INTERNATIONAL STANDARD

ISO 4722-1

First edition
2023-10

Water quality — Thorium 232 —

Part 1: Test method using alpha spectrometry

Qualité de l'eau — Thorium 232 —

Partie 1: Méthode d'essai par spectrométrie alpha

Reference number
ISO 4722-1:2023(E)

ISO copyright office
CP 401 • Ch. de Blandonnet 8
CH-1214 Vernier, Geneva
Phone: +41 22 749 01 11
Email: copyright@iso.org
Website: www.iso.org

Published in Switzerland

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*.

A list of all parts in the ISO 4722 series can be found on the ISO website.

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, 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, 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, ^{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 Chornobyl 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. For example, during either a planned or existing situation, the WHO guidance level for ^{232}Th in drinking water is 1 $Bq{\cdot}l^{-1}$ (see NOTE). 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[5] and ISO 5667-20[6].

NOTE 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].

In the event of a nuclear emergency, the WHO Codex Guideline Levels[7] states that the activity concentration can possibly be not greater than 1 $Bq{\cdot}l^{-1}$ and 10 $Bq{\cdot}l^{-1}$ for ^{232}Th, respectively, for infants and other than infants.

This document contains a method to determine ^{232}Th in water samples. The test method has been developed to support laboratories to determine ^{232}Th in water samples.

The detection limit for measurement of a test portion of about 500 ml is approximately 5 $mBq{\cdot}l^{-1}$ with a counting time of about 200 000 s.

The methods described in this document can be used for various types of waters (see Clause 1). 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. This can be done for several reasons such as emergency situations, lower national guidance limits and operational requirements.

Water quality — Thorium 232 —

Part 1: Test method using alpha spectrometry

WARNING — Persons using this document should be familiar with normal laboratory practice. This document does not purport to address all 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 the method and the conditions for the determination of ^{232}Th activity concentration in samples of environmental water (including sea waters) and waste waters before release to the environment using alpha spectrometry and ^{229}Th as a recovery tracer. A chemical separation allows to separate and purify thorium from a test portion of the sample.

The general principles outlined in this document can be applied for the analysis of other alpha-emitting thorium isotopes such as ^{228}Th and ^{230}Th in aqueous samples.

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 11929-1, *Determination of the characteristic limits (decision threshold, detection limit and limits of the coverage interval) for measurements of ionizing radiation — Fundamentals and application — Part 1: Elementary applications*

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

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

3 Terms, definitions and symbols

3.1 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 11929-1 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

The symbols used in this document are listed in Table 1.

Table 1 — Symbols

Symbol	Description	Unit
A	Activity of the ^{229}Th tracer added	Bq
c_A	Activity concentration of ^{232}Th measured in the sample	Bq·l^{-1}
c_A^*	Decision threshold	Bq·l^{-1}
$c_A^\#$	Detection limit	Bq·l^{-1}
$c_A^\triangleleft, c_A^\triangleright$	Lower and upper limits of the probabilistically symmetric coverage interval of the measurand, respectively	Bq·l^{-1}
$c_A^<, c_A^>$	Lower and upper shortest coverage interval	Bq·l^{-1}
$\tilde{c}_A$	Possible or assumed true quantity values of the measurand	Bq·l^{-1}
k_p	Quantiles of the standardized normal distribution for the probability, p (for instance, $p = 1-\alpha$, $p = 1-\beta$ or $p = 1-\gamma / 2$)	—
p	Probability for "success", $p = 1-\alpha$, $p = 1-\beta$ or $p = 1-\gamma / 2$	—
q	Probability for "failure",	—
R	Total recovery	—
R_c	Chemical recovery	—
r_g	Gross count rate in the region of interest of ^{232}Th, the isotope to measure	s^{-1}
r_{gT}	Gross count rate in the region of interest of the ^{229}Th tracer	s^{-1}
r_{0T}	Background count rate in the region of interest of the ^{229}Th tracer	s^{-1}
r_0	Background or blank count rate in the region of interest of ^{232}Th, the isotope to measure	s^{-1}
t_0	Counting time of the background by alpha spectrometry	s
t_g	Sample counting time by alpha spectrometry	s
U	Expanded uncertainty	—
u_c	Standard uncertainty	—
$u(c_A)$	Standard uncertainty of the activity concentration of ^{232}Th	Bq·l^{-1}
$\tilde{u}(\tilde{c}_A)$	Standard uncertainty of the estimator c_A as a function of an assumed true value $\tilde{c}_A$ of the measurand	Bq·l^{-1}
u_{rel}	Standard uncertainty of the estimator c_A as a function of its detection limit	—
w	Estimate of the calibration factor	—
V	Sample volume	l
α	Probability of the false positive decision	—
β	Probability of the false negative decision	—
ε	Counting efficiency	—
$1-\gamma$	Probability for the coverage interval of the measurand	—
Φ	Distribution function of the standardized normal distribution	—
ω	Auxiliary quantity	—

4 Principle

The test sample is mixed with an aliquot of ^{229}Th tracer, followed by equilibration of the sample prior to analysis, chemical isolation of thorium by a concentration step (e.g. a precipitation) and a specific separation step (e.g. using ion exchange chromatography).

Uranium isotopes, ^{210}Po, ^{237}Np, ^{238}Pu or ^{241}Am can be present in water and can interfere with the counting of ^{232}Th and the ^{229}Th tracer if no chemical separation is carried out to remove these radionuclides from the water sample.

The measured thin source is prepared by electrodeposition or co-precipitation and measured by alpha spectrometry using a grid chamber or a semiconductor-type apparatus. Measurements rely on the interaction of alpha particles with the detecting medium. This interaction creates a charge, which is amplified and output as a voltage pulse proportional to the deposited energy of the incoming alpha-particle.

The electric pulse from the detector is analysed by the electronic systems. Data analysis software provides a spectrum, in which the number of pulses (counts) recorded in each energy interval is shown.

The analysis of the count rates in the ^{232}Th alpha energy window allows the determination of the test sample activity concentration for ^{232}Th, after correcting for the blank count rate, the volume of the test sample and the total measurement recovery (chemical recovery and detection efficiency).

The chemical recovery and detection efficiency are not necessarily determined separately but are determined together by measuring the total measurement recovery from the net count rate of ^{229}Th, added as a chemical recovery tracer.

For quality control and to quantify potential impurities in the tracer solution, a blank sample shall be prepared using grade 3 laboratory water in compliance with ISO 3696 with the addition of tracer. The radioactive characteristics of the main thorium isotopes are given in Table 2 (see References [8], [9] and [10]).

Table 2 — Characteristics of the main thorium isotopes

Thorium isotope	Half-life (uncertainty) years	Main alpha particle emission energy (uncertainty) keV	Intensity %
228	1,912 6 (9)	5 340,35 (22)	26,0
		5 423,24 (22)	73,4
229	7 880 (12)	4 845,3 (12)	56,2
		4 901,0 (12)	10,2
230	75 380 (30)	4 687,0 (15)	76,3
		4 620,5 (15)	23,4
232	$14{,}02\ (6) \times 10^{9}$	4 011,2 (14)	21,0
		3 948,5 (14)	78,9

5 Chemical reagents and equipment

5.1 General

The chemical reagents and equipment used for chemical treatment and preparation of the source are described in Annexes A to C, which give various options. Where there are choices, at least one of the options presented shall be used.

Use only reagents of recognized analytical grade.

5.2 Chemical reagents

5.2.1 Laboratory water, used as a blank, as free as possible of chemical or radioactive impurities (e.g. uranium or thorium isotopes), complying with ISO 3696, grade 3.

Unless otherwise stated, water refers to deionised water.

5.2.2 Tracer solution containing ^{229}Th can be used to determine the total recovery. It can also be used to calculate the chemical recovery. The solution is prepared by the dilution of a suitable standard that provides traceability to national and international standards. The tracer solution shall be homogeneous and stable.

The tracer solution concentration should be calculated to allow adding a small amount of this solution to be in the range of activity contained in the test portion. For example, the tracer solution concentration can be between 0,05 Bq·g^{-1} and 1 Bq·g^{-1}.

It is recommended that the activity and the purity of the tracer solution dilution be checked before use and at regular intervals after preparation. This can be done, for example, by liquid scintillation counting, but an account needs to be taken of progeny radionuclide ingrowth. Performing a blank analysis with tracer is a potential way to identify any presence of thorium isotope analytes in the tracer.

5.3 Equipment

Usual laboratory equipment and, in particular, the following.

5.3.1 Alpha spectrometer of the grid chamber (with higher detection recovery but lower resolution) or semiconductor type (with lower detection recovery, but higher resolution). Operation at constant temperature is recommended. Follow the manufacturer's instructions.

For semiconductor-type apparatus, the measurements using alpha spectrometry depend on the interaction of alpha particles with ion-implanted silicon. This interaction instantly changes the conductivity of the silicon, proportional to the energy of the incoming alpha particle. To achieve well-resolved spectra, the detection system needs to be maintained at a pressure <1 Pa. Resolution can be further enhanced by increasing the distance between the source and the detector. However, it has to be noted that counting efficiency will decrease which increases the measurement time.

5.3.2 Pipette, suitable for the accurate transfer of (e.g. 100 µl) ^{229}Th tracer solution with a total precision within ±1 %.

5.3.3 Balance capable of achieving ±0,1 mg precision.

6 Sampling, handling and storage

6.1 Sampling

Conditions of sampling shall conform to ISO 5667-1.

Filter the sample to remove solids and then acidify to pH less than 2 with nitric acid as soon as possible after sampling prior to analysis, as specified in ISO 5667-3. Acidification prior to filtration can result in leaching of thorium from the solid component of the sample.

It is important that the laboratory receive a representative sample, unmodified during transport or storage and in an undamaged container.

6.2 Sample storage

If the sample is not going to be analysed immediately, the sample shall be stored in accordance to ISO 5667-3.

7 Separation and measurement

7.1 Chemical steps

Suggested separation and source preparation strategies are outlined in Annexes A, B and C.

7.2 Measurement

7.2.1 Quality control

Equipment quality control sources shall be measured to verify that the measurement equipment is performing within the limits specified by the laboratory.

A thin source of $^{239/240}$Pu (other alpha-emitters such as ^{230}Th, ^{239}Pu, ^{244}Cm and ^{241}Am are also possible) can be employed to check the energy calibration and the resolution (alpha-emissions are in the 5,10 MeV to 5,20 MeV energy region); there should be no appreciable decay over the working life of the source.

7.2.2 Chemical recovery

The chemical recovery can be considered as a quality control parameter. In general, around 90 % chemical recovery can be achieved under normal controlled conditions. For very low chemical recovery which is not fit for purpose, the laboratory can decide to repeat the sample analysis.

The chemical recovery, R_c, of the process can be calculated using Formula (1):

$$R_c = \frac{R}{\varepsilon} \tag{1}$$

The total recovery, R, is the product of the chemical recovery, R_c, and the counting efficiency, ε.

The total recovery, R, is calculated from the sample spectrum using Formula (2):

$$R = \frac{\left(r_{gT} - r_{0T}\right)}{A} \tag{2}$$

7.2.3 Background

The background rate of each detector is determined with an empty source support. This shall take at least as much time as the counting of a sample.

The optimum time for the measurement of the background source can be shown to be equal to that of the source from very low activity sources.

The blank sample analysis (i.e. analysis carried out with laboratory water containing no detectable thorium isotope without adding tracer) value shall be compared to the totality of the background values obtained from the same detector.

This value can be comparable to the background value measured with an empty source support in the energy regions of ^{232}Th and of the tracer if there is no reagent or laboratory equipment contamination.

8 Expression of results

8.1 Spectrum analysis

The activity concentration of thorium is calculated by integrating the number of counts in the region of interest (ROI) of the ^{232}Th analyte and in the ROI corresponding to the tracer peak.

The results of these integrations are divided by the counting time and give the gross count rates.

Gross count rates are corrected for the detector background and the blank contribution in the same ROI.

8.2 Calculation of activity concentration

The activity concentration, c_A, expressed in becquerels per litre, of a radionuclide present in a sample is given by Formula (3):

$$c_A = \frac{r_g - r_0}{R.V} = (r_g - r_0).w \tag{3}$$

with $w = \frac{1}{R.V}$

8.3 Standard uncertainty

In the case of the measurement of radionuclides by alpha spectrometry, only the uncertainties of the following parameters are retained:

a) gross counts from measured thorium isotope and tracer;

b) background counts per second from thorium isotope and tracer;

c) tracer activity;

d) volume of test sample.

The other uncertainties can be neglected to a first approximation (counting time, etc.).

According to ISO/IEC Guide 98-3,[5] combined uncertainty of c_A is calculated by Formula (4):

$$u(c_A) = \sqrt{w^2\left[u^2(r_g) + u^2(r_0)\right] + c_A^2 u_{rel}^2(w)} = \sqrt{w^2\left(\frac{r_g}{t_g} + \frac{r_0}{t_0}\right) + c_A^2 u_{rel}^2(w)} \tag{4}$$

where the uncertainty of the counting time is neglected and the standard uncertainty of w is calculated using Formula (5):

$$u_{rel}^2(w) = u_{rel}^2(R) + u_{rel}^2(V) \tag{5}$$

The relative standard uncertainty in R is calculated using Formula (6):

$$u_{rel}^2(R) = u_{rel}^2(r_{gT} - r_{0T}) + u_{rel}^2(A) = (r_{gT}/t_g + r_{0T}/t_0)/(r_{gT} - r_{0T})^2 + u_{rel}^2(A) \tag{6}$$

where $u_{rel}^2(A)$ includes all the uncertainties related to the tracer activity: the standard solution activity, preparation of the tracer solution; addition of the tracer solution to the sample; correction for interferences; etc.

For the characteristic limits, $\tilde{u}(\tilde{c}_A)$, i.e. the combined uncertainty of c_A as a function of its true value (see also ISO 11929-1), shall be calculated with Formula (7):

$$\tilde{u}(\tilde{c}_A)=\sqrt{w^2\left[(\tilde{c}_A/w+r_0)/t_g+r_0/t_0\right]+\tilde{c}_A^2u_{rel}^2(w)} \tag{7}$$

NOTE If the mass of the test portion, m, is used, it is expressed in grams. The intermediate calculations are done with similar formulae. Activity concentration can also be converted to specific activity [m replacing V in Formulae (3) and (5)]. If activity per volume is converted by dividing by the density ρ, expressed in gram per litre, an uncertainty associated with the density is added in Formula (5).

8.4 Decision threshold

The decision threshold, c_A^*, expressed in becquerels per litre, is obtained from Formula (8) for $\tilde{c}_A=0$ (see ISO 11929-1):

$$c_A^*=k_{1-\alpha}\tilde{u}(0)=k_{1-\alpha}\cdot w\cdot\sqrt{(r_0/t_g)+(r_0/t_0)} \tag{8}$$

where α = 0,05 with $k_{1-\alpha}$ = 1,65 is often chosen by default.

8.5 Detection limit

The detection limit, $c_A^\#$, expressed in becquerels per litre, can be calculated by solving Formula (9):

$$c_A^\#=c_A^*+k_{1-\beta}\cdot\tilde{u}\left(c_A^\#\right)=c_A^*+k_{1-\beta}\sqrt{w^2\left[\left(c_A^\#/w+r_0\right)/t_g+\frac{r_0}{t_0}\right]+c_A^{\#2}u_{rel}^2(w)} \tag{9}$$

The detection limit can be calculated by solving Formula (9) for $c_A^\#$ or more simply by iteration with a starting approximation $c_A^\#=2c_A^*$ in terms of the right-hand side of Formula (10).

With $k_{1-\alpha}=k_{1-\beta}=k$:

$$c_A^\#=\frac{\dfrac{2c_A^*+k^2w}{t_g}}{1-k^2u_{rel}^2(w)} \tag{10}$$

Values $\alpha=\beta$ = 0,05 and therefore $k_{1-\alpha}=k_{1-\beta}$ = 1,65 are often chosen by default.

9 Limits of coverage intervals

9.1 Limits of the probabilistically symmetric coverage interval

The lower, $c_A^\triangleleft$, and upper, $c_A^\triangleright$, coverage limits are calculated using Formulae (11) and (12) according to ISO 11929-1:

$$c_A^\triangleleft=c_A-k_pu(c_A)\quad;\quad p=\omega\left(1-\frac{\gamma}{2}\right) \tag{11}$$

$$c_A^\triangleright=c_A+k_qu(c_A)\quad;\quad q=1-\frac{\omega\gamma}{2} \tag{12}$$

where $\omega=\Phi[c_A/u(c_A)]$, Φ being the distribution function of the standardized normal distribution.

The value of ω can be set to 1, if $c_A \geq 4u(c_A)$. In this case:

$$c_A^{\triangleleft}, c_A^{\triangleright} = c_A \pm k_{1-\gamma/2} u(c_A) \tag{13}$$

γ = 0,05 with $k_{1-\gamma/2}$ = 1,96 is often chosen by default.

9.2 Limits of the shortest coverage interval

As described in detail in ISO 11929-1, the lower limit of the shortest coverage interval, $c_A{}^{<}$, and the upper limit of the shortest coverage interval, $c_A{}^{>}$, are calculated from a primary measurement result, c_A, of the measurand and the standard uncertainty, $u(c_A)$, associated with c_A, either by Formula (14):

$$c_A{}^{<}, c_A{}^{>} = c_A \pm k_p \cdot u(c_A) \quad ; \quad p = [1 + \omega \cdot (1 - \gamma)]/2 \tag{14}$$

or if $c_A{}^{<} < 0$ were the result, by Formula (15):

$$c_A{}^{<} = 0 \quad ; \quad c_A{}^{>} = c_A \pm k_q \cdot u(c_A) \quad ; \quad q = 1 - \omega \cdot \gamma \tag{15}$$

where

$\omega = \Phi[y/u(y)]$, Φ is the distribution function of the standardized normal distribution;

The relations $0 \leq c_A{}^{<} < c_A{}^{>}$ apply and the approximation of Formula (13) is valid.

10 Test report

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

a) reference to this document (i.e. ISO 4722-1:2023);

b) the method used;

c) identification of the sample;

d) units in which the results are expressed;

e) the test result:

   1) when the activity concentration, c_A, is compared with the decision threshold (refer to the ISO 11929 series);

      — if the result is less than the decision threshold, the result of the measurement is expressed as $\leq c_A^*$,

      — if the result is greater than the decision threshold, the result of the measurement is expressed as $c_A \pm u_c(c_A)$ or $c_A \pm U$ with the associated k value,

   2) when the activity concentration, c_A, is compared with the detection limit;

      — if the result is less than the detection limit, the result of the measurement is expressed as $\leq c_A^{\#}$,

      — if the result is greater than the detection limit, the result of the measurement is expressed as $c_A \pm u_c(c_A)$ or $c_A \pm U$ with the associated k value.

f) any deviations from the procedure;

g) any unusual features observed;

h) the date of the test.

Complementary information can be provided such as:

i) the uncertainty can also be expressed as the limits of the probabilistically symmetric coverage interval $c_A^{\triangleleft}, c_A^{\triangleright}$ and/or the limits of the shortest coverage interval $c_A^{<}, c_A^{>}$;

j) probabilities α, β and $(1 - \gamma)$;

k) the decision threshold and the detection limit;

l) if the detection limit exceeds the guideline value, it shall be documented that the method is not suitable for the measurement purpose;

m) mention of any relevant information likely to affect the results.

NOTE Occasionally, it is requested by the customer or regulator to compare the primary measurement result, c_A, with the detection limit in order to decide whether the physical effect is recognized or not. Such stipulations are not in accordance with the ISO 11929 series. They have the consequence that it is decided too frequently that the physical effect is absent when in fact it is not absent.

Annex A
(informative)

Chemical separation of thorium

A.1 Sample preparation

The removal of suspended matter from a raw aqueous sample shall be performed as soon as possible after sampling.

Take a test portion of *V*, expressed in litres, (e.g. 0,5 l) or determine the mass, *m*, in kilograms, for analysis.

The sample test portion should be acidified to pH < 2.

There are several possibilities for the chemical separation of thorium. Examples are given in Clause A.2.

A.2 Thorium separation and purification examples

This procedure is based on References [11] and [12].

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 Nitric acid solution, c_{HNO3} = 2 mol·l^{-1}.

A.2.1.2 Ammonia solution, c_{NH4OH} = 14,5 mol·l^{-1}.

A.2.1.3 Carrier salt or solution. Calcium chloride ($CaCl_2$) or yttrium chloride (YCl_3) or iron(III) chloride ($FeCl_3$).

A.2.1.4 Ion-exchange or extraction chromatographic resin specific for tetravalent actinides.

A.2.1.5 Hydrochloric acid solution, c_{HCl} = 9 mol·l^{-1}, 8 mol·l^{-1}, 3 mol·l^{-1}, 0,1 mol·l^{-1}, 0,01 mol·l^{-1}.

A.2.1.6 Nitric acid solution, c_{HNO3} = 8 mol·l^{-1}, 6 mol·l^{-1}, 3 mol·l^{-1}.

A.2.1.7 Hydrochloric acid solution in oxalic acid. Dissolve 5 mol of HCl in 1 l of 0,05 mol·l^{-1} $C_2H_2O_4$.

A.2.1.8 Aluminium nitrate solution in nitric acid. Dissolve 1 mol $Al(NO_3)_3$ in 1 l of 3 mol·l^{-1} HNO_3.

A.2.1.9 Laboratory water, used as a blank, as free as possible of chemical or radioactive impurities (e.g. uranium or thorium isotopes), complying with ISO 3696, grade 3.

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 and tubes.

A.2.3 Tracer addition

Add an activity A of ^{229}Th recovery tracer which matches the order of magnitude of the ^{232}Th activity expected in the test sample.

Allow the tracer to equilibrate with the samples by stirring for 10 min.

Decay progeny radionuclides (^{225}Ra, ^{225}Ac etc.) grow in from ^{229}Th can recoil into the detector and interfere with the ^{232}Th analysis. Therefore, the background for each detector should be monitored regularly.

A.2.4 Concentration step

To concentrate the thorium in the sample, the solution can be evaporated (A.2.2.2) or coprecipitated.

It is possible to coprecipitate thorium with iron (III) or yttrium hydroxides or calcium phosphates.

Add the corresponding carrier salt or solution (A.2.1.3) in excess.

Stir and adjust to pH 9 for hydroxide precipitation or pH 12 for phosphate precipitation with a concentrated ammonia solution (A.2.1.2).

Allow to precipitate.

Centrifuge (A.2.2.3) and discard the supernatant.

Wash precipitate with water.

Centrifuge and discard the supernatant.

A.2.5 Separation and purification

A.2.5.1 Anion exchange option

Transfer the precipitate from A.2.4 to a clean, labelled beaker and then dissolve the precipitate in 20 ml 8 mol·l^{-1} of nitric acid (A.2.1.6).

Prepare a column (approximately 1 cm in diameter and approximately 7,5 cm long) containing 5 g of anion exchange resin[1)] (A.2.1.4) with 8 % cross-linking and a particle size of 100 mesh to 200 mesh, and condition with 10 ml of 8 mol·l^{-1} of nitric acid (A.2.1.6).

Introduce the sample to the column and let it pass through the column.

Wash the column twice with 15 ml of 8 mol·l^{-1} nitric acid (A.2.1.6); the column eluate can be discarded. Iron, uranium, radium, americium and Np(V) are removed by this treatment.

Remove thorium from the column by washing with 10 ml of 9 mol·l^{-1} hydrochloric acid (A.2.1.5) and collect the eluate in a clean glass beaker. Thorium is efficiently eluted from the column with 9 mol·l^{-1} hydrochloric acid (A.2.1.5) while Pu(IV), Np(IV) and residual uranium are retained on the resin.

The thorium solution is ready for use in the preparation of an alpha spectrometry source.

1) AG1 is an example of a suitable product available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of this product.

A.2.5.2 Extraction chromatography option

Transfer the precipitate (A.2.4) to a clean, labelled beaker and then dissolve the precipitate in 6 $mol \cdot l^{-1}$ of nitric acid (A.2.1.6).

Gently evaporate the resulting solution to dryness and then re-dissolve in 10 ml of $Al(NO_3)_3$ solution in HNO_3 (A.2.1.8).

Prepare a pre-packed column or cartridge containing 2 ml of resin specific for tetravalent actinides[2)] and condition with 5 ml of 3 $mol \cdot l^{-1}$ HNO_3 (A.2.1.6):

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

— wash the column with 30 ml of 3 $mol \cdot l^{-1}$ HNO_3 (A.2.1.6) to remove any uranium, radium or americium traces that can be present and discard the column eluate;

— elute thorium from the column by washing it with 15 ml of 9 $mol \cdot l^{-1}$ hydrochloric acid (A.2.1.5) and collect the eluate in a clean glass beaker.

This solution is ready for use in the preparation of counting sources for alpha spectrometry by electrodeposition (see Annex B) or coprecipitation (see Annex C).

A.2.5.3 Information about the source preparation technique choice

Both electrodeposition and microprecipitation methods have been commonly used for preparation of a thin-layer source for counting of thorium isotopes by alpha spectrometry. Selection of the source preparation method depends on laboratory preference. Each method has its own advantages over the other. The electrodeposition method usually yields better energy resolution, while microprecipitation method saves time for source preparation and is easier to set up for batch processing for high sample analysis throughput. Both methods can be affected by the presence of impurities in the sample matrix. For instance, organic residues in the sample can yield a lower counting efficiency and a worse resolution for alpha source prepared by electrodeposition; on the other hand, milligram levels of calcium in the sample cause a thicker alpha source using the fluoride microprecipitation method.

2) TEVA is an example of a suitable product available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of this product.

Annex B
(informative)

Preparation of the source by electrodeposition

B.1 Principle

A DC power supply is used to apply different voltages between two electrodes, resulting in the reduction of the metal cations dissolved in the electrolyte. The reduction that takes place at the cathode leads to the formation of a deposit of actinides in hydroxide form.

B.2 Reagents

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

B.2.1 Nitric acid solution, w_{HNO3} = 65 % mass fraction.

B.2.2 Sodium sulfate solution, c_{Na2SO4} = 0,3 mol·l^{-1}.

B.2.3 Sulfuric acid solution, w_{H2SO4} = 95 % to 97 % mass fraction.

B.2.4 Thymol blue, 0,4 g·l^{-1}.

B.2.5 Ammonia solution, ρ_{NH4OH} = 250 g·l^{-1}.

B.2.6 Sulfuric acid solution, ρ_{H2SO4} = 10 g·l^{-1}.

B.2.7 Ammonia solution, ρ_{NH4OH} = 1 g·l^{-1}.

B.2.8 Deionised water, used as a blank, as free as possible of chemical or radioactive impurities (e.g. thorium and uranium isotopes), complying with ISO 3696, grade 3.

B.3 Equipment

The electrodeposition apparatus is generally composed of the following components.

B.3.1 Glass, polytetrafluoroethylene (PTFE), or polyethylene electrodeposition cell.

B.3.2 Platinum wire (anode).

B.3.3 Stainless steel disk (cathode) with a diameter adapted to the electrodeposition cell.

B.3.4 DC power supply.

B.3.5 Hot plate.

B.3.6 Petri dish.

B.4 Procedure

B.4.1 General

This procedure is based on Reference [13] and ASTM C1284[14].

B.4.2 Assembly of the electrodeposition cell

This procedure refers to the electrodeposition apparatus designed for deposits on small diameter stainless steel disks (see Figure B.1). It can be possible to engrave identifying information on the reverse of the disk. The electrodeposition procedure for this type of apparatus is as follows.

Place the clean and degreased stainless-steel disk (B.3.3) in the cap assembly.

Screw the cell (B.3.1) with the cap assembly.

Fill the cell with water to check for leaks.

Empty the cell.

Fix the platinum wire (B.3.2) vertically to its support.

Attach the lower end of the wire to the side contact of the disk support; the distance between the wire and the disk is approximately 3 mm.

B.4.3 Electrodeposition

Using the preparation obtained from the chemical separation of thorium (see Annex A), carry out, for example, the following operations.

Evaporate to incipient dryness.

Add 1 ml of concentrated HNO_3 (B.2.1) and evaporate to near dryness. Repeat this step three times.

Add 1 ml of Na_2SO_4 solution (B.2.2) and evaporate to dryness.

Add 500 µl of concentrated H_2SO_4 (B.2.3).

Add 10 ml of water and three drops of thymol blue (B.2.4), and stir.

Adjust the pH to between 2,1 and 2,3 by adding concentrated ammonia solution (B.2.5) (colour changes from red to orange).

Transfer this solution (final volume between 10 ml and 15 ml) into the electrodeposition cell.

Rinse the beaker with dilute H_2SO_4 (B.2.6), whose pH is previously adjusted to 2,3; add the rinsing to the electrodeposition cell.

Set up the anode and carry out the electrodeposition (B.3.4) at a constant current density (about 0,1 $A \cdot cm^2$) for approximately 2 h.

Cool the plating cell, if necessary.

Add 1 ml of concentrated NH_4OH (B.2.5), 1 min before switching off the power supply.

Wait 1 min, remove the anode before switching off the power supply and quickly empty the cell.

Dismantle the apparatus, rinse the disk in water, then in dilute NH_4OH (B.2.7) and dry it [if necessary, on a hot plate (B.3.5)].

Identify the disk and place it in a plastic Petri dish (B.3.6).

The source is ready to be measured by alpha spectrometry.