INTERNATIONAL STANDARD

ISO 16796

Second edition
2022-01

Nuclear energy — Determination of Gd_2O_3 content in gadolinium fuel blends and gadolinium fuel pellets by atomic emission spectrometry using an inductively coupled plasma source (ICP-AES)

Énergie nucléaire — Dosage de Gd_2O_3 dans des mélanges de poudres et dans des pastilles combustibles au gadolinium par spectrométrie par émission atomique à plasma à couplage inductif (ICP-AES)

Reference number
ISO 16796:2022(E)

ISO copyright office
CP 401 • Ch. de Blandonnet 8
CH-1214 Vernier, Geneva
Phone: +41 22 749 01 11
Email: copyright@iso.org
Website: www.iso.org

Published in Switzerland

Contents

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.

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).

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. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

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.

ISO 16796 was prepared by Technical Committee ISO/TC 85, *Nuclear energy, nuclear technologies, and radiological protection*, Subcommittee SC 5, *Nuclear installations, processes and technologies*.

This second edition cancels and replaces the first edition (ISO 16796:2004), which has been technically revised.

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 — Determination of Gd_2O_3 content in gadolinium fuel blends and gadolinium fuel pellets by atomic emission spectrometry using an inductively coupled plasma source (ICP-AES)

1 Scope

This document is applicable to the determination of gadolinium as Gd_2O_3 in powder blends and sintered pellets of Gd_2O_3 + UO_2 and ((U, Gd) O_2) from mass fraction 10 g/kg to 100 g/kg (i.e. 1 % to 10 %), using a suitable ICP-AES instrument.

This methodology is capable of demonstrating compliance with agreed upon fuel specifications and associated data quality objectives provided the user has performed qualification measurements under their established measurement control program to demonstrate that measurement uncertainty requirements will be met with the desired level of confidence at the specification.

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 3696, *Water for analytical laboratory use — Specification and test methods*

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 https://www.electropedia.org/

4 Principle

The test sample is weighed and dissolved in nitric acid. The test sample solutions are aspirated into an inductively coupled plasma using argon as a carrier. The emitted light from the test sample in the plasma is dispersed, and the gadolinium line at 335,0 nm is measured by a spectrometer.

The intensity of the gadolinium line is proportional to the concentration of gadolinium present.

Impurity interferences have not been observed for the usual test samples of the nuclear grade material.

5 Apparatus

5.1 Inductively coupled plasma atomic emission spectrometer (ICP-AES). A typical value for resolution is 0,555 nm/mm in the first order.

5.2 Analytical balance; sensitivity ±0,1 mg.

5.3 Three-dimensional shaker mixer.

5.4 Hot plate.

5.5 Micropipettes; accurate to ±0,25 %.

5.6 Volumetric flasks; accurate to ±0,25 %.

5.7 Glass beakers.

5.8 Percussion mortar.

5.9 Pellet press.

5.10 Muffle furnace.

6 Reagents

6.1 Concentrated nitric acid, analytical reagent grade.

6.2 Demineralized water, in accordance with the Grade 2 purity requirements of ISO 3696.

6.3 Nitric acid, 1:1, prepare by diluting equal volumes of concentrated nitric acid and demineralized water.

6.4 Uranium dioxide, nuclear grade reference material, obtained from a qualified supplier.

6.5 Gadolinium oxide, Gd_2O_3, minimum mass fraction 999,9 g/kg, reference material, obtained from a qualified supplier.

7 Standard blends

Standard powder blends are prepared under laboratory conditions from the UO_2 and Gd_2O_3 high-purity reference materials listed in Clause 6. These standards will contain Gd_2O_3 mass fraction in the range of 10 g/kg to 100 g/kg, depending on the anticipated Gd_2O_3 content in the test samples.

Guidance on preparing working reference materials is available in ASTM C1128[3].

7.1 Drying of reference materials

The UO_2 and Gd_2O_3 powders are dried at 110 °C for 2 h and allowed to cool in a desiccator (or dried and cooled as directed by the reference material supplier) before preparing the standard blends.

7.2 Preparing standard blends

The appropriate amounts of Gd_2O_3 and UO_2 are weighed on an analytical balance into different plastic vials to obtain the standard blends containing Gd_2O_3 mass fraction in the range from 10 g/kg to 100 g/kg.

When preparing standard powder blends that will be pelletized and fired, the desired mass of the UO_2 reference material shall be calculated based on the stoichiometry of the reference material, as given in Formula (1):

$$m_{UO_{(2+x)}} = m_{UO_2}\left(1+\frac{xA_O}{A_U+2A_O}\right) \tag{1}$$

where

$m_{UO_{(2+x)}}$	is the desired mass of reference material powder, in grams;
m_{UO_2}	is the mass of stoichiometric UO_2 powder needed in the blend, in grams;
A_U	is the atomic mass of uranium;
A_O	is the atomic mass of oxygen;
x	is the excess fraction of oxygen atoms calculated from the values on the reference material certificate.

7.3 Blending

Each blend is mixed in the three-dimensional shaker mixer for 4 h (or the time necessary to guarantee the homogeneity of the blend).

7.4 Preparing pellets standards

After blending, the powders are pressed into pellets. Care shall be taken to clean the press before pressing the standard pellets. The first set of pressed pellets for each Gd_2O_3 mass fraction shall be discarded. As sintering conditions may strongly impact the analytical results, sintering of the pellet standards shall be performed under the same conditions as production. The Gd_2O_3 content of the standard pellets shall be validated, using the procedure described in this document, before being used for calibration or quality control.

7.5 Identification

Each blend shall be identified and retained as an appropriate standard.

8 Standard and test sample preparation

8.1 Preparation of standard solution from powder reference materials

8.1.1 Weigh 5,0 g of each standard into a beaker, weighed to the nearest 0,001 g.

8.1.2 Add 25 ml of nitric acid (1:1) to each standard.

8.1.3 Heat on the hot plate until the blend is completely dissolved, then evaporate the excess nitric acid by boiling for several minutes.

8.1.4 Cool the solution and transfer quantitatively to a 100 ml volumetric flask.

8.1.5 Dilute to 100 ml with demineralized water and mix the solution.

8.1.6 Pipette 1 ml of the prepared solution into a 100 ml volumetric flask.

8.1.7 Dilute to 100 ml with demineralized water.

8.2 Preparation of the powder test samples of Gd_2O_3 plus UO_2

8.2.1 Weigh 5,0 g of test sample into a beaker, weighed to the nearest 0,001 g.

8.2.2 Prepare the test sample as described in 8.1, steps 8.1.2 through 8.1.7.

8.3 Preparation of pellet standards and test samples

8.3.1 Crush the pellet using a percussion mortar (5.8).

8.3.2 Weigh 5,0 g into a crucible, weighed to the nearest 0,001 g.

8.3.3 Heat the crucible with the test sample in a muffle furnace at 420 °C ± 25 °C minimum for 2 h to 3 h.

8.3.4 Quantitatively transfer the content from the crucible to a glass beaker. Then proceed as described in 8.1, steps 8.1.2 through 8.1.7.

9 Calibration and analysis of test samples

9.1 General

Standards as prepared in Clause 7 and 8.1 are used to calibrate the equipment.

Calibration standards shall be traceable to the SI and shall bracket the anticipated concentration range for the dissolved test samples being measured.

a) In the event that a test sample result is outside of the calibration range: the instrument shall be recalibrated and the measurements repeated; or the test sample dilution scheme shall be adjusted so the concentration of the dissolved test sample is within the calibration range when the measurement is repeated.

b) Independence between reference materials used to prepare calibration standards and quality control standards is required. At a minimum, different lots of gadolinium reference material from the same supplier may be used to prepare calibration and quality control standards, however using different suppliers is recommended.

9.2 Calibration

The measurement system shall be calibrated using traceable reference materials procured from competent and qualified suppliers.

The ICP-AES analytical conditions are developed by each laboratory.

- Instrument wavelength calibration, camera alignment, and tuning shall be performed in accordance with manufacturer's guidance.
- Optical intensity and plasma position should be verified as part of the calibration process, in accordance with manufacturer's guidance.
- No specific intensity is required other than that it should not change significantly from the last series of analyses.

- The measurement of optical intensity is typically performed each day at a single wavelength using the same concentration analyte (for example 10 µg/g manganese standard solution at 257,610 nm).
- The intensity is normally measured radially with respect to the plasma. Gadolinium measurements at high concentration are typically measured radially while low concentration gadolinium is typically measured axially.

To calibrate the measurement system for powder test samples, the standard solutions prepared in accordance with 8.1 are measured in at least duplicate and the calibration curve produced from the intensity-versus-concentration curve.

To calibrate the measurement system for pellet test samples, the standard solutions prepared in accordance with 8.3 are measured in at least duplicate and the calibration curve produced from the intensity-versus-concentration curve.

Calibration curves are evaluated using acceptance criteria established by each laboratory, based upon their historical performance; e.g., linear regression fit (R^2), slope, and coefficient of error.

See example in Annex A.

9.3 Analysis of the test samples and quality control standards

The test samples prepared in 8.2 and 8.3 shall be analysed after making the calibration curve. Test samples shall be measured in at least duplicate and spiked test samples should be measured at a defined frequency such as one test sample per batch of ten or fewer similar test samples. To avoid daily correction and achieve the required precision, a new calibration curve is prepared for each batch of test sample determinations.

Process blank measurements should be performed periodically to ensure that background levels are in the expected range; however, background corrections are not normally necessary.

Quality control (QC) standards shall be prepared and measured in the same manner as test samples.

Compare the emission intensities of the test samples and QC standards to the calibration curve and calculate the Gd_2O_3 concentrations for each of the test samples and QC standards.

QC standards shall be used as both opening and closing controls, and should be control charted to monitor measurement and analyst performance.

If any of the test samples contain products other than UO_2 and Gd_2O_3, the calibration and the instrument control measurements shall be performed using reference material blends having the same matrix as the test samples.

9.4 Measurement control program

The measurement control program, procedure system, record retention program, method qualification, and staff training for measuring gadolinium by ICP-AES method shall conform with the accepted practices at the user laboratory. Guidance on record retention, method qualification, and staff training is available in ISO/IEC 17025[2]. Guidance on a measurement control program is available in ANSI N15.51[4]

QC standards shall be traceable and of sufficient quality to demonstrate control of measurement parameters and performance/proficiency of analysts.

Periodic spiking of a predetermined percentage of test samples with known quantities of gadolinium is recommended. Spike recoveries should be consistent with measurement uncertainty determined from quality control standards and should support the conclusion that the measurement method may be applied to demonstrate that materials meet product specification.

Measurement of process blanks is recommended to detect unexpected gadolinium background levels.

If any measurements, such as process blanks, will be performed at or near the method detection limit (MDL), then the MDL and the method reporting limit (MRL) should be determined using accepted practices at the user laboratory.

Secondary absorption lines for gadolinium such as 342,247 nm and 376,839 nm may be used for routine or periodic comparison purposes or to support method qualification or demonstration activities; however, this document has not been validated or demonstrated using these secondary absorption lines.

10 Precision and accuracy

Measurement and sampling uncertainties shall be adequately understood to demonstrate that specifications are being satisfied with an appropriate level of confidence. The calculation of uncertainty for the measurement method shall be performed using accepted statistical practices. Implementation of ISO/IEC Guide 98-3[1] is recommended.

Typical results obtained by one laboratory are the following:

— For 20 determinations of each of 6 standards containing Gd_2O_3 mass fractions ranging from 20 g/kg to 100 g/kg, the maximum coefficient of variation was 0,99 % for Gd_2O_3 at 70 g/kg, and the minimum was 0,32 % for Gd_2O_3 at 40 g/kg.

— Maximum relative error was 0,98 %.

— See Annex B.

The precision and accuracy requirements (i.e., acceptance criteria) shall be agreed upon with individual customers requesting analytical services. Prior method qualification shall have demonstrated that the laboratory can meet the customer's requirements before any request for analytical services is accepted.

11 Test report

The test report shall include the following information:

a) identification of the test sample;

b) a reference to this document, i.e. ISO 16796:2022;

c) the method used with reference to this document;

d) the results (i.e., values, expanded uncertainties, and coverage factors) and their units of measurement;

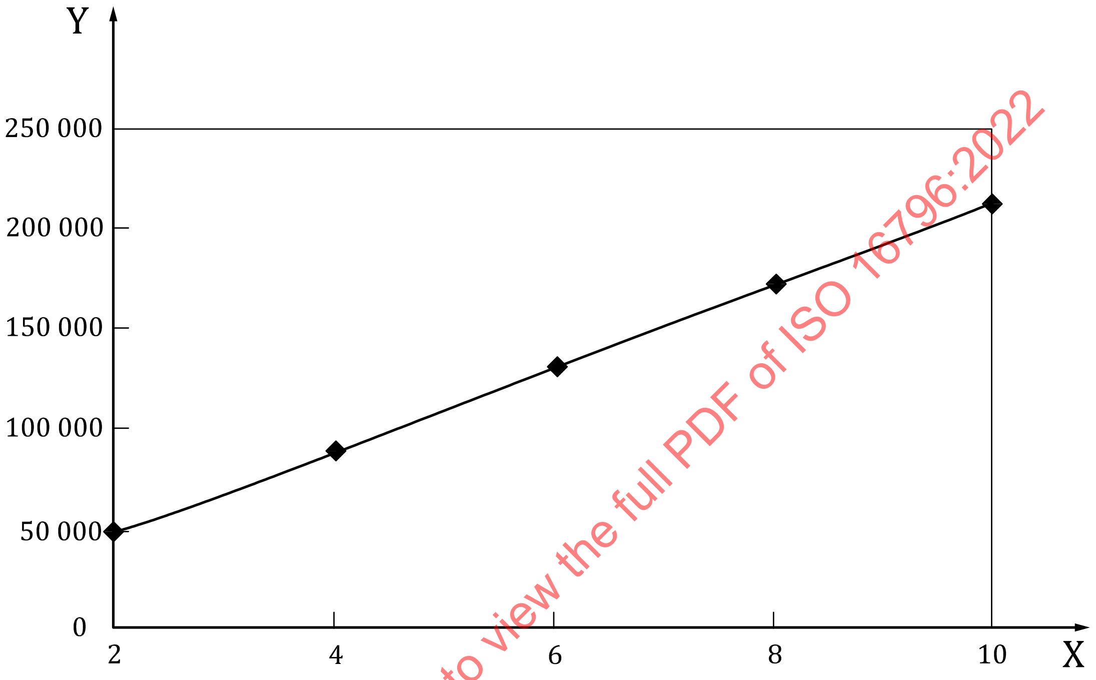
e) any unusual features noted during the test;

f) any operations not included in this document;

g) a note indicating whether or not buoyancy corrections have been applied.

Annex A
(informative)

Calibration curve



Key

X Gd_2O_3, mass fraction in g/kg

Y intensity

NOTE To carry out the pattern curve, each standard is read twice.

Figure A.1 — Calibration curve

Table A.1

Data used to calculate the pattern curve		**Linear regression results**	
		Y-intercept	−4,11 0
Gd_2O_3 g/kg	Intensity	Estimation error in Y	±0,571
20,075	48 780	R^2	0,999 8
40,146	89 691	Number of data	5
60,215	129 232	Freedom degrees	3
80,281	172 216	Slope	4,945 9E-04
100,343	210 333	Coefficient of error	±4,5E-06