International Standard

ISO 4722-2

First edition
2024-12

Water quality — Thorium 232 —

Part 2:
Test method using ICP-MS

Qualité de l'eau — Thorium 232 —

Partie 2: Méthode d'essai par ICP-MS

Reference number
ISO 4722-2:2024(en)

Contents

Page

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 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).

ISO draws attention to the possibility that the implementation of this document may involve the use of (a) patent(s). ISO takes no position concerning the evidence, validity or applicability of any claimed patent rights in respect thereof. As of the date of publication of this document, ISO had not received notice of (a) patent(s) which may be required to implement this document. However, implementers are cautioned that this may not represent the latest information, which may be obtained from the patent database available at www.iso.org/patents. ISO shall not be held responsible for identifying any or all such patent rights.

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

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.

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 ^{3}H, ^{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 to 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 ^{232}Th in drinking water is 1 Bq·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 l·d^{-1} of drinking water for one year, results in an effective dose of 0,1 mSv·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 that need to determine ^{232}Th 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 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, the limit of quantification and the 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 — Thorium 232 —

Part 2:
Test method using ICP-MS

WARNING — Persons using this document should be familiar with normal laboratory practice. It is the responsibility of the user to establish appropriate safety and health practices and to determine the applicability of any other restrictions. 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 thorium 232 (^{232}Th) by inductively coupled plasma mass spectrometry (ICP-MS). The mass concentrations obtained can be converted into activity concentrations.

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 2 $mBq \cdot l^{-1}$ (or $mBq \cdot kg^{-1}$), which is lower than the WHO criteria for safe consumption of drinking water (1 $Bq \cdot l^{-1}$)[4].

The method described in this document covers the measurement of ^{232}Th in water at activity concentrations between 2 $mBq \cdot l^{-1}$ and 5 $Bq \cdot l^{-1}$. Samples with higher activity concentrations than 5 $Bq \cdot l^{-1}$ can be measured if a dilution is performed.

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

Filtration of the test sample is necessary for the method described in this document. The analysis of ^{232}Th 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	Mass activity	$Bq{\cdot}kg^{-1}$
C_s	Specific activity corresponding to one gram of the radionuclide	$Bq{\cdot}g^{-1}$
C_T	Activity of the tracer	Bq
C_{TS}	Mass activity of the tracer added to a sample	$Bq{\cdot}g^{-1}$
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	$Counts{\cdot}s^{-1}$
L_Q	Limit of quantification, the lowest mass concentration that can be quantified with statistical uncertainty	$Counts{\cdot}s^{-1}$
m	Mass of the sample	kg
m / z	Mass-to-charge ratio measured by ICP-MS	—
m_A	Mass of analyte 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 solution added to a sample	g
m_{CS}	Mass of the calibration standard solution added to a sample	g
m_{IS}	Mass of the internal standard added to a blank and a sample	g
m_{ISS}	Mass of the internal standard solution added to a blank or a sample	g
m_T	Mass of the tracer solution added to a blank and a sample	g
m_{TB}	Mass of the tracer solution added to a reagent blank	g
m_{TS}	Mass of the tracer solution added to a blank or a sample	g

N	Number of counts per second measured by ICP-MS of a sample at a given mass-to-charge ratio	Counts·s^{-1}
N_0	Number of counts per second measured by ICP-MS of a blank sample at a given mass-to-charge ratio	Counts·s^{-1}
$\bar{N}_0$	Average number of counts per second of several blank samples measured by ICP-MS at a given mass-to-charge ratio	Counts·s^{-1}
$\mathrm{N}_{\mathrm{net}}$	Net number of counts per second, $N - N_0$	Counts·s^{-1}
$\mathrm{N}_{\mathrm{netIS}}$	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}	Number of 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 measuring of 10 test portions of the blank sample	Counts·s^{-1}
U	Expanded uncertainty and the coverage factor k with k = 1, 2, ..., $U = k \cdot u$	Bq·kg^{-1}
$u(C)$	Standard uncertainty of the mass activity result	Bq·kg^{-1}
$u(\rho)$	Standard uncertainty associated with the measurement result	g·kg^{-1}
ρ	Mass concentration of the analyte	g·kg^{-1}
ρ_{A}	Mass concentration of the analyte in the standard solution	g·g^{-1}
ρ_{C}	Mass concentration calibration standard solution	g·g^{-1}
ρ_{IS}	Mass concentration of the internal standard element or isotope per unit volume of the internal standard solution	g·g^{-1}
ρ_{T}	Mass concentration of the tracer solution	g·g^{-1}
ρ_V	Mass concentration of the analyte per sample unit volume	g·l^{-1}
V	Volume of the sample	l
α	Measurement bias constant which allows a correction for signal intensity bias between the tracer and the analyte	—

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 ^{232}Th in water samples[8],[9].

The results can be converted in activity concentrations using the specific activity as a conversion factor given in Table 1.

Table 1 — Half-life and specific activity of ^{232}Th[10]

Isotope	Half-life years	Specific activity Bq·g^{-1}
^{232}Th	14,02 (7) 10^{9}	4,067 (17)·10^{3}

An example of the limit of detection that can be obtained with ICP-MS is given in Table 2, with a typical measurement time of several minutes per sample, including sample uptake, counting time and washout before the next sample.

Table 2 — Example of a limit of detection[8],[9]

Isotope	Limit of detection µg·l^{-1}	Limit of detection Bq·l^{-1}
^{232}Th	0,5	2,0×10^{-3}

Radionuclide measurement by ICP-MS is affected by several interferences which are outlined in Table 3.

Table 3 — Interferences affecting ICP-MS measurement

Type of interference	Description	^{232}Th interference
Isobaric	Stable or radioactive isotopes with a similar mass to the analyte	None
Polyatomic	Stable or radioactive isotopes combining in plasma to form a polyatomic ion with a similar mass to the analyte	^{231}Pa^{1}H, ^{197}Au^{35}Cl, ^{192}Pt^{40}Ar
Tailing interference	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	^{231}Pa, ^{233}U

Depending on the potential interferences, ^{232}Th measurement can either be performed directly or after a chemical separation. This also removes elements that can form polyatomic and tailing interferences. It is important to ensure that all potential interferences have been removed prior to measurement. There are limited interferences affecting ^{232}Th measurement by ICP-MS, but polyatomic and tailing interferences shall be considered.

It is important to know the interference separation factor achievable by chemical separation and the ICP-MS instrument used. This can initially be assessed by measuring the concentration of interferences at increasing concentrations to monitor the impact at m / z = 232 before and after either chemical separation or instrumental separation, or both.

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 dilution 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 such as seawater without prior dilution.

If any interference has an impact on the ^{232}Th 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 ^{232}Th 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. Potential tracers are ^{229}Th and ^{230}Th, which can be measured using alpha spectrometry or ICP-MS. In case of a direct measurement, using a tracer is not necessary.

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.