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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 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).

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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 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 $Bq \cdot l^{-1}$, 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 $l \cdot d^{-1}$ of drinking water for one year, results in an effective dose of 0,1 $mSv \cdot a^{-1}$ 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 decision threshold, limit of detection, 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 practices. 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 and to determine the applicability of any other restrictions.

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 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 0,1 Bq·l^{-1} (or Bq·kg^{-1}), which is the same as the WHO criteria for safe consumption of drinking water (0,1 Bq·l^{-1})[4].

The method described in this document covers the measurement of ^{231}Pa in water at activity concentrations between 0,1 Bq·l^{-1} and 100 Bq·l^{-1}. Samples with higher activity concentrations than 100 Bq·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	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 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 analyte solution added to a control sample or for measurement calculation	g
m_C	Mass of calibration standard solution tracer added to a sample	g
m_{CS}	Mass of calibration standard solution added to a sample	g
m_{IS}	Mass of internal standard added to a blank and a sample	g
m_{ISS}	Mass of internal standard solution added to a blank or a sample	g
m_T	Mass of tracer solution added to a blank and a sample	g
m_{TB}	Mass of tracer solution added to a reagent blank	g
m_{TS}	Mass of 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	$Counts \cdot s^{-1}$

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 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}	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 measurement of 10 test portions of the blank sample	Counts·s^{-1}
U	Expanded uncertainty and the coverage factor k with $k = 1, 2, \ldots$, $U = k \cdot u$	Bq·kg^{-1}
u_{rel}	Relative standard uncertainty	—
$u(C)$	Standard uncertainty of the mass activity result	Bq·kg^{-1}
$u(\rho)$	Standard uncertainty associated with the measurement result	g·kg^{-1}
V	Volume of sample	l
α	Measurement bias constant which allows a correction for signal intensity bias between the tracer and the analyte	—
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 of the 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 of analyte per sample unit volume	g·l^{-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 ^{231}Pa in water samples[8],[9].

Protactinium-231 is a naturally occurring radionuclide.

The results can be converted in activity concentrations using the 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 ^{231}Pa[10]

Isotope	Half-life years	Specific activity $Bq \cdot g^{-1}$
^{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 $\mu g \cdot l^{-1}$	Limit of detection $Bq \cdot l^{-1}$
^{231}Pa	5,7 · 10^{-5}	0,1

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	^{231}Pa 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	$^{230}Th^1H$, $^{199}Hg^{16}O_2$, $^{191}Ir^{40}Ar$
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 neither been damaged nor modified during transportation or storage.

The sample is filtered to remove suspended matter using a 0,45 µm 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 contamination and losses is of primary concern. Impurities in the reagents and dust on the laboratory equipment 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 either a positive or a negative bias in the determination of trace elements by superficial desorption or adsorption.

7 Chemical reagents and apparatus

7.1 General

The chemical reagents and equipment used for chemical treatment and preparation of the samples are described in Annexes A and B.

Use only reagents of recognized analytical grade.

7.2 Chemical reagents

7.2.1 Ultrapure water, with a resistivity of more than 18,2 MΩ·cm at 25 °C and a total organic carbon less than 1 $\mu g \cdot l^{-1}$.

Unless otherwise stated, water refers to ultrapure water.

7.2.2 Instrument blank, for example 0,3 $mol \cdot l^{-1}$ nitric acid, 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.

7.2.3 Protactinium-231 standard solution, used to prepare calibration standards to calculate the concentration in the sample.

7.2.4 Internal standard solution, prepared with a stable element.

7.2.5 Tracer solution, to determine the chemical recovery. This solution is prepared by dilution of a standard that is traceable to national and international standards.

7.2.6 Argon gas, for the plasma in the ICP-MS, at least 99,99 % pure.

7.3 Apparatus

Usual laboratory apparatus and in particular the following:

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

7.3.2 Argon supply, equipped with pressure control and suitable extract and gas regulation system.

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

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

7.3.5 **Balance**, for example, capable of achieving ±0,1 mg precision.

8 Separation

It is the user's responsibility to ensure that all potential interferences have been removed. The extent of removal of interferences is a result of the decontamination factor of the separation method. Suggested chemical separation options are outlined in Annexes A and B.

Alternative chemical separation procedures can be used that are outside of the scope of this document (such as those in References [11], [12], [21], [22], [23], [24] and [25]).

9 Quality control

9.1 General

Measurement methods shall be performed by suitably skilled staff under a quality assurance program, such as the one that is described in ISO/IEC 17025.

If an analyst has not performed this procedure before, a precision and bias test should be performed by running a duplicate measurement of either a reference or spiked material. Acceptance limits should be within limits specified by the laboratory.

A similar evaluation procedure should be performed by the analyst who routinely applies this procedure, with a periodicity defined by the laboratory. Acceptance limits should be within limits specified by the laboratory.

9.2 Variables that can influence the measurement

Special care shall be taken in order to limit the influence of parameters that can bias the measurement and lead to a non-representative result. Failure to take sufficient precautions during the different steps of the measurement process such as sampling, transportation and storage, reagents used, sample transfer, can require corrective factors to be applied to the measured results.

9.3 Instrument verification

Follow the instructions provided by the instrument manufacturer and the steps described in ISO 17294-1:2024, Clauses 7 and 9 and ISO 17294-2:2023, Clauses 8 to 11.

The instrument sensitivity, limit of detection, measurement precision and measurement bias should be determined for every analysis performed on the instrument.

Before any sample measurement, measure a quality control solution. Ensure that the measured value of the concentration does not deviate from the expected value (within measurement limits). If the deviation exceeds the established laboratory measurement limits (e.g. sensitivity, stability and uncertainty), follow the recommendations of the instrument's manufacturer and perform the optimization of parameters again.

The instrument sensitivity can be determined from ^{231}Pa calibration standards run by ICP-MS prior to samples. The concentration of calibration standard solutions should be known with high precision, using a certified standard if possible.

If a dual-mode detector or similar is used, then detector cross calibration can be required depending on the activity range of calibration standards measured.

A known mass of calibration standard solution, m_{CS}, at a known mass concentration, ρ_C, shall be added for each standard, with the mass of calibration standard, m_C, calculated using Formula (1):

$$m_C = \rho_C \cdot m_{CS} \quad (1)$$

The uncertainty on m_C can be calculated using Formula (2):

$$u(m_C) = m_C \sqrt{u_{rel}^2(\rho_C) + u_{rel}^2(m_{CS})} \quad (2)$$

A calibration plot can be produced using either the ICP-MS instrument software or a spreadsheet. The calibration standard concentration can be plotted against the counts per second. A linear calibration line gives the instrument sensitivity based on Formula (3):

$$y = D \cdot x + E \quad (3)$$

where

D is the gradient of the calibration line;

y is the counts per second for the analyte in the sample;

x is the analyte mass concentration;

E is the intercept for the y-axis when $x = 0$.

A linear calibration line gives values for D and E. If a calibration curve is used to determine the mass concentration of the measurand, the sample matrix effects on the instrument sensitivity are not always accounted for. The determination of the mass concentration using a recovery tracer is a more robust approach.

Equipment quality control solutions shall also be measured at regular intervals during the procedure to verify that the measurement equipment is performing within agreed limits.

An internal standard shall be prepared to monitor and correct for any change in the instrument's response during a run, using an element which has a similar mass and ionization energy to ^{231}Pa and that is not present in the sample being measured, for example ^{209}Bi.

9.4 Method verification

The method should be validated periodically through replicate measurements of appropriate samples such as spiked samples, reference materials or participation in inter-comparison exercises.

The repeatability of the method should be verified (e.g. by replicate measurements).

10 Expression of results

10.1 Data analysis

The output from the instrument is typically in counts per second. Gross count rates for samples are corrected for background and change in the instrument's response using the internal standard. A correction for chemical recovery is also required.

If dilutions are carried out, apply the appropriate factor to the values of the sample.

10.2 Background

The blank solution is measured as a sample. The obtained value shall be subtracted from the measured sample values. A blank solution should also be measured regularly throughout the procedure.

A rinsing sequence is usually performed. The sample introduction system is rinsed between each sample using a solution of dilute HNO_3. A blank solution shall be measured at regular intervals to verify that all remaining ^{231}Pa is removed from the system by returning to background level.

Depending on the interfering element concentration, more than one rinsing solution of different concentrations can be required to return the count rate to the background level.

Depending on the instrument software used, it is possible to set a threshold count rate that shall be reached during the rinsing sequence before moving on to the next sample.

The ICP-MS instrument software can have built-in background correction capability. The user shall take care that only one background correction is applied.

10.3 Internal standard

An internal standard shall be added to samples before measurement, including a blank sample. The signal for internal standard monitors for changes in instrument performance during a run. This can be due to small variations in, for example, plasma gas flow rate, or, for higher matrix samples such as seawater, internal components such as interface cones becoming partially blocked during a run, reducing sample transmission.

A known mass of internal standard, m_{IS}, shall be added to the sample and the blank. For this purpose, a solution of known mass concentration of internal standard, ρ_{IS}, ideally with great precision, is needed. The mass of internal standard solution, m_{ISS}, added is recorded. The mass of internal standard added, m_{IS}, can be calculated using Formula (4):

$$m_{IS} = \rho_{IS} \cdot m_{ISS} \tag{4}$$

The uncertainty on m_{IS} can be calculated using Formula (5):

$$u(m_{IS}) = m_{IS}\sqrt{u_{rel}^2(\rho_{IS}) + u_{rel}^2(m_{ISS})} \tag{5}$$

Some ICP-MS instruments are equipped with online internal standard lines in the sample introduction that can measure a separate solution containing the internal standard.

The net count rate for the internal standard in each sample should be corrected based on the net count rate in the first background sample and this correction factor applied to each sample.

The ICP-MS instrument software can have a built-in internal standard correction capability. The user shall take care that only one internal standard correction is applied.

10.4 Expression of results using ^{233}Pa as a recovery tracer

10.4.1 Calculation of activity of the tracer and mass of the analyte

The sample activity is determined using a recovery tracer, which corrects for losses during the sample preparation. The instrumental deviations during the measurement are corrected using an internal standard. The mass activity of the tracer solution, C_{TS}, and the internal standard mass concentration, ρ_{IS}, shall be known, ideally with great precision. A certified standard is usually employed for ^{233}Pa. A defined mass activity of the tracer solution, C_{TS}, is added to each sample and the mass of the tracer solution added, m_{TS}, is recorded.

The activity of the tracer, C_T, added to each sample can be calculated using Formula (6):

$$C_T = C_{TS} \cdot m_{TS} \quad (6)$$

Note that the activity of tracer added is calculated at a reference date. Consider the isotope decay when calculating the recovery obtained from the gamma spectrometry method.

The uncertainty on C_T can be calculated using Formula (7):

$$u(C_T) = C_T \sqrt{u_{rel}^2(C_{TS}) + u_{rel}^2(m_{TS})} \quad (7)$$

To calculate the measurement bias from the internal standard and prepare control solutions, a known mass of ^{231}Pa, m_A, shall be added to the solution. For this purpose, a solution of known mass concentration of ^{231}Pa, ρ_A, ideally with great precision, is needed. The mass of the analyte solution added, m_{AS}, is recorded. The mass of ^{231}Pa, m_A, can be calculated using Formula (8):

$$m_A = \rho_A \cdot m_{AS} \quad (8)$$

The uncertainty on m_A can be calculated using Formula (9):

$$u(m_A) = m_A \sqrt{u_{rel}^2(\rho_A) + u_{rel}^2(m_{AS})} \quad (9)$$

10.4.2 Chemical recovery

The ^{233}Pa tracer is counted by gamma spectrometry. The chemical recovery, R_c, is calculated by dividing the measured activity by the expected activity. The decay of the ^{233}Pa tracer shall be calculated. The chemical recovery is calculated using Formula (10):

$$R_c = \frac{(N_{netT})_i - (N_{netT})_f}{(N_{netT})_f} \quad (10)$$

where

i is the initial sample measured prior to separation;

f is the final sample after separation.

Additional samples can be measured at different stages of the separation procedure to monitor the yield.

If dilutions are carried out, apply the appropriate factor to the values of the sample.

10.4.3 Measurement bias

The measurement bias is a correction factor that corrects for all the measurement deviations between the tracer and the analyte. It includes correction for the mass bias and the variation of signal intensity between the tracer and the analyte. When a stable tracer or internal standard is used, it also corrects for the fact that only one isotope of the element is used for the measurement.

The measurement bias, α, is first determined by measuring with the ICP-MS instrument the number of counts per second (cps) obtained for ^{231}Pa, N_{net}, and for the internal standard, N_{netIS}, using a solution containing a known mass of ^{231}Pa, m_A, and of internal standard, m_{IS}. The measurement bias is determined using Formula (11):

$$\alpha = (m_A \cdot N_{netIS}) / (m_{IS} \cdot N_{net}) \quad (11)$$

The uncertainty on the measurement bias is determined using Formula (12):

$$u(\alpha) = \alpha\sqrt{u_{\text{rel}}^2(m_{\text{A}}) + u_{\text{rel}}^2(m_{\text{IS}}) + u_{\text{rel}}^2(N_{\text{net}}) + u_{\text{rel}}^2(N_{\text{netIS}})} \quad (12)$$

10.4.4 Sample mass concentration

The sample mass concentration, ρ, in ^{231}Pa is calculated using Formula (13):

$$\rho = (\alpha \cdot m_{\text{IS}} \cdot N_{\text{net}})/(R_{\text{c}} \cdot m \cdot N_{\text{netIS}}) \quad (13)$$

The uncertainty on the sample mass concentration is calculated using Formula (14):

$$u(\rho) = \rho\sqrt{u_{\text{rel}}^2(m_{\text{IS}}) + u_{\text{rel}}^2(N_{\text{net}}) + u_{\text{rel}}^2(N_{\text{netIS}}) + u_{\text{rel}}^2(\alpha) + u_{\text{rel}}^2(m) + u_{\text{rel}}^2(R_{\text{c}})} \quad (14)$$

10.5 Limit of detection

The limit of detection, L_{D}, corresponds to the equivalent concentration of three times the standard deviation of the measurement of 10 test portions of a blank sample. The blank sample shall have passed through all steps of the method. The limit of detection is calculated using Formula (15):

$$L_{\text{D}} = \overline{N_0} + 3 \cdot S_{N_0} \quad (15)$$

10.6 Limit of quantification

The limit of quantification, L_{Q}, is 10 times the standard deviation of the measurement of 10 test portions of the blank. This can be calculated using Formula (16):

$$L_{\text{Q}} = \overline{N_0} + 10 \cdot S_{N_0} \quad (16)$$

NOTE The calculation of the limit of detection and limit of quantification using atom counting is different to that using decay counting techniques.

10.7 Correcting for ^{231}Pa contamination in the tracer

The tracer can contain a ^{231}Pa contamination that interferes with sample measurement if it is not corrected for. To correct for this, a blank sample should be prepared containing a known mass of tracer, m_{TB}, and the counts at $m / z = 231$ compared between the spiked, N_{SP}, and unspiked, N_{US}, blank using Formula (17):

$$N_{\text{T}} = N_{\text{SP}} - N_{\text{US}} \quad (17)$$

If a chemical separation is performed, the contribution of ^{231}Pa from the tracer, N_{T}, varies with the chemical recovery, R_{c}. The net numbers of counts for each sample, N_{netT}, can be calculated using Formula (18):

$$N_{\text{netT}} = (N - N_0) - (N_{\text{US}} + (R_{\text{c}} \cdot N_{\text{T}} \cdot m_{\text{T}} / m_{\text{TB}})) \quad (18)$$

The uncertainty on the tracer counts can be calculated using Formula (19):

$$\text{u}(N_{\text{netT}}) = \sqrt{(u(N))^2 + (u(N_0))^2 + (u(N_{\text{US}}))^2 + \left[u_{\text{rel}}^2(R_{\text{c}}) + u_{\text{rel}}^2(N_{\text{T}}) + u_{\text{rel}}^2(m_{\text{T}}) + u_{\text{rel}}^2(m_{\text{TB}})\right]^2} \quad (19)$$

10.8 Conversion of mass concentration to mass activity

The specific activity, C_s, of ^{231}Pa can be multiplied by the mass concentration, ρ, limit of detection, L_D, and limit of quantification, L_Q, to convert from mass concentration to mass activity, C, using Formula (20):

$$C = \rho \cdot C_s \tag{20}$$

The uncertainty of the mass activity is calculated using Formula (21):

$$u(C) = C\sqrt{u_{rel}^2(\rho) + u_{rel}^2(C_s)} \tag{21}$$

The L_D and L_Q are estimated values and do not require an uncertainty calculation.

10.9 Conversion from mass to volume units

A conversion from mass (grams per kilogram) to volume (grams per litre) units can be achieved using the analyte mass, ρ, mass, m, and volume, V, of the sample recorded during the procedure. The conversion is carried out using Formula (22):

$$\rho_v = \frac{m \cdot \rho}{V} \tag{22}$$

The uncertainty in this conversion can be calculated using Formula (23):

$$u(\rho_v) = \rho_v\sqrt{u_{rel}^2(\rho) + u_{rel}^2(m) + u_{rel}^2(V)} \tag{23}$$

11 Test report

The test report should conform to ISO/IEC 17025 requirements. The test report shall contain the following information:

a) reference to this document i.e. ISO 4717:2024;

b) identification of the sample;

c) units in which the results are expressed;

d) the test result can be given according to method 1 or method 2; the method used shall be clearly stated in the report.

- Method 1
  - if the result is less than the limit of detection, the result of the measurement is expressed as $\leq L_D$,
  - if the result is between the limit of detection and the limit of quantification, the result of the measurement is expressed as $\leq L_Q$,
  - if the result is greater than limit of quantification, the result of the measurement is expressed as ($\rho \pm k \cdot u(\rho)$ or $\rho \pm U$) or as ($C \pm k \cdot u(C)$ or $C \pm U$) with the associated k value.

  If the limit of detection exceeds the guideline value, it shall be documented that the method is not suitable for the measurement purpose.
- Method 2
  - if the result is less than the limit of quantification, the result of the measurement is expressed as $\leq L_Q$,

— if the result is greater than limit of quantification, the result of the measurement is expressed as ($\rho \pm k \cdot u(\rho)$ or $\rho \pm U$) or as ($C \pm k \cdot u(C)$ or $C \pm U$) with the associated k value.

If the limit of quantification exceeds the guideline value, it shall be documented that the method is not suitable for the measurement purpose.

e) the date used to calculate the sample mass activity;

f) the date of issue of the report.

Complementary information can be provided such as:

g) relevant dates such as the date of sampling, the date of the sample receipt and the date of the analysis start, where these dates are critical to the validity and application of the results;

h) the limit of application;

i) the limit of detection and the limit of quantification;

j) any mention of relevant deviation from this document likely to affect the results and any unusual features observed.

Annex A
(informative)

Chemical separation of protactinium by extraction chromatography

A.1 Principle

This Annex gives options for the extraction chromatography separation and pre-concentration of Pa. The pre-concentration procedure is good for low activity samples, while extraction chromatography chemical separation is fast and well-suited for monitoring protactinium activity in waters by ICP-MS. This procedure is based on References [26] and [27].

A.2 Technical resources

A.2.1 Reagents

Unless otherwise stated, use only reagents of recognized analytical grade and distilled or demineralized water or water of equivalent purity

A.2.1.1 Octanol-based extraction chromatography resin (e.g. Triskem TK400[1)]).

A.2.1.2 Hydrochloric acid, $c(HCl) = 12\ mol \cdot l^{-1}$, $0,1\ mol \cdot l^{-1}$.

A.2.1.3 Nitric acid, $c(HNO_3) = 0,3\ mol \cdot l^{-1}$.

A.2.1.4 Ultrapure water, with a resistivity of more than 18,2 MΩ·cm at 25 °C and total organic carbon less than $1\ \mu g \cdot l^{-1}$.

A.2.2 Equipment

Usual laboratory equipment and, in particular, the following.

A.2.2.1 Analytical balance.

A.2.2.2 Hot plate.

A.2.2.3 Centrifuge tubes.

A.3 Procedure

A.3.1 General

This procedure is carried out with two main steps: extraction and elution of protactinium. In all steps, if not specified, the flow rate should be of approximately $1\ ml \cdot min^{-1}$.

NOTE In some cases, the flow through resin columns is very poor because of sample impurities. Working with vacuum is therefore very helpful to support the flow.

1) Triskem TK400 resin is an example of suitable extraction chromatography media. This information is given for the convenience of users of this document and does not constitute an endorsement of ISO of this product.

A.3.2 Chemical separation

A.3.2.1 Tracer addition

Add ^{233}Pa as a yield tracer that is detectable by gamma spectrometry.

NOTE The half-life of ^{233}Pa is 26,98(2) days; see Reference [9].

A.3.2.2 Concentration step

To concentrate the protactinium in the sample, the solution can be evaporated (A.2.2.2).

A.3.2.3 Separation and purification

This procedure is based on References [15] and [16].

Transfer the evaporated sample residue (A.3.2.2) to a clean, labelled glass beaker and then, redissolve the sample in 12 mol·l^{-1} hydrochloric acid (A.2.1.2).

Prepare a pre-packed TK400 column or cartridge containing 2 ml of resin (A.2.1.1) and condition with 5 ml of 12 mol·l^{-1} hydrochloric acid (A.2.1.2):

— introduce the sample into the column, and allow it to pass through;

— wash the column with 30 ml of 12 mol·l^{-1} hydrochloric acid (A.2.1.2) to remove interfering elements and retain Pa on the column;

— elute protactinium from the column with 15 ml of 0,1 mol·l^{-1} hydrochloric acid (A.2.1.2) and collect the eluate in a clean glass beaker.

A.3.3 Measurement

A.3.3.1 Perform an ICP-MS measurement of ^{231}Pa.

A.3.3.2 Perform a gamma spectrometry measurement of ^{233}Pa tracer.