Rate of oxidation of Pu(IV) to Pu(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 or 3 mol/l nitric acid.

With argentic oxide, the oxidation is very rapid, noticeably faster than with cerium(IV).

### 3.3 Destruction of the excess oxidant

With cerium(IV) the excess reagent does not interfere and need not be destroyed.

With argentic oxide as oxidant, the excess reagent shall be destroyed by reaction with a small excess of sulfamic acid or by heating (to about 80 °C).

### 3.4 Molar extinction coefficient of Pu(VI)

The absorbance falls

- when the nitrate ion concentration is increased. The decrease in absorbance becomes more rapid at higher nitrate levels. At about 3 mol/l nitrate, an increase of 0,1 mol/l in the total nitrate content causes a decrease of about 0,7 % in the absorbance;

1) This acidity has been chosen in order to avoid dilution with water due to the fact that the solutions to be measured are wet precipitates with a nitrate ion concentration of 3 mol/l. Dilution with water would risk causing plutonium hydrolysis.

- when the acidity is increased. This change is generally less than 0,1 % for a free acid change of 0,1 mol/l. Thus the influence of free acidity is an order of magnitude less than that of the nitrate content;
- when the temperature is increased. The decrease in absorbance is about 0,5 % per °C.

## 4 Reagents

All reagents shall be of analytical reagent grade.

### 4.1 Method using argentic oxide as oxidant

**4.1.1 Nitric acid**, 3 mol/l, adjusted to  $\pm 0,05$  mol/l.

**4.1.2 Sulfamic acid** ( $\text{NH}_2\text{SO}_3\text{H}$ ), 0,5 mol/l solution in water (48,5 g/l).

**4.1.3 Argentic oxide** ( $\text{Ag}_2\text{O}$ ).

This reagent can be prepared as follows.

Dissolve 72 g of sodium hydroxide in 1 litre of water in a very clean pyrex conical flask or beaker and heat to 85 °C.

Add, with stirring, 75 g of potassium persulfate ( $\text{K}_2\text{S}_2\text{O}_8$ ) to the hot solution.

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

Add, whilst still stirring, a solution of 51 g of silver nitrate in a minimum of water (about 40 ml). Heat the mixture to 90 °C and stir for 15 min.

Allow to cool, then filter on a No. 4 glass frit.

Wash with 0,25 mol/l sodium hydroxide solution (10 g/l) until free from sulfate ions, as verified by testing the effluent solution for precipitation with barium; the volume necessary is generally between 0,5 litre and 1 litre.

Wash with water until neutral.

Allow to dry in air at room temperature, stirring occasionally with care to form a powder (use a sieve if necessary).

**WARNING — Never dry at a temperature above 35 °C (danger of explosion).**

Dry in a desiccator for 1 day and store in a stoppered brown glass bottle.

**4.1.4 Plutonium reference solution**, containing about 0,5 g of plutonium per litre in 3 mol/l nitric acid.

### 4.2 Method using cerium(IV) as oxidant

**4.2.1 Nitric acid**, 3 mol/l, adjusted to  $\pm 0,05$  mol/l.

**4.2.2 Cerium(IV)**, 0,4 mol/l solution in 3 mol/l nitrate medium.

Dissolve 219,3 g of ceric ammonium nitrate  $[(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6]$  in 600 ml of 1 mol/l nitric acid and dilute to 1 litre with water.

**4.2.3 Plutonium reference solution**, containing about 0,5 g of plutonium per litre in 3 mol/l nitric acid.

## 5 Apparatus

Normal laboratory equipment and equipment normally found in a high-activity laboratory analysing plutonium solutions, and

**5.1 Double-beam spectrophotometer**, equipped for measurements in a shielded cell, having, where possible, the following characteristics:

- bandwidth about 0,3 nm at 831 nm with low detector baseline noise (fluctuations of the order of 0,001 in optical density);
- spectrum scanning speed no greater than the value obtained on dividing the bandwidth by the period; this period is the time for the pen to reach 98,6 % of its total displacement when triggered by a signal;

- stable baseline.

These characteristics are required to obtain a linear relationship between the optical density and the plutonium concentration, the molar extinction coefficient being close to 490 in a 3 mol/l nitrate medium. The peak width at half-height is 2,8 nm.

**5.2 Equipment**, comprising for example:

- a shielded cell or a glove box for sample preparation;
- a system for transferring the prepared sample to the spectrophotometer cuvette;
- an assembly of two flow-through cuvettes in closed loops in a small ventilated enclosure. This assembly shall be optically compatible with the characteristics of the spectrophotometer, without introducing stray light and shall maintain a stable temperature to within  $\pm 0,5$  °C.

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## 6 Operating procedure

The procedure specified in this clause is intended for use with cuvettes of 4 cm optical path length and for 25 ml final volume of solution.

NOTE 1 The best relative precisions are theoretically obtained at about 0,8 optical density with a photomultiplier as detector (0,4 with a lead sulfide cell). The operating procedure (concentration of the reference solution, volume of the aliquots, etc.) should, if necessary, be modified accordingly if these parameters are changed.

### 6.1 Calibration

#### 6.1.1 Oxidation

##### 6.1.1.1 By argentic oxide

Using calibrated pipettes, transfer respectively 1 ml, 2 ml, 3 ml, 4 ml and 5 ml of the plutonium reference solution (4.1.4) into five 25 ml calibrated flasks reserved for the calibration.

Add 10 ml of 3 mol/l nitric acid (4.1.1) and a small excess of argentic oxide (4.1.3) to give a persistent dark colour. Allow to react for 5 min, mixing from time to time. Destroy the excess argentic oxide by adding sulfamic acid solution (4.1.2) dropwise until the brown colour disappears (avoid adding too high an excess of sulfamic acid). Adjust to 25 ml with 3 mol/l nitric acid (4.1.1) and measure the absorbance on the spectrophotometer.

##### 6.1.1.2 By cerium(IV)

Using calibrated pipettes, transfer respectively 1 ml, 2 ml, 3 ml, 4 ml and 5 ml of the plutonium reference solution (4.2.3) into five 25 ml calibrated flasks reserved for the calibration.

Add 5 ml of cerium(IV) solution (4.2.2); mix and allow to stand for 5 min. Adjust to 25 ml with 3 mol/l nitric acid (4.2.1) and measure the absorbance on the spectrophotometer.

#### 6.1.2 Spectrophotometry

Between all measurements, the cuvettes shall be kept full of 3 mol/l nitric acid. Ensure that the spectrophotometer settings (slit width, spectrum scanning speed, pen damping, etc.) are selected to obtain the best conditions for the plutonium(VI) peak. These settings shall be kept exactly the same for all measurements.

Choose and, if required, set the measurement scales of the spectrophotometer and recorder.

With the cuvettes filled with 3 mol/l nitric acid, set the baseline (or zero) of the spectrophotometer and recorder.

Rinse and refill the sample cuvette with the solution to be measured. Record the spectra between 860 nm and 800 nm at least twice, the reference cuvette being filled with 3 mol/l nitric acid.

Rinse the sample cuvette copiously with 3 mol/l nitric acid.

#### 6.1.3 Measurement

Draw the tangent to the two troughs at the foot of the peak, and the perpendicular from the summit to the theoretical spectrophotometer baseline. Measure the optical density along the perpendicular between the summit and the intersection with the tangent to the feet of the Pu(VI) peak.

Plot a graph of the measured optical densities against the concentration of plutonium in the cuvette, or calculate the coefficients of the regression curve.

NOTE 2 Other measurement procedures are suitable; for instance the peak-trough measurement.

The "trough" value can be measured at 805 nm or 860 nm where the Pu(VI) optical density is zero. This procedure, which has to be the same for the calibration and for the sample determination, should be chosen according to the apparatus used (shape of the real baseline, connected computer, etc.) and to the other elements present. The procedure described minimizes the Am(III) (peak at 812 nm) and Nd(III) (peaks at 795 nm and 865 nm) interference but is strictly accurate only if the "trough" line is tangent to the spectrum at constant wavelengths.

### 6.2 Sample determination

Make the determination in duplicate.

Transfer the sample aliquot containing an amount of plutonium within the calibration range (between 0,5 mg and 2,5 mg) into a 25 ml calibrated flask. Adjust the nitrate concentration to 3 mol/l by adding dilute or concentrated nitric acid.

Proceed as for the calibration (see 6.1).

NOTE 3 It is not necessary to take into account a supplementary blank. The reagents do not contain plutonium and the blank is taken into account by the measurement (double beam) and the ordinate at the zero point of the calibration curve.

## 7 Expression of results

### 7.1 Method of calculation

From the sample absorbance measurement, deduce the plutonium concentration in the cuvette,  $C$ , in milligrams per litre, using the calibration curve or, better, the regression equation of the curve. Calculate the final result from the formula

$$C_s = C \frac{V_1}{V}$$

where

- $C_s$  is the concentration in the sample, in milligrams per litre;
- $V$  is the volume of the sample aliquot, in millilitres;
- $V_1$  is the volume of the flask used, in millilitres (= 25 ml).

### 7.2 Repeatability, $r$

The coefficient of repeatability variation is about 0,4 % (at the 2 mg sample level), if the chemical parameters of the method are well controlled, particularly the nitrate concentration and the temperature of the solutions at the time of measurement.

### 7.3 Systematic error

The mean of the results obtained in a reprocessing campaign was found to differ by less than 0,2 % from the mean of those obtained by the mass spectrometric isotope dilution method. The comparison was performed on about 350 results.

## 8 Interferences

### 8.1 Anions

Any anions likely to form complexes with the  $\text{PuO}_2^{2+}$  ion can interfere by changing the molar extinction coefficient. Anions  $\text{Pu(IV)}$  or  $\text{Ce(IV)}$  can interfere with the oxidation by cerium.

Tests have been made leading to the following conclusions:

- $\text{ClO}_4^-$  Perchlorate ions do not interfere even at a concentration of 0,1 mol/l.
- $\text{NO}_3^-$  The concentration of nitrate ions has a major influence on the molar extinction coefficient (see 3.4).
- $\text{F}^-$  Fluoride ions have a very large effect in the absence of complexing cations with the  $\text{AgO}$  oxidation method: fluoride ions should be complexed by replacing some of the 3 mol/l nitric acid in the method by the mixture 0,1 mol/l  $\text{Al(NO}_3)_3$  — 2,7 mol/l  $\text{HNO}_3$ , in order to obtain an Al/F ratio of at least 3. Under these conditions there is no interference.
- $\text{Cl}^-$  Chloride ions can form a complex with  $\text{Pu(VI)}$  and precipitate silver, but they are not present in process solutions.

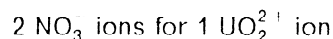
$\text{SO}_4^{2-}$  The concentration of sulfate ions should be known and the calibration should be made in the same medium, since sulfates influence the molar extinction coefficient. For example, this is about 298 in 0,5 mol/l  $\text{H}_2\text{SO}_4$  — 4 mol/l  $\text{HNO}_3$  compared with 455 in 4 mol/l  $\text{HNO}_3$  (the peak develops a shoulder at 834 nm). Moreover, sulfates can impede the quantitative oxidation of plutonium by  $\text{Ce(IV)}$ .

$\text{PO}_4^{3-}$  Tests have shown that the presence of 0,2 mmol of phosphate in the sample aliquot does not impede the quantitative oxidation of 4 mg of Pu by  $\text{Ce(IV)}$  and does not affect the molar extinction coefficient of  $\text{Pu(VI)}$ . Only a very slow precipitation of cerium has been observed. At the levels normally present in plant solutions (about  $10^{-5}$  mol/l), there is no effect.

### 8.2 Cations

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

If the concentration of foreign 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:



Tests have been made leading to the following conclusions:

- $\text{H}^+$  Protons have a very small influence on the molar extinction coefficient. It is, however, inadvisable to operate with a concentration of free protons below 1 mol/l because the plutonium species become less stable.
- $\text{Fe}$  The molar extinction coefficient of  $\text{Fe}^{3+}$  is constant between 800 nm and 860 nm.
- $\text{Cr}$  Chromium ions do not interfere even at a Cr/Pu ratio of 10.
- $\text{Mn, Ni, Cu}$  The concentrations of these ions in reprocessing solutions are usually sufficiently low not to pose any problems.
- $\text{Mo}$  Molybdenum ions do not interfere even at a Mo/Pu ratio of 5.

Na	Sodium ions do not interfere even at a Na/Pu ratio of $2 \times 10^4$ .	Am	For an Am/Pu ratio of about 10, there is 5 % interference (if no precautions are taken in the chart measurements). The Am content of reprocessing solutions is sufficiently low not to cause interference.
U	It is possible to measure 25 ppm of plutonium in uranium, taking into account the associated nitrate.		
Al	Aluminium ions do not interfere, even at an Al/Pu ratio greater than 100.	Nd	Fission neodymium does not cause any interference with reprocessing plant feed solutions provided that it is not used as an internal standard.
Np	Neptunium ions not interfere, even at a Np/Pu ratio of 1 000.		Reducing agents in very large amounts consume cerium(IV); the volume of ceric nitrate solution in the oxidation step should then be increased.

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