
Water quality — Uranium isotopes — Test method using alpha-spectrometry

*Qualité de l'eau — Isotopes de l'uranium — Méthode d'essai par
spectrométrie alpha*

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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 documents 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).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

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, *Radiological methods*.

This second edition cancels and replaces the first edition (ISO 13166:2014), of which it constitutes a minor revision. The changes compared to the previous edition are as follows:

- update of the common introduction;
- update of the text considering the new ISO 11929 series published in 2019.

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

Radioactivity from several naturally occurring and anthropogenic sources is present throughout the environment. Thus, water bodies (e.g. surface waters, ground waters, sea waters) can contain radionuclides of natural, human-made, or both origins:

- Natural radionuclides, including ^{40}K , ^3H , ^{14}C , and those originating from the thorium and uranium decay series, in particular ^{226}Ra , ^{228}Ra , ^{234}U , ^{238}U , and ^{210}Pb , can be found in water for natural reasons (e.g. desorption from the soil and wash off by rain water) or can be released from technological processes involving naturally occurring radioactive materials (e.g. the mining and processing of mineral sands or phosphate fertilizer production and use);
- Human-made radionuclides, such as transuranium elements (americium, plutonium, neptunium, curium), ^3H , ^{14}C , ^{90}Sr , and gamma emitting radionuclides can also be found in natural waters. Small quantities of these radionuclides are discharged from nuclear fuel cycle facilities into the environment as the result of authorized routine releases. Some of these radionuclides used for medical and industrial applications are also released into the environment after use. Anthropogenic radionuclides are also found in waters as a result of past fallout contaminations resulting from the explosion in the atmosphere of nuclear devices and accidents such as those that occurred in Chernobyl and Fukushima.

Radionuclide activity concentration in water bodies can vary according to local geological characteristics, and climatic conditions and can be locally and temporally enhanced by releases from nuclear installation during planned, existing and emergency exposure situations^[1]. Drinking-water may thus contain radionuclides at activity concentrations which could present a risk to human health.

The radionuclides present in liquid effluents are usually controlled before being discharged into the environment^[2] and water bodies. Drinking water is monitored for its radioactivity content as recommended by the World Health Organization (WHO)^[3] so that proper actions can be taken to ensure that there is no adverse health effects to the public. Following these international recommendations, national regulation usually specify radionuclide authorized concentration limits for liquid effluent discharged to the environment and radionuclide guidance levels for water bodies and drinking waters for planned, existing and emergency exposure situations. Compliance with these limits can be assessed using measurement results with their associated uncertainties as specified by ISO/IEC Guide 98-3 and ISO 5667-20^[4].

Depending on the exposure situation, there are different limits and guidance levels that would result in an action to reduce health risk. As an example, during a planned or existing situation, the WHO guidance level in drinking water for ^{238}U and ^{234}U is 10 and 1 Bq · l⁻¹, respectively. The provisional guideline value for the concentration of uranium in drinking water is 30 µg · l⁻¹ based on its chemical toxicity, which is predominant compared with its radiological toxicity.

NOTE 1 The guidance level is the activity concentration with an intake of 2 l/d of drinking water for one year that results in an effective dose of 0,1 mSv/a for members of the public. This is an effective dose that represents a very low level of risk and which is not expected to give rise to any detectable adverse health effects^[3].

In the event of a nuclear emergency, the WHO Codex Guideline Levels^[5] mentioned that the activity concentration might be greater.

NOTE 2 The Codex guidelines levels (GLs) apply to radionuclides contained in foods destined for human consumption and traded internationally, which have been contaminated following a nuclear or radiological emergency. These GLs apply to food after reconstitution or as prepared for consumption, i.e., not to dried or concentrated foods, and are based on an intervention exemption level of 1 mSv in a year for members of the public (infant and adult)^[5].

Thus, the test method can be adapted so that the characteristic limits, decision threshold, detection limit and uncertainties ensure that the radionuclide activity concentrations test results can be verified to be below the guidance levels required by a national authority for either planned/existing situations or for an emergency situation^{[6][7]}.

Usually, the test methods can be adjusted to measure the activity concentration of the radionuclide(s) in either wastewaters before storage or in liquid effluents before being discharged to the environment. The test results will enable the plant/installation operator to verify that, before their discharge, wastewaters/liquid effluent radioactive activity concentrations do not exceed authorized limits.

The test method(s) described in this document may be used during planned, existing and emergency exposure situations as well as for wastewaters and liquid effluents with specific modifications that could increase the overall uncertainty, detection limit, and threshold.

The test method(s) may be used for water samples after proper sampling, sample handling, and test sample preparation (see the relevant part of the ISO 5667 series).

This document has been developed to answer the need of test laboratories carrying out these measurements that are sometimes required by national authorities, as they may have to obtain a specific accreditation for radionuclide measurement in drinking water samples.

This document is one of a family of International Standards on test methods dealing with the measurement of the activity concentration of radionuclides in water samples.

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Water quality — Uranium isotopes — Test method using alpha-spectrometry

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 absolutely essential that tests conducted according to this document be carried out by suitably trained staff.

1 Scope

This document specifies the conditions for the determination of uranium isotope activity concentration in samples of environmental water (including sea waters) using alpha-spectrometry and ^{232}U as a yield tracer.

A chemical separation is required to separate and purify uranium from a test portion of the sample.

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 11929-3, *Determination of the characteristic limits (decision threshold, detection limit and limits of the coverage interval) for measurements of ionizing radiation — Fundamentals and application — Part 3: Applications to unfolding methods*

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

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

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

3 Terms, definitions and symbols

For the purposes of this document, the terms, definitions, and symbols given in ISO 80000-10, ISO 11929-1 and the following apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— IEC Electropedia: available at <http://www.electropedia.org/>

— ISO Online browsing platform: available at <http://www.iso.org/obp>

Table 1 — Symbols and definitions

Symbol	Definition
A	activity of ^{232}U tracer added, in becquerel, at the date of measurement
c_A	activity concentration of ^{238}U or ^{235}U or ^{234}U , in becquerels per litre
c_A^*	decision threshold, in becquerels per litre
$c_A^\#$	detection limit, in becquerels per litre
$c_A^{\triangleleft}, c_A^{\triangleleft}$	lower and upper limits of the probabilistically symmetric coverage interval, in becquerels per litre
$c_A^{<}, c_A^{>}$	lower and upper limits of the shortest coverage interval, in becquerels per litre
R	total measurement yield
r_0, r_{0T}	background count rate per second for the uranium analytes and tracer in the respective regions of interest (ROI) of the blank sample spectrum
R_c	chemical yield
r_g, r_{gT}	gross count rate per second for the uranium analytes and tracer in the respective regions of interest (ROI) of the test sample spectrum
t_0	background counting time, in seconds
t_g	sample counting time, in seconds
U	expanded uncertainty, calculated by $U = ku(c_A)$ with $k = 1, 2, \dots$, in becquerels per litre
$u(c_A)$	standard uncertainty associated with the measurement result; in becquerels per litre
V	volume of test sample, in litres
ε	counting efficiency

4 Principle

The test sample is mixed with an aliquot of ^{232}U tracer, followed by equilibration of the sample prior to analysis. Chemical isolation of uranium is achieved by a concentration step (e.g. a precipitation) followed by a specific separation step (e.g. using ion exchange chromatography).

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

Natural radionuclides such as ^{230}Th , ^{226}Ra and ^{228}Th can be present in water and can interfere with the counting of uranium isotopes if no chemical separation is carried out to remove these radionuclides from the test portion. Plutonium isotopes can also interfere, if present with detectable activities in the sample.

The measured thin source is prepared by electrodeposition or coprecipitation 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 uranium isotopes alpha-energy windows allows the determination of the test sample activity concentration for ^{238}U , ^{235}U and ^{234}U , after correcting for the blank count rate, volume of the test sample and the total measurement yield (chemical yield and detection efficiency).

The chemical yield and detection efficiency are not necessarily determined separately, but are determined together by measuring the total measurement yield from the net count rate of ^{232}U , added as a chemical yield tracer.

In order 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 a laboratory water.

For quality control, in order to quantify potential impurities in the tracer solution, another blank sample shall be prepared with addition of tracer.

The radioactive characteristics of the main uranium isotopes are given in [Table 2](#) (References [8], [9]).

Table 2 — Radioactive characteristics of the main uranium isotopes

Uranium isotope	Half-life years	Main emission energy keV	Intensity %
232	70,6 ($\pm 1,1$)	5 263,48	30,6
		5 320,24	69,1
233	159,1 ($\pm 0,2$) $\times 10^3$	4 783,5	13,2
		4 824,2	84,3
234	2,455 ($\pm 0,006$) $\times 10^5$	4 722,4	28,42
		4 774,6	71,37
235	704 (± 1) $\times 10^6$	4 366,1	18,8
		4 397,8	57,19
		4 414,9	3,01
236	23,43 ($\pm 0,06$) $\times 10^6$	4 445	26,1
		4 494	73,8
238	4,468 ($\pm 0,005$) $\times 10^9$	4 151	22,33
		4 198	77,54

With a spectral resolution (FWHM full-width half-maximum height) of around 20 keV in best cases, alpha-spectrometry cannot easily resolve ^{233}U and ^{234}U , nor ^{235}U and ^{236}U , due to the similarity in their respective emission energies. However, ^{233}U and ^{236}U are normally not present in environmental samples or in quantities above their detection limits using alpha spectrometry (see [Annex D](#)).

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 alternatives. Where there are options, 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 isotopes), conforming to ISO 3696, grade 3.

Fresh rainwater is an example of water with a very low uranium activity concentration. The uranium activity concentration of this water can be evaluated at the same time as interferences from reagents or using another type of precise measurement, e.g. thermal ionization or inductively coupled plasma mass spectrometry.

5.2.2 ^{232}U tracer solution, used to determine the total yield. It can also be used to calculate the chemical yield. 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 in order to be in the range of activity contained in the test portion. For example, the tracer solution concentration could be between $0,05 \text{ Bq} \cdot \text{g}^{-1}$ and $1 \text{ Bq} \cdot \text{g}^{-1}$.

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 account needs to be taken of progeny radionuclide ingrowth. Performing a blank analysis with tracer is a potential way to identify any presence of uranium isotope analytes in the tracer.

^{228}Th is present in the ^{232}U tracer solution as a member of its decay series and has very close energy to that of ^{232}U . Therefore, separation between Th and U is required (References [10], [11]) to minimize the interference of ^{228}Th so that the counting yield of ^{232}U is not overestimated (see [Clause 4](#)).

5.3 Equipment

Usual laboratory apparatus and in particular the following:

5.3.1 Alpha-spectrometer, of the grid chamber (with higher detection yield, but lower resolution) or semiconductor type (with lower detection yield, 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 $<1 \text{ Pa}$. Resolution can be further enhanced through increasing distance between source and detector.

5.3.2 Pipette, suitable for the accurate transfer of (for example $100 \mu\text{l}$) ^{232}U tracer solution with a total precision within $\pm 1 \%$.

5.3.3 Balance, for example, capable of achieving $\pm 0,1 \text{ mg}$ precision.

6 Sampling and samples

6.1 Sampling

Conditions of sampling shall conform to ISO 5667-1.

Filter the sample to remove solids and then acidify to $< \text{pH } 2$ with nitric acid or hydrochloric 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 uranium from solids component of 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 required, the sample is shall be stored according 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](#) respectively.

7.2 Measurement

7.2.1 Quality control

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

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

7.2.2 Chemical yield

The chemical yield can be considered as a quality control parameter. In general, the chemical yield obtained is around 90 %. For very low chemical yields, it is recommended to redo the sample analysis.

The chemical yield R_c of the process can be calculated using [Formula \(1\)](#):

$$R_c = \frac{R}{\varepsilon} \quad (1)$$

Total yield R is the product of the chemical yield and the counting efficiency ε .

Total yield, R , is calculated from the sample spectrum using [Formula \(2\)](#):

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

7.2.3 Background

The background rate of each detector is determined with an empty source support with the lowest activity possible present on, 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 uranium 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 uranium isotopes and of the tracer if there is no reagent or laboratory equipment contamination.

r_0 is the blank value or can be the background value of the detector if similar.

8 Expression of results

8.1 Spectrum analysis

The activity concentration of the different isotopes of uranium is calculated by integrating the number of counts in the corresponding region of interest (ROI) of each uranium isotope 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, if needed, the blank contribution in the same ROI.

For ^{235}U , a correction factor is needed to take into account the percentage of emission in its ROI: as this isotope has 21 alpha-emissions, it is difficult to include them all in the classical ROI. A percentage around 80 % is usually reached.

8.2 Calculation of activity concentration

The symbols used are defined in [Clause 3](#).

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

$$c_A = \frac{r_g - r_0}{RV} = (r_g - r_0)w \quad (3)$$

$$w = \frac{1}{RV}$$

8.3 Standard uncertainty

In the particular case of the measurement of radionuclide by alpha-spectrometry, only the elementary uncertainties of the following parameters are retained:

- gross counts from measured uranium isotope and tracer;
- background counts per second from uranium isotope and tracer;
- tracer activity;
- volume of test sample.

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

According to ISO/IEC Guide 98-3, combined uncertainty of c_A is calculated by:

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

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

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

The relative standard uncertainty in R is calculated using [Formula \(6\)](#):

$$u_{\text{rel}}^2(R) = u_{\text{rel}}^2(r_{gT} - r_{0T}) + u_{\text{rel}}^2(A) = \left(\frac{r_{gT}}{t_g} + \frac{r_{0T}}{t_0} \right) / (r_{gT} - r_{0T})^2 + u_{\text{rel}}^2(A) \quad (6)$$

where $u_{\text{rel}}^2(A)$ 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 calculation of 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 series), is required, calculated by:

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

NOTE If the mass of the test portion, m , is used, it is expressed in grams. The intermediate calculations are done with similar equations. 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 in gram per litre, an uncertainty associated with the density is added in [Formula \(5\)](#).

8.4 Decision threshold

In accordance with ISO 11929-1 and ISO 11929-3, the decision threshold, c_A^* , in becquerels per litre, is obtained from [Formula \(7\)](#) for $\tilde{c}_A = 0$:

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

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

8.5 Detection limit

In accordance with ISO 11929-1 and ISO 11929-3, the detection limit, $c_A^\#$, in becquerels per litre, can be calculated by solving [Formula \(9\)](#):

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

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 \(9\)](#).

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

$$c_A^\# = \frac{2c_A^* + (k^2 w)/t_g}{1 - [k^2 u_{\text{rel}}^2(w)]} \quad (10)$$

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

8.6 Limits of the coverage interval

8.6.1 Limits of the probabilistically symmetric coverage interval

The lower, $c_A^<$, and upper, $c_A^>$, coverage limits, are calculated using (according to ISO 11929-1 and ISO 11929-3) [Formulae \(11\)](#) and [\(12\)](#):

$$c_A^< = c_A - k_p u(c_A); p = \omega \left(1 - \frac{\gamma}{2}\right) \quad (11)$$

$$c_A^> = c_A + k_q u(c_A); q = 1 - \frac{\omega\gamma}{2} \quad (12)$$

where

$$\omega = \Phi \left[\frac{c_A}{u(c_A)} \right]$$

Φ being the distribution function of the standardized normal distribution and $1 - \gamma$, the probability that the true value of c_A is situated in the coverage interval.

Set $\omega = 1$, if $c_A \geq 4 u(c_A)$. In this case:

$$c_A^{<>} = c_A \pm k_{1-\gamma/2} u(c_A) \quad (13)$$

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

8.6.2 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:

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

or if $c_A < 0$, by:

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

where

$$\omega = \Phi \left[\frac{c_A}{u(c_A)} \right]$$

Φ being the distribution function of the standardized normal distribution.

The relation: $0 \leq c_A^< < c_A^>$ applies and the approximation of [Formulae \(11\)](#) and [\(12\)](#) is valid.

9 Test report

The test report shall conform to the requirements of ISO/IEC 17025 and should contain at least the following information:

- a) reference to the measurement and evaluation procedure used and to this document (ISO 13166:2020);
- b) identification of the sample;
- c) units in which the results are expressed;
- d) test result,
 - 1) when the activity concentration, c_A , is compared with the decision threshold (see 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 $c_A \pm u(c_A)$ 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 $c_A \pm u(c_A)$ or $c_A \pm U$ with the associated k -value.

NOTE Note that $U = k u(c_A)$ with $k = 1$ or 2 .

Complementary information can be provided such as:

- e) chemical yield;
- f) probabilities α , β and $(1 - \gamma)$;
- g) decision threshold and the detection limit;

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

- h) the uncertainty can also be expressed as the limits of the probabilistically symmetric coverage interval $c_A^<, c_A^>$ and/or the limits of the shortest coverage interval $c_A^<, c_A^>$;
- i) mention of any relevant information likely to affect or explaining the results.

Annex A (informative)

Chemical separation of uranium

A.1 Sample preparation

If necessary on a raw sample, the removal of suspended matter shall be performed as soon as possible after the sampling.

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

Acidify the sample test portion to $< \text{pH } 2$.

There are several possibilities for the chemical separation of uranium. Examples are given in [A.2](#).

A.2 Uranium separation and purification examples

This procedure is based on References [\[10\]](#), [\[11\]](#), [\[12\]](#).

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 Concentrated nitric acid, $w(\text{HNO}_3) = 65\%$ (mass fraction).

A.2.1.2 Concentrated ammonia, $c(\text{NH}_4\text{OH}) = 250 \text{ g l}^{-1}$.

A.2.1.3 Carrier salt or solution. Calcium phosphate $[\text{Ca}_3(\text{PO}_4)_2]$ or yttrium chloride (YCl_3), or iron(III) chloride (FeCl_3).

A.2.1.4 Anion exchange resin or chromatographic extraction resin.

A.2.1.5 Hydrochloric acid, $c(\text{HCl})$: 9 mol/l, 8 mol/l, 3 mol/l, 0,1 mol/l, 0,01 mol/l.

A.2.1.6 Nitric acid, $c(\text{HNO}_3)$: 7,2 mol/l, 7 mol/l, 6 mol/l, 3 mol/l.

A.2.1.7 Hydrochloric acid solution in oxalic acid. Dissolve 5 mol of HCl in 1 l of 0,05 mol/l $\text{C}_2\text{H}_2\text{O}_4$.

A.2.1.8 Aluminium nitrate solution in nitric acid. Dissolve 1 mol $\text{Al}(\text{NO}_3)_3$ in 1 l of 3 mol/l HNO_3 .

A.2.1.9 Laboratory water, used as a blank, as free as possible of chemical or radioactive impurities (e.g. uranium isotopes), conforming to 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 ^{232}U yield tracer similar to the activities of the uranium isotopes to be measured in the test portion.

Allow the tracer to equilibrate with the samples by warming.

NOTE The half-life of ^{232}U is $70,6 \pm 1,1$ years; see Reference [9].

The progeny radionuclides (^{228}Th , ^{224}Ra , et seq.) grow in from ^{232}U , and may interfere with other analytes.

Thorium-228 may recoil into the detector from decay of ^{232}U , and the background for each detector should be monitored for this potential source of interference.

A.2.4 Concentration step

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

It is possible to coprecipitate uranium 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 concentrated ammonia solution (A.2.1.2).

Allow to precipitate.

Centrifuge (A.2.2.3) and discard the supernatant.

Wash 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 50 ml 7 mol/l nitric acid (A.2.1.6). Gently evaporate the resulting solution to dryness and then redissolve in the minimum volume of 8 mol/l hydrochloric acid (A.2.1.5) (around 20 ml).

Prepare a column containing 5 g of anion exchange resin¹⁾ (A.2.1.4) with 8 % cross-linking and a particle size of 100 mesh to 200 mesh (approximately 1 cm diameter and approximately 7,5 cm long), and condition with 10 ml 8 mol/l hydrochloric acid.

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

Wash the column twice with 15 ml 8 mol/l hydrochloric acid; the column eluate can be discarded. Any thorium and radium is removed by this treatment.

Wash the column with 10 ml 3 mol/l hydrochloric acid (A.2.1.5), discarding the eluate. Neptunium and plutonium are removed by this treatment.

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.

Wash the column with no more than 15 ml 7,2 mol/l nitric acid (A.2.1.6). Iron is removed by this treatment.

Remove uranium from the column by washing with 10 ml 0,1 mol/l hydrochloric acid (A.2.1.5) and collect the eluate in a clean glass beaker.

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

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/l nitric acid (A.2.1.6).

Gently evaporate the resulting solution to dryness and then redissolve in 10 ml of $\text{Al}(\text{NO}_3)_3$ solution in HNO_3 (A.2.1.8).

If plutonium, neptunium, and thorium require removal (Reference [11]), first prepare a prepacked chromatographic extraction column containing 2 ml of specific resin (A.2.1.4) and a particle size of 100 mesh to 150 mesh, and condition with 5 ml 3 mol/l HNO_3 (A.2.1.6):

- introduce the sample into the column, and allow it to pass through the column;
- wash the column with 5 ml 3 mol/l HNO_3 ; the column eluate contains uranium — any thorium and radium is retained by the extraction chromatography medium²⁾ (as is plutonium and neptunium).

Prepare the specific uranium chromatography medium³⁾ pre-packed column containing 2 ml of resin and a particle size of 100 mesh to 150 mesh, and condition with 5 ml 3 mol/l HNO_3 (Reference [9]):

- introduce the sample into the column, and allow it to pass through;
- wash the column with 6 ml 3 mol/l HNO_3 , discard the column eluate;
- wash the column with 5 ml 9 mol/l hydrochloric acid (A.2.1.5) — the resin is converted to the chloride form;
- wash the column with 20 ml hydrochloric acid solution in oxalic acid (A.2.1.7) to remove any thorium, plutonium and neptunium that may be present;
- remove purified uranium from the column by washing it with 15 ml 0,01 mol/l hydrochloric acid (A.2.1.5) and collect the eluate in a clean glass beaker.

The solution is ready for use in the preparation of an alpha-spectrometry source: See Annexes B and 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 uranium 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 a 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 of the methods might be affected by the presence of impurities in the sample matrix. For instance, organic residues in the sample could 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.

3) UTEVA 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)

Precipitation 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 Concentrated nitric acid, $w(\text{HNO}_3) = 65\%$ mass fraction.

B.2.2 Sodium sulfate, $c(\text{Na}_2\text{SO}_4) = 0,3\text{ mol/l}$.

B.2.3 Concentrated sulfuric acid, $w(\text{H}_2\text{SO}_4)$: 95 % to 97 % mass fraction.

B.2.4 Thymol blue, $0,4\text{ g l}^{-1}$.

B.2.5 Concentrated ammonia, $\rho(\text{NH}_4\text{OH}) = 250\text{ g l}^{-1}$.

B.2.6 Sulfuric acid, $\rho(\text{H}_2\text{SO}_4) = 1,84\text{ g l}^{-1}$.

B.2.7 Ammonia, $\rho(\text{NH}_4\text{OH}) = 1\text{ g l}^{-1}$.

B.2.8 Laboratory water, used as a blank, as free as possible of chemical or radioactive impurities (e.g. uranium isotopes), conforming to ISO 3696, grade 3.

B.3 Equipment

The electrodeposition apparatus is generally composed of the following components.

B.3.1 Glass, Teflon 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 may 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 uranium ([Annex A](#)), carry out, for example, the following operations.

Evaporate to near dryness, taking care to avoid evaporating the sample to complete 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 3 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 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 rinsings 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. 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.