INTERNATIONAL STANDARD

ISO 17294-2

Second edition
2016-07-15

Water quality — Application of inductively coupled plasma mass spectrometry (ICP-MS) —

Part 2:

Determination of selected elements including uranium isotopes

Qualité de l'eau — Application de la spectrométrie de masse avec plasma à couplage inductif (ICP-MS) —

Partie 2: Dosage des éléments sélectionnés y compris les isotopes d'uranium

Reference number
ISO 17294-2:2016(E)

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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The committee responsible for this document is ISO/TC 147, *Water quality*, Subcommittee SC 2, *Physical, chemical and biochemical methods*.

This second edition cancels and replaces the first edition (ISO 17294-2:2003), which has been technically revised.

ISO 17294 consists of the following parts, under the general title *Water quality — Application of inductively coupled plasma mass spectrometry (ICP-MS)*:

— *Part 1: General guidelines*

— *Part 2: Determination of selected elements including uranium isotopes*

Introduction

When applying this part of ISO 17294, it is necessary in each case, depending on the range to be tested, to determine if and to what extent additional conditions are to be established.

Water quality — Application of inductively coupled plasma mass spectrometry (ICP-MS) —

Part 2:
Determination of selected elements including uranium isotopes

WARNING — Persons using this part of ISO 17294 should be familiar with normal laboratory practice. This part of ISO 17294 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 and to ensure compliance with any national regulatory conditions.

IMPORTANT — It is absolutely essential that tests, conducted in accordance with this part of ISO 17294, be carried out by suitably qualified staff.

1 Scope

This part of ISO 17294 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, tungsten, uranium and its isotopes, vanadium, yttrium, ytterbium, zinc and zirconium in water (for example, drinking water, surface water, ground water, waste water and eluates).

Taking into account the specific and additionally occurring interferences, these elements can also be determined in digests of water, sludges and sediments (for example, 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 (xLQ) 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 pg/l and mg/l depending on the element and pre-defined 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 17294-1:2004, 8.2).

Table 1 — Lower limits of quantification (*x*LQ) for unpolluted water

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

[c] In order to reach these limits, depending on interferences, the use of a collision/reaction cell is recommended

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. 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*

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 and estimation of performance characteristics — Part 1: Statistical evaluation of the 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 17294-1:2004, *Water quality — Application of inductively coupled plasma mass spectrometry (ICP-MS) — Part 1: General guidelines*

3 Terms and definitions

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

3.1
limit of application
lowest concentration of an analyte that can be determined with a defined level of accuracy and precision

4 Principle

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 (for example, by pneumatic nebulization) where energy transfer processes from the plasma cause desolvation, decomposition, atomization and ionization of elements;

— as an additional option, collision and reaction cell technology may be 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 to be used for 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 has to be applied. For the determination of uranium isotopes, the specific procedure detailed in Annex A has to 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 part of ISO 17294, the user is responsible for demonstrating that the chosen approach is fit for purpose and achieves the necessary performance.

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 (for example, ^{114}Cd and ^{114}Sn).

Element interferences from isobars may 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 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 ^{109}Ag	—	ZrO NbO, ZrOH
As	^{75}As	—	ArCl, CaCl
Au	^{197}Au	—	TaO
B	^{10}B		
	^{11}B	—	BH
Ba	^{138}Ba	La^+, Ce^+	—
Be	^{9}Be	—	$^{18}O_2$
Ca	^{43}Ca	—	CNO
	^{44}Ca	—	COO
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

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 above.

Table 2 *(continued)*

Element	Isotope	Inter-element interferences caused by isobars and doubly charged ions	Interferences caused by polyatomic ions
Eu	^{151}Eu	—	BaO
	^{153}Eu	—	BaO
Fe	^{54}Fe	—	$^{37}Cl^{16}O^{1}H^{+}$ $^{40}Ar^{14}N$
	^{56}Fe	—	$^{40}Ar^{16}O^{+}$ $^{40}Ca^{16}O^{+}$
	^{57}Fe	—	$^{40}Ar^{16}O^{1}H^{+}$ $^{40}Ca^{16}O^{1}H^{+}$ $^{40}Ar^{17}O^{+}$
Ga	^{69}Ga	Ba^{++}	CrO, ArP, ClOO
Ge	^{74}Ge	Se^{+}	ArS, ClCl
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
W	^{184}W	Os^{+}	—
Zn	^{64}Zn	Ni^{+}	AlCl, SS, SOO, CaO
	^{66}Zn	Ba^{++}	PCl, SS, FeC, SOO
	^{68}Zn	Ba^{++}, Ce^{++}	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 above.

Table 3 — Examples for 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
	^{75}As	$-3{,}127\ (^{77}Se + 0{,}322\ 0\ ^{78}Se)$
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	$-0{,}110\ 6\ ^{101}Ru$

Table 3 *(continued)*

Element	Recommended isotope and inter-element correction	
Ni	^{58}Ni	−0,048 25 ^{54}Fe
Pb	^{208}Pb	+^{207}Pb + ^{206}Pb
Se	^{82}Se	−1,009 ^{83}Kr
Sn	^{120}Sn	−0,013 44 ^{125}Te
V	^{51}V	^{51}V −3,127 (^{53}Cr −0,113 4 ^{52}Cr)
W	^{184}W	−0,001 242 ^{189}Os

5.2.3 Polyatomic interferences

Polyatomic ions are formed by coincidence of plasma gas components, reagents and sample matrix (for example, interference of the relative mass ^{75}As by ^{40}Ar^{35}Cl and ^{40}Ca^{35}Cl). Examples for 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 (for example, As, Cr, Se, V).

It is recommended that the analyst checks the magnitude of this interference regularly for the particular instrument.

In the case of mathematical corrections, it shall be taken into account that the magnitude of interference depends both on the plasma adjustment (for example, oxide formation rate) and on the mass concentration of the interfering element, which will usually be 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^{++}
		0,3	ArP
		1,0	ClOO
	^{71}Ga	0,2 to 0,6	ArP

[a] Indicates the magnitude of interference without corrective measures. User should check the interferences and decide how to reduce or eliminate them.

Table 4 *(continued)*

Element	Isotope	Simulated mass concentration[a] µg/l	Type of interference
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	$ArMgBa^{++}$
		5	SS, SOO
		4	PCl
		2	Ba^{++}
	^{68}Zn	50	ArS, SS, SOO
		4	Ba^{++}

[a] Indicates the magnitude of interference without corrective measures. User should check the interferences and decide how to reduce or eliminate them.

6 Reagents

For the determination of elements at trace and ultratrace level, 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, grade 1 as specified in ISO 3696, for all sample preparation and dilutions.

6.2 Nitric acid, $\rho(HNO_3) = 1{,}4$ g/ml.

NOTE Nitric acid is available both as $\rho(HNO_3) = 1{,}40$ g/ml [$w(HNO_3) = 650$ g/kg] and $\rho(HNO_3) = 1{,}42$ g/ml [$w(HNO_3) = 690$ 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, $\rho(HCl) = 1{,}16$ g/ml.

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

6.5 Sulfuric acid, $\rho(H_2SO_4) = 1{,}84$ g/ml.

6.6 Hydrogen peroxide, $w(H_2O_2) = 30\ \%$.

NOTE Hydrogen peroxide is often stabilized with phosphoric acid.

6.7 Element stock solutions, $\rho = 1\ 000$ 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 (for example, 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, $\rho = 1\ 000$ 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 (for example, 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 (for example, precipitation).

The examples given below 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.

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

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

- ρ(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.

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) 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 may 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, Hg, Mo, Sb, Sn, W, Zr) = 5 mg/l.

Pipette 2,5 ml of each element stock solution (Au, Hg, Mo, Sb, Sn, W, Zr) (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.

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

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.

NOTE For the determination of mercury (Hg), it can be helpful to add gold (Au) in order to avoid interferences to the reference-element solution to allow a final concentration of 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 may 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 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 reference-element solution (6.9.3) to a concentration of, for example, 50 µg/l of the reference-element before bringing up to volume.

6.11 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.

Pipette 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 hexafluoroethene 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.

Pipette 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 perfluoroalkoxy (PFA) or hexafluoroethene 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 B shall be adjusted to that of the digests.

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 may be as follows:

- $\rho(\text{Ca}) = 200$ mg/l;
- $\rho(\text{Cl}^-) = 300$ mg/l;
- $\rho(\text{PO}_4{}^{3-}) = 25$ mg/l;
- $\rho(\text{SO}_4{}^{2-}) = 100$ 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 might replace the use of the matrix solution. This has to be validated accordingly by the user of this part of ISO 17294.

7 Apparatus

The stability of samples 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 perfluoroalkoxy (PFA), hexafluoroethene propene (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 [for example, $w(HNO_3)$ = 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 might 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 inductively coupled plasma (ICP) suitable for multi-element and isotope analysis is required. The spectrometer should be capable of scanning a mass range from 5 m/z (AMU) to 240 m/z (AMU) with a resolution of at least 1 m_r/z peak width at 5 % of peak height (m_r = relative mass of an atom species; z = charge number). The instrument may 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 may be of benefit in reducing some types of interferences (for example, 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, 5.1.2.

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, high density polyethene (HDPE) or polytetrafluoroethene (PTFE) bottles are sufficient for the storage of samples. For the determination of elements in an ultratrace level, bottles made from perfluoroalkoxy (PFA) or hexafluoroethene propene (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 ISO 5667-3. Due to the extremely high requirements concerning purity in trace and ultratrace 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) per 100 ml of sample. Ensure that the pH is less than 2; otherwise, add nitric acid as required.

In the case of determination of elements forming compounds that tend to be hydrolyzed, for example, Hg, Sb, Sn, W or Zr, add to an additional sample 1,0 ml of hydrochloric acid (6.3) per 100 ml of water. Ensure that the pH is less than 1; otherwise, add more hydrochloric acid as required.

9 Sample pre-treatment

9.1 Determination of the mass concentration of dissolved elements without digestion

Continue according to Clause 10, using the acidified filtrate specified in Clause 8. If experience has shown that no significant amounts of particles occur, the filtration may be omitted. Those samples shall be colourless and shall have a turbidity of <1,5 FNU (formazin nephelometric unit, see ISO 7027-1).

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 will be 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 (for example, silicates and aluminium oxide) will be dissolved incompletely using this procedure.

For the determination of tin, the following digestion may 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 might be necessary if Sb, W or Zr is to be determined.

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

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 may 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 (for example, oxide formation, formation of doubly charged ions) allowing sufficient sensitivity.

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

Define the rinsing times 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 $\rho(\mathrm{Y, Re}) = 50\ \mu\mathrm{g/l}$ 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, e.g. using four to five measuring points (for example, 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 enough but check the validity of the calibration curve with a certified reference sample, a standard sample, or a suitable internal control sample (consider also comments in ISO 17294-1:2004, 9.1).

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 (for example, relevant for Li, Pb, U).

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

In order to evaluate and to update the correction factors, measure the matrix solutions (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 samples.

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

Some elements (for example, Ag, B, Be, Bi, Li, Th and Sb) are rinsed very slowly from the sample 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 (see 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).

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.

EXAMPLES	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 part of ISO 17294, i.e. ISO 17294-2;

b) complete identification of the sample;

c) expression of results as indicated in Clause 11;

d) sample pre-treatment, if appropriate;

e) any deviations from this part of ISO 17294, and details of all circumstances which could have affected the result.

For the determination of uranium isotopes, see Annex A.

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 (for example, drinking water, surface water, ground water, waste water and eluates) by inductively coupled plasma mass spectrometry. On the basis of the concentrations obtained, the activity concentrations of the different isotopes can be calculated.

For the most chemical environmental monitoring purposes, it is important and sufficient do 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 dosis estimation (see References [13], [15] and [16]).

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.

A.2 Symbols and abbreviated terms

Quantity	Symbol/abbreviated term	Unit symbol	Term
Mass concentration	C	µg/l	Mass of analyte per unit volume of the sample
Mass concentration of the internal standard solution	C_T	µg/l	Mass of internal standard element per unit volume of the internal standard solution
Internal standard mass	m_T	µg	Mass of the isotope dilution tracer added
Standard uncertainty	u(C)	unit of the quantity C	Standard uncertainty associated with the measurement result
Expanded uncertainty	U	unit of the quantity C	Product of the standard uncertainty and the coverage factor k with $k = 1, 2, \ldots, U = k \cdot u(C)$
Standard uncertainty	U	unit of the quantity C	
Instrumental detection limit	IDL	µg/l	IDL 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 ten replicates of the blank
Limit of quantification	xLQ	µg/l	xLQ can be determined by ten times the standard deviation obtained with ten replicates of the blank
Limit of quantification	$x\text{LQ}_{\text{ins}}$	µg/l	$x\text{LQ}_{\text{ins}}$ is the xLQ expressed in counts for the chosen m/z, due to the blank and the instrument

Quantity	Symbol/ abbreviated term	Unit symbol	Term
Limit of application	LOA	µg/l	Lowest or highest concentration of an analyte that can be determined with a defined level of accuracy and precision
Blank standard deviation	s_{N_0}		
Volume of the sample	V	l	
Background	N_0	Counts	Counts for a given mass in the blank solution
Counts	N	Counts	Raw counts
Net counts	N_{net}	Counts	$N-N_0$ Define N_{netT} in case of the internal standard
Counts calculated when using isotopic dilution	N_{dl}	Counts	
Regression line slope	a	Counts.µg^{-1}·l	$N_{net} = a \cdot C + b$
Coordinate at the origin of the regression line	b	Counts	
Internal standard correction factor	c_{int}		Sample matrix effect correction when an internal standard is added to the sample
Bias per unit mass	α		
Fractionation coefficient deviation	β		
Isotope distribution in the standard solution of ^{233}U	T		Used for isotopic dilution
Measured isotopic ratio	r		
True isotopic ratio	R		

A.3 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 y	Specific activity Bq/g
234	2,455 (±0,006) × 10^5	2,312 × 10^8
235	704 (±1) × 10^6	7,997 × 10^4
236	23,43 (±0,006) × 10^6	2,392 × 10^6
238	4,468 (±0,005) × 10^9	1,244 × 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 may 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 17294-1:2004, 6.3.5). For isotopic determination of uranium in water, 233-Uranium is commonly used but 204-Thallium 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 sample test portion;
- external calibrations with ^{238}U certified standard solution can provide ^{238}U concentration in the sample test portion; then the isotopic ratios measured in the sample test portion without internal standard addition lead to the ^{235}U and ^{234}U concentrations in the sample test portion;
- 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 sample 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 and 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	x_{LQ} µg·l^{-1}	x_{LQ} mBq·l^{-1}
234-Uranium	<0,000 1	<20
235-Uranium	<0,001	<0,1
238-Uranium	0,1	<1

A.4 Reagents

Use only reagents of recognized analytical grade.

A.4.1 Laboratory water.

A.4.2 Blank.

Diluted acid solution used to determine the background spectra for the various masses.

A.4.3 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.4.4 Calibration solutions.

Prepare these solutions by successive dilutions of the certified standard solution in 1 % to 2 % nitric acid (volume). Adjust concentrations in line with the measuring range to be calibrated. The calibration curve is established with at least five measuring points (for example, the blank calibration solution and four calibration solutions).

A.4.5 Internal standard solution (for example, of uranium 233 as an internal standard).

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

A.4.6 Quality control solution.

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

A.4.7 Argon gas, at least 99,995 % pure.

A.4.8 Diluted nitric acid, 2 % volume, for example.

A.5 Apparatus

Usual laboratory apparatus and, in particular, the following.

A.5.1 Analytical balance, accurate to within 1/10 mg or 1/100 mg.

A.5.2 Argon supply, equipped with low pressure control.

A.5.3 ICP-MS apparatus with associated software, installed in an air-conditioned room.

A.5.4 Auto-sampler device.

A.6 Sampling

A.6.1 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.6.2 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.6.3 Storage

See ISO 5667-3. Perform the analysis as soon as possible.

A.7 Procedure

A.7.1 General

Follow the instructions provided by the instrument manufacturer and the steps described in this part of ISO 17294.

For each analysis performed on this instrument, the sensitivity, the instrumental 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 sample analysis by cleaning the system with the blank solution. Repeat this operation after each sample.

A.7.2 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 (for example, 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.7.3 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 are determined by linear regression using the least square method.

Analyse the quality control solutions to validate the external calibrations.

Perform samples 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.7.4 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 Tl.

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.

Sample 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.7.5 Internal calibration by isotopic dilution

The uranium concentration will be quantified in relation to the ^{233}U standard solution isotopic composition and concentration introduced in the samples.

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

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

Perform samples 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.8 Expression of results

A.8.1 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 sample.

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

A.8.2 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 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.

This 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. Two examples are given:

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

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

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

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

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 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 [6]).

A.8.3 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 with Formula (A.4):

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

It is recommended to have the mass concentration in the sample 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 (Uranium 233, for example) is useful to correct the signal fluctuations. In cases where an internal standard is used, a correction factor α 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):

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

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

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

A.8.4 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):

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

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

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

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

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

A.8.5 Internal calibration by isotopic dilution

Uranium 233 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 µg.l^{-1}, is equal to Formula (A.10):

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

with Formula (A.11):

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

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:

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

with Formula (A.13):

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

where T (^{23i}U) 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 Uranium 234 by isotopic dilution.

A.9 Uncertainties

A.9.1 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):

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

with Formula (A.15):

$$u\left(N_{\mathrm{net}}\left({}^{23i}\mathrm{U}\right)\right)=\left[\left(N\left({}^{23i}\mathrm{U}\right)\right)^{2}\times u^{2}\left(c_{\mathrm{int}}\right)+c_{\mathrm{int}}{}^{2}\times u^{2}\left(N\left({}^{23i}\mathrm{U}\right)\right)+u^{2}\left(N_{0}\left({}^{23i}\mathrm{U}\right)\right)\right]^{\frac{1}{2}} \quad \text{(A.15)}$$

A.9.2 External calibration and isotopic ratios

For ^{238}U mass concentration, the uncertainty is expressed as in A.9.1.

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

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

A.9.3 Isotope dilution

The measurement uncertainty is expressed by Formula (A.17):

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

with Formula (A.18):

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

A.9.4 Instrumental detection limit

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

$$\mathrm{DL}\left({}^{23i}\mathrm{U}\right)=\left(3s_{N_{0}\left({}^{23i}\mathrm{U}\right)}\right)\Big/a \quad \text{(A.19)}$$