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Nuclear technology — Nuclear fuels — Procedures for the measurement of elemental impurities in uranium- and plutonium-based materials by inductively coupled plasma mass spectrometry

Technologie nucléaire — Combustibles nucléaires — Modes opératoires pour le mesurage des impuretés élémentaires des matériaux à base d'uranium et de plutonium par spectrométrie de masse avec plasma à couplage inductif

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Contents

Page

Foreword iv

Introduction v

1 Scope 1

2 Normative references 1

3 Principle 1

4 Reagents and materials 2
4.1 Water 2
4.2 Acids and other reagents 2
4.3 Standards 3
4.4 Matrix material 3
4.5 Calibration standards for instrumental analysis 3
4.6 Quality control standards for instrumental analysis 3
4.7 Quality control standards for the method control 3
4.8 Recovery control standard 3
4.9 Internal standard 4

5 Apparatus 4
5.1 Mass spectrometer 4
5.2 Radioactivity containment 4
5.3 Dissolution containers and process apparatus 5

6 Procedure 5
6.1 Interferences 5
6.2 Test portion 7
6.3 Preparation of test portion 7
6.4 Instrumental analysis 8
6.5 Instrument and method calibration 9

7 Calculation 11

8 Precision 11

9 Quality assurance and control 11
9.1 Instrument performance 11
9.2 Method performance 12

10 Test report 12

Annex A (informative) Table of elements measurable by ICP-MS 13

Annex B (informative) Specific examples of dissolution and extraction procedures 15

Annex C (informative) General information 19

Bibliography 21

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.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. 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.

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.

ISO 26062 was prepared by Technical Committee ISO/TC 85, *Nuclear energy*, Subcommittee SC 5, *Nuclear fuel cycle.*

Introduction

The technique presented in this International Standard is capable of being used to perform quantitative measurements of elements with the specific exceptions of H, He, C, N, O, F, Cl, Br, and the noble gases. The measurement of other elements such as Si, P, S, K and I will require specialized sample introduction options, specialized solutions, mass analysers or in-line systems for the measurement.

This International Standard is presented in general terms for actinide samples because of the complexity and variation of the ICP-MS technique and its sample introduction accessories. Sufficient and appropriate method development should be undertaken to ensure that the procedure used for the determination of impurities in uranium and plutonium matrices is validated.

It is assumed that the user of this International Standard has a basic understanding of standard sample control, chemical extraction techniques and operation of ICP-MS instrumentation. Blank control is critical when undertaking ICP-MS analysis. Assessment of reagents and standards may be required when undertaking ultra trace analysis.

Nuclear technology — Nuclear fuels — Procedures for the measurement of elemental impurities in uranium- and plutonium-based materials by inductively coupled plasma mass spectrometry

1 Scope

This International Standard specifies a procedure for the determination of trace impurities in uranium- or plutonium-based, or mixed uranium- and plutonium-based, materials by inductively coupled plasma mass spectrometry (ICP-MS). It provides both guidelines and specific options for the determination of an element or group of elements.

It is applicable to solutions such as uranyl or plutonium nitrate, solids such as the oxides and to mixed actinide materials such as unirradiated mixed oxide material in either solid or dissolved forms. It is not directly suitable for the analysis of uranium or plutonium matrices containing significant quantities of other elements such as uranium–gadolinium mixtures. It may nevertheless form the basis of a process for analysing this type of matrix, provided that the impact of the gadolinium component is ascertained.

2 Normative references

The following referenced documents are indispensable for the application 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 Principle

The method is based upon the dissolution of solid samples, the use of an optional chemical treatment to remove the actinide matrix, followed by the spectroscopic determination of the analytes using inductively coupled plasma mass spectrometry (ICP-MS).

In principle, the ICP-MS technique relies on the introduction of the sample in an aerosol form into the inductively coupled plasma. In the plasma, the sample atoms are ionized then extracted from the plasma through a series of differential pumping chambers into the analyser region. The ionized species are mass separated using a mass analyser and then measured using an appropriate detection system. Quantitative measurements can be performed using a number of techniques, including standard addition and isotope dilution analysis; however, the generation of calibration graphs from measured standards is the conventional technique.

To provide an indication of the application of the technique, Table A.1 lists the elements commonly measured in uranium, plutonium and mixed actinide materials. The table includes the optimum isotope to be measured, the mass analyser options and comments regarding the measurement of that element.

The process is presented in a series of stages, as given in the following list. For each stage a series of criteria or principles that require consideration is presented. Annex B gives summaries of specific procedures for the dissolution and optional chemical extraction stages.

a) Dissolution to dissolve solid samples:

general details provided for hot plate and microwave oven based dissolution;

b) Optional chemical extraction procedure to remove the sample matrix:

general details provided for solvent extraction process and chromatography process;

c) Direct analysis of samples in the actinide matrix:

general principles to be considered if using this option;

d) Analysis of the extracted sample:

general principles of calibration, quality control and sample measurement are provided.

No details are provided for the specific instrumental set up, owing to the significant range of options available from the variety of instruments currently available commercially, for example,

- quadrupole mass analyser vs. magnetic sector mass analyser vs. time-of-flight mass analyser,
- conventional nebulisation sample introduction vs. specialised applications e.g. flow injection or ultra sonic nebuliser,
- the use of “collision/reaction cell” or “cool plasma” systems,
- quantitative techniques.

A brief description of the relative merits of these options is provided in Annex C. However, detailed information should be obtained from textbooks, journals or from manufacturers' manuals.

4 Reagents and materials

Use only reagents of recognized analytical grade, unless otherwise specified.

4.1 Water

Normal industry practice is to use high purity water designated 18 MΩ·cm, judged as being suitable for this guideline. Water complying with better than grade 2 as defined in ISO 3696:1987 is the recommended water quality.

4.2 Acids and other reagents

High purity reagents shall be used for all ICP-MS analysis. The quality of the reagents used in the process shall be validated by undertaking suitable blank measurements before use. Procedural blanks should be used at the sample preparation, sample extraction (where applicable) and instrument measurement stages.

4.2.1 Nitric acid, 16 M

4.2.2 Hydrofluoric acid, 40 %

4.2.3 Nitric acid/hydrofluoric acid cleaning solution

Fill a 2,5 l plastic bottle with approximately 2 l of the high purity water. Add 470 ml of 16 M nitric acid slowly to the water, swirl gently to mix. Add 5 ml of hydrofluoric acid with a mass fraction of 40 %. Dilute the acid mixture to 2,5 l and mix.

4.3 Standards

Suitable certified and reference standards traceable to a certifying authority shall be used for all quantitative analysis. Use standards from different suppliers for calibration and quality control standards to monitor for preparation problems.

4.4 Matrix material

The use of matrix-matched standards is required to ensure a high level of quality control. Ensure that a suitable material is used that does not affect the measurement. Undertake appropriate and sufficient method development to validate the procedure.

4.5 Calibration standards for instrumental analysis

The ICP-MS instrument shall be calibrated to allow quantitative analysis, for example external calibration, using the conventional technique described in 6.4. Suitable standards can be prepared from commercially available elemental standards. Matrix matching the standards is required for direct analysis of analytes in strong actinide solution to correct for the impact of the sample matrix on signal intensities (i.e. signal suppression or possible enhancement).

4.6 Quality control standards for instrumental analysis

A suitable quality control standard shall be measured to ensure that the calibration has been performed correctly. Prepare quality control standards by diluting commercially available elemental standards down to suitable concentrations for the application. Matrix matching the standards may be required for direct analysis of analytes in strong actinide solution.

4.7 Quality control standards for the method control

A suitable quality control standard shall be processed alongside the samples to monitor the performance of the analytical method. Prepare a suitable quality control standard that contains the desired analytes at levels appropriate for the material being analysed. The quality control standard should be prepared in a suitable matrix to reflect the concentration of the matrix in the sample solution produced after the dissolution phase.

Ideally, a certified reference material should be used. In the absence of a suitable reference material, the alternative approach is to prepare a standard from an appropriate dilution of a commercial elemental standard in a matrix that matches the samples being analysed.

4.8 Recovery control standard

Where a chemical extraction is used, the recovery through the process shall be monitored and, if necessary, appropriate correction of the analytical result should be made, ensuring that appropriate uncertainty associated with recovery correction is taken into account.

Prepare a suitable standard that contains the desired analytes at levels appropriate for the material being analysed. The matrix of the standard should reflect the concentration of the matrix in the sample solution produced after the dissolution phase.

Ideally, a certified reference material should be used. In the absence of a suitable standard, the alternative approach is to prepare a standard by preparing an appropriate dilution of a commercial elemental standard in a matrix that matches the samples being analysed.

Specialized options such as isotope dilution analysis can be used. However, these are outside the scope of this standard, and textbooks on ICP-MS provide details of these techniques.

4.9 Internal standard

Internal standards are used to evaluate variations in measurement arising from drift caused by changing plasma or instrument conditions and the effect of the sample/standard matrix on measurements. All blanks, standards and samples shall be spiked with the internal standard. The selection of suitable internal standards depends upon factors such as the following:

- the element is not present in blanks, standards or samples;
- the isotope of the element used is not subject to interference from other elements;
- the element does not interfere with analyte isotopes;
- the element is preferably mono-isotopic;
- the physical-chemical behaviour of the internal standard element should be similar to those of the analytes in the instrumental measurement processes.

There are a number of elements routinely recommended for ICP-MS measurements, such as beryllium or scandium for low-mass analytes, indium or rhodium for mid-mass elements and bismuth or iridium for high-mass elements. With only one internal standard it may not be possible to correct efficiently for all elements across the mass range. It is therefore advisable to use a mixture of three internal standards (i.e. one for low masses, one for intermediate masses and one for high masses).

The selection of a suitable standard is widely covered in standard ICP-MS textbooks.

5 Apparatus

5.1 Mass spectrometer

A computer-controlled inductively coupled plasma mass spectrometer designed for elemental analysis suitable for handling radioactive material.

The use of platinum-tipped cones is recommended for the analysis of samples where a hydrofluoric acid based dissolution process is used. These reduce the chemical corrosion of the cone orifice and hence maintain instrument performance and reduce blank contribution from the cone metal.

5.2 Radioactivity containment

The process should be undertaken in containment facilities suitable for handling powdered and liquid forms of uranium- and plutonium-based samples.

5.3 Dissolution containers and process apparatus

The consumable apparatus used in the measurement process should be chosen to ensure stability of the analytes, compatibility with the chemicals used and prevention of contamination of the samples and process. The following list provides an indication of the types of consumables required, and the comments apply equally to all apparatus used, e.g. for the preparation of standards, calibration processes, sample preparation, and subsequent measurements. Assessment of the suitability of equipment should be addressed during the validation of the standard.

- Nalgene®[1] volumetric flasks or those prepared from other inert materials are recommended.
- Solvent resistant containers are required to undertake the solvent extraction process described in this International Standard.
- All flasks/centrifuge tubes, polytetrafluoroethylene (PTFE) beakers and sample vials used in this operation should be soaked in a cleaning mixture such as nitric acid/hydrofluoric acid cleaning solution (4.2.3) for a minimum of 72 h before use. Suitable tests should be made to validate the process to be adopted. This is beneficial for removing the potential for contamination of the samples from impurities in these consumable items.
- Glass apparatus should be avoided because of the risk of leaching of potential interferences from the glass such as boron, silicon and lanthanides. Some quartz apparatus is available that is suitable for the impurities analysis described in this International Standard.
- If extremely low levels of analytes are to be measured, the impact of plastic-based apparatus should be assessed, in order to ensure stability of the analyte due to the risk of adsorption onto the apparatus.

6 Procedure

6.1 Interferences

The determination of elements by ICP-MS suffers from interference from a number of sources. The potential for interference has to be assessed for individual operations, although general details are readily available in standard textbooks on ICP-MS and from scientific journals, and provided by instrument manufacturers. A summary of the impact is provided in 6.1.1 to 6.1.3.

6.1.1 Isobaric interference

Isobaric interferences arise from two sources:

- isobaric interference from other elements;
- molecular isobaric interference from other plasma species.

Isobaric interference arises from ions produced by isobars from other elements, e.g. interference on ^{114}Cd from ^{114}Sn. Isobaric interferences are readily identifiable from the study of the isotopic composition of the elements of interest and their adjacent neighbours in the periodic table. This interference may be removed by a number of methods, including the following:

- sample preparation to remove the interfering element prior to measurement;
- use of blank correction if the interference is constant;

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[1] Nalgene® is an example of a suitable product available commercially. This information is given for the convenience of users of this International Standard and does not constitute an endorsement by ISO of this product.