



FINAL DRAFT International Standard

Water quality — Protactinium-231 — Test method using ICP-MS

Qualité de l'eau — Protactinium 231 — Méthode d'essai par ICP-MS

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Foreword

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Introduction

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

- Naturally-occurring radionuclides, including ^3H , ^{14}C , ^{40}K and those originating from the thorium and uranium decay series, in particular ^{210}Pb , ^{210}Po , ^{222}Rn , ^{226}Ra , ^{228}Ra , ^{227}Ac , ^{231}Pa , ^{234}U and ^{238}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 production and use of phosphate fertilisers).
- Anthropogenic radionuclides, such as ^{55}Fe , ^{59}Ni , ^{63}Ni , ^{90}Sr and ^{99}Tc , transuranic elements (e.g. Np, Pu, Am and Cm), and some gamma emitting radionuclides, such as ^{60}Co and ^{137}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 into the environment^[1] and water bodies. Anthropogenic radionuclides used in 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^{[2],[3]}. 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^[4] 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 ^{231}Pa in drinking water is $0,1 \text{ Bq}\cdot\text{l}^{-1}$, 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 and ISO 5667-20^[5].

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 [6] and [7].

NOTE 2 The guidance level calculated in Reference [4] is the activity concentration that, with an intake of $2 \text{ l}\cdot\text{d}^{-1}$ of drinking water for one year, results in an effective dose of $0,1 \text{ mSv}\cdot\text{a}^{-1}$ to members of the public. 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^[4].

This document contains method(s) to support laboratories, which need to determine ^{231}Pa in water samples.

The method described in this document can be used for various types of waters (see [Clause 1](#)). For radiometric methods, minor modifications such as sample volume and counting time can be made if needed to ensure that the characteristic limit, decision threshold, detection limit, and uncertainties are below the required limits. For ICP-MS methods, minor modifications to, for example, the sample pre-concentration volume and the interference separation, can be made if needed to ensure that the limit of detection, limit of quantification 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 — Protactinium-231 — 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.

IMPORTANT — It is essential that tests conducted according to this document be carried out by suitably trained staff.

1 Scope

This document specifies a method to determine ^{231}Pa by inductively coupled plasma mass spectrometry (ICP-MS). The mass concentrations obtained can be converted into an activity concentration.

The method described in this document is applicable to test samples of drinking water, rainwater, surface and ground water, marine water, as well as cooling water, industrial water, domestic and industrial wastewater after proper sampling and handling and test sample preparation.

The limit of detection depends on the sample volume, the instrument used, the background count rate, the detection efficiency and the chemical yield. In this document, the limit of detection of the method using currently available apparatus is approximately $0,1 \text{ Bq}\cdot\text{l}^{-1}$ (or $\text{Bq}\cdot\text{kg}^{-1}$), which is the same as the WHO criteria for safe consumption of drinking water ($0,1 \text{ Bq}\cdot\text{l}^{-1}$)^[4].

The method described in this document covers the measurement of ^{231}Pa in water at activity concentrations between $0,1 \text{ Bq}\cdot\text{l}^{-1}$ and $100 \text{ Bq}\cdot\text{l}^{-1}$. Samples with higher activity concentrations than $100 \text{ Bq}\cdot\text{l}^{-1}$ can be measured if a dilution is performed.

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

Filtration of the test sample is necessary for the method described in this document. The analysis of ^{231}Pa 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/IEC Guide 98-3, *Uncertainty of measurement — Part 3: Guide to the expression of uncertainty in measurement (GUM:1995)*

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

ISO 17294-1:2024, *Water quality — Application of inductively coupled plasma mass spectrometry (ICP-MS) — Part 1: General guidelines*

ISO 17294-2:2023, *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*

3 Terms and definitions

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

4 Symbols

C	Activity concentration	Bq·g ⁻¹
C_s	Specific activity corresponding to one gram of the radionuclide	Bq·g ⁻¹
C_T	Activity of the tracer	Bq
C_{TS}	Activity concentration of the tracer added to a sample	Bq·g ⁻¹
k	Coverage factor for uncertainties	
L_D	Limit of detection in mass concentration, the lowest mass concentration that can be considered statistically different from a blank sample	g·kg ⁻¹
L_Q	Limit of quantification, the lowest mass concentration that can be quantified with statistical uncertainty	g·kg ⁻¹
m	Mass of sample	kg
m/z	Mass-to-charge ratio measured by ICP-MS	
m_A	Analyte mass added to a spiked solution	g
m_{AS}	Mass of the analyte solution added to a control sample or for measurement calculation	g
m_C	Mass of the calibration standard tracer added to sample	g
m_{CS}	Mass of calibration standard solution added to sample	g
m_{IS}	Mass of the internal standard solution added to blank and sample	g
m_{ISS}	Mass of the internal standard solution added to blank or a sample	g
m_T	Mass of tracer added to blank and sample	g
m_{TB}	Mass of tracer added to the reagent blank	g
m_{TS}	Mass of tracer solution added to blank or sample	g
N	Counts per second measured when performing ICP-MS measurement for a sample at a given mass-to-charge ratio	Counts·s ⁻¹
N_0	Counts per second measured when performing ICP-MS measurement of a blank sample at a given mass-to-charge ratio	Counts·s ⁻¹

\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 ⁻¹
N_{net}	Net number of counts per second, $N - N_0$	Counts·s ⁻¹
N_{netIS}	Net number of counts per second at the internal standard mass-to-charge ratio	Counts·s ⁻¹
N_{netT}	Net number of counts per second in samples where a tracer has been added to assess chemical recovery	Counts·s ⁻¹
N_{SP}	Net number of counts per second in the spiked reagent blank	Counts·s ⁻¹
N_{T}	Counts per second at analyte mass-to-charge ratio present as impurities	Counts·s ⁻¹
N_{US}	Net number of counts per second in the unspiked reagent blank sample	Counts·s ⁻¹
R_c	Chemical recovery following purification measured by ICP-MS	
S_{N_0}	Standard deviation obtained by measurement of 10 test portions of the blank sample	Counts·s ⁻¹
U	Expanded uncertainty and the coverage factor k with $k = 1, 2, \dots$, $U = k \cdot u$	Bq
$u(C)$	Standard uncertainty of the activity concentration result	Bq
$u(\rho)$	Standard uncertainty associated with the measurement result	g
V	Volume of sample	l
α	Measurement bias constant which allows a correction for signal intensity bias between the tracer and the analyte	
ρ	Analyte concentration	g·g ⁻¹
ρ_A	Mass concentration of the analyte standard solution	g·g ⁻¹
ρ_{IS}	Mass of internal standard element or isotope per unit volume of the internal standard solution	g·l ⁻¹
ρ_{T}	Mass concentration of tracer solution	g·g ⁻¹

5 Principle

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

ICP-MS has been successfully used to measure the concentration of ²³¹Pa in water samples^{[8],[9]}.

Protactinium-231 is a naturally occurring radionuclide.

The results can be converted in activity concentrations using specific activity as a conversion factor given in [Table 1](#).

The typical measurement time is several minutes per sample, including sample uptake, counting time and washout before the next sample.

Table 1 — Half-life and specific activity of ²³¹Pa^[10]

Isotope	Half-life years	Specific activity Bq·g ⁻¹
²³¹ Pa	3,267 0 (260) · 10 ⁴	1,753 (14) · 10 ⁹

An example of the limit of detection that can be obtained with ICP-MS is given in [Table 2](#).

Table 2 — Example of limit of detection^[1]

Isotope	Limit of detection $\mu\text{g}\cdot\text{l}^{-1}$	Limit of detection $\text{Bq}\cdot\text{l}^{-1}$
^{231}Pa	$5,7 \cdot 10^{-4}$	0,01

Radionuclide measurement by ICP-MS is affected by several interferences which are outlined in [Table 3](#).

Table 3 — Interferences affecting ICP-MS measurement

Name of interference	Description	^{231}Pa interference
Isobaric interference	Stable or radioactive isotopes with a similar mass to the analyte	None
Polyatomic interference	Stable or radioactive isotopes combining in plasma to form a polyatomic ion with a similar mass to the analyte	$^{230}\text{Th}^1\text{H}$, $^{199}\text{Hg}^{16}\text{O}_2$, $^{191}\text{Ir}^{40}\text{Ar}$
Tailing	Stable or radioactive isotopes of one or two mass units on either side of the analyte with a relatively high abundance ($>10^6$) relative to the analyte	^{232}Th

It is important to ensure that all potential interferences have been removed prior to measurement in order to remove interferences and pre-concentrate ^{231}Pa prior to measurement.

Chemical separation of ^{231}Pa is required prior to measurement. This also removes elements that can form polyatomic and tailing interferences.

It is important to know the interference separation factor achievable by chemical separation. This can initially be assessed by running stable element standards at increasing concentrations to monitor the impact at $m/z = 231$.

An aliquot of a water sample can be directly measured by ICP-MS to determine the stable element composition. High matrix samples, such as seawater, can need to be diluted to a greater extent before this measurement, depending on the sample introduction system of the instrument used; some designs offer online aerosol dilution capability that can run high matrix samples without prior dilution.

If any interference has an impact on the ^{231}Pa result that cannot be corrected for, then the result cannot be considered to be valid.

Chemical separation can be required to remove interferences and pre-concentrate ^{231}Pa prior to measurement. As described in the ISO 17294 series, a tracer is needed to evaluate the recovery in chemical separation. The tracer can be mixed with an aliquot of sample, followed by chemical isolation of the analyte. Protactinium-233 is a suitable tracer that can be quantified by gamma spectrometry.

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 ultrapure water.

6 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 [13] to [20]. 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 a pH less than 2 with HNO_3 .

Minimising all contamination or losses is of primary concern. Impurities in the reagents or dust on the laboratory equipment, which is in contact with the samples can be potential sources of stable element contamination that increases the background at $m/z = 231$. The sample containers can lead to positive or negative bias in the determination of trace elements by superficial desorption or adsorption.