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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 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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For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see www.iso.org/iso/foreword.html.

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 9463:2009), which has been technically revised. The main change compared to the previous edition is the use of silver (II) oxide powder for the plutonium valence adjustment.

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.

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

1 Scope

This document specifies an analytical method by spectrophotometry, for determining the plutonium concentration in nitric acid solutions, with spectrophotometer implemented in hot cell and glove box allowing the analysis of high activity solutions. Commonly, the method is applicable, without interference, even in the presence of numerous cations, for a plutonium concentration higher than 0,5 mg·l^{-1} in the original sample with a standard uncertainty, with coverage factor k = 1, less than 5 %.

The method is intended for process controls at the different steps of the process in a nuclear fuel reprocessing plant or in other nuclear facilities.

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 terminological databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at http://www.electropedia.org/

4 Principle

Plutonium is quantitatively oxidized to the hexavalent state either with cerium (IV) or with silver oxide. The excess of silver oxide is destroyed by the addition of sulfamic acid. The optical density of the plutonium (VI) (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).

5 Chemical conditions

5.1 Stability of Pu(VI)

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

5.2 Rate of oxidation of Pu(IV) to Pu(VI)

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

As an example, the oxidation of Pu(IV) in 4 mol·l^{-1} nitric acid is complete in between 10 min and 15 min when the Ce/Pu initial ratio is higher than 20[2].

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

In addition, the Ag^{2+}/Ag^{+} redox potential is higher than that of Ce^{4+}/Ce^{3+} and is better adapted to cope with the presence of organic traces in solution.

On the other hand, cerium presents the advantage to be stable in sulfuric acid so that it can be added as a precise quantity in solution.

5.3 Destruction of the excess oxidant

With cerium the excess reagent and product Ce(III), does not interfere (no absorption above 450 nm) and does not need to be destroyed[2].

With silver oxide as oxidant, the excess reagent shall be destroyed by reaction with a small excess of sulfamic acid or rise of temperature[2].

5.4 Comparison of Ce(IV) and Ag(II)

As regards Pu(IV) oxidation into Pu(VI), the reactivity and use of Ce(IV) and Ag(II) are compared in Table 1, in order to guide the analyst in the selection of the best reactant for oxidation.

Table 1 — Comparison of Ce(IV) and Ag(II)

Oxidizer	Ag(II)	Ce(IV)
Introduction of reactants	−	+
Spectral interferences	−	+
Oxidizing power	++	+
Oxidation kinetics	++	−
Oxidizer excess destruction	Sulfamic acid or rise of temperature	Not necessary
Operating temperature	Room temperature	

5.5 Molar extinction coefficient of Pu(VI)

The nominal molar extinction coefficient[1]i.e. the molar attenuation coefficient of Pu(VI) in nitric acid solution varies between 400 l·mol^{-1}·cm^{-1} and 500 l·mol^{-1}·cm^{-1}[3], with a very narrow full width at half maximum (FWHM) of about 4 nm.

The molar extinction coefficient and therefore absorbance depends upon a number of parameters, for example:

— **The 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.

— **The 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.

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