
**Water quality — Plutonium and
neptunium — Test method using ICP-
MS**

*Qualité de l'eau — Plutonium et neptunium — Méthode d'essai par
ICP-MS*

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Published in Switzerland

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

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

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For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 147, *Water quality*, Subcommittee SC 3, *Radioactivity measurements*.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

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Introduction

Radioactivity from several naturally-occurring and anthropogenic sources is present throughout the environment. Thus, water bodies (e.g. surface waters, ground waters, sea waters) can contain radionuclides of natural, human-made, or both origins.

- Natural radionuclides, including ^{40}K , ^3H , ^{14}C and those originating from the thorium and uranium decay series, in particular ^{226}Ra , ^{228}Ra , ^{234}U , ^{238}U , ^{210}Po and ^{210}Pb can be found in water for natural reasons (e.g. desorption from the soil and washoff by rain water) or can be released from technological processes involving naturally occurring radioactive materials (e.g. the mining and processing of mineral sands or phosphate fertilizers production and use).
- Human-made radionuclides, such as transuranium elements (americium, plutonium, neptunium, curium), ^3H , ^{14}C , ^{90}Sr and gamma emitting radionuclides, can also be found in natural waters. Small quantities of these radionuclides are discharged from nuclear fuel cycle facilities into the environment as a result of authorized routine releases. Some of these radionuclides used for medical and industrial applications are also released into the environment after use. Anthropogenic radionuclides are also found in waters as a result of past fallout contaminations resulting from the explosion in the atmosphere of nuclear devices and accidents such as those that occurred in Chernobyl and Fukushima.

Radionuclide activity concentration in water bodies can vary according to local geological characteristics and climatic conditions and can be locally and temporally enhanced by releases from nuclear installation during planned, existing, and emergency exposure situations[1]. Drinking-water may thus contain radionuclides at activity concentrations which could present a risk to human health.

The radionuclides present in liquid effluents are usually controlled before being discharged into the environment[2] and water bodies. Drinking waters are monitored for their radioactivity as recommended by the World Health Organization (WHO)[3] so that proper actions can be taken to ensure that there is no adverse health effect to the public. Following these international recommendations, national regulations usually specify radionuclide authorized concentration limits for liquid effluent discharged to the environment and radionuclide guidance levels for waterbodies and drinking waters for planned, existing, and emergency exposure situations. Compliance with these limits can be assessed using measurement results with their associated uncertainties as specified by ISO/IEC Guide 98-3[4] and ISO 5667-20[5].

Depending on the exposure situation, there are different limits and guidance levels that would result in an action to reduce health risk. As an example, during a planned or existing situation, the WHO guidelines for guidance level in drinking water is 1 Bq/l activity concentration for ^{239}Pu , ^{240}Pu and ^{241}Pu .

NOTE 1 The guidance level is the activity concentration with an intake of 2 l/d of drinking water for one year that results in an effective dose of 0,1 mSv/a for members of the public. This is an effective dose that represents a very low level of risk and which is not expected to give rise to any detectable adverse health effects[3].

In the event of a nuclear emergency, the WHO Codex guideline levels (GLs)[7] states that the activity concentration might not be greater than 1 Bq/l and 10 Bq/l for ^{239}Pu , ^{240}Pu , ^{241}Pu , respectively, for infant and for others than infant.

NOTE 2 The Codex GLs apply to radionuclides contained in foods destined for human consumption and traded internationally, which have been contaminated following a nuclear or radiological emergency. These GLs apply to food after reconstitution or as prepared for consumption, i.e. not to dried or concentrated foods, and are based on an intervention exemption level of 1 mSv in a year for members of the public (infant and adult)[7].

Thus, the test method can be adapted so that the characteristic limits, decision threshold, detection limit and uncertainties ensure that the test results of the radionuclide activity concentrations can be verified to be below the guidance levels required by a national authority for either planned/existing situations or for an emergency situation[6][7][8].

Usually, the test methods can be adjusted to measure the activity concentration of the radionuclide(s) in either wastewaters before storage or in liquid effluents before being discharged to the environment.

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The test results will enable the plant/installation operator to verify that, before their discharge, wastewaters/liquid effluent radioactive activity concentrations do not exceed authorized limits.

The test method(s) described in this document may be used during planned, existing and emergency exposure situations as well as for wastewaters and liquid effluents with specific modifications that could increase the overall uncertainty, detection limit, and threshold.

The test method(s) may be used for water samples after proper sampling, sample handling, and test sample preparation (see the relevant part of the ISO 5667 series).

An International Standard on a test method for ^{239}Pu , ^{240}Pu , ^{241}Pu and ^{237}Np concentration in water samples is justified for test laboratories carrying out these measurements, required sometimes by national authorities, as laboratories may have to obtain a specific accreditation for radionuclide measurement in drinking water samples.

This document is one of a set of International Standards on test methods dealing with the measurement of the activity concentration of radionuclides in water samples.

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Water quality — Plutonium and neptunium — Test method using ICP-MS

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 methods used to determine the concentration of plutonium and neptunium isotopes in water by inductively coupled plasma mass spectrometry (ICP-MS) (^{239}Pu , ^{240}Pu , ^{241}Pu and ^{237}Np). The concentrations obtained can be converted into activity concentrations of the different isotopes^[9].

Due to its relatively short half-life and ^{238}U isobaric interference, ^{238}Pu can hardly be measured by this method. To quantify this isotope, other techniques can be used (ICP-MS with collision-reaction cell, ICP-MS/MS with collision-reaction cell or chemical separation). Alpha spectrometry measurement, as described in ISO 13167^[10], is currently used^[11].

This method is applicable to all types of water having a saline load less than $1\text{ g}\cdot\text{l}^{-1}$. A dilution of the sample is possible to obtain a solution having a saline load and activity concentrations compatible with the preparation and the measurement assembly.

A filtration at $0,45\ \mu\text{m}$ is needed for determination of dissolved nuclides. Acidification and chemical separation of the sample are always needed.

The limit of quantification depends on the chemical separation and the performance of the measurement device.

This method covers the measurement of those isotopes in water in activity concentrations between around^[12]^[13]:

- $1\text{ mBq}\cdot\text{l}^{-1}$ to $5\text{ Bq}\cdot\text{l}^{-1}$ for ^{239}Pu , ^{240}Pu and ^{237}Np ;
- $1\text{ Bq}\cdot\text{l}^{-1}$ to $5\text{ Bq}\cdot\text{l}^{-1}$ for ^{241}Pu .

In both cases, samples with higher activity concentrations than $5\text{ Bq}\cdot\text{l}^{-1}$ can be measured if a dilution is performed before the chemical separation.

It is possible to measure ^{241}Pu following a pre-concentration step of at least 1 000.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

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

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 5667-10, *Water quality — Sampling — Part 10: Guidance on sampling of waste waters*

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

ISO 17294-2:2016, *Water quality — Application of inductively coupled plasma mass spectrometry (ICP-MS) — Part 2: Determination of selected elements including uranium isotopes*

ISO 80000-10, *Quantities and units — Part 10: Atomic and nuclear physics*

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

3 Terms, definitions, symbols and abbreviated terms

For the purposes of this document, the terms, definitions, symbols and abbreviated terms given in ISO 80000-10 and the following apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

- ISO Online browsing platform: available at <https://www.iso.org/obp>
- IEC Electropedia: available at <http://www.electropedia.org/>

Term	Symbol or abbreviated term	Unit symbol	Definition
Mass concentration	ρ	$\mu\text{g}\cdot\text{l}^{-1}$	Analyte mass for a given radionuclide per sample unit volume.
Mass concentration of the internal standard solution	ρ_{T}	$\mu\text{g}\cdot\text{l}^{-1}$	Mass of internal standard radionuclide element per unit volume of the internal standard solution.
Internal standard mass	m_{T}	μg	Mass of the isotope dilution tracer added
Standard uncertainty	$u(\rho)$	$\mu\text{g}\cdot\text{l}^{-1}$	Standard uncertainty associated with the measurement result
Expanded uncertainty	$U(x)$		Product of the standard uncertainty and the coverage factor k with $k = 1, 2, \dots$, $U = k \cdot u$
Standard uncertainty	$u(x)$		Standard uncertainty associated with the measurement result of x
Detection limit	DL	$\mu\text{g}\cdot\text{l}^{-1}$	DL is the lowest amount of an analyte that is detectable using an instrument, as determined by repeated measurement of a reagent blank.
Limit of quantification	LOQ	$\mu\text{g}\cdot\text{l}^{-1}$ $\text{mBq}\cdot\text{l}^{-1}$	LOQ is the smallest concentration of an analyte in the test sample which can be determined with a fixed precision.
Standard deviation of the blank	s_{N_0}		Standard deviation of replicates of the blank.
Instrumental limit of quantification	LOQ_{ins}	$\text{Counts}\cdot\text{s}^{-1}$	LOQ_{ins} is the LOQ expressed in counts rate for the chosen mass on charge ration (m/z), due to the blank and the instrument.
Instrumental detection limit	IDL	$\text{Counts}\cdot\text{s}^{-1}$	IDL is the DL expressed in counts rate for the chosen mass on charge ration (m/z).
Volume of the sample	V	l	
Background	N_0	$\text{Counts}\cdot\text{s}^{-1}$	Counts rates for a given mass in the blank solution.
Counts	N	$\text{Counts}\cdot\text{s}^{-1}$	Gross counts rates: uncorrected counts rate of a measurement.
Net counts	N_{net}	$\text{Counts}\cdot\text{s}^{-1}$	$N - N_0$

Term	Symbol or abbreviated term	Unit symbol	Definition
Net counts of the internal standard	N_{netT}	Counts.s ⁻¹	At the internal standard mass.
Bias per unit mass	α		
Mass	m		Isotope mass number.
Mass difference	Δm		$m_i - m_j$
Measured isotopic ratio	r		
True isotopic ratio	R		
Specific activity	C_s	Bq.g ⁻¹	Activity corresponding to one gram of the radionuclide.
Activity concentration	C	Bq.l ⁻¹	Corresponding to the mass concentration ρ measured for a given radionuclide.

4 Principle

The principle of measurement of analysis using ICP-MS is described in ISO 17294-1 and ISO 17294-2.

ICP-MS can be used to measure the mass concentrations of plutonium isotopes (²³⁹Pu, ²⁴⁰Pu, ²⁴¹Pu) and ²³⁷Np in water samples.

The results can be converted in activity concentrations using conversion factors given in [Table 1](#).

Table 1 — Plutonium and neptunium isotopes half-lives and specific activities[12][13]

Plutonium isotope	Half-life years	Specific activity Bq.g ⁻¹
²³⁹ Pu	24 100 (±11)	2,296·10 ⁹ (±2,000·10 ⁶)
²⁴⁰ Pu	6 561 (±7)	8,396·10 ⁹ (±9,000·10 ⁶)
²⁴¹ Pu	14,33 (±0,04)	3,829·10 ¹² (±1,100·10 ¹⁰)
²⁴² Pu	3,73 (±0,03)·10 ⁵	1,465·10 ⁸ (±1,180·10 ⁶)
²⁴⁴ Pu	81,1 (±0,6)·10 ⁶	6,683·10 ⁵ (±7,600·10 ³)
Neptunium	Half-life years	Specific activity Bq.g ⁻¹
²³⁷ Np	2,144 (±0,007)·10 ⁶	2,603·10 ⁷ (±9,000·10 ⁴)

The water sample has to be measured after filtration (at 0,45 µm porosity) for the determination of dissolved radionuclides and a specific chemical separation shall be performed to limit potential interferences due to uranium isotopes[14]. An example of chemical separation is given in [Annex A](#).

As described in the ISO 17294 series, a tracer is needed to evaluate the recovery in chemical separation and to perform an isotopic dilution. A known amount of pure certified tracer standard solution is added to the sample test portion and the calculation of isotope concentration is based on the isotopic ratios.

Even if activity certified standard solutions are available, external calibration is not used as it is quite difficult to find mass certified standard solutions of plutonium isotopes (²³⁹Pu, ²⁴⁰Pu, ²⁴¹Pu) and ²³⁷Np.

For the determination of plutonium isotopes in water, ²⁴²Pu is commonly used but ²⁴⁴Pu can also be chosen.

The chemical yield obtained for plutonium may be applied to neptunium. This may lead to a potential bias that shall be quantified. Other methods should be used such as external calibration, addition of the short lived ²³⁹Np as tracer, standard additions of ²³⁷Np in several tests portions of the sample, etc.

It is also important to evaluate the mass bias and to correct it (see 10.2).

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

Table 2 — Examples of limits of quantification[15][16]

Isotope	LOQ $\mu\text{g}\cdot\text{l}^{-1}$	LOQ $\text{mBq}\cdot\text{l}^{-1}$
^{237}Np	3,85E-07	0,01
^{239}Pu	8,70E-07	2
^{240}Pu	4,76E-07	4
^{241}Pu	3,93E-07	1 500

Through chemical separation, high uranium decontamination factor can be achieved but remaining uranium concentration is likely to be still above the typical ^{238}Pu concentration expected in water. In addition, this ^{238}Pu concentration is expected to be lower than the LOQ reported. For this reason, current instrumentation is not suited for ^{238}Pu measurements, in normal conditions. However, assuming that a collision-reaction cell could be installed onto a more sensitive instrument, such a newer instrument could be more suited for the separation of isobaric interferences.

5 Reagents

Use only reagents of recognized analytical grade.

5.1 Laboratory water, grade 3 quality as specified in ISO 3696.

5.2 Blank.

A blank sample is taken through the entire procedure, including chemical separation.

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

5.3 Certified standard solutions of isotopes.

Use of a certified standard solution with known isotopic composition is recommended to evaluate the mass bias.

Use of a reference solution with known actinide isotopic composition is recommended for standard bracketing (measured at least twice, before and after the sample, in several repetitions).

5.4 Tracer solution (for example ^{242}Pu).

Prepare this solution by successive dilutions of the certified standard solution, the last dilution being in 1 % to 2 % nitric acid (volume). Concentration is adjusted in link with the method validation. The water samples are spiked with a known amount of this solution at the beginning of the procedure.

5.5 Quality control solution.

Solution of certified plutonium concentration, different than the one used for isotopic dilution should be used.

5.6 Argon gas, at least 99,995 % pure.

5.7 Diluted nitric acid, 2 % volume, for example.