BS ISO 26062:2010

BSI Standards Publication

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

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National foreword

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The UK participation in its preparation was entrusted to Technical Committee NCE/9, Nuclear fuel cycle technology.

A list of organizations represented on this committee can be obtained on request to its secretary.

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ISBN 978 0 580 55786 6

ICS 27.120.30

Compliance with a British Standard cannot confer immunity from legal obligations.

This British Standard was published under the authority of the Standards Policy and Strategy Committee on 31 October 2010.

Amendments issued since publication

Date	Text affected

BS ISO 26062:2010

INTERNATIONAL STANDARD

ISO 26062

First edition
2010-09-15

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

Reference number
ISO 26062:2010(E)

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Published in Switzerland

Contents

Page

Foreword

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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.

INTERNATIONAL STANDARD ISO 26062:2010(E)

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;

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.

— use of mathematical correction based on the measurement of the interfering element;

— use of sector ICP-MS for polyatomic species, such as ArO^+.

6.1.2 Molecular ion interference

The second group of isobaric interfering ions is more complex and arises from the reactions within the plasma between the plasma ions, the sample ions and the solvent used for the sample. These species are more commonly referred to as molecular ions.

Molecular ions from the argon plasma itself include species such as Ar^+ or its oxide, ArO^+, affecting K or Fe respectively. The solvent contributes molecular ions; nitric acid generates ions such as its oxides whilst other acids present more serious interferences. An example is the effect of the presence of chloride ions, such as from hydrochloric acid, where the production of the $ArCl^+$ ion interferes with the measurement of ^{75}As.

A second example of interference from molecular ions is particularly pertinent to the measurement of elemental impurities in uranium or plutonium matrices, where the formation of doubly charged ions and oxide ions will interfere with elements with isotopes within the mass range 110 to 140. The formation of these doubly charged ions and oxide ions, such as U^{2+}, UO^+, UO^{2+}, Pu^{2+}, PuO^+ and PuO^{2+}, depends upon the plasma conditions and the level of the matrix component.

To provide an indication of these interferences, Table 1 shows the masses likely to be affected by the most commonly produced species arising from actinides with atomic masses ranging from 232 to 242.

Table 1 — Potential ions generated from actinide elements

Source mass	Mass of M^{2+} ion[a]	Affected element	Mass of $(MO)^{2+}$ ion[a]	Affected element	Mass of $(MO_2)^{2+}$ ion[a]	Affected element[b]
232	116	Cd/Sn	124	Sn, Te	132	Ba
234	117	Sn	125	Te	133	Cs
235	117,5	—	125,5	—	133,5	—
236	118	Sn	126	Te	134	Ba
237	118,5	—	126,5	—	134,5	—
238	119	Sn	127	I	135	Ba
239	119,5	—	127,5	—	135,5	—
240	120	Te, Sn	128	—	136	Ba, Ce
241	120,5	—	128,5	—	136,5	—
242	121	Sb	129	—	137	Ba

[a] M represents the source isotope from the actinide matrix.

[b] Only natural isotopes are given; radionuclides from fission and other nuclear processes would also be affected: e.g. ^{125}Sb, ^{134}Cs, ^{135}Cs, ^{137}Cs and ^{129}I.

This interference may be removed by a number of methods:

— sample preparation to remove the interfering element prior to measurement;

— use of different reagents;

— the use of blank correction if the interference is constant;

— the use of mathematical correction based on the measurement of the interfering element;

— adjustment of the plasma conditions can reduce the doubly charged and oxide ion formation, although this can have a deleterious effect on the sensitivity of the analyte measurement;

— the use of instrumental options such as collision cell technology or different mass analysers such as high-resolution sector ICP-MS.

6.1.3 Peak overlap

The overlap of a major peak onto an adjacent mass peak will cause interference on the adjacent peak. The measure of the peak overlap of a mass spectrometer is the abundance sensitivity and for most quadrupole-based instruments this is around 10^5. Put simply, this means that the overlap from a 100 µg/ml ^{238}U peak on mass 237 is around 1 ng/ml.

There are two options for managing this interference:

— removal of the matrix species;

— the use of instrumental options such as high-resolution sector ICP-MS.

6.2 Test portion

The quantity of sample selected for analysis should reflect a number of parameters, including:

— level of analyte present in the sample;

— required precision and accuracy;

— required detection limits;

— measurement techniques;

— solubility of the matrix in the dissolution medium.

Annex B provides typical sample quantities for a number of dissolution techniques.

6.3 Preparation of test portion

6.3.1 Dissolution

Specific dissolution requirements should be developed for specific applications. General provisions are the following:

— provide complete dissolution of the sample and the analytes required;

— since the solubility of the actinide solution is a product of the relationship between concentration, temperature and acidity, care should be taken to ensure that solubility can be achieved;

— minimize the risk of contamination through control of reagents, apparatus and segregation of high/low samples be minimized;

— a procedural blank is required;

— minimize losses of volatile elements such as B, Ru and Tc;

— provide a final solution that is suitable for the subsequent stages of the analysis, either direct analysis or extraction chemistry to remove the actinide matrix.

See Annex B for summaries of three specific processes: open beaker, reflux and microwave dissolution, are described in Annex B. Appropriate validation of the process to be adopted should be undertaken to ensure that the process meets those general guidelines.

Once the sample is dissolved, two options are available: to use an extraction process to isolate the analytes from the actinide matrix or analyse the sample directly.

6.3.2 Extraction process

The use of an extraction process is an option for removing the actinide-based matrix and/or for improving the potential detection limits of the measurement. If the analyte levels are sufficiently high for direct measurement in the actinide matrix then this stage can be omitted. Any extraction process used shall consider the use of the following criteria. The selection of the criteria to be used should reflect the specific application:

— the use of a recovery standard is required to measure the extraction of the analytes;

— provide a final solution that is suitable for the subsequent stages of the analysis;

— a procedural blank is required;

— minimize the risk of contamination through control of reagents, apparatus and segregation of high/low samples;

— acid washing of the solvent extraction mixture or clean up of the ion exchange columns is advisable before use.

Annex B provides summaries of two processes: chromatography and solvent extraction.

6.4 Instrumental analysis

6.4.1 Dynamic range of the instruments

The dynamic range of modern ICP-MS instruments is considerable, covering several orders of magnitude. The selection of a dynamic range is dependent upon the level of quality required and the variability in both the material to be analysed and the sample preparation used to isolate the impurities of interest. In terms of general guidelines, the dynamic range should be minimized to 2 to 3 orders of magnitude.

6.4.2 Quantitative analysis options

Two options are available: either to analyse the sample directly after dissolution (step 6.3.1) or analyse the sample following the chemical extraction (step 6.3.2). Both processes have their relative advantages and disadvantages, some of which are described in 6.4.2.1 and 6.4.2.2. The choice should be made accordingly to reflect the specific application.

6.4.2.1 Direct analysis

This is undertaken directly on the sample solution after dissolution. The concentration of the matrix under routine operations should be approximately 1 mg/ml. Higher concentrations can be used, but these can lead to blockages of nebulizers and cones. The advantages of direct analysis are the following:

— it limits analyte loss and reduces risk of contamination in the sample preparation stage;

— it avoids the requirement to process the sample, thus minimizing waste and the handling of radioactive material.

Drawbacks to take into account:

— significant amounts of the matrix are introduced into the mass spectrometer, resulting in matrix effects such as signal suppression and generating a high background for the matrix elements that prevents or restricts subsequent measurement of those elements;

— suitable matrix material for use in matrix matched standards and blanks may not be available;

— the potential detection limits are restricted by the amount of matrix tolerated by the instrument and any matrix effects induced by the matrix.

Direct analysis is beneficial where speed is important and the analyte levels are sufficient to provide an appropriate analytical result that meets the desired level of quality and quantification.

6.4.2.2 Chemical separation

The main advantage of undertaking chemical separation is to isolate the analytes from the sample matrix and potential interferences. Analysis after chemical extraction is beneficial where ultra trace analysis is required and/or there is a need to prevent contamination of the mass spectrometer from the matrix elements. Other advantages are

— the removal of the matrix and the potential to improve limit of detection, and

— the removal of the matrix to avoid contamination of the instrumentation from the matrix elements.

The process does have some disadvantages to consider:

— the necessary sample processing will lead to a certain amount of analyte losses and contamination;

— sourcing suitable matrix material for use in recovery correction can prove problematic;

— many extractants are organic-based, which can present problems for waste disposal.

6.5 Instrument and method calibration

The steps described in 6.5.1 to 6.5.6 provide the criteria to be adopted for the control of the instrumental analysis. The choice will reflect the nature of the analysis being undertaken.

6.5.1 Instrument calibration

Instrument optimization operations shall be undertaken to ensure that parameters such as sensitivity, gas flows, sample introduction rates, oxide ion formation and reflected power (as recommended by the manufacturer) are all within acceptable ranges for optimum performance.

Undertake the appropriate pre-analysis instrument checks such as mass calibration, resolution check and detector calibration as recommended by the manufacturer.

These instrument parameters and checks are critical to ensure that the instrument is operating correctly and must be undertaken. The actual parameters used will depend on the type of instrument used and the checks recommended by the instrument manufacturer.

6.5.2 Method calibration

The instrument shall be calibrated to determine the analytes in these samples by appropriate measurement of blanks and standards in order to generate an appropriate concentration vs. response graph (routinely undertaken by the operating software of the instrument).

The concentration range of the standards shall be appropriate to ensure that the analyte concentrations fall roughly mid-calibration wherever possible, with the standards evenly spread. A calibration regime such as 1, 2, 5, 10 and 20 ng/ml provides additional standards at the low end of the concentration range to improve the quality of the measurement.

Matrix-matching the standards and blanks is critical in some applications, particularly those involving the direct analysis of a high-actinide matrix. Both the acid concentration and in the case of direct analysis, the actinide matrix will have an effect on the accuracy and precision of the measurement. When undertaking validation of the method, the potential effects of these matrices should be assessed.

If some impurity levels are significantly higher than the majority of elements, adjust the calibration range accordingly for these specific analytes. This may occur for elements such as Cr, Ni, Fe, Ca, Al, K and Na.

Other options, such as standard addition and isotope dilution analysis, are available. These are outside the scope of this International Standard and further information is available in ICP-MS textbooks.

6.5.3 Internal standardization

The use of an internal standard is recommended to monitor measurement to measurement variation, i.e. drift, within an analytical run due to changing plasma conditions. Internal standardization can compensate for the effect of the drift arising from a number of factors including variations in instrument parameters, plasma conditions and matrix effects (this is especially pertinent for direct analysis).

All blanks, standards and samples should be spiked with the internal standard(s).

6.5.4 Instrument quality control

To determine the performance of the instrument, suitable blanks and quality control standards are analysed. The quality control standards should be selected to reflect the range of analytes and the matrix present in the samples and to assess the performance of the method calibration.

6.5.5 Sample preparation and measurement

The number of replicates to be measured and any dilution of the samples should be chosen on the basis of the quality demands on the analytical measurement.

Undertake the analysis by measuring the various blanks, samples and standards from the sample preparation stages alongside the instrument blanks, calibration standards and quality control standards in a sequence appropriate to meeting analytical demands and quality requirements.

If the analysis is to be performed directly on the dissolved sample, ensure that the final solution being nebulised does not contain the matrix at a level that could result in blocking of the nebuliser and/or cones. It is recommended that the concentration not be greater than 1 mg/ml. If higher concentrations are used, ensure that the impact is assessed. Ensure that the samples are matrix-matched using a suitable material that is suitably pure, to prevent cross contamination and/or blank issues.

6.5.6 Instrument conditions

No specific details are provided because of the range of commercial instruments and accessories available.

7 Calculation

Calculate the concentration of the analytes in the solution being analysed using the software packages available with the instrumentation and, subsequently, relative to the original amount of sample taken. Correct the result as appropriate for

— sample dilution,

— blank measurements,

— interference correction,

— recovery measurements, and

— non-natural isotopic abundances of fission product elements such as Zr, Mo or Gd (see Table A.1).

8 Precision

The performance capability of the standard will depend upon the combination of sample preparation and instrument configuration and protocol. As a guide, the following should be achievable.

The typical coefficient of variation from a conventional quadrupole-based ICP-MS is 10 % to 20 % (1 sigma). Elements that do not suffer significant interference through the sample processing and instrumental analysis, such as lead or beryllium, will achieve precisions of less than 10 %. Elements such as B, Fe, Nb and W will have worse precision owing to poor reproducibility through the processing and/or poor measurement precision.

The limit of detection is heavily dependent upon the options chosen, but levels of 0,1 µg/g original sample to 1 µg/g original sample are achievable for most elements, based upon a 3× standard deviation of the blank figure, using a conventional quadrupole-based instrument and chemical processing.

The typical coefficient of variation from a sector-based ICP-MS is 12 % (1 sigma). The instrumental measurement of elements such as Li, Be, B Si and P will be significantly poorer and alternative techniques should be considered.

The limit of detection for a sector-based ICP-MS instrument is heavily dependent upon the options chosen, but levels between 0,2 ng/g with respect to the original sample and 200 ng/g with respect to the original sample for most analytes are achievable using a direct analysis based upon a 3× standard deviation of the blank figure and on analysis of a 50 µg/ml solution with respect to uranium.

9 Quality assurance and control

The quality of the measurement should be verified by performing the various quality control checks and instrumental parameters.

9.1 Instrument performance

Assess the performance of the instrument, taking into account the following items:

— instrument blanks level;

— verification of the performance of the instrumental quality control standards; the acceptability will depend upon the instrument used, the element being determined and the calibration regime;

— monitoring of the internal standard signals;

— checking the sensitivity and trending in the signal of the internal standard performance; this will provide an indication of factors including:

  — in direct analysis applications, variability in sensitivity or significant reduction in sensitivity, indicating effects such as cone or nebuliser blockage,

  — in applications using an extraction process, significant suppression of the internal standard signal, signifying the break though of significant levels of the actinide sample matrix;

— comparison of results from multiple isotopes (where available), which will indicate any possible isotopic interference.

9.2 Method performance

Assess the performance of the method by:

— assessing the performance of the method blanks, the levels achieved being dependent upon factors such as the quality of the reagents, the facilities used and the performance of the instrument;

— assessing the performance of the method recovery factor if an extraction process has been used; the expected levels for most analytes should be around 95 % to 100 %; for elements such as Ag and the lanthanides and thorium, the recovery will drop to 50 % to 60 %.

NOTE Further improvements in the quality of the analytical procedure can be achieved through measurement and monitoring of the overall measurement uncertainty. However, this is outside the scope of this International Standard.

10 Test report

The test report shall contain the following information:

a) all information necessary for identification of the sample tested;

b) a reference to the procedure used;

c) the method used;

d) the results of the test, including the results of the individual determinations and their mean, calculated using the method specified in Clause 7;

e) any deviations from the procedure specified;

f) any unusual feature (anomaly) observed during the test;

g) the date of the test.

Annex A
(informative)

Table of elements measurable by ICP-MS

A.1 Table A.1 is by no means exhaustive and so can only provide a brief overview of some of the potential interferences and measurement requirements.

A.2 The isotopic abundance of an element is required if the element is fission-product-generated.

A.3 Method validation can identify the potential interferences, measurement criteria, etc., and additional information is available from textbooks, journals or from manufacturer's manuals.

Table A.1 — Elements measurable by ICP-MS

Element	Optimum mass	Applicability to quadrupole instrument	Applicability to sector instrument	General comments[a]
Li	7	✓	✓	—
Be	9	✓	✓	—
B	11	✓	✓	Memory effects
Na	23	✓	✓	Risk of contamination from reagents and apparatus
Mg	24	✓	✓	Risk of contamination from reagents and apparatus
Al	27	✓	✓	Risk of contamination from reagents and apparatus
Si	28	—	✓	High background from quartz spray chamber and torch, Resolution $\geqslant$ 3 000 required
P	31	—	✓	Resolution $\geqslant$ 3 000 required
S	32	—	✓	Resolution $\geqslant$ 3 000 required
K	39	—	✓	Resolution $\geqslant$ 7 000 required
Ca	44	✓	✓	Resolution $\geqslant$ 3000 on sector instrument, poor on quadrupole
Ti	48	✓	✓	—
V	51	✓	✓	Potential interference from ClO^- if it is present in the sample
Cr	52	✓	✓	Potential interference from ArC arising from the presence of organic material in the sample
Mn	55	✓	✓	—
Fe	56	✓	✓	Resolution $\geqslant$ 3 000 on sector instrument, poor on quadrupole
Ni	58	✓	✓	Background from cones
Co	59	✓	✓	—
Cu	63	✓	✓	—
Zn	64	✓	✓	—
As	75	✓	✓	Potential interference from ArCl
Sr	88	✓	✓	Potential fission product in sample
Zr	90,91,92	✓	✓	Potential fission product in sample
Nb	93	✓	✓	Potential fission product in sample

Table 1 (*continued*)

Element	Optimum mass	Applicability to quadrupole Instrument	Applicability to sector Instrument	General comments[a]
Mo	95	✓	✓	Potential fission product in sample
Mo	98	✓	✓	Potential fission product in sample
Tc	99	✓	✓	—
Ru	102	✓	✓	Potential fission product in sample
Ag	109	✓	✓	Potential fission product in sample
Cd	111	✓	✓	Potential fission product in sample
In	115	✓	✓	—
Sb	123	✓	✓	Potential fission product in sample
Sn	124	✓	✓	Potential fission product in sample
I	127	✓	✓	Requires specialist sample treatment due to instability of iodine in acidic solutions
Cs	133	✓	✓	Potential fission product in sample
Ba	138	✓	✓	Potential fission product in sample
La	139	✓	✓	—
Ce	140	✓	✓	Potential fission product in sample
Pr	141	✓	✓	—
Nd	143	✓	✓	Potential fission product in sample
Sm	147	✓	✓	Potential fission product in sample
Eu	153	✓	✓	Potential fission product in sample
Gd	158	✓	✓	Potential fission product in sample
Dy	162	✓	✓	Potential fission product in sample
Ta	181	✓	✓	—
W	184	✓	✓	—
Pb	208	✓	✓	—
Bi	209	✓	✓	—
Th	232	✓	✓	Memory effects
Np	237		✓	Resolution $\geqslant$ 3 000 in uranium
Np	237	✓	✓	In plutonium
U		✓	✓	U in Pu possible after separation on quadrupole instrument
Pu	239		✓	Pu in U possible after separation on quadrupole instrument
Am	241	✓	✓	Separation of Pu required because of interference from Pu 241 unless sufficient Am 243 present
Cm		✓	✓	—
This table is provided as a guide only and the performance of the standard should be validated on the individual system.				

[a] Isotopic interferences should be identified through method development and reference sources.

Annex B
(informative)

Specific examples of dissolution and extraction procedures

B.1 Dissolution options

B.1.1 General

The advantage of the first two options (see B.1.2 and B.1.3) is that relatively simple equipment can be used, a distinct advantage in a glove-box-based application, whereas the microwave dissolution applications (B.1.4) are faster.

The choice of process will reflect the application and equipment available. The processes should be validated to ensure performance is acceptable.

B.1.2 Open-beaker hot-plate dissolution

B.1.2.1 Reagents

B.1.2.1.1 0,5 g of PuO_2 or MOX dissolved in 10 ml of 12 M HNO_3/0,05 M HF.

B.1.2.1.2 7 g of UO_3 dissolved in 40 ml of 12 M HNO_3/0,05 M HF.

B.1.2.2 Procedure

B.1.2.2.1 Transfer an appropriate amount of sample into a PTFE beaker. Weighing into an intermediate container, such as an inert weighing boat, is recommended because of the problem of electrostatic charge on PTFE beakers. Ensure that a quantitative transfer is made by washing with a minimum amount of 12 M HNO_3/0,05 M HF.

B.1.2.2.2 Add an appropriate amount of 12 M HNO_3/0,05 M HF.

B.1.2.2.3 Place a loose-fitting PTFE cap on the beaker (to prevent contamination). Place on a hot plate at 150 °C for a period of 3 h to 4 h. The exact time will depend upon the refractivity of the material being analysed. In the event of incomplete dissolution, continue heating until the sample dissolves. The addition of small amounts of HF may aid dissolution.

B.1.3 Reflux dissolution

B.1.3.1 Transfer 4 g MOX material into a dissolution vessel with a reflux condenser.

B.1.3.2 Dissolve the sample in 16 M $HNO_3 + 0{,}1$ M HF (about 15 ml) at 130 °C under reflux until complete dissolution occurs.

B.1.3.3 Reduce the heat to 80 °C for a further 2 h without the reflux condenser in place to expel nitrous compounds.

B.1.4 Microwave dissolution

The conditions will depend upon the type and power of microwave oven available; however, appropriate safety interlocks should be used to prevent over-pressurisation and over-heating. The following procedure is suitable for a Questron QWAVE 3000[2] microwave or similar.

B.1.4.1 Transfer between 0,5 g and 0,8 g of PuO_2 or MOX dissolved in 10 ml 12 M HNO_3/0,1 M HF into the microwave dissolution vessel.

B.1.4.2 Heat the sample in a clean microwave vessel to 215 °C over 10 min. Maintain temperature for 20 min. The pressure should be limited to 2 758 kPa (400 psi).

B.1.4.3 On completion of the run, allow to cool and quantitatively transfer to a suitable vessel using 4 M HNO_3.

B.2 Extraction options

B.2.1 Separation using chromatography

The following is an example of a chromatography-based separation procedure that is suitable for isolation of the elements listed in Table B.1 from a uranium and plutonium matrix.

Specific details are available from the resin supplier. The residual actinide present in the samples is less than 1 µg/ml, giving an extraction efficiency of greater than 99,9 %. Other chromatography resins are available.

The choice of process will reflect the application and equipment available. The processes should be validated to ensure performance is acceptable.

B.2.1.1 Extraction process for uranium matrix

The uranium is retained on an Eichrom UTEVA®[3] chromatography column allowing elements of interest to pass through the column for collection and subsequent analysis.

Condition such a column (2 ml) with 3 × 2 ml of 3 M nitric acid. Load the sample (1 ml), containing up to 30 mg of actinide, onto the column in a 3 M nitric acid solution, collect the eluate.

Elute the bulk of the impurities using nitric acid (3 M, 4 × 2 ml) collecting the eluate. Zirconium can be eluted in this phase if both the sample solution and elution acid contain a 0,2 M hydrofluoric acid.

Elute silver and thorium using hydrochloric acid (6M, 3 × 2 ml) to give recoveries in the region of 90 % to 100 %.

Following elution, the acid solution can be submitted for analysis.

2) Q-WAVE 3000 is the trade name of a product supplied by Questron Technologies Corp. This information is given for the convenience of users of this International Standard and does not constitute an endorsement by ISO of the product named. Equivalent products may be used if they can be shown to lead to the same results.

3) UTEVA® is the trade name of a product supplied by Eichrom Industries Inc. This information is given for the convenience of users of this International Standard and does not constitute an endorsement by ISO of the product named. Equivalent products may be used if they can be shown to lead to the same results.

Table B.1 — Typical recoveries achieved through separation using chromatography

Element	Recovery %	Element	Recovery %	Element	Recovery %	Element	Recovery %	Element	Recovery %
Li	96	Ti	99	Co	96	Cd	100	Gd	100
Be	94	V	100	Ni	95	Sn	100	Dy	99
B	99	Cr	94	Cu	96	Ba	100	W	100
Mg	90	Mn	97	Zn	90	Sm	99	Pb	100
Al	100	Fe	100	Mo	100	Eu	100	Bi	100

B.2.2 Separation using tributyl phosphate-based solvent extraction

Tributyl phosphate (TBP) is a versatile extractant commonly used in extraction chemistry. For the purposes of this International Standard the process is reliant on the extractability of four and six valent uranium and plutonium ions into the organic phase, thereby leaving the analytes of interest in the aqueous phase.

The retention of the analytes of interest in the aqueous phase is dependent upon a number of factors, including acid strength, type of acid, state of the element (valency, complexes, etc.) and the presence of other elements.

The following list describes examples of the general behaviour of elements in a TBP-based extraction process.

— Trivalent actinides such as americium are not extracted and are retained in the aqueous phase.

— Elements such as Sc, Y, Lanthanides and Th are partially extracted into the organic phase from high acid matrix.

— Elements such as Pd, Pt, Au, Bi, Po and Ru can be partially extracted into the organic phase if the acid strength is allowed to drop below approximately 5 M HNO_3.

— Tc and Re are moderately extracted when present as the (VII) state and the acid strength is low. Uranium levels and the presence of elements such as zirconium that can complex with the technetium to form an extractable complex affect these elements.

— The extractability of Np is difficult to quantify because of the equilibrium mixtures of oxidation state(s). Np (IV), Np (V) and Np (VI) form an equilibrium mixture but only the Np (IV) Np (VI) valencies are readily extracted into the organic phase.

— The extraction of nitric acid into the organic phase can lead to sufficient reduction in acidity such that it can lead to plutonium hydrolysis and hence prevent any further extraction of plutonium.

The choice of diluent for the extraction varies; two commonly used and related diluents are odourless kerosene and dodecane.

B.2.2.1 Extraction process for uranium and plutonium matrix using 30 % TBP in odourless kerosene

The method should be validated for specific applications and as a guide the steps given in B.2.2.1.1 and B.2.2.1.2 detail a process utilising 30 % TBP in odourless kerosene as the extractant to remove the plutonium and uranium from a 12 M HNO_3/0,05 M HF solution.

B.2.2.1.1 30 % TBP in odourless kerosene

Dilute 30 ml of TBP to 100 ml using odourless kerosene. Transfer the TBP/odourless kerosene into a separating funnel to remove impurities. Add 100 ml of 8M HNO_3 to the separating funnel. Mix thoroughly the contents of the separating funnel for 1 min and then allow settling for 5 min. Dispose of the bottom aqueous layer and pour the top solvent layer into a 500 ml bottle.

B.2.2.1.2 Extraction procedure

Solvent-extract an appropriate quantity of sample with an equal or greater volume of 30 % TBP/odourless kerosene, retaining the aqueous phase at each stage. Typically, 5 ml of the sample solution to 5 ml of the extractant is suitable. For uranium-rich matrices, at least four extractions are required. For plutonium matrices, up to five extractions are required. Based on applying the extraction process to a solution of 200 mg/ml uranium or 30 mg/ml plutonium, the final level of actinide will be typically less than 0,02 mg/ml, giving an extraction efficiency of better than 99,9 %. On completion of the extraction process, the aqueous phase can be submitted for analysis.

For an extraction process using 30 % TBP in odourless kerosene to remove the actinide matrix on a 30 mg/ml actinide solution in 12 M HNO_3/0,05 M HF, the recovery through the process is as given in Table B.2 (i.e. the residual amount of element remaining in the aqueous phase after the extraction process)

Table B.2 — Typical recoveries achieved through TBP/odourless kerosene extraction

Element	Recovery %	Element	Recovery %	Element	Recovery %	Element	Recovery %
Li	70 to 95	K	75 to 95	Co	80 to 100	Sm	70 to 85
Be	75 to 100	Ca	80 to 100	Cu	80 to 100	Eu	70 to 85
B	75 to 100	Ti	75 to 95	Zn	70 to 95	Gd	65 to 85
Na	60 to 100	V	75 to 95	Mo	80 to 100	Dy	60 to 80
Mg	70 to 95	Cr	80 to 100	Cd	80 to 100	W	80 to 100
Al	75 to 100	Mn	75 to 95	In	85 to 100	Pb	70 to 100
P	85 to 100	Fe	75 to 100	Sn	70 to 100	Bi	70 to 90
S	65 to 95	Ni	75 to 100	Ba	75 to 100	Th	55 to 75
Silver and silicon have been evaluated using the TBP/odourless kerosene extraction; however, recoveries are significantly variable from batch to batch.							

Annex C
(informative)

General information

This annex presents a very brief summary of the relative merits of the options provided in this International Standard. For detailed information, contact manufacturers or appropriate textbooks.

C.1 Instrument options

Quadrupole-based ICP-MS relies upon a quadrupole mass analyser to separate the ions. The key advantages relative to the other instrument options are its low cost, compact design, and that it is a well-established and extensively used instrumental technique. The key disadvantage lies in the impact of isobaric interference on the measurement of some nuclide isotopes. To overcome these interferences, options are available for modifying the plasma conditions using specialist additional equipment such as collision cells or operation using non-routine plasma parameters, see below.

Sector ICP-MS relies upon an electromagnet-based mass analyser to separate the ions. The key advantage of this technique is the ability to use the resolving power of the sector-based analyser to separate interfering molecular based ions. The instrument also offers improved sensitivity compared with the quadrupole instruments. This is offset by the higher cost compared with quadrupole instruments.

Time of flight ICP-MS relies upon the time taken to pass down the mass spectrometer flight tube to separate the ions. This is a relatively new technique and was only just being established at the time of preparation of this International Standard: consequently, no details are provided.

C.2 Sample introduction techniques

The conventional technique for introducing the sample into the plasma is through the use of a nebuliser and spray chamber. This is the well-established technique and provides adequate performance for most applications. Performance can be improved using techniques such as spray chamber heating and Peltier cooling. Other specialized techniques exist, such as ultrasonic nebulisation or direct-insert nebulisers.

C.3 Collision cell systems

The problem of interference by molecular ions such as ArO^+ has led to the development of collision/reaction cells. These are located in the ion beam on quadrupole instruments in particular. By introducing a suitable doping gas, the interfering ion can be neutralized or converted into another ion with a different mass, thus reducing the interference.

C.4 Cool plasma systems

These operate by reducing the power of the plasma and thus reducing the ionisation energy and hence the production of molecular ions. This also affects the analytes of interest, but the signal-to-noise level is still sufficient for determining the analyte.

C.5 Quantitative techniques

This International Standard uses the conventional technique of comparing the sample signal to a calibration graph generated from the measurement of a number of standards. This is the standard technique for ICP-MS and provides suitable sensitivity, precision and accuracy for most applications. A number of alternatives are available, but only for specialist applications where enhanced sensitivity and specificity are required. Both standard addition and isotope dilution analysis techniques can be used for the technique. The applicability of these options can be found in many of the textbooks on ICP-MS, and so are outside the scope of this International Standard.

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