जल और अपशिष्ट जल के नमूने लेने तथा परीक्षण (भौतिक एवं रसायन) की पद्धतियाँ

भाग 65 उपपादन द्वारा मिलकर प्लाज्मा मास स्पेक्ट्रोमेट्री (आईसीपी-एमएस) के अनुप्रयोग — यूरेनियम आइसोटोपस सहित चयनित तत्त्वो का निर्धारण

(दूसरा पुनरीक्षण)

Methods of Sampling and Test (Physical and Chemical) for Water and Wastewater

Part 65 Application of Inductively Coupled Plasma Mass Spectrometry (ICP-MS) — Determination of Selected Elements Including Uranium Isotopes

(Second Revision)

ICS 13.060.50

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Water Quality Sectional Committee, CHD 36

NATIONAL FOREWORD

This Indian Standard which is identical to ISO 17294-2 : 2023 'Water quality — Application of inductively coupled plasma mass spectrometry (ICP-MS) — Part 2: Determination of selected elements including uranium isotopes' issued by the International Organization for Standardization (ISO) was adopted by the Bureau of Indian Standards on the recommendation of Water Quality Sectional Committee and approval of the Chemical Division Council.

This standard was published in 2014 and subsequently revised in 2022 which was identical to ISO 17294-2 : 2016. This second revision has been undertaken to adopt the latest version of ISO 17294-2 published in 2023. In this revision the following changes have been incorporated:

a) With the incorporation of mercury in the previous edition, mercury has now been excluded as a hydrolysable and has now become a non-hydrolysable element because it was not in line with the other existing standards for the determination of mercury;

b) The addition of a modifier has been clarified; and

c) Titanium has been added to the scope.

BIS has also published separate standard IS 3025 (Part 64) which specifies the principles of inductively coupled plasma mass spectrometry (ICP-MS) and provides general requirements for the use of this technique to determine elements in water, digests of sludges and sediments which is identical adoption of ISO 17294 (Part 1).

The text of ISO standard has been approved as suitable for publication as an Indian Standard without deviations. Certain conventions are, however, not identical to those used in Indian Standards. Attention is particularly drawn to the following:

a) Whenever the words 'International Standard; appears referring to this standard, they should be read as 'Indian Standard'; and

b) Comma (,) has been used as a decimal marker, while in Indian Standards, the current practice is to use a point (.) as the decimal marker.

In this adopted standard, reference appears to certain International Standards where the standard atmospheric conditions to be observed are stipulated which are not applicable to tropical/subtropical countries. The applicable standard atmospheric conditions for Indian conditions are 27 ± 2 °C and 65 ± 5 percent relative humidity and shall be observed while using this standard.

In this adopted standard, references appear to certain International Standards for which Indian Standards also exist. The corresponding Indian Standards, which are to be substituted in their respective places, are listed below along with their degree of equivalence for the editions indicated:

International Standard	Corresponding Indian Standard	Degree of Equivalence
IS0 5667-1 Water quality — Sampling — Part 1: Guidance on the design of sampling programmes and sampling techniques	IS 17614 (Part): XXXX/ISO 5667-1: 2023 Water quality — Sampling: Part 1 Guidance on the design of sampling programmes and sampling techniques (*under preparation*)	Identical

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Indian Standard

METHODS OF SAMPLING AND TEST (PHYSICAL AND CHEMICAL) FOR WATER AND WASTEWATER

PART 65 APPLICATION OF INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY (ICP-MS) — DETERMINATION OF SELECTED ELEMENTS INCLUDING URANIUM ISOTOPES

(Second Revision)

WARNING — Persons using this document should be familiar with normal laboratory practice. This document does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices.

IMPORTANT — It is absolutely essential that tests, conducted in accordance with this document, be carried out by suitably qualified staff.

1 Scope

This document specifies a method for the determination of the elements aluminium, antimony, arsenic, barium, beryllium, bismuth, boron, cadmium, caesium, calcium, cerium, chromium, cobalt, copper, dysprosium, erbium, gadolinium, gallium, germanium, gold, hafnium, holmium, indium, iridium, iron, lanthanum, lead, lithium, lutetium, magnesium, manganese, mercury, molybdenum, neodymium, nickel, palladium, phosphorus, platinum, potassium, praseodymium, rubidium, rhenium, rhodium, ruthenium, samarium, scandium, selenium, silver, sodium, strontium, terbium, tellurium, thorium, thallium, thulium, tin, titanium, tungsten, uranium and its isotopes, vanadium, yttrium, ytterbium, zinc and zirconium in water (e.g. drinking water, surface water, ground water, waste water and eluates).

Taking into account the specific and additionally occurring interferences, these elements can be determined in water and digests of water and sludge (e.g. digests of water as described in ISO 15587-1 or ISO 15587-2).

The working range depends on the matrix and the interferences encountered. In drinking water and relatively unpolluted waters, the limit of quantification (L_{0Q}) lies between 0,002 µg/l and 1,0 µg/l for most elements (see Table 1). The working range typically covers concentrations between several ng/l and mg/l depending on the element and specified requirements.

The quantification limits of most elements are affected by blank contamination and depend predominantly on the laboratory air-handling facilities available on the purity of reagents and the cleanliness of glassware.

The lower limit of quantification is higher in cases where the determination suffers from interferences (see Clause 5) or memory effects (see ISO 17294-1).

Elements other than those mentioned in the scope can also be determined according to this document provided that the user of the document is able to validate the method appropriately (e.g. interferences, sensitivity, repeatability, recovery).

Table 1 — Lower limits of quantification for unpolluted water

Element	Isotope often used	L_{OQ}[a] µg/l	Element	Isotope often used	L_{OQ}[a] µg/l	Element	Isotope often used	L_{OQ}[a] µg/l
Ag	^{107}Ag	0,5	Hf	^{178}Hf	0,1	Ru	^{102}Ru	0,1
Ag	^{109}Ag	0,5	Hg	^{202}Hg	0,05	Sb	^{121}Sb	0,2
			Hg	^{201}Hg	0,1	Sb	^{123}Sb	0,2
Al	^{27}Al	1	Ho	^{165}Ho	0,1	Sc	^{45}Sc	5
As	^{75}As[c]	0,1	In	^{115}In	0,1	Se	^{77}Se[c]	1
Au	^{197}Au	0,5	Ir	^{193}Ir	0,1	Se	^{78}Se[c]	0,1
B	^{10}B	1	K	^{39}K[C]	5	Se	^{82}Se	1
B	^{11}B	1	La	^{139}La	0,1	Sm	^{147}Sm	0,1
Ba	^{137}Ba	3	Li	^{6}Li	10	Sn	^{118}Sn	1
Ba	^{138}Ba	0,5	Li	^{7}Li	1	Sn	^{120}Sn	1
Be	^{9}Be	0,1	Lu	^{175}Lu	0,1	Sr	^{86}Sr	0,5
Bi	^{209}Bi	0,5	Mg	^{24}Mg	1	Sr	^{88}Sr	0,3
Ca	^{43}Ca	100	Mg	^{25}Mg	10	Tb	^{159}Tb	0,1
Ca	^{44}Ca	50	Mn	^{55}Mn	0,1	Te	^{126}Te	2
Ca	^{40}Ca	10	Mo	^{95}Mo	0,5	Th	^{232}Th	0,1
Cd	^{111}Cd	0,1	Mo	^{98}Mo	0,3	Tl	^{203}Tl	0,2
Cd	^{114}Cd	0,5	Na	^{23}Na	10	Tl	^{205}Tl	0,1
Ce	^{140}Ce	0,1	Nd	^{146}Nd	0,1	Ti	^{47}Ti	10
						Ti	^{48}Ti	1
						Ti	^{49}Ti	10
Co	^{59}Co	0,2	Ni	^{58}Ni[c]	0,1	Tm	^{169}Tm	0,1
Cr	^{52}Cr[c]	0,1	Ni	^{60}Ni[c]	0,1	U	^{238}U	0,1
Cr	^{53}Cr	5	P	^{31}P	5	U	^{235}U	$1,10^{-4}$
Cs	^{133}Cs	0,1	Pb	^{206}Pb[b]	0,2	U	^{234}U	$1,10^{-5}$
Cu	^{63}Cu	0,1	Pb	^{207}Pb[b]	0,2	V	^{51}V[c]	0,1
Cu	^{65}Cu	0,1	Pb	^{208}Pb[b]	0,1	W	^{182}W	0,3
Dy	^{163}Dy	0,1	Pd	^{108}Pd	0,5	W	^{184}W	0,3
Er	^{166}Er	0,1	Pr	^{141}Pr	0,1	Y	^{89}Y	0,1
Fe	^{56}Fe[c]	5	Pt	^{195}Pt	0,5	Yb	^{172}Yb	0,2
Ga	^{69}Ga	0,3	Rb	^{85}Rb	0,1	Yb	^{174}Yb	0,2
Ga	^{71}Ga	0,3	Re	^{185}Re	0,1	Zn	^{64}Zn	1
Gd	^{157}Gd	0,1	Re	^{187}Re	0,1	Zn	^{66}Zn	1
Gd	^{158}Gd	0,1	Rh	^{103}Rh	0,1	Zn	^{68}Zn	1
Ge	^{74}Ge	0,3	Ru	^{101}Ru	0,2	Zr	^{90}Zr	0,2

[a] Depending on the instrumentation, significantly lower limits can be achieved.

[b] Lead (Pb) is reported as the sum of the signal intensities of ^{206}Pb, ^{207}Pb and ^{208}Pb.

[c] These limits are achieved by the use of a collision/reaction cell.

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 5667-1, *Water quality — Sampling — Part 1: Guidance on the design of sampling programmes and sampling techniques*

ISO 5667-3, *Water quality — Sampling — Part 3: Preservation and handling of water samples*

ISO 8466-1, *Water quality — Calibration and evaluation of analytical methods — Part 1: Linear calibration function*

ISO 15587-1, *Water quality — Digestion for the determination of selected elements in water — Part 1: Aqua regia digestion*

ISO 15587-2, *Water quality — Digestion for the determination of selected elements in water — Part 2: Nitric acid digestion*

ISO/IEC 17025, *General requirements for the competence of testing and calibration laboratories*

ISO 17294-1:2004, *Water quality — Application of inductively coupled plasma mass spectrometry (ICP-MS) — Part 1: General guidelines*

3 Terms, definitions and symbols

3.1 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 17294-1 and the following apply.

ISO and IEC maintain terminology 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/

3.1.1
analyte
element to be determined

3.1.2
background
N_0
counts for a given mass in the blank solution

Note 1 to entry: Background is expressed in Counts.

3.1.3
blank calibration solution
solution prepared in the same way as the *calibration solution* (3.1.4) but leaving out the *analyte* (3.1.1)

3.1.4
calibration solution
solution used to calibrate the instrument, prepared from a *stock solution(s)* (3.1.24) or from a certified standard

3.1.5
determination
entire process from preparing the *test sample solution* (3.1.26) up to and including the measurement and calculation of the final *result* (3.1.22)

3.1.6
expanded uncertainty
U
product of the standard uncertainty, $u(C)$, and the coverage factor, k, with $k = 1, 2,...,$ as follows: $U = k \cdot u(C)$

Note 1 to entry: Expanded uncertainty is expressed in the unit of the quantity C.

3.1.7
instrument detection limit
L_{DI}
smallest concentration that can be detected with a defined statistical probability using a contaminant-free instrument and a *blank calibration solution* (3.1.3)

Note 1 to entry: It is the lowest value that can be measured by the instrument in the most optimal set up and is determined by three times the standard deviation obtained with 10 replicates of the blank.

Note 2 to entry: Instrument detection limit is expressed in µg/l.

3.1.8
instrumental limit of quantification
$L_{OQ,ins}$
limit of quantification (3.1.13) expressed in counts for the chosen m/z, due to the blank and the instrument

Note 1 to entry: Instrumental limit of quantification is expressed in µg/l.

3.1.9
internal standard correction factor
c_{int}
sample matrix effect correction when an internal standard is added to the sample

3.1.10
internal standard mass
$m_{\mathbf{T}}$
mass of the isotope dilution tracer added

Note 1 to entry: Internal standard mass is expressed in µg.

3.1.11
laboratory sample
sample as prepared for sending to the laboratory and intended for inspection or testing

[SOURCE: ISO 6206:1979, 3.2.10]

3.1.12
limit of application
L_{OA}
lowest or highest concentration of an *analyte* (3.1.1) that can be determined with a defined level of accuracy and *precision* (3.1.18)

Note 1 to entry: Limit of application is expressed in µg/l.

3.1.13
limit of quantification
L_{OQ}
value determined by 10 times the standard deviation obtained with 10 replicates of the blank

Note 1 to entry: Limit of quantification is expressed in µg/l.

3.1.14
linearity
functional relationship between the indicated values and the content

3.1.15
mass concentration
C
mass of *analyte* (3.1.1) per unit volume of the sample

Note 1 to entry: Mass concentration is expressed in µg/l.

3.1.16
mass concentration of the internal standard solution
C_T
mass of internal standard element per unit volume of the internal standard solution

Note 1 to entry: Mass concentration of the internal standard solution is expressed in µg/l.

3.1.17
optimization solution
solution serving for mass calibration and for the optimization of the apparatus conditions

EXAMPLE   Adjustment of maximal *sensitivity* (3.1.23) with respect to minimal oxide formation rate and minimal formation of doubly charged ions.

3.1.18
precision
closeness of agreement between independent test *results* (3.1.22) obtained under stipulated conditions

Note 1 to entry: Precision depends only on the distribution of random errors and does not relate to the true value or the specified value.

[SOURCE: ISO 5725-1:2023, 3.12, modified — Notes 2 and 3 to entry have been deleted.]

3.1.19
pure chemical
chemical with the highest available purity and known stoichiometry and for which the content of *analyte* (3.1.1) and contaminants is known with an established degree of certainty

3.1.20
repeatability
r
precision (3.1.18) under repeatability conditions

[SOURCE: ISO 5725-1:2023, 3.13, modified — the symbol "*r*" has been added and Note 1 to entry has been deleted.]

3.1.21
reproducibility
R
precision (3.1.18) under reproducibility conditions

[SOURCE: ISO 5725-1:2023, 3.18, modified — the symbol "*R*" has been added, and Notes 1 and 2 to entry have been deleted.]

3.1.22
result
outcome of a measurement

Note 1 to entry: The result is typically calculated as *mass concentration* (*C*) (3.1.15), expressed in µg/l or mg/l.

3.1.23
sensitivity
S
ratio of the variation of the magnitude of the signal (ΔI) to the corresponding variation in the concentration of the *analyte* (3.1.1) (ΔC) expressed by Formula (1):

$$S = \frac{\Delta I}{\Delta C}$$

(1)

3.1.24
stock solution
solution with accurately known *analyte* (3.1.1) concentration(s), prepared from *pure chemicals* (3.1.19)

Note 1 to entry: Stock solutions are reference materials as explained in ISO Guide 30.

3.1.25
test sample
sample prepared from the *laboratory sample* (3.1.11), for example, by grinding or homogenizing

3.1.26
test sample solution
solution prepared with the fraction (test portion) of the *test sample* (3.1.25) according to the appropriate specifications, such that it can be used for the envisaged measurement

3.2 Symbols

k	coverage factor	—
N	raw counts	—
N_{dl}	counts calculated when using isotopic dilution	Counts
N_{net}	net counts ($N - N_0$), $N_{net} = a \cdot C + b$ where a is the regression line slope, expressed in Counts·µg^{-1}·l; b is the coordinate at the origin of the regression line, expressed in Counts	Counts
r	measured isotopic ratio	Counts
R	true isotopic ratio	—
s_{N0}	blank standard deviation	—
T	isotope distribution in the standard solution of ^{233}U (used for isotopic dilution)	—
$u(C)$	standard uncertainty associated with the measurement result	unit of the quantity C
V	volume of the sample	l
α	bias per unit mass	—
β	fractionation coefficient deviation	—

4 Principle

When applying this document, it is necessary in each case, depending on the range to be tested, to determine if and to what extent additional conditions shall be established. Guidance is given in ISO 17294-1.

Multi-element determination of selected elements, including uranium isotopes, by inductively coupled plasma mass spectrometry (ICP-MS) consists of the following steps:

— introduction of a measuring solution into a radiofrequency plasma (e.g. by pneumatic nebulization) where energy transfer processes from the plasma cause desolvation, decomposition, atomization and ionization of elements;

— as an additional option, collision or reaction cell technology may be used to overcome several interferences (see 5.1);

— extraction of the ions from plasma through a differentially pumped vacuum interface with integrated ion optics and separation on the basis of their mass-to-charge ratio by a mass spectrometer (for instance, a quadrupole MS);

— transmission of the ions through the mass separation unit (for instance, a quadrupole) and detection, usually by a continuous dynode electron multiplier assembly, and ion information processing by a data handling system;

— quantitative determination after calibration with suitable calibration solutions.

The relationship between signal intensity and mass concentration is usually a linear one over a broad range (usually over more than several orders of magnitude).

The method used for the determination of uranium isotopes is described in Annex A.

With instruments equipped with a magnetic sector field, higher mass resolution spectra can be obtained. This can help to separate isotopes of interest from interfering species.

5 Interferences

5.1 General

In certain cases, isobaric and non-isobaric interferences can occur. The most important interferences in this respect are coinciding masses and physical interferences from the sample matrix. For more detailed information, see ISO 17294-1.

Common isobaric interferences are given in Table 2 (for additional information, see ISO 17294-1). It is recommended that different isotopes of an element be determined in order to select an isotope that does not suffer from interference. If there are none that meet this requirement, a mathematical correction shall be applied. For the determination of uranium isotopes, the specific procedure detailed in Annex A shall be followed.

Small drifts or variations in intensities should be corrected by the application of the internal standard correction. In general, in order to avoid physical and spectral interferences, the mass concentration of dissolved matter (salt content) should not exceed 2 g/l (corresponding to a conductivity of less than 2 700 µS/cm).

NOTE   With the use of collision and reaction cell technology, it is possible to overcome several interferences. As the various options and parameters of those techniques cannot be described in detail in this document, the user is responsible for demonstrating that the chosen approach is fit for purpose and achieves the necessary performance.

Table 2 — Important isobaric and polyatomic interferences

Element	Isotope	Inter-element interferences caused by isobars and doubly charged ions	Interferences caused by polyatomic ions
Ag	^{107}Ag	—	ZrO
	^{109}Ag	—	NbO, ZrOH
As	^{75}As	—	ArCl, CaCl
Au	^{197}Au	—	TaO
B	^{10}B	—	—
	^{11}B	—	BH
Ba	^{138}Ba	La^+, Ce^+	—
Be	^9Be	—	$^{18}O_2$
Ca	^{43}Ca	Sr^{2+}	CNO
	^{44}Ca	Sr^{2+}	COO
NOTE In the presence of elements in high mass concentrations, interferences can be caused by the formation of polyatoms or doubly charged ions which are not listed in this table.			

Table 2 *(continued)*

Element	Isotope	Inter-element interferences caused by isobars and doubly charged ions	Interferences caused by polyatomic ions
Cd	^{111}Cd	—	MoO, MoOH, ZrOH
	^{114}Cd	Sn^+	MoO, MoOH
Co	^{59}Co	—	CaO, CaOH, MgCl
Cr	^{52}Cr	—	ArO, ArC, ClOH
	^{53}Cr	Fe^+	ClO, ArOH,
Cu	^{63}Cu	—	ArNa, POO, MgCl
	^{65}Cu	—	SOOH
Eu	^{151}Eu	—	BaO
	^{153}Eu	—	BaO
Fe	^{54}Fe	—	$^{37}Cl^{16}O^1H$, $^{40}Ar^{14}N$
	^{56}Fe	—	$^{40}Ar^{16}O$, $^{40}Ca^{16}O$
	^{57}Fe	—	$^{40}Ar^{16}O^1H$, $^{40}Ca^{16}O^1H$, $^{40}Ar^{17}O$
Ga	^{69}Ga	Ba^{2+}	CrO, ArP, ClOO
Ge	^{74}Ge	Se^+	ArS, ClCl
Hg	^{201}Hg	—	$^{184}W^{17}O$
	^{202}Hg	—	$^{186}W^{16}O$
In	^{115}In	Sn^+	—
Ir	^{193}Ir	—	HfO
Mg	^{24}Mg	—	CC
	^{25}Mg	—	CC
Mn	^{55}Mn	—	NaS, ArOH, ArNH
Mo	^{98}Mo	Ru^+	—
Ni	^{58}Ni	Fe^+	CaO, CaN, NaCl, MgS
	^{60}Ni	—	CaO, CaOH, MgCl, NaCl
Pd	^{108}Pd	Cd^+	MoO, ZrO
Pt	^{195}Pt	—	HfO
Re	^{187}Re	Os^+	—
Ru	^{102}Ru	Pd^+	—
Sb	^{123}Sb	Te^+	—
Sc	^{45}Sc	—	COO, COOH
Se	^{77}Se	—	CaCl, ArCl, ArArH
	^{78}Se	Kr^+	ArAr, CaCl
	^{82}Se	Kr^+	HBr
Sn	^{120}Sn	Te^+	—
V	^{51}V	—	ClO, SOH, ClN, ArNH
Ti	^{47}Ti	Zr^{2+}	NO_2, PO, SiO, CCl, SNH, SiOH, SN, N_2, NO_2H
	^{49}Ti	—	SOH
W	^{184}W	Os^+	—
Zn	^{64}Zn	Ni^+	AlCl, SS, SOO, CaO
	^{66}Zn	Ba^{2+}	PCl, SS, FeC, SOO
	^{68}Zn	Ba^{2+}, Ce^{2+}	FeN, PCl, ArS, FeC, SS, ArNN, SOO

NOTE   In the presence of elements in high mass concentrations, interferences can be caused by the formation of polyatoms or doubly charged ions which are not listed in this table.

5.2 Spectral interferences

5.2.1 General

For more detailed information on spectral interferences, see ISO 17294-1:2004, 6.2.

5.2.2 Isobaric elemental

Isobaric elemental interferences are caused by isotopes of different elements of the same nominal mass-to-charge ratio and which cannot be separated due to an insufficient resolution of the mass spectrometer in use (e.g. ^{114}Cd and ^{114}Sn).

Element interferences from isobars can be corrected for taking into account the influence from the interfering element (see Table 3). In this case, the isotopes used for correction shall be determinable without any interference and with sufficient precision. Possible proposals for correction are often included in the instrument software.

Table 3 — Examples of suitable isotopes with their relative atomic masses and formulae for correction

Element	Recommended isotope and inter-element correction	
As	^{75}As	$-3{,}127$ (^{77}Se $-$ $0{,}815$ ^{82}Se) or $-3{,}127$ (^{77}Se $+$ $0{,}322$ 0 ^{78}Se)
Ba	^{138}Ba	$-0{,}000\ 900\ 8$ ^{139}La $-$ $0{,}002\ 825$ ^{140}Ce
Cd	^{114}Cd	$-0{,}026\ 84$ ^{118}Sn
Ge	^{74}Ge	$-0{,}138\ 5$ ^{82}Se
In	^{115}In	$-0{,}014\ 86$ ^{118}Sn
Mo	^{98}Mo	$-0{,}110\ 6$ ^{101}Ru
Ni	^{58}Ni	$-0{,}048\ 25$ ^{54}Fe
Pb	^{208}Pb	$+^{207}$Pb $+$ ^{206}Pb
Sn	^{120}Sn	$-0{,}013\ 44$ ^{125}Te
V	^{51}V	$-3{,}127$ (^{53}Cr $-0{,}113\ 4$ ^{52}Cr)
W	^{184}W	$-0{,}001\ 242$ ^{189}Os
NOTE When using collision or reaction cell technology, some of these interferences can be overcome.		

5.2.3 Polyatomic interferences

Polyatomic ions are formed by coincidence of plasma gas components, reagents and sample matrix (e.g. interference of the relative mass ^{75}As by ^{40}Ar^{35}Cl and ^{40}Ca^{35}Cl). Examples of correction formulae are given in Table 3 and information on the magnitude of interferences are stated in Table 4. This interference is of particular relevance for several elements (e.g. As, Cr, Se, V). It is recommended that the analyst checks the magnitude of this interference regularly.

In the case of mathematical corrections, it shall be taken into account that the magnitude of interference depends both on the plasma adjustment (e.g. oxide formation rate) and on the mass concentration of the interfering element, which is usually a variable component of the sample solution.

5.3 Non-spectral interferences

For detailed information on non-spectral interferences, see ISO 17294-1:2004, 6.3.

Table 4 — Important interferences by solutions of

Na, K, Ca, Mg, Cl, S, P (ρ = 100 mg/l) and Ba (ρ = 1 000 µg/l)

Element	Isotope	Simulated mass concentration[a] µg/l	Type of interference
As	^{75}As	1,0	ArCl
Co	^{59}Co	0,2 to 0,8	CaO, CaOH
Cr	^{52}Cr	1,0	ClOH
		1,0	ArC
	^{53}Cr	5,0	ClO
Cu	^{63}Cu	1,0 to 3,0	ArNa
		1,0 to 1,6	POO
	^{65}Cu	2,0	ArMg
		2,0	POO
		2,0	SOOH
Ga	^{69}Ga	1,0 to 25	Ba^{2+}
		0,3	ArP
		1,0	ClOO
	^{71}Ga	0,2 to 0,6	ArP
Ge	^{74}Ge	0,3	ClCl
		0,3	ArS
Mn	^{55}Mn	3,0	KO
		3,0	NaS
		3,0	NaS
Ni	^{58}Ni	2,5	CaO, CaN
	^{60}Ni	3 to 12	CaO, CaOH
Se	^{77}Se	10	ArCl
V	^{51}V	1 to 5	ClO, ClN
		1,0	SOH
Zn	^{64}Zn	7	ArMg
		3	CaO
		8	SS, SOO
		1	POOH
	^{66}Zn	2,0	ArMgBa^{2+}
		5	SS, SOO
		4	PCl
		2	Ba^{2+}
	^{68}Zn	50	ArS, SS, SOO
		4	Ba^{2+}

[a] Indicates the magnitude of interference without corrective measures. Users should check the interferences and decide how to reduce or eliminate them (e.g. by use of collision or reaction cell technology).

6 Reagents

For the determination of elements at trace and ultra-trace levels, the reagents shall be of adequate purity. The concentration of the analyte or interfering substances in the reagents and the water should be negligible compared to the lowest concentration to be determined.

For preservation and digestion, nitric acid should be used to minimize interferences by polyatoms.

For uranium isotopes concentration determination, see Annex A.

6.1   Water, demineralized.

6.2   Nitric acid, $\rho(\text{HNO}_3)$ = 1,4 g/ml.

NOTE   Nitric acid is available both as $\rho(\text{HNO}_3)$ = 1,40 g/ml [$w(\text{HNO}_3)$ = 650 g/kg] and $\rho(\text{HNO}_3)$ = 1,42 g/ml [$w(\text{HNO}_3)$ = 690 g/kg]. Both are suitable for use in this method provided that there is minimal content of the analytes of interest.

6.3   Hydrochloric acid, $\rho(\text{HCl})$ = 1,16 g/ml.

6.4   Hydrochloric acid, $c(\text{HCl})$ = 0,2 mol/l.

6.5   Sulfuric acid, $\rho(\text{H}_2\text{SO}_4)$ = 1,84 g/ml.

6.6   Hydrogen peroxide, $w(\text{H}_2\text{O}_2)$ = 30 %.

NOTE   Hydrogen peroxide is often stabilized with phosphoric acid.

6.7   Element stock solutions, ρ = 1 000 mg/l each of Ag, Al, As, Au, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ge, Hf, Hg, Ho, In, Ir, K, La, Li, Lu, Mg, Mn, Mo, Na, Nd, Ni, P, Pb, Pd, Pr, Pt, Rb, Re, Rh, Ru, Sb, Sc, Se, Sm, Sn, Sr, Tb, Te, Th, Tl, Tm, U, V, W, Y, Yb, Zn and Zr.

Both single-element stock solutions and multi-element stock solutions with adequate specification stating the acid used and the preparation technique are commercially available. Element stock solutions with different concentrations of the analytes (e.g. 2 000 mg/l or 10 000 mg/l) are also allowed.

These solutions are considered to be stable for more than one year, but in reference to guaranteed stability, the recommendations of the manufacturer should be considered.

6.8   Anion stock solutions, ρ = 1 000 mg/l each of Cl^-, PO_4^{3-}, SO_4^{2-}.

Prepare these solutions from the respective acids. The solutions are also commercially available. Anion stock solutions with different concentrations of the analytes (e.g. 100 mg/l) are also allowed.

These solutions are considered to be stable for more than one year, but in reference to guaranteed stability, the recommendations of the manufacturer should be considered.

6.9   Multi-element standard solutions.

Depending on the scope, different multi-element standard solutions can be necessary. In general, when combining multi-element standard solutions, their chemical compatibility and the possible hydrolysis of the components shall be regarded. Care shall be taken to prevent chemical reactions (e.g. precipitation).

The examples given in 6.9.1 and 6.9.2 also consider the different sensitivities of various mass spectrometers.

The multi-element standard solutions are considered to be stable for several months, if stored in the dark.

This does not apply to multi-element standard solutions that are prone to hydrolysis, in particular, solutions of Bi, Mo, Sn, Sb, Te, W, Hf and Zr.

NOTE   Mercury (Hg) standard solutions can also be stabilized with HCl; therefore, one of the procedures described in 6.9.1 o 6.9.2 can be used depending on the preservation of the samples with either HNO_3 or HCl.

In reference to guaranteed stability of all standard solutions, refer to the recommendations of the manufacturer.

6.9.1   Multi-element standard solution A, for example, consisting of the following:

— $\rho(\text{As, Se})$ = 20 mg/l;

— ρ(Ag, Al, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Fe, La, Li, Mg, Mn, Ni, Pb, Rb, Sr, Th, Tl, U, V and Zn) = 10 mg/l.

— option: ρ(Hg) = 1 mg/l;

Transfer with a pipette 20 ml of each element stock solution (As, Se) (6.7) and 10 ml of each element stock solution (Ag, Al, B, Ba, Be, Bi, Cd, Ce, Co, Cr, Cs, Cu, Fe, La, Li, Mn, Ni, Pb, Rb, Sr, Th, Tl, U, V and Zn) (6.7) and 1 ml of stock solution (Hg) (6.7) into a 1 000 ml volumetric flask.

Add 10 ml of nitric acid (6.2).

Bring to volume with water (6.1) and transfer to a suitable storage bottle.

Multi-element standard solutions with more elements can be used provided that it is verified that these solutions are stable and no chemical reactions occur. This shall be checked again a few days after the first use (sometimes precipitation can occur after preparation).

6.9.2   Multi-element standard solution B, for example, consisting of the following:

— ρ(Au, Mo, Sb, Sn, W, Zr) = 5 mg/l.

— option: ρ(Hg) = 1 mg/l;

Transfer with a pipette 2,5 ml of each element stock solution (Au, Mo, Sb, Sn, W, Zr) and 0,5 ml of stock solution (Hg) (6.7) into a 500 ml volumetric flask.

Add 40 ml of hydrochloric acid (6.3).

Bring to volume with water (6.1) and transfer to a suitable storage bottle.

6.9.3   Reference-element solution (internal standard solution).

The choice of elements for the reference-element solution depends on the analytical problem. Solutions of these elements should cover the mass range of interest. The concentrations of these elements in the sample should be negligibly low. The elements In, Lu, Re, Rh and Y have been found suitable for this purpose. Other elements can also be used, depending on the purpose of the analysis, such as stable Bi and Tl.

For example, ρ(Y, Re) = 5 mg/l reference-element solution can be used.

Transfer with a pipette 5 ml of each element stock solution (Y, Re) (6.7) into a 1 000 ml volumetric flask.

Add 10 ml of nitric acid (6.2).

Bring to volume with water (6.1) and transfer to a suitable storage bottle. The reference element solution can be added to all sample solutions or added to the diluent before the nebulizer.

For the determination of mercury (Hg), it is recommended to add a gold (Au) solution in diluted HCl to the reference-element solution to allow a final concentration of at least 50 µg/l in the solution to be measured [ρ(Au) ≥ 50 µg/l].

6.10   Multi-element calibration solutions.

Choose the mass concentrations of the calibration solutions to allow for a sufficient precision and reproducibility and ensure that the working range is covered.

The stability of the calibration solutions should be checked regularly. Due to their rather low respective mass concentrations, they should be replaced by freshly prepared solutions at least every month or more frequently for elements which are prone to hydrolysis. In special cases, daily preparation is necessary. The user has to determine the maximum stability period of the calibration solutions.

Transfer the calibration solution(s) A (6.10.1) and B (6.10.2) to suitable storage bottles.

If the determination is carried out after previous digestion (9.2), the matrix of the calibration solution(s) A (6.10.1) and B (6.10.2) below shall be adjusted to that of the digests after dilution, where appropriate.

The working range in general can cover the range of 0,1 µg/l to 50 µg/l or a part of this.

6.10.1 Multi-element calibration solution(s) A.

Prepare the calibration solution(s) A that cover the required working range by diluting the multi-element standard solution A (see 6.9.1). Add sufficient nitric acid (6.2) and other acids, if required, per litre to matrix match with prepared sample solutions and bring up to volume with water (6.1). If necessary, add the reference-element solution (6.9.3) to a concentration of, for example, 50 µg/l of the reference-element, before bringing up to volume.

6.10.2 Multi-element calibration solution(s) B.

Prepare the calibration solution(s) B that cover the required working range by diluting the multi-element standard solution B (6.9.2). Add sufficient hydrochloric acid (6.3) and other acids, if required, per litre to matrix match with prepared sample solutions and bring up to volume with water (6.1). If necessary, add the reference-element solution (6.9.3) to a concentration of, for example, 50 µg/l of the reference-element, before bringing up to volume.

NOTE   The measurement of gold (Au) is interrupted in case gold (Au) is added as a stabilizer for mercury (Hg) according to 6.9.3.

6.11 Blank calibration solutions.

High demands shall be set concerning the purity. The user should ensure that the background levels of the analytes are not significant to the results of the analysis.

6.11.1 Blank calibration solution A.

Add a sufficient volume of nitric acid (6.2) and other acids, if required to matrix match with prepared sample solutions, to a volumetric flask made, for example, from perfluoroalkoxy (PFA) or hexafluoro-ethene propene (FEP) and bring to volume with water (6.1). If necessary, add reference-element solution (6.9.3) to a concentration of, for example, 50 µg/l of the reference-element, before bringing up to volume.

If the determination is carried out after previous digestion (9.2), the matrix of the blank calibration solution A shall be adjusted to that of the digests.

6.11.2 Blank calibration solution B.

Add a sufficient volume of hydrochloric acid (6.3) and other acids, if required to matrix match with prepared sample solutions, to a volumetric flask made, for example, from PFA or FEP and bring to volume with water (6.1). If necessary, add reference-element solution (6.9.3) to a concentration of, for example, 50 µg/l of the reference-element, before bringing up to volume.

If the determination is carried out after previous digestion (9.2), the matrix of the blank calibration solution B shall be adjusted to that of the digests.

NOTE   The measurement of gold (Au) is interrupted in case gold (Au) is added as a stabilizer for mercury (Hg) according to 6.9.3.

6.12 Optimization solution.

The optimization solution serves for mass calibration and for optimization of the apparatus conditions, for example, adjustment of maximal sensitivity with respect to minimal oxide formation rate and minimal formation of doubly charged ions.

It should contain elements covering the entire mass range, as well as elements prone to a high oxide formation rate or to the formation of doubly charged ions. For example, an optimization solution containing Mg, Cu, Rh, In, Ba, La, Ce, U and Pb is suitable. Li, Be and Bi are less suitable because they tend to cause memory effects.

The mass concentrations of the elements used for optimization should be chosen to allow count rates of more than 10 000 Counts/s.

For further information, see general remarks in ISO 17294-1.

6.13 Matrix solution.

The matrix solutions serve to determine the correction factors for the corresponding formulae. High demands are made concerning the purity of the basic reagents due to the high mass concentrations. The user should ensure that the background levels of the analytes in the matrix solution are not significant to the results of the analysis. The composition can be as follows but can contain additional analytes:

— $\rho(Ca)$ = 200 mg/l;

— $\rho(Cl^-)$ = 300 mg/l;

— $\rho(PO_4^{3-})$ = 25 mg/l;

— $\rho(SO_4^{2-})$ = 100 mg/l.

Pipette 200 ml of element stock solution (Ca) (6.7), 300 ml of anion stock solution (Cl⁻) (6.8), 25 ml of anion stock solution (PO_4^{3-}) (6.8) and 100 ml of anion stock solution (SO_4^{2-}) (6.8) to a 1 000 ml volumetric flask.

Add 10 ml of nitric acid (6.2).

Bring to volume with water (6.1) and transfer to a suitable storage bottle.

The reaction or collision cell technology can replace the use of the matrix solution. This shall be validated accordingly by the user of this document.

7   Apparatus

The stability of sample and measuring and calibration solutions depends to a high degree on the container material. The material shall be checked according to the specific purpose. For the determination of elements in a very low concentration range, glass or polyvinyl chloride (PVC) should not be used. Instead, it is recommended to use PFA, FEP or quartz containers, cleaned with hot, concentrated nitric acid in a closed system. For the determination of elements in a higher concentration range, high density polyethene (HDPE) or polytetrafluoroethene (PTFE) containers are also allowed for the collection of samples.

Immediately before use, all glassware should be washed thoroughly with diluted nitric acid [e.g. $w(HNO_3)$ = 10 %], and then rinsed several times with water (6.1).

The use of piston pipettes is permitted and also enables the preparation of lower volumes of calibration solutions. The application of dilutors is also allowed. Mind that contaminated consumables like pipette tips, disposable vessels and filters can lead to increased blank levels and increase the uncertainty of the analytical result.

For more detailed information on the instrumentation, see ISO 17294-1:2004, Clause 5.

7.1   Mass spectrometer.

A mass spectrometer with ICP suitable for multi-element and isotope analysis is required. The spectrometer should be capable of scanning a mass range from 5 m/z [arbitrary mass unit (AMU)] to 240 m/z (AMU) with a resolution of at least 1 m/z peak width at 5 % of peak height (where m is the relative mass of an atom species and z is the charge number). The instrument can be fitted with a conventional or extended dynamic range detection system.

7.2   Mass-flow controller.

A mass-flow controller on the nebulizer gas supply is required. Mass-flow controllers for the plasma gas and the auxiliary gas are also useful. A water-cooled spray chamber can be of benefit in reducing some types of interferences (e.g. from polyatomic oxide species).

NOTE   The plasma is very sensitive to variations in the gas flow rate.

7.3   Nebulizer with variable speed peristaltic pump, for which information on different types of nebulizers is given in ISO 17294-1:2004, 5.2.3.

7.4   Argon gas supply, of high purity grade, for instance >99,99 %.

7.5   Glassware, consisting of the following:

7.5.1   Volumetric flasks, for example, 50 ml, 100 ml, 500 ml and 1 000 ml.

7.5.2   Conical (Erlenmeyer) flasks, for example, 100 ml.

7.5.3   Pipettes, for example, 1 ml, 2,5 ml, 10 ml, 20 ml and 25 ml.

7.6   Storage bottles, for the stock, standard, calibration and sample solutions.

For the determination of elements in a normal concentration range, HDPE or PTFE bottles are sufficient for the storage of samples. For the determination of elements in an ultra-trace level, bottles made from PFA or FEP should be preferred. In any case, the user has to check the suitability of the chosen containers.

8   Sampling

Carry out the sampling in accordance with ISO 5667-1 and preserve the sample in accordance with ISO 5667-3. Due to the extremely high requirements concerning purity in trace and ultra-trace analysis, any impurity shall be avoided.

The mass concentrations of the elements can change rather rapidly after sampling due to adsorption or desorption effects. This is of special importance, for example, in the case of Ag, As, B, Se and Sn. The choice of the container material depends on the mass concentration of the elements to be determined.

For the determination of the dissolved fraction of the elements, filter the sample through a membrane filter, nominal pore size 0,45 μm. Membrane filters shall be tested for impurities by appropriate blank tests. Use several portions of the sample to rinse the filter assembly, discard and then collect the required volume of filtrate.

Add 0,5 ml of nitric acid (6.2) or HCl (6.3) per 100 ml of sample (see 6.9). Ensure that the pH is less than 2; otherwise, add more acid as required.

9   Sample pre-treatment

9.1   Determination of the mass concentration of dissolved elements without digestion

Continue in accordance with Clause 10, using the acidified filtrate specified in Clause 8. If experience has shown that no significant amounts of particles occur (e.g. drinking or tap water), the filtration can be omitted. Those samples shall be colourless and shall have a turbidity of <1,5 FNU (formazin nephelometric unit, see ISO 7027-1) and in fact the total mass concentration is determined.

For the determination of mercury (Hg), it is recommended to add a gold (Au) solution in diluted HCl, to stabilize the mercury in the acidified sample to a final concentration of at least 50 μg/l in the solution to be measured [$\rho(Au) \geq 50$ μg/l].

9.2 Determination of the total mass concentration after digestion

The mass concentration determined according to this subclause does not in all cases represent the total mass concentration. Instead, only the portion that is determinable according to the distinct digestion for a given element composition is analysed.

A nitric acid digestion shall be carried out in accordance with ISO 15587-2. If aqua regia is chosen, the procedure shall be carried out in accordance with ISO 15587-1, in which case, possible interferences caused by the high content of chloride have to be considered accordingly.

Some elements and their respective compounds (e.g. silicates and aluminium oxide) are dissolved incompletely using this procedure.

For the determination of tin, the following digestion can be used:

a) add 0,5 ml of sulfuric acid (6.5) and 0,5 ml of hydrogen peroxide (6.6) to 50 ml of the homogenized water sample;

b) evaporate the mixture until SO_3 vapour is formed;

c) in case of incomplete digestion, add a small portion of water (6.1) after cooling, add hydrogen peroxide (6.6) once more and repeat the treatment;

d) dissolve the residue in diluted hydrochloric acid (6.4) and adjust the volume to 50 ml with water;

e) treat a blank in the same way.

Special digestion methods can be necessary if Sb, W or Zr is to be determined.

If experience has shown that the elements are recovered quantitatively without decomposition, the digestion can be omitted.

NOTE   For drinking water, tap water and potable water, the digestion step can commonly be omitted. The determination of the total mass concentration can be performed in the laboratory sample.

10 Procedure

10.1 General

In ICP-MS methods, the relationship between measured count rates and mass concentrations of an element is known to be linear over several orders of magnitude. Therefore, linear calibration curves can be used for quantification. In routine measurements, check the linearity of the calibration curves at regular intervals. This check shall be carried out in accordance with ISO 8466-1.

Adjust the instrumental parameters of the ICP-MS system in accordance with the manufacturer's manual.

About 30 min prior to measurement, adjust the instrument to working condition.

Before each series of measurement, the sensitivity and the stability of the system should be checked using the optimization solution (6.12). Check the resolution and the mass calibration as often as required by the manufacturer.

Adjust the instrument with the aid of the optimization solution (6.12) to minimize interfering effects (e.g. oxide formation, formation of doubly charged ions) allowing sufficient sensitivity.

According to Table 3, select the relative atomic masses and the corresponding corrections.

Select the rinsing time depending on the length of the flow path; in the case of large variations in mass concentrations in the measuring solutions, allow for longer rinsing periods.

The use of a reference-element solution is recommended. Add the reference-element solution (6.9.3) to the matrix solution (see 6.13), to all multi-element calibration solutions (6.10), to the blank calibration

solutions ([6.11](#)) and to all measuring solutions. The mass concentration of the reference-elements shall be the same in all solutions.

A mass concentration of ρ(Y, Re) = 50 µg/l is often suitable.

NOTE   ICP-MS has excellent multi-element capability. The sensitivity of determination depends on a number of parameters (nebulizer flow, radiofrequency power, lens voltage, lens voltage mode, etc.). The optimal instrument settings cannot be achieved for all elements simultaneously.

10.2 Calibration of the ICP-MS system

When the analytical system is first evaluated and at intervals afterwards, establish a calibration curve for each element to be determined, for example, using four to five measuring points (e.g. the blank calibration solution and three or four calibration solutions).

For work on a daily basis, one blank solution and one to two calibration solutions are suitable; check the validity of the calibration curve with a certified reference sample, an independent standard solution or a suitable internal control sample (consider also ISO 17294-1:2004, 9.2).

Typically, proceed as follows.

— Prepare and measure the blank calibration solutions ([6.11](#)) and the multi-element calibration solutions ([6.10](#)). Set up a calibration graph according to the manufacturer's instruction and in line with ISO 8466-1. Each reference point should be the mean of at least two replicates.

— Take into account possible discrepancies in the isotope composition between the calibration solutions and the measuring solutions (e.g. relevant for Li, Pb, U).

10.3 Measurement of the matrix solution for evaluation of the correction factors

In order to evaluate and/or to update the correction factors, measure the matrix solution ([6.13](#)) or extracts of matrix matched CRM's at regular intervals within a measuring cycle.

10.4 Measurement of the samples

After establishing the calibration curves, measure the blanks and the test samples solutions.

Within sufficient small intervals (e.g. every 10 samples), check the accuracy of at least one certified reference sample or one independent standard solution or one internal control sample. If necessary, re-calibrate.

Some elements (e.g. Ag, B, Be, Bi, Li, Th and Sb) are rinsed very slowly from the inlet system. After high count rates, these memory effects shall be checked by measuring a blank calibration solution ([6.11](#)).

11 Calculation

The mass concentrations for each element may be determined with the aid of the instrument software. Carry out the following single steps for each element.

a) Correct the count rates according to the respective formulae in [Table 3](#).

b) For uranium isotopes, the calculation of the concentration is described in [Annex A](#).

c) Make allowance for the count rates from the blank calibration, calibration and measuring solutions, and relate to the count rates of the reference-elements. Determine the slope and the intercept on the ordinate.

d) Determine the mass concentrations of samples with the aid of the count rates and the calibration graphs.

e) Correct the results taking into account the mass concentrations from the blank calibration solutions and incorporate all dilution steps in the calculation. If the sample is digested (see [9.2](#)), a correction for the procedure blank shall be used if appropriate (digestion blank solution).

For the determination of uranium isotopes, see Annex A. Additional information on the validation is provided in Annex B and Annex C.

According to the requirements set by the analytical quality control, the determination of the mass concentrations using the software of the apparatus shall be verifiable and shall be documented. In all cases, it shall be clear which corrections have been carried out with the aid of the software.

Alternatively, it is also allowed to process the raw data (count rates) by validated in-house software applications.

Report the results to as many significant figures as are acceptable according to the precision of the measuring values.

EXAMPLE   Copper (Cu)   0,142 mg/l

Cadmium (Cd)   0,50 µg/l

12 Test report

The test report shall contain at least the following information:

a)   test method used, together with a reference to this document, i.e. ISO 17294-2:2023;

b)   identity of the sample;

c)   expression of results as indicated in Clause 11;

d)   the sample and sample pre-treatment where appropriate;

e)   any deviations from this document and details of all circumstances which can have affected the result;

f)   any unusual features observed;

g)   the date of the test.

Annex A
(normative)

Determination of the mass concentration of uranium isotopes

A.1 General

This annex describes methods for measuring the concentration of uranium isotopes in water (e.g. drinking water, surface water, ground water, waste water and eluates) by ICP-MS. On the basis of the concentrations obtained, the activity concentrations of the different isotopes can be calculated.

For most chemical environmental monitoring purposes, it is important and sufficient to determine the mass concentration of uranium.

For nuclear environmental monitoring purposes, it is important to determine the activity concentrations of each isotope of uranium in order to be able to perform the right dose estimation (see References [16], [18] and [19]).

This method is applicable to all types of water having a saline load less than 1 g/l. Dilution is possible to obtain a solution having a saline load and activity compatible with preparation and the measurement assembly.

Filtration at 0,45 µm and acidification are recommended.

For a full description of the terms and symbols used in this clause, refer to Clause 3.

A.2 Principle

ICP-MS can be used to measure the mass concentrations of the different uranium isotopes in a water test portion.

If necessary, the results can be converted in activity concentrations using conversion factors given in Table A.1.

Table A.1 — Uranium isotopes half-lives and specific activities

Uranium isotope	Half-life	Specific activity
	y	Bq/g
^{234}U	$2,455 \ (\pm0,006) \times 10^5$	$2,312 \times 10^8$
^{235}U	$704 \ (\pm1) \times 10^6$	$7,997 \times 10^4$
^{236}U	$23,43 \ (\pm0,006) \times 10^6$	$2,392 \times 10^6$
^{238}U	$4,468 \ (\pm0,005) \times 10^9$	$1,244 \times 10^4$

Abundances of 99,274 5 % for ^{238}U, 0,720 0 % for ^{235}U and 0,005 5 % for ^{234}U would usually be observed in natural waters.

^{236}U has a low natural abundance and is not usually measured in water samples. But as ^{236}U is a good fingerprint to demonstrate the presence of uranium isotopes in water from anthropogenic sources, the measurement of this isotope can be sometimes required.

The water sample can be directly measured after filtration (at 0,45 µm porosity) without specific chemical separation.

As the water sample is directly measured, matrix effect correction with an internal standard is needed (as described in ISO 17294-1). For isotopic determination of uranium in water, ^{233}U is commonly used but ^{205}Tl or ^{193}Ir can also be chosen.

It is also important to evaluate the mass bias and to correct it, if necessary.

The following different possibilities are offered:

— external calibrations with ^{238}U, ^{235}U and ^{234}U certified standard solutions can provide ^{238}U, ^{235}U and ^{234}U mass concentrations in the test portion;

— external calibrations with ^{238}U certified standard solution can provide ^{238}U concentration in the test sample solution; then the isotopic ratios measured in the test portion without internal standard addition lead to the ^{235}U and ^{234}U concentrations in the test sample solution;

— isotopic dilution using ^{233}U (^{236}U is also possible, provided that this isotope is not present in the sample) is another possibility; a known amount of pure ^{233}U certified standard solution is added to the test portion and the concentration of the uranium isotopes is based on the isotopic ratios.

In the first case, it can be difficult for the laboratory to get the three different pure and certified standard solutions; three external standard calibration curves have to be prepared.

In the second case, only one certified standard solution is needed, but the test portion shall be measured twice; first with internal standard to get ^{238}U mass concentration and then without internal standard addition to evaluate isotopic ratios.

In the last case, the method is more convenient, but requires corrections for the interference of natural uranium isotopes (^{235}U and ^{234}U) in the internal standard solution, the mass bias and spectral interferences like hydrides.

Examples of limits of quantification that can be obtained with a quadrupole ICP-MS are given in Table A.2.

Table A.2 — Examples of limits of quantification

Isotope	L_{OQ} $\mu g \cdot l^{-1}$	L_{OQ} $mBq \cdot l^{-1}$
^{234}U	<0,000 1	<20
^{235}U	<0,001	<0,1
^{238}U	0,1	<1

A.3 Reagents

Use only reagents of recognized analytical grade.

A.3.1 Laboratory water.

A.3.2 Blank, diluted acid solution used to determine the background spectra for the various masses.

A.3.3 Certified standard solutions of isotopes.

Certified standard solution with known isotopic ratios to evaluate the mass bias or reference solution with known isotopic ratios are used for standard bracketing (measure at least twice, before and after sampling; several repetitions are recommended).

A.3.4 Calibration solutions.

Prepare these solutions by successive dilutions of the certified standard solution in 1 % to 2 % nitric acid (volume fraction). Adjust concentrations in line with the measuring range to be calibrated. The calibration

curve is established with at least five measuring points (e.g. the blank calibration solution and four calibration solutions).

A.3.5 Internal standard solution (e.g. of ^{233}U as an internal standard).

Prepare this solution by successive dilutions of the certified standard solution in 1 % to 2 % nitric acid (volume fraction). Adjust the concentration in line with the validation method chosen. Spike samples with a known amount of this solution before measurement.

A.3.6 Quality control solution.

Solution of certified uranium concentration, different than the one used for calibration.

A.3.7 Argon gas, at least 99,995 % pure.

A.3.8 Diluted nitric acid, 2 % volume fraction, for example.

A.4 Apparatus

Usual laboratory apparatus and, in particular, the following.

A.4.1 Analytical balance, accurate to within 1/10 mg or 1/100 mg.

A.4.2 Argon supply, equipped with low pressure control.

A.4.3 ICP-MS apparatus with associated software, installed in an air-conditioned room.

A.4.4 Auto-sampler device.

A.5 Sampling

A.5.1 General

For the determination of trace amounts of uranium, the prevention of all contamination or losses shall be of primary concern. Dust in the laboratory, impurities in the reagents and on the laboratory equipment which is in contact with the sample are all potential sources of contamination. The sample containers can lead to positive or negative errors in the determination of trace elements by superficial desorption or adsorption.

Perform the following conservation and pre-treatment steps (filtration and acidification) when sampling or immediately afterwards.

The sample collection conditions shall comply with ISO 5667-1.

It is important that the laboratory receive a sample that is truly representative and has not been damaged or modified during transport or storage.

A.5.2 Sample preparation for the determination of dissolved uranium

Filter the sample on a 0,45 μm membrane filter as soon as possible, using a glass or single-use filtration apparatus.

Acidify with nitric acid to ensure that the pH of the sample is less than 2.

A.5.3 Storage, according to ISO 5667-3.

Perform the analysis as soon as possible.

A.6 Procedure

A.6.1 General

Follow the instructions provided by the instrument manufacturer and the steps described in this document.

For each analysis performed on this instrument, the sensitivity, the instrument detection limit, precision, and the interferences should be established for the masses of interest.

Before analysing a sample or prior to a series of samples, analyse the quality control solution as if it was a sample. Ensure that the measured value of the concentration does not deviate from the expected value (within measurement limits). If the deviation exceeds the established measurement limits (optimum sensitivity, optimum stability), follow the recommendations of the instrument manufacturer and perform the adjustment again.

The value of the blank solution is measured using the same procedure as for the samples. This value shall be subtracted from those measured in the samples.

Begin measurement of test sample solutions by cleaning the system with the blank solution. Repeat this operation after each sample.

A.6.2 Quantification

Uranium isotopes can be quantified in the following three different ways:

— using an external calibration solution for each isotope;

— using an external calibration solution for one of the isotopes (e.g. for ^{238}U) with an internal standard and isotopic ratios to determine the other isotopes of uranium;

— using an internal standard solution and corrections (isotopic dilution).

A.6.3 External calibration

Prepare the calibration solutions by adding an internal standard (^{233}U or stable thallium can be used).

The formula of the calibration curves is determined by linear regression using the least square method.

Analyse the quality control solutions to validate the external calibrations.

Perform test sample solution measurements.

Total uranium concentration is sometimes quantified using the calibration of ^{238}U. Then, it is recommended to check that isotopic compositions of the sample and the working solution are identical, otherwise it is necessary to perform corrections.

A.6.4 External calibration for ^{238}U and isotopic ratios

Prepare the calibration solutions for ^{238}U by adding ^{233}U as an internal standard, for example. It is also possible to choose stable elements such as ^{205}Tl or ^{193}Ir.

The formula of the ^{238}U calibration curve is determined by linear regression using the least square method.

Analyse the standard solution to validate the external calibration.

Test portion is measured twice: first time with ^{233}U, as an internal tracer to correct matrix effects, to determine ^{238}U concentration, second time without ^{233}U to determine isotopic ratios.

A.6.5 Internal calibration by isotopic dilution

The uranium concentration is quantified in relation to the ^{233}U standard solution isotopic composition and concentration introduced in the test sample solution.

Isotopic ratios in the standard tracer solution shall be different than the one in the test sample solution.

The mass of tracer ^{233}U added shall be closed to the one of the uranium isotopes in the test sample solution.

Perform test sample solution measurements.

As the ^{233}U certified standard solution is not pure, impurities of uranium natural isotopes shall be quantified with precision and corrections shall be made as well as for mass bias.

A.7 Expression of results

A.7.1 General

The results are expressed in mass concentration with their associated uncertainty. The coverage factor is specified in the presentation of the results.

If dilutions were carried out, apply the appropriate factor to the values of the test sample solution.

The result is expressed as an estimate of the "true" value, to which an uncertainty is associated, itself a combination of elementary uncertainties.

A.7.2 Mass bias evaluation

The mass bias is a fundamental notion in mass spectrometry and the user shall take it into account during calculations to obtain a good accuracy of measurement. This is a systematic error produced by the instrument. However, the mass bias may be small for heavy ions as they are better focused through the skimmer cone after the sampling cone.

The fractionation coefficient deviation, β, can be defined as a function of the different masses studied. The true ratio of isotopes A and B (R) can be expressed from the ratio measured (r) by different relations called linear law, power law, kinetic law, equilibrium law or generalized power law.

The bias per unit mass, α, determined measuring a certified solution or a reference solution when using standard bracketing. Three examples are:

Linear law, given in Formula (A.1):

$$\frac{r}{R} = 1 + \alpha \Delta m \tag{A.1}$$

where $\Delta m = m_A - m_B$

Exponential (kinetic) law, given in Formula (A.2):

$$\beta = \ln\left(\frac{R}{r}\right) / \ln(m_A / m_B) \tag{A.2}$$

And power law, given in Formula (A.3):

$$R = r\left(\frac{m_A}{m_B}\right)^{\beta} \tag{A.3}$$

The linear law is commonly used for the determination of uranium isotopes concentration in water.

In the following, the raw counts will be corrected of the mass bias, if necessary.

The associated uncertainty shall be determined, depending on the law chosen (see Reference [9]).

A.7.3 External calibration

The calibration curve is established from a series of working solutions of known and increasing concentrations, including the expected concentrations (at least five points that can be four different mass concentrations and the blank) and is expressed as indicated in Formula (A.4):

$$N_{\text{net}} = a \cdot C + b \tag{A.4}$$

It is recommended to have the mass concentration in the test sample solution very close to the centroid of the curve in order to minimize the standard uncertainty linked to the calibration curve.

The formula of the calibration curve is determined by the least squares method. Construct a calibration curve by isotope that can be measured in the standard.

Additionally, the use of an internal standard (e.g. ^{233}U) is useful to correct the signal fluctuations. In cases where an internal standard is used, a correction factor, c_{int}, is introduced. This correction is applied by the software.

The mass concentration of the uranium isotopes, expressed in µg·l^{-1}, is equal to Formula (A.5) and Formula (A.6):

$$\rho\left(^{23i}\text{U}\right) = \frac{N_{\text{net}}\left(^{23i}\text{U}\right) - b}{a} \tag{A.5}$$

$$N_{\text{net}}\left(^{23i}\text{U}\right) = c_{\text{int}} \times N\left(^{23i}\text{U}\right) - N_0\left(^{23i}\text{U}\right) \tag{A.6}$$

with i = 4, 5, 6 or 8 depending on the uranium isotope quantified.

A.7.4 External calibration and isotopic ratios

The ^{238}U mass concentration is determined as explained in Clause 8.

The concentration of the ^{238}U, expressed in µg·l^{-1}, is equal to Formula (A.7) and Formula (A.8):

$$\rho\left(^{238}\text{U}\right) = \frac{N_{\text{net}}\left(^{238}\text{U}\right) - b}{a} \tag{A.7}$$

$$N_{\text{net}}\left(^{238}\text{U}\right) = c_{\text{int}} \times N\left(^{238}\text{U}\right) - N_0\left(^{238}\text{U}\right) \tag{A.8}$$

Then, the isotopic ratios are used to determine the concentration of the other isotopes based on the counts obtained in the test sample solution measured without internal standard, as given in Formula (A.9):

$$\rho\left(^{23i}\text{U}\right) = \rho\left(^{238}\text{U}\right) \times \frac{N_{\text{net}}\left(^{23i}\text{U}\right)}{N_{\text{net}}\left(^{238}\text{U}\right)} \times \frac{1}{\left(1 + a_{(i-8)}\right)} \tag{A.9}$$

with i = 4, 5, or 6 on the basis of the uranium isotope quantified.

A.7.5 Internal calibration by isotopic dilution

^{233}U is generally used as isotope dilution tracer: a known quantity of ^{233}U, generally determined by weighing, is added to each sample and is thus used to calculate the concentration of other uranium isotopes present in the sample.

The mass concentration of the uranium isotopes, expressed in $\mu g \cdot l^{-1}$, is given in Formula (A.10):

$$\rho\left(^{23i}U\right) = \frac{m\left(^{23i}U\right)}{V} \tag{A.10}$$

with Formula (A.11):

$$m\left(^{23i}U\right) = m_T \times \frac{N_{net}\left(^{23i}U\right)}{N_{net}\left(^{233}U\right)} \times \frac{1}{\left(1+\alpha_{(i-3)}\right)} \tag{A.11}$$

and the value of N_{net}, which is expressed as given in Formula (A.12) for the various isotopes to be analysed and the isotope dilution tracer:

$$N_{net} = N_{dl} - N_0 \tag{A.12}$$

with Formula (A.13):

$$N_{dl}\left(^{23i}U\right) = N\left(^{23i}U\right) - N_{net}\left(^{233}U\right) \times T\left(^{23i}U\right) \tag{A.13}$$

where $T\left(^{23i}U\right)$ is the rate of the isotope $23i$ (i = 4, 5, 6 or 8) present as impurity in the tracer used.

This correction is particularly significant for the measurement of ^{234}U by isotopic dilution.

A.8 Uncertainties

A.8.1 Uncertainties associated with external calibration

The measurement uncertainty is expressed in relation to the error associated with the calibration and the error associated with the measurement, as given in Formula (A.14):

$$u\left[C\left(^{23i}U\right)\right] = \left[u^2\left(cal\right) + u^2\left(N_{net}\left(^{23i}U\right)\right)\right]^{\frac{1}{2}} \tag{A.14}$$

with Formula (A.15):

$$u\left(N_{net}\left(^{23i}U\right)\right) = \left[\left(N\left(^{23i}U\right)\right)^2 \times u^2\left(c_{int}\right) + c_{int}^2 \times u^2\left(N\left(^{23i}U\right)\right) + u^2\left(N_0\left(^{23i}U\right)\right)\right]^{\frac{1}{2}} \tag{A.15}$$

A.8.2 External calibration and isotopic ratios

For ^{238}U mass concentration, the uncertainty is expressed as given in A.8.1.

For the other isotopes, the uncertainty is expressed as given in Formula (A.16):

$$u\left[\rho\left(^{23i}U\right)\right] = \left[u_{rel}^2\left(\rho\left(^{238}U\right)\right) + u_{rel}^2\left(N_{net}\left(^{23i}U\right)/N_{net}\left(^{238}U\right)\right) + u_{rel}^2\left(1/\left(1+\alpha_{(i-8)}\right)\right)\right]^{\frac{1}{2}} \tag{A.16}$$

A.8.3 Isotope dilution

The measurement uncertainty is expressed as given in Formula (A.17):

$$u\left(c\left({}^{23i}\mathrm{U}\right)\right)=\left[u_{\mathrm{rel}}^{2}\left(\mathrm{m}\left({}^{23i}\mathrm{U}\right)\right)+u_{\mathrm{rel}}^{2}\left(V\right)\right]^{\frac{1}{2}} \tag{A.17}$$

with Formula (A.18):

$$u\left[C\left({}^{238}\mathrm{U}\right)\right]=\left[u_{\mathrm{rel}}^{2}\left(C\left(m_{\mathrm{T}}\right)\right)+u_{\mathrm{rel}}^{2}\left(N_{\mathrm{net}}\left({}^{238}\mathrm{U}\right)/N_{\mathrm{net}}\left({}^{233}\mathrm{U}\right)\right)+u_{\mathrm{rel}}^{2}\left(1/\left(1+a_{(i-3)}\right)\right)\right]^{\frac{1}{2}} \tag{A.18}$$

A.8.4 Instrument detection limit

The instrument detection limit, for a given mass, is obtained from an extension of the standard deviation associated with the measurements obtained for 10 test portions of the blank.

The instrument detection limit (L_{DI}) is expressed in µg·l^{-1} dividing three times the background counts standard deviation, s, by the slope of the regression line when using external calibration, as given in Formula (A.19):

$$L_{\mathrm{DI}}({}^{23i}\mathrm{U})=\left(3s_{N_0({}^{23i}\mathrm{U})}\right)/a \tag{A.19}$$

In the case of isotope dilution (e.g. with ^{233}U), the formula is as given in Formula (A.20):

$$L_{\mathrm{DI}}=\rho_{T}\times\frac{L_{\mathrm{DI,ins}}({}^{23i}\mathrm{U})}{N_{\mathrm{netT}}} \tag{A.20}$$

A.8.5 Limit of quantification

The limit of quantification, for a given mass, can be evaluated as 10 times the standard deviation associated with the measurements obtained for 10 test portions of the blank, as given in Formula (A.21):

$$L_{\mathrm{OQ,ins}}({}^{23i}\mathrm{U})=10s_{N_0({}^{23i}\mathrm{U})} \tag{A.21}$$

The limit of quantification can be expressed in µg·l^{-1} dividing L_{OQ} by the slope of the regression line when using external calibration, as given in Formula (A.22):

$$L_{\mathrm{OQ}}({}^{23i}\mathrm{U})=\frac{10s_{N_0({}^{23i}\mathrm{U})}}{a} \tag{A.22}$$

and in the case of isotope dilution (e.g. with ^{233}U), as given in Formula (A.23):

$$L_{\mathrm{OQ}}=\rho_{T}\times\frac{L_{\mathrm{OQ,ins}}({}^{23i}\mathrm{U})}{N_{\mathrm{net}T}} \tag{A.23}$$

A.9 Test report

The test report shall conform to the requirements of ISO/IEC 17025 and shall contain at least the following information:

a) the measurement and evaluation procedure used, together with a reference to this document, i.e. ISO 17294-2:2023;

b) identification of the sample;

c) test result, including the expanded uncertainty with the coverage factor, k, and units in which the results are expressed;

d) the sample and sample pre-treatment, where appropriate;

e) any deviations from this document and details of all circumstances which can have affected the result;

f) any unusual features observed;

g) the date of the test.

The following complementary information can be provided:

a) limit of application;

b) any relevant information likely to affect and/or explain the results;

c) if necessary, the mass concentrations can be transformed in activity concentrations expressed in $Bq \cdot l^{-1}$.

Annex B
(informative)

Description of the matrices of the samples used for the interlaboratory trial

B.1 Surface water

The surface water sample for the interlaboratory trial (see Table C.1) was taken from the little stream "Meitze" which is located in the low, German mountain range, Harz ("Lower Saxony"). The sample was homogenized and filtered through a membrane filter with a pore size of 0,45 µm. Then, it was acidified with a volume fraction of 1 % of concentrated nitric acid. The following matrix elements were quantified (see Table B.1):

Table B.1 — Matrix of the surface water used for the interlaboratory trial

Parameter or ion	Unit	Result
pH value		6,2
Electrical conductivity at 25 °C	µS/cm	310
Calcium (Ca^{2+})	mg/l	30,0
Magnesium (Mg^{2+})	mg/l	4,6
Sodium (Na^+)	mg/l	41,0
Potassium (K^+)	mg/l	5,6
Iron (Fe^{2+})	mg/l	1,7
Chloride (Cl^-)	mg/l	25,0
Sulfate (SO_4^{2-})	mg/l	28,0
Nitrate (NO_3^-)	mg/l	10,5
Hydrogen carbonate (HCO_3^-)	mg/l	141

The following elements were spiked using the respective single-element stock solutions (6.7):

— arsenic;

— beryllium;

— bismuth;

— cadmium;

— caesium;

— chromium;

— gallium;

— selenium;

— thallium;

— uranium.

B.2 Synthetic standard

The synthetic standard for the interlaboratory trial (see Table C.3) was prepared by diluting the respective single-element stock solutions (6.7). Ten millilitres of hydrochloric acid (6.3) per litre was added and the solution was filled up to volume with water (6.1).

B.3 Bottled water

The samples submitted to the Association Générale des Laboratoires d'Analyses et d'Essais (AGLAE) Proficiency Testing (PT) schemes 22M3A.2 (PT A) were bottled water that were acidified with nitric acid to a pH below 2.

The following elements were analysed in the matrix before spiking and acidification (see Table B.2)

Table B.2 — Bottled water matrix used for proficiency test

	PT A
Total organic carbon (mg of C/l)	<0,3
Conductivity (µS/cm at 25 °C)	606,7
pH	7,85 at 21,3 °C
Turbidity in NFU	<0,1

In this matrix, other elements were added by spiking. The values observed by the participants were also determined (see Table B.3).

Table B.3 — Spiking carried out and values observed by participants

Parameters PT A	$\bar{\bar{x}}$ µg/l
Al	196,61
As	3,842 5
B	72,603
Be	59,711
Bi	71,668
Cd	17,507
Cu	4,018 1
Fe	316,95
Gd	8,090 7
Mo	100,688
Pb	17,679
S	5 260,3
Sb	4,618 9
Se	6,572 7
Sn	7,285 0
Te	38,759
Tl	1,938 3
W	19,472
Zr	26,340

B.4 Wastewater

The wastewater samples submitted to the AGLAE Proficiency Testing schemes 22M3B.1 (PT B) was water coming out from a wastewater treatment plant (WWTP) that had been sieved at 2 mm beforehand. Then, this was stabilized by addition of nitric acid to a pH below 2.

The following elements were analysed in the matrix before spiking and acidification (see Table B.4)

Table B.4 — Wastewater matrix used for proficiency test

	PT B
Total organic carbon (mg of C/l)	11,64
Conductivity (μS/cm at 25 °C)	1 382
Chemical oxygen demand (mg of O_2/l)	32,8
Total suspended solids (mg/l)	11,20
pH	7,62 at 20,6 °C
Turbidity in NFU	5,54

In this matrix, other elements were added by spiking. The values observed by the participants were also determined (see Table B.5)

Table B.5 — Spiking carried out and values observed by participants

Parameters PT B	$\bar{\bar{x}}$ μg/l
Al	271,08
As	38,967
B	707,87
Ba	427,32
Cd	13,914
Co	32,530
Cr	23,335
Li	482,42
Ni	67,732
Sn	46,040
Te	404,56
Ti	89,784
Tl	330,01
V	307,42
W	173,63
Zr	95,71

Annex C
(informative)

Performance data

An interlaboratory trial was carried out in Germany in 1997. The results are given in Tables C.1 to Table C.3. For the description of the sample matrices, see Annex B.

An independent interlaboratory trial for the uranium isotopes was carried out by AGLAE in France in 2013. The trial yielded the results given in Table C.4.

Table C.1 — Performance data for the matrix surface water[a] [b]

Element	l	n	o	$\bar{\bar{x}}$	s_R	$C_{V,R}$	s_r	$C_{V,r}$
			%	µg/l	µg/l	%	µg/l	%
As	37	145	3,3	6,90	0,954	13,8	0,432	6,3
Ba	38	149	5,7	41,1	2,53	6,1	1,04	2,5
Cd	37	147	5,2	5,75	0,491	8,5	0,234	4,1
Co	38	151	2,6	2,33	0,269	11,6	0,140	6,0
Cr	38	151	0,0	3,39	0,634	18,7	0,294	8,7
Cu	38	151	2,6	26,7	2,02	7,6	0,93	3,5
Mn	39	155	2,5	205,0	13,2	6,4	5,9	2,9
Mo	38	150	2,6	4,45	0,402	9,0	0,187	4,2
Ni	35	137	11,0	5,44	0,786	14,5	0,397	7,3
Pb	39	155	2,5	13,6	1,13	8,3	0,64	4,7
Sn	34	132	3,6	1,19	0,241	20,3	0,157	13,2
Sr	40	158	0,0	117,0	8,1	6,9	3,4	3,0
Tl	31	124	8,1	0,272	0,046 0	16,9	0,029 2	10,7
V	33	129	8,5	1,15	0,311	27,0	0,121	10,5
Zn	36	143	7,7	27,6	2,56	9,3	1,43	5,2

Key

l number of laboratories

n number of values

o percentage of outliers

$\bar{\bar{x}}$ total mean

s_R reproducibility standard deviation

$C_{V,R}$ coefficient of variation of reproducibility

s_r repeatability standard deviation

$C_{V,r}$ coefficient of variation of repeatability

[a]   Antimony (total mean 0,33 µg/l) and zirconium (total mean 0,98 µg/l) have been measured as well in the matrix surface water. In both cases, a satisfactory reproducibility coefficient of variation cannot be achieved.

[b]   All data refer to the determination of the mass concentration of dissolved elements (see 9.1).

Table C.2 — Performance data for the matrix aqua regia digest

Element	l	n	o %	$\overline{\overline{x}}$ µg/l	s_R µg/l	$C_{V,R}$ %	s_r µg/l	$C_{V,r}$ %
As	37	145	3,3	20,1	4,36	21,7	1,44	7,2
Ba	37	147	7,0	437,0	19,6	4,5	11,7	2,7
Cd	37	141	5,4	2,11	0,542	25,7	0,227	10,8
Co	39	154	2,5	145,0	8,4	5,8	5,7	3,9
Cr	38	151	5,0	363,0	24,1	6,6	12,3	3,4
Cu	38	150	5,1	3 334,0	239,6	7,2	117,0	3,5
Mn	39	155	2,5	1 029,0	73,2	7,1	36,4	3,5
Mo	39	154	2,5	15,2	1,14	7,5	0,57	3,7
Ni	37	146	8,2	184,0	17,4	9,4	7,2	3,9
Pb	37	146	7,6	793,0	49,0	6,2	27,9	3,5
Sb	36	143	7,7	170,0	12,5	7,4	5,5	3,2
Sn	38	150	2,6	415,0	37,4	9,0	16,3	3,9
Sr	40	155	1,3	89,9	6,21	6,9	3,37	3,8
Tl	29	112	8,9	0,276	0,076 5	27,7	0,049 4	17,9
V	36	140	5,4	44,0	8,87	20,2	2,06	4,7
Zn	38	150	2,6	711,0	58,1	8,2	32,9	4,6
Zr	31	117	7,1	2,87	0,752	26,2	0,403	14,0

For an explanation of the symbols, see Table C.1.

Table C.3 — Performance and recovery data for the matrix synthetic standard

Element	l	n	o %	X µg/l	$\overline{\overline{x}}$ µg/l	η %	s_R µg/l	$C_{V,R}$ %	s_r µg/l	$C_{V,r}$ %
As	37	146	5,2	192,0	186,0	97,1	14,8	7,9	6,4	3,4
Ba	37	147	7,5	8,0	7,90	98,8	0,580	7,3	0,319	4,0
Cd	34	135	12,9	2,0	1,98	99,1	0,190	9,6	0,135	6,8
Co	40	159	0,0	42,0	41,5	98,8	3,02	7,3	1,55	3,7
Cr	36	142	7,8	9,0	9,35	103,9	1,986	21,2	0,721	7,7
Cu	39	155	0,0	48,0	48,2	100,3	3,83	8,0	1,64	3,4
Mn	39	155	2,5	97,0	95,3	98,2	6,52	6,8	3,05	3,2
Mo	37	146	8,2	7,0	6,85	97,8	0,474	6,9	0,256	3,7
Ni	40	157	1,3	93,0	91,2	98,0	8,55	9,4	3,91	4,3
Pb	36	142	8,4	6,0	6,43	107,2	0,491	7,6	0,287	4,5
Sb	39	154	0,0	114,0	114,0	99,9	11,1	9,8	4,0	3,5
Sn	38	149	3,2	120,0	117,0	97,9	8,4	7,1	4,2	3,5
Sr	40	157	1,3	24,0	23,3	97,1	1,66	7,1	1,07	4,6
Tl	31	121	14,8	0,9	0,892	99,1	0,059 7	6,7	0,041 9	4,7
V	35	138	12,7	245,0	240,0	97,9	26,9	11,2	11,3	4,7
Zn	39	155	0,0	183,0	188,0	102,5	17,2	9,2	7,1	3,8
Zr	31	119	7,8	4,0	4,47	111,8	0,967	21,6	0,334	7,5

Key

X assigned value

η recovery rate

For an explanation of the other symbols, see Table C.1.

Table C.4 — Performance data for uranium isotopes in the matrix mineral water (natural mineral water, bottled, without carbon dioxide)

Element	l	n	o	$\overline{\overline{x}}$	s_R	$C_{V,R}$
			%	µg/l	µg/l	%
U	8	8	0	14,6	0,42	2,9
Isotope	l	n	o	$\overline{\overline{x}}$	s_R	$C_{V,R}$
			%	Bq/l	Bq/l	%
^{234}U	8	8	0	0,255	0,021	8,17
^{235}U	8	8	0	0,008 3	0,000 19	2,26
^{238}U	8	8	0	0,179	0,005 5	3,08

An interlaboratory trial was carried out by AGLAE in France in 2022. The samples were prepared according to Clauses B.3 and B.4. The results are given in Table C.5.

Table C.5 — Performance data for titanium in the matrix bottled and waste water

Ti	l	n	o	$\overline{\overline{x}}$	s_R	$C_{V,R}$	s_r	$C_{V,r}$
			%	µg/l	µg/l	%	µg/l	%
PT A (bottled water)	40	160	6,98	39,247	2,014 0	5,1	0,503 9	1,3
PT B (waste water)	26	104	3,70	92,631	6,929 3	7,5	2,613 6	2,8

Key

l number of laboratories after outlier rejection

n number of individual test results after outlier rejection

o percentage of outliers

$\overline{\overline{x}}$ total mean overall (without outliers)

s_R reproducibility standard deviation

$C_{V,R}$ coefficient of variation of reproducibility

s_r repeatability standard deviation

$C_{V,r}$ coefficient of variation of repeatability

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International Standard	Corresponding Indian Standard	Degree of Equivalence
ISO 5667-3 Water quality — Sampling — Part 3: Preservation and handling of water samples	IS 17614 (Part 3): 2024/ISO 5667-3: 2024 Water quality — Sampling: Part 3 Preservation and handling of water samples	Identical
ISO 8466-1 Water quality — Calibration and evaluation of analytical methods — Part 1: Linear calibration function	IS 18612 (Part 1) : 2024/ISO 8466-1 : 2021 Water quality Calibration and evaluation of analytical methods: Part 1 Linear calibration function	Identical
ISO/IEC 17025 General requirements for the competence of testing and calibration laboratories	IS/ISO/IEC 17025 : 2017 General requirements for the competence of testing and calibration laboratories (*second revision*)	Identical
ISO 17294-1: 2004 Water quality — Application of inductively coupled plasma mass spectrometry (ICP-MS) — Part 1: General guidelines	IS 3025 (Part XXXXX) 17294-1: 2024 Methods of sampling and test (physical and chemical) for water and wastewater: Part 64 Application of inductively coupled plasma mass spectrometry (ICP-MS) — General Guidelines (*under preparation*)	Identical

The Committee responsible for the preparation of this standard has reviewed the provisions of the below mentioned ISO/IEC standards and has decided that they are acceptable for use in conjunction with this standard.

International Standard	Title
ISO 15587-1	Water quality — Digestion for the determination of selected elements in water — Part 1: Aqua regia digestion
ISO 15587-2	Water quality — Digestion for the determination of selected elements in water — Part 2: Nitric acid digestion

In reporting the result of a test or analysis made in accordance with this standard, if the final value, observed or calculated, is to be rounded off, it shall be done in accordance with IS 2 : 2022 'Rules for rounding off numerical values (*second revision*)'.

Amendments Issued Since Publication

Amend No.	Date of Issue	Text Affected