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## Water quality — Radium 226 — Test method using ICP-MS

*Qualité de l'eau — Radium 226 — Méthode d'essai par ICP-MS*

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CP 401 • Ch. de Blandonnet 8  
CH-1214 Vernier, Geneva  
Phone: +41 22 749 01 11  
Email: [copyright@iso.org](mailto:copyright@iso.org)  
Website: [www.iso.org](http://www.iso.org)

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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 document 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](http://www.iso.org/directives)).

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This document was prepared by 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](http://www.iso.org/members.html).

## Introduction

Radionuclides are present throughout the environment; thus, water bodies (e.g. surface waters, ground waters, sea waters) contain radionuclides, which can be of either natural or anthropogenic origin:

- Naturally-occurring radionuclides, including  $^3\text{H}$ ,  $^{14}\text{C}$ ,  $^{40}\text{K}$  and those originating from the thorium and uranium decay series, in particular  $^{210}\text{Pb}$ ,  $^{210}\text{Po}$ ,  $^{222}\text{Rn}$ ,  $^{226}\text{Ra}$ ,  $^{228}\text{Ra}$ ,  $^{227}\text{Ac}$ ,  $^{232}\text{Th}$ ,  $^{231}\text{Pa}$ ,  $^{234}\text{U}$ , and  $^{238}\text{U}$ , can be found in water bodies due to either natural processes (e.g. desorption from the soil and runoff by rain water) or released from technological processes involving naturally occurring radioactive materials (e.g. mining, mineral processing, oil, gas, and coal production, water treatment and the production and use of phosphate fertilisers).
- Anthropogenic radionuclides such as  $^{55}\text{Fe}$ ,  $^{59}\text{Ni}$ ,  $^{63}\text{Ni}$ ,  $^{90}\text{Sr}$ ,  $^{99}\text{Tc}$ , transuranic elements (e.g. Np, Pu, Am, and Cm), and some gamma emitting radionuclides such as  $^{60}\text{Co}$  and  $^{137}\text{Cs}$  can also be found in natural waters. Small quantities of anthropogenic radionuclides can be discharged from nuclear facilities to the environment as a result of authorized routine releases. The radionuclides present in liquid effluents are usually controlled before being discharged to the environment<sup>[1]</sup> and water bodies. Anthropogenic radionuclides used for medical and industrial applications can be released to the environment after use. Anthropogenic radionuclides are also found in waters due to contamination from fallout resulting from above-ground nuclear detonations and accidents such as those that have occurred at the Chernobyl and Fukushima nuclear facilities.

Radionuclide activity concentrations in water bodies can vary according to local geological characteristics and climatic conditions and can be locally and temporally enhanced by releases from nuclear facilities during planned, existing, and emergency exposure situations.<sup>[2][3]</sup> Some drinking water sources can thus contain radionuclides at activity concentrations that can present a human health risk. The World Health Organization (WHO) recommends to routinely monitor radioactivity in drinking waters<sup>[4]</sup> and to take proper actions when needed to minimize the health risk.

National regulations usually specify the activity concentration limits that are authorized in drinking waters, water bodies and liquid effluents to be discharged to the environment. These limits can vary for planned, existing, and emergency exposure situations. As an example, during either a planned or existing situation, the WHO guidance level for  $^{226}\text{Ra}$  in drinking water is  $1 \text{ Bq}\cdot\text{l}^{-1}$ ,<sup>[4]</sup> see NOTES 1 and 2. Compliance with these limits is assessed by measuring radioactivity in water samples and by comparing the results obtained, with their associated uncertainties, as specified by ISO/IEC Guide 98-3<sup>[5]</sup> and ISO 5667-20<sup>[6]</sup>.

NOTE 1 If the value is not specified in Annex 6 of Reference [4], the value has been calculated using the formula provided in Reference [4] and the dose coefficient data from References [7] and [8].

NOTE 2 The guidance level calculated in Reference [4] is the activity concentration that results in an effective dose of  $0,1 \text{ mSv}\cdot\text{a}^{-1}$  to members of the public for an intake of  $2 \text{ l}\cdot\text{d}^{-1}$  of drinking water for one year. This is an effective dose that represents a very low level of risk to human health and which is not expected to give rise to any detectable adverse health effects.<sup>[4]</sup>

This document contains method(s) to support laboratories, which need to determine  $^{226}\text{Ra}$  in water samples. The method(s) described in this document can be used for various types of waters. Minor modifications such as sample volume and counting time can be made if needed to ensure that the decision threshold, detection limit, and uncertainties are below the required limits. This can be done for several reasons such as emergency situations, lower national guidance limits and operational requirements.



# Water quality — Radium 226 — 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 essential that tests conducted according to this document be carried out by suitably trained staff.

## 1 Scope

This document specifies methods used to determine  $^{226}\text{Ra}$  concentration by inductively coupled plasma mass spectrometry (ICP-MS). The mass concentrations obtained can be converted into an activity concentration.

The method is applicable to test samples of drinking water, rainwater, surface and ground water, after proper sampling and handling, and test sample preparation.

The detection limit depends on the sample volume, the instrument used, the background count rate, the detection efficiency, the counting time and the chemical yield. The detection limit of the method described in this document, using currently available equipment, is approximately  $10 \text{ mBq}\cdot\text{l}^{-1}$ , which is better than the WHO criteria for safe consumption of drinking water ( $1 \text{ Bq}\cdot\text{l}^{-1}$ ).<sup>[4]</sup>

This method covers the measurement of  $^{226}\text{Ra}$  in water at activity concentrations between  $0,001 \text{ Bq}\cdot\text{l}^{-1}$  and  $100 \text{ Bq}\cdot\text{l}^{-1}$ . Samples with concentrations higher than  $1 \text{ Bq}\cdot\text{l}^{-1}$  can be measured if a dilution is performed.<sup>[9]</sup>

The method described in this document is applicable in the event of an emergency situation.

In this method, filtration of the test sample is necessary. The analysis of  $^{226}\text{Ra}$  adsorbed to suspended matter is not covered by this method. The analysis of the insoluble fraction requires a mineralization step that is not covered by this document. In this case, the measurement is made on the different phases obtained.

It is the user's responsibility to ensure the validity of this test method for the water samples tested.

## 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/IEC Guide 98-3, *Uncertainty of measurement — Part 3: Guide to the expression of uncertainty in measurement (GUM:1995)*

ISO/IEC Guide 99, *International vocabulary of metrology — Basic and general concepts and associated terms (VIM)*

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 water*

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 Term, definitions and symbols

#### 3.1 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO/IEC Guide 98-3, ISO/IEC Guide 99 and ISO 80000-10 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/>

#### 3.2 Symbols

**Table 1 — Symbols**

Symbol	Description	Unit
$c_s$	Specific activity corresponding to one gram of the radionuclide	Bq·g <sup>-1</sup>
$L_D$	Detection limit in mass concentration, the lowest mass concentration that can be considered statistically different from a blank sample	Bq·kg <sup>-1</sup>
$L_Q$	Limit of quantification, the lowest mass concentration that can be quantified with statistical uncertainty	g·kg <sup>-1</sup>
$f$	Correction factor	
$m$	Mass of sample	kg
$m/z$	Mass to charge ratio measured by ICP-MS	—
$m_c$	Mass of the calibration standard tracer added to sample	g
$m_{cs}$	Mass of calibration standard added to standard	g
$m_{IS}$	Mass of the internal standard added to blank and sample	g
$m_{ISS}$	Mass of the internal standard solution added to a blank or a sample	g
$N_0$	Counts per second measured when performing ICP-MS measurement of a blank sample at a given mass-to-charge ratio	Counts·s <sup>-1</sup>
$\bar{N}_0$	Average number of counts per second for several blank samples measured by ICP-MS at a given mass-to-charge ratio	Counts·s <sup>-1</sup>
$U$	Expanded uncertainty and the coverage factor $k$ with $k = 1, 2, \dots$ , $U = k \cdot u$	—
$u$	Uncertainty such as counts per second, mass added etc.	—
$u(c)$	Standard uncertainty of the activity concentration result	Bq·kg <sup>-1</sup>
$u(\rho)$	Standard uncertainty associated with the measurement result	—
$u(\rho_V)$	Standard uncertainty associated with mass concentration of the calibration standard solution	g·g <sup>-1</sup>
$\rho$	Analyte mass for a given radionuclide per sample unit volume	g·g <sup>-1</sup>
$\rho_c$	Mass concentration of the calibration standard solution	g·g <sup>-1</sup>



**Table 1 (continued)**

Symbol	Description	Unit
$\rho_{IS}$	Mass of internal standard element or isotope per unit volume of the internal standard solution.	$\text{g}\cdot\text{l}^{-1}$
$\rho_V$	Volume concentration of the calibration standard solution	$\text{g}\cdot\text{l}^{-1}$
$V$	Volume	L
$z$	Electric charge of an ion	

## 4 Principle

The principles of analysis using ICP-MS are described in ISO 17294-1 and ISO 17294-2.

$^{226}\text{Ra}$  is natural in origin, occurring in the  $^{238}\text{U}$  decay chain.

ICP-MS has been successfully used to measure the concentration of  $^{226}\text{Ra}$  in water samples.<sup>[9],[10]</sup>

The results can be converted to activity concentrations using specific activity as a conversion factor given in [Table 2](#).

**Table 2 —  $^{226}\text{Ra}$  half-life and specific activity<sup>[11]</sup>**

Isotope	Half-life years	Specific activity $\text{Bq}\cdot\text{g}^{-1}$
Radium-226	$1,600\cdot(7)\cdot 10^3$	$3,658\cdot(16)\cdot 10^{10}$

An example of the limit of detection that can be obtained with ICP-MS is given in [Table 3](#), with a typical measurement time of several minutes per sample, including sample uptake, analysis time and washout before the next sample.

**Table 3 — Examples of detection limit<sup>[9],[10]</sup>**

Isotope	Limit of detection $\mu\text{g}\cdot\text{l}^{-1}$	Limit of detection $\text{Bq}\cdot\text{l}^{-1}$
Radium-226	$2,70\cdot 10^{-7}$	0,01

Measurement by ICP-MS is affected by several interferences, which are shown in [Table 4](#).

Table 4 —  $^{226}\text{Ra}$  interferences affecting ICP-MS measurement

Interference name	Description	$^{226}\text{Ra}$ interference
Isobaric	An isotope with a similar mass to the analyte	None
Polyatomic	Isotopes combining in the plasma to form an ion with a similar mass to the analyte	$^{86}\text{Sr}$ $^{140}\text{Ce}$ $^{87}\text{Sr}$ $^{139}\text{La}$ $^{88}\text{Sr}$ $^{138}\text{Ba}$ $^{40}\text{Ca}_2$ $^{146}\text{Nd}$ $^{209}\text{Bi}$ $^{16}\text{O}$ $^1\text{H}$ $^{208}\text{Pb}$ $^{18}\text{O}$ $^{186}\text{Os}$ $^{40}\text{Ar}$ $^{188}\text{Os}$ $^{38}\text{Ar}$ $^{190}\text{Os}$ $^{36}\text{Ar}$ $^{186}\text{W}$ $^{40}\text{Ar}$ $^{203}\text{Tl}$ $^{23}\text{Na}$
Tailing	Isotopes with one or two mass units superior or inferior than the analyte to measure with a relatively high abundance ( $>10^6$ ) relative to analyte	None

It is important to ensure that all potential interferences have been removed prior to measurement. The most significant interference affecting  $^{226}\text{Ra}$  measurement by ICP-MS is specific polyatomic.

The half-life of  $^{226}\text{Ra}$  for ICP-MS measurement means direct measurement without chemical separation is possible. A pre-concentration and chemical separation can be required prior to measurement if removal of elements that can form polyatomic interferences is required. The test method is based on chemical separation of  $^{226}\text{Ra}$  from interfering elements by ion-exchange and extraction chromatography followed by ICP-MS analysis.

It is important to know the interference decontamination factor. This can initially be assessed by running stable element standards at increasing concentrations to monitor the impact at  $m/z = 226$ .

If any interference has an impact on the  $^{226}\text{Ra}$  result that cannot be corrected for, then the result cannot be considered to be valid.

The sample can be measured directly, if necessary, after filtration (at 0,45  $\mu\text{m}$  porosity), without chemical separation of radium. In this case, it is necessary to use a matrix effect correction with an internal standard, as described in ISO 17294-1. An internal standard, for example  $^{205}\text{Tl}$  or  $^{195}\text{Pt}$ , is added to correct the matrix effects.

To quantify any potential interference coming from the reagents, a blank sample is prepared in the same way as the test sample. This blank sample is prepared using laboratory water.

## 5 Sampling and sample storage

Sampling, handling and storage of the water shall be done as specified in ISO 5667-1, ISO 5667-3 and ISO 5667-10 and guidance is given for the different types of water in References [12] to [19]. It is important that the laboratory receives a sample that is truly representative and has not been damaged or modified during transportation or storage.

The sample is filtered to remove suspended matter using a 0,45  $\mu\text{m}$  filter. A smaller pore size filter can also be used, but the filtration can be more tedious and time consuming. The sample shall be acidified after filtration to 1 % (v/v)  $\text{HNO}_3$ .

Conditions of sampling shall conform to ISO 5667-1.

## 6 Chemical reagents and equipment

### 6.1 General

The chemical reagents and equipment used for chemical treatment and preparation of the samples are described in [Annex A](#).

Reagents of an appropriate purity should be used depending on the detection limit required, impact of interferences on the measurement and the ICP-MS instrument design used for measurement.

### 6.2 Chemical reagents

**6.2.1** Laboratory water, used as a blank, as free as possible of chemical or radioactive impurities, with a resistivity of more than 18,2 MΩ cm at 25 °C and total organic carbon less than 1 µg·l<sup>-1</sup>.

Unless otherwise stated, water refers to laboratory water.

**6.2.2** An instrument blank, approximately 0,3 mol l<sup>-1</sup> nitric acid, is used to determine the background count rate of the instrument at selected mass to charge ratios.

The same reagent is also used to prepare the calibration standards and final samples for measurement.

**6.2.3** <sup>226</sup>Ra standard solution can be used to prepare calibration standards to calculate the activity concentration in the sample.

**6.2.4** An internal standard solution prepared with a stable element. For example, isotope <sup>205</sup>Tl and <sup>195</sup>Pt have been found suitable for this purpose. Their typical concentrations can be  $c(^{205}\text{Tl}) = 50 \mu\text{g}\cdot\text{l}^{-1}$  and  $c(^{195}\text{Pt}) = 0,25 \mu\text{g}\cdot\text{l}^{-1}$ .

**6.2.5** Argon gas for the plasma in the ICP-MS. The user should consult the instrument manufacturer on the minimum gas purity required.

### 6.3 Equipment

Usual laboratory equipment and in particular the following:

**6.3.1** ICP-MS (quadrupole (with or without collision or reaction cell capability), tandem, sector field or multi-collector) and associated software. Operation at constant temperature is recommended. Follow the manufacturers instruction for laboratory setup and instrument operation.

**6.3.2** Argon supply, equipped with pressure control and suitable extract system.

**6.3.3** Autosampler if available, and compatible tubing for running multiple samples automatically.

**6.3.4** Pipette, suitable for the accurate transfer of calibration standard and internal standard solution with a total precision within ±1 %.

## 7 Separation

It is the user's responsibility to ensure that all potential interferences have been removed. The removal of potential interferences is limited by the decontamination factor of the method. Suggested chemical separation options are outlined in [Annex A](#).