International
Standard

ISO 13165-3

Second edition
2024-12

Water quality — Radium-226 —

Part 3:
Test method using coprecipitation and gamma-ray spectrometry

Qualité de l'eau — Radium-226 —

Partie 3: Méthode d’essai par coprécipitation et spectrométrie gamma

Reference number
ISO 13165-3:2024(en)

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Published in Switzerland

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Foreword

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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*, in collaboration with the European Committee for Standardization (CEN) Technical Committee CEN/TC 230, *Water analysis*, in accordance with the Agreement on technical cooperation between ISO and CEN (Vienna Agreement).

This second edition cancels and replaces the first edition (ISO 13165-3:2016), which has been technically revised.

The main changes are as follows:

- the introduction has been completely revised;
- the principal of measurement in Clause 5 has been expanded;
- the instrument verification subclause (formerly 9.3) has been deleted;
- formulae for the coverage intervals according to ISO 11929 series have been updated;
- requirements of the test report have been updated.

A list of all parts in the ISO 13165 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 (see Annex A), 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 the 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, Cm) and some gamma emitting radionuclides, such as ^{60}Co, ^{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 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. As an example, during either a planned or existing situation, the WHO guidance level for ^{226}Ra in drinking water is 1 $\mathrm{Bq \cdot l^{-1}}$, 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 $\mathrm{l \cdot d^{-1}}$ of drinking water for one year, results in an effective dose of 0,1 $\mathrm{mSv \cdot a^{-1}}$ 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 ^{226}Ra in water samples.

The method described in this document can be used for various types of waters (see Clause 1). Minor modifications to, for example, the sample volume and the 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.

This document deals with the measurement of the activity concentration of radionuclides in water samples.

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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 are carried out by suitably trained staff.

1 Scope

This document specifies a method to determine radium-226 (^{226}Ra) activity concentration in all types of water by coprecipitation followed by gamma-ray spectrometry (see ISO 20042[7]).

The method covers the measurement of soluble ^{226}Ra activity concentrations greater than 0,002 Bq·l^{-1} using a sample volume of up to 100 l of any water type.

For water samples with a volume of less than a volume of 1 l, direct gamma-ray spectrometry can be performed following ISO 10703 but with a higher detection limit. The typical detection limit for samples of 1 l to 5 l is in the range of 0,002 to 0,000 40 Bq·l^{-1}[8].

NOTE This test method can be adapted to determine other naturally occurring isotopes of radium, such as ^{223}Ra, ^{224}Ra and ^{228}Ra, if the respective ingrowth periods are taken into account.

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 5667-3, *Water quality — Sampling — Part 3: Preservation and handling of water samples*

ISO 10703, *Water quality — Gamma-ray emitting radionuclides — Test method using high resolution gamma-ray spectrometry*

ISO 11929 (all parts), *Determination of the characteristic limits (decision threshold, detection limit and limits of the coverage interval) for measurements of ionizing radiation*

ISO 12749-1, *Nuclear energy — Vocabulary — Part 1: General terminology*

ISO 12749-2, *Nuclear energy, nuclear technologies, and radiological protection — Vocabulary — Part 2: Radiological protection*

ISO 12749-3, *Nuclear energy, nuclear technologies, and radiological protection — Vocabulary — Part 3: Nuclear installations, processes and technologies*

ISO 12749-4, *Nuclear energy, nuclear technologies, and radiological protection — Vocabulary — Part 4: Dosimetry for radiation processing*

ISO 12749-5, *Nuclear energy, nuclear technologies, and radiological protection — Vocabulary — Part 5: Nuclear reactors*

ISO 12749-6, *Nuclear energy, nuclear technologies, and radiological protection — Vocabulary — Part 6: Nuclear medicine*

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 and definitions

For the purposes of this document, the terms and definitions given in ISO 12749-1, ISO 12749-2, ISO 12749-3, ISO 12749-4, ISO 12749-5, ISO 12749-6, ISO 80000-10 and the following 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/

3.1
activity
number of spontaneous nuclear disintegrations occurring in a given quantity of material during a suitably small interval of time divided by that interval of time

4 Symbols

For the purposes of this document, the following symbols apply.

A	Activity of each radionuclide in calibration source, at the time of calibration	Bq
c_A	Activity concentration of ^{226}Ra, without and with corrections	$\text{Bq}\cdot\text{l}^{-1}$
c_A^*	Decision threshold, without and with corrections	$\text{Bq}\cdot\text{l}^{-1}$
$c_A^\#$	Detection limit, without and with corrections	$\text{Bq}\cdot\text{l}^{-1}$
$\tilde{c}_A$	Possible or assumed true quantity values of the measurand	$\text{Bq}\cdot\text{l}^{-1}$
$c_A^\triangleleft$	Lower limit of the probabilistically symmetric coverage interval of the measurand	$\text{Bq}\cdot\text{l}^{-1}$
$c_A^\triangleright$	Upper limit of the probabilistically symmetric coverage interval of the measurand	$\text{Bq}\cdot\text{l}^{-1}$
$c_A^<$	Lower limit of the shortest coverage interval of the measurand	$\text{Bq}\cdot\text{l}^{-1}$
$c_A^>$	Upper limit of the shortest coverage interval of the measurand	$\text{Bq}\cdot\text{l}^{-1}$
ε_E	Detection efficiency at energy, E, at actual measurement geometry	—
f_E	Correction factor considering all necessary corrections	—
k_p	Quantiles of the standardised normal distribution for the probabilities p (for instance $p=1-\alpha$, $p=1-\beta$ or $p=1-\gamma/2$)	—
k_q	Quantiles of the standardised normal distribution for the probabilities q (for instance $q=1-\alpha$, $q=1-\beta$ or $q=1-\gamma/2$)	—

$m_{\text{carbonate}}$	Mass of barium carbonate	g
m_{nitrate}	Mass of barium nitrate	g
m_{sulfate}	Mass of barium sulfate	g
$n_{\text{b},E}$	Number of counts in the background of the peak considered, at energy E, in the sample	—
$n_{\text{b0},E}$	Number of counts in the background of the peak considered, at energy E, in the background	—
$n_{\text{bs},E}$	Number of counts in the background of the peak considered, at energy E, in the standard	—
$n_{\text{g},E}$	Number of counts in the gross area of the peak considered, at energy E, in the sample	—
$n_{\text{g0},E}$	Number of counts in the gross area of the peak considered, at energy E, in the background	—
$n_{\text{gs},E}$	Number of counts in the gross area of the peak considered, at energy E, in the standard	—
$n_{\text{N},E}$	Number of counts in the net area of the peak considered, at energy E, in the sample	—
$n_{\text{N0},E}$	Number of counts in the net area of the peak considered, at energy E, in the background	—
$n_{\text{Ns},E}$	Number of counts in the net area of the peak considered, at energy E, in the standard	—
P_E	Probability of the emission of a gamma-ray with energy E of each radionuclide, per decay	—
R_c	Chemical yield	—
t_0	Background spectrum counting time	s
t_g	Sample spectrum counting time	s
t_s	Standard spectrum counting time	s
U	Expanded uncertainty calculated with $k = 2$	$\text{Bq}\cdot\text{l}^{-1}$
$u(c_A)$	Standard uncertainty associated with the measurement result	$\text{Bq}\cdot\text{l}^{-1}$
$\tilde{u}(\tilde{c}_A)$	Standard uncertainty of the estimator c_A as a function of an assumed true value $\tilde{c}_A$ of the measurand	$\text{Bq}\cdot\text{l}^{-1}$
$u(\text{fit})$	Standard uncertainty associated with fitting efficiency curve	$\text{Bq}\cdot\text{l}^{-1}$
V	Volume of the test sample	l
Φ	Distribution function of the standardized normal distribution	—
w	Estimated value for the calibration factor	—
ω	Auxiliary quantity	—

5 Principle

Measurement of ^{226}Ra activity concentration in water is carried out in two separate steps: a sample preparation step, followed by a measurement using gamma-ray spectrometry[9],[10].

After filtration and acidification of the water sample (see ISO 5667-3), to ensure that only the soluble fraction of the ^{226}Ra is measured, the ^{226}Ra is coprecipitated as its sulfate salt using a barium carrier. Radium and barium sulfates are then washed, dried and weighed. The chemical yield is obtained gravimetrically.

For water samples that can have an existing concentration of soluble barium, another tracer should be used to avoid a chemical yield above 100 %.

When a radiometric tracer, such as ^{133}Ba is used as an internal standard, the recovery yield is used instead of the chemical yield, R_c, in Formulae (2) and (5). A correction of counting losses due to coincidence is then required for the determination of ^{133}Ba.

The ^{226}Ra activity concentration of the precipitate is measured by gamma-ray spectrometry using a high purity germanium detector.

Secular equilibrium between ^{222}Rn and its progenies is a prerequisite when measuring ^{226}Ra using ^{214}Bi and ^{214}Pb gamma rays. The equilibrium is reached four weeks after the last coprecipitation step. The sample container shall be air-tight to achieve equilibrium conditions.

The presence of other gamma-ray emitters, such as ^{235}U, in the precipitate can interfere with the quantification of ^{226}Ra activity.

NOTE Since the coprecipitation described in this test method does not allow for the determination of specific radium isotopes, it can be adapted to determine other naturally occurring isotopes of radium, such as ^{223}Ra, ^{224}Ra and ^{228}Ra, if the respective ingrowth periods are taken into account. For this method, however, the equilibrium time of four weeks does not allow for the determination of ^{223}Ra, ^{224}Ra or ^{228}Ra.

6 Reagents and equipment

6.1 Reagents

Unless otherwise stated, use only reagents of recognized analytical grade.

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

6.1.2 Concentrated nitric acid solution, $c(HNO_3) = 14{,}5\ mol \cdot l^{-1}$ to $15{,}5\ mol \cdot l^{-1}$.

6.1.3 Nitric acid solution, $c(HNO_3) = 0{,}4\ mol \cdot l^{-1}$.

6.1.4 Nitric acid solution, $c(HNO_3) = 3{,}2\ mol \cdot l^{-1}$.

6.1.5 Carrier solution, $c(Ba^{2+}) = 10{,}0\ g \cdot l^{-1}$.

Slowly dissolve barium nitrate $Ba(NO_3)_2$ (19,0 g) or barium carbonate $BaCO_3$ (14,3 g) in one litre of nitric acid solution (6.1.3). The salt mass shall be weighed accurately (better than 1 %) and recorded.

It is recommended to use a $Ba(NO_3)_2$ or $BaCO_3$ reagent with a low ^{226}Ra activity concentration. The presence of ^{226}Ra in the reagent shall be controlled using a blank sample prepared with distilled or demineralized water.

6.1.6 Concentrated sulfuric acid solution, $c(H_2SO_4) = 18{,}3\ mol \cdot l^{-1}$.

6.1.7 Cellulose ester filter, of porosity 0,45 µm.

6.2 Equipment

Usual laboratory equipment and, in particular, the following.

6.2.1 Peristaltic or membrane pump.

6.2.2 Magnetic bar stirrer.

6.2.3 Centrifuge tubes.

6.2.4 Analytical balance, for example, capable of achieving ±0,1 mg precision.

6.2.5 Drying oven.

6.2.6 Gas-tight container.

6.2.7 Gamma-ray spectrometry system, with low background capability.

Major instrument parameters (energy calibration, efficiency calibration as a function of energy and background spectrum) shall be periodically checked within a quality assurance programme established by the laboratory and following the manufacturer's instructions (see ISO 10703 and ISO 20042[7]).

7 Sampling

7.1 General

The method can be used on water samples up to 100 l.

7.2 Sample collection

The sampling conditions shall comply with ISO 5667-3 and ISO 10703. For sampling, polyethylene bottles should be used, cleaned with 1 mol·l^{-1} hydrochloric acid, followed by leaching with dilute nitric acid solution and rinsed with distilled or demineralised water (other cleaning treatments can be used if their effectiveness is demonstrated).

Depending on the elapsed time between sampling and measurement (e.g. if storage is more than seven days), the sample should be acidified to pH 1 with nitric acid. If particulate matter is removed by filtration, this shall be carried out before acidification.

The volume of the water sample to be collected for measurement depends on the detection limits required.

7.3 Sample transportation and storage

The water sample shall be transported and stored in accordance with ISO 5667-3.

When pre-concentration is desired, acidify the filtered sample to a pH between 1 and 3 with HNO_3. Acidification of the water sample minimizes the loss of radioactive material from solution by adsorption. It is advisable to store liquids at lower temperatures.

The test shall be performed as soon as possible.

8 Procedure

8.1 Blank sample preparation

Prepare a blank with distilled or demineralized water by performing the steps described in 8.2 a) to i).

8.2 Sample preparation

Sample preparation is carried out as follows.

a) To prevent adsorption effects and proliferation of algae, the water sample is filtered and acidified to pH 1 with concentrated nitric acid solution (see 6.1.2). The water sample volume can be up to 100 l.

Acidification of the sample shall not be performed with hydrochloric acid as barium sulfate is partially soluble in it.

b) Pour dropwise, precisely, 50 ml of carrier solution (see 6.1.5) into the solution to be analysed, with vigorous stirring. In the case of natural water rich in sulfate ions, such as seawater, the barium and radium have to be mixed before the sulfate is precipitated.

c) Add 20 ml of concentrated H_2SO_4 (see 6.1.6) to precipitate the sulfate.

d) Mix for a few minutes to homogenize the mixture, and then stop mixing.

e) Leave the barium radium sulfate precipitate $Ba(Ra)SO_4$ to settle for 24 h or until no further precipitation occurs.

f) Remove most of the supernatant, for example using a pump, and centrifuge the remaining mixture at 2 000 r/min for 5 min or filter to recover the precipitate.

g) Wash the precipitate with 3,2 mol·l^{-1} nitric acid (see 6.1.4) in the centrifuge tube, shake and centrifuge again. Repeat steps f) and g) twice.

h) Discard the supernatant.

i) Rinse the precipitate with water (e.g. shaking and centrifuging each time).

j) Dry the precipitate in an oven at 105 °C for at least 24 h.

k) Weigh a gas-tight container.

l) Place the precipitate in the weighed gas-tight container and seal tightly to prevent any loss of radon (see ISO 20042[7]).

m) Weigh the container.

8.3 Counting procedure

In order to achieve low detection limits using gamma-ray spectrometry, the ^{226}Ra activity is determined using the detection of emissions of ^{214}Pb at 351,9 keV and/or ^{214}Bi at 609,3 keV following an ingrowth period of approximately four weeks after which, secular equilibrium with ^{226}Ra is reached.[12] However, it requires that the sample is in a gas-tight container. Calibration shall be performed using the same geometry as the one used to count the sample precipitate.

The ^{226}Ra activity concentration can also be determined directly from its own energy emission at 186,2 keV, without the need for decay products ingrowth[11]. The disadvantages of this technique are that the emission probability of this gamma photopeak is low (3,28 %), and furthermore, ^{235}U, which has a gamma-ray emission at 185,7 keV with a high emission probability of 57,2 % can interfere.

9 Quality assurance and quality control programme

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.

9.2 Interferences

Special precautions shall be taken to minimize the interferences that can affect the measurement results:

— loss of ^{222}Rn from the container;

— ^{226}Ra present in the $Ba(NO_3)_2$ or $BaCO_3$ reagent; the presence of ^{226}Ra in the reagents shall be assessed by measuring a blank sample;

- significant radon activity concentration variations which can be observed in the atmosphere of the laboratory. The continuous monitoring of the ^{222}Rn activity concentration in the laboratory using a radon measuring device is recommended, since even in well-ventilated rooms, considerable variations are possible in special weather conditions (see ISO 11665-1[12] and ISO 11665-5[13]).[14] In case of significant ^{222}Rn activity, this can be accounted for by ensuring identical environmental conditions between the background and sample measurement, and, in some cases, sufficiently long counting times can be used for both sample and background to eliminate short term background fluctuations;
- release of radon from material within the laboratory walls. In order to limit the release of radon from material within the walls, the walls of the laboratory should be painted with a suitable material such as epoxy paint.[12] To maintain a constant temperature and relative humidity, the air should be continuously renewed through an air-conditioning system.

A case can be added around the detector and filled with a radon-free gas (e.g. N_2, air passed through a granulated activated charcoal filter) in order to prevent any accumulation of radon in the vicinity of the detector.

9.3 Method verification

Periodic verifications of the accuracy of the method shall be performed.[15] These verifications can be accomplished by:

- participating in intercomparison exercises;
- analysing reference materials.

Method repeatability shall also be checked, for example, by replicate measurements.

The acceptance limits of the verification tests shall be defined.

9.4 Demonstration of analyst capability

If an analyst has not used this procedure before, a precision and bias test shall be performed by running measurements of a reference or spiked material. Acceptance limits shall be specified by the laboratory.

A similar test shall be performed by analysts routinely using this procedure with a periodicity defined by the laboratory. Acceptance limits shall be specified.

10 Expression of results

10.1 General

Except for the chemical yield, R_c, computation for calculation of the activity concentration is described in ISO 10703, and in Clause 10, only the final formulae are presented.

10.2 Water-soluble ^{226}Ra activity concentration

The activity concentration measured by gamma-ray spectrometry, expressed in $\text{Bq}\cdot\text{l}^{-1}$, shall be corrected for the barium sulfate or other precipitation yield (R_c) determination. Formula (1) describes how to incorporate the gravimetrically determined yield. As described in Clause 5, it is also possible to use a radiometric tracer, such as ^{133}Ba to assess the recovery yield and to use that instead of R_c in Formulae (1), (2) and (5).

This recovery yield is the ratio of the mass of separated barium sulfate to the mass of barium nitrate or barium carbonate:

$$R_c = \frac{m_{\text{sulfate}}}{m_{\text{nitrate}}} \cdot 1{,}119\ 8 \quad \text{or} \quad R_c = \frac{m_{\text{sulfate}}}{m_{\text{carbonate}}} \cdot 0{,}845\ 5 \qquad (1)$$

where 1,119 8 and 0,845 5 are the molar mass ratios.

Thus, for an undisturbed peak at an energy, E, the activity concentration measured by gamma-ray spectroscopy is expressed in Bq·l^{-1} as shown in Formula (2):

$$c_A = \frac{n_{\mathrm{g},E} - n_{\mathrm{b},E}}{P_E \cdot \varepsilon_E \cdot V \cdot R_\mathrm{c} \cdot f_E \cdot t_\mathrm{g}} = \left(n_{\mathrm{N},E}\right) \cdot \frac{w}{t_\mathrm{g}} \tag{2}$$

with $w = \dfrac{1}{P_E \cdot \varepsilon_E \cdot V \cdot R_\mathrm{c} \cdot f_E}$

where ε_E is given by the calibration curve in the measurement set-up.

$$\varepsilon_E = \frac{n_{\mathrm{Ns},E} / t_\mathrm{s}}{A \cdot P_E} \tag{3}$$

It should be considered that for the purpose of this document, the correction factor, f_E, that appears in ISO 10703, is taken to be equal to 1. If the determination of the ^{226}Ra is based on the activity of the ^{214}Bi, a correction of counting losses due to coincidence should be required, the correction factor, f_E, that appears in ISO 10703 should be different than 1.

10.3 Standard uncertainty of activity concentration

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

$$u(c_A) = \sqrt{\left(w / t_\mathrm{g}\right)^2 \cdot \left[u^2\left(n_{\mathrm{g},E}\right) + u^2\left(n_{\mathrm{b},E}\right)\right] + c_A^2 \cdot u_\mathrm{rel}^2(w)} \tag{4}$$

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

$$u_\mathrm{rel}^2(w) = u_\mathrm{rel}^2(P_E) + u_\mathrm{rel}^2(V) + u_\mathrm{rel}^2(\varepsilon_E) + u_\mathrm{rel}^2(R_\mathrm{c}) + u_\mathrm{rel}^2(f_E) \tag{5}$$

The standard uncertainty of the efficiency is given by Formula (6):

$$u_\mathrm{rel}^2(\varepsilon_E) = u_\mathrm{rel}^2\left(n_{Ns,E}\right) + u_\mathrm{rel}^2(A) + u_\mathrm{rel}^2(P_E) = u_\mathrm{rel}^2\left(n_{\mathrm{gs},E} - n_{\mathrm{bs},E}\right) + u_\mathrm{rel}^2(A) + u_\mathrm{rel}^2(P_E) + u_\mathrm{rel}^2(fit) \tag{6}$$

Details about the calculation of $u_\mathrm{rel}^2(\varepsilon_E)$ can be found in ISO 10703.

For the calculation of the characteristic limits (see ISO 11929-1), $\tilde{u}(\tilde{c}_A)$, is needed, i.e. the combined standard uncertainty of c_A as a function of its true value. For a true value, $\tilde{c}_A$, it is expected $n_{\mathrm{g},E} / t_\mathrm{g} = \tilde{c}_A / w + n_{\mathrm{b},E} / t_\mathrm{g}$ and with $u^2\left(n_{\mathrm{g},E}\right) = n_{\mathrm{g},E}$, $\tilde{u}(\tilde{c}_A)$, is calculated by Formula (7):

$$\tilde{u}(\tilde{c}_A) = \sqrt{w^2 \cdot \left[\left(\tilde{c}_A / w + n_{\mathrm{b},E} / t_\mathrm{g}\right) / t_\mathrm{g} + u^2\left(n_{\mathrm{b},E}\right) / t_\mathrm{g}^2\right] + \tilde{c}_A^2 \cdot u_\mathrm{rel}^2(w)} \tag{7}$$

10.4 Decision threshold

According to the ISO 11929 series, the decision threshold, c_A^*, is obtained from Formula (7) for $\tilde{c}_A = 0$. This yields the following given in Formula (8):

$$c_A^* = k_{1-\alpha} \cdot w \cdot \sqrt{2} \cdot \frac{u\left(n_{\mathrm{b},E}\right)}{t_\mathrm{g}} = k_{1-\alpha} \cdot w \cdot \frac{\sqrt{2 n_{\mathrm{b},E}}}{t_\mathrm{g}} \tag{8}$$

where

$\alpha = 0{,}05$;

$k_{1-\alpha} = 1{,}645$ is often chosen by default.

10.5 Detection limit

The detection limit, $c_A^{\#}$, is calculated according to ISO 11929 series using the implicit Formula (9):

$$c_A^{\#} = c_A^{*} + k_{1-\beta} \cdot \sqrt{w^2 \cdot \left[\left(c_A^{\#} / w + n_{\mathrm{b},E} / t_{\mathrm{g}} \right) / t_{\mathrm{g}} + u^2 \left(n_{\mathrm{b},E} \right) / t_{\mathrm{g}}^2 \right] + c_A^{\#2} \cdot u_{\mathrm{rel}}^2 (w)} \tag{9}$$

where

$\beta = 0{,}05$;

$k_{1-\beta} = 1{,}645$ is often chosen by default.

The detection limit can be calculated by solving Formula (9) for $c_A^{\#}$ or, more simply, by iteration with a starting approximation, $c_A^{\#} = 2 \cdot c_A^{*}$.

When taking $k_{1-\alpha} = k_{1-\beta} = k$, the solution of Formula (9) is given by Formula (10):

$$c_A^{\#} = \frac{2 \cdot c_A^{*} + \left(k^2 \cdot w \right) / t_{\mathrm{g}}}{1 - k^2 \cdot u_{\mathrm{rel}}^2 (w)} \tag{10}$$

10.6 Limits of the coverage intervals

10.6.1 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 and ISO 11929-3:

$$c_A^{\triangleleft} = c_A - k_p \cdot u(c_A); p = \omega \cdot (1 - \gamma / 2) \tag{11}$$

$$c_A^{\triangleright} = c_A + k_q \cdot u(c_A); q = 1 - \omega \cdot \gamma / 2 \tag{12}$$

where

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

$1 - \gamma$ is the probability for the coverage interval of the measurand;

$\omega = 1$ can be set if $c_A \geq 4 \cdot u(c_A)$. In this case:

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

where

$\gamma = 0{,}05$;

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

10.6.2 Shortest coverage interval

As specified 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):

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

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

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

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

10.7 Corrections for contributions from other radionuclides and background

10.7.1 General

If the determination of soluble ^{226}Ra activity concentration is determined directly from the gamma-ray emissions of ^{226}Ra at 186,2 keV, then correction for the interference from ^{235}U, which has a gamma-ray emission line at 185,7 keV with an emission probability of 57,0 %, shall be applied. Uranium-235 has another gamma-ray spectral line at 143,8 keV, with an emission probability of 10,94 %, from which the contribution to the line in question can be estimated, taking into account the branching ratios of the gamma-ray emissions (see 10.7.2)[16].

If the determination of soluble ^{226}Ra activity concentration is estimated by the measurement of its decay products ^{214}Pb and ^{214}Bi at equilibrium, reached four weeks after the coprecipitation step (see Figure A.1), it should be taken into account that the gamma-ray line of the radionuclide to be determined occurs also in the background of the spectrometer. By measuring a background spectrum without a sample for a counting time, t_0, this contribution can be corrected for, taking into account the different counting times of the two spectra.

In both cases, the activity concentration can be calculated using a model according to Formula (16):

$$c_A = \left(\frac{n_{\mathrm{N},E}}{t_\mathrm{g}} - \frac{n_{\mathrm{N0},E}}{t_0} \right) \cdot w \tag{16}$$

In both cases, this model gives the necessary corrections, which are developed in ISO 10703.

10.7.2 Contribution from other radionuclides

The gamma-ray line to be corrected at the energy E_1, has the net peak area n_{N,E_1}. The contribution of another radionuclide having more than one gamma-ray line at energy, E_1, is calculated through the ratio of the respective emission probability, deducted from the gamma-ray line, E_2. Using Formula (16) with $x = \frac{P_{E_1} \cdot \varepsilon_1}{P_{E_2} \cdot \varepsilon_2}$ and $t_0 = t_g$, this yields Formula (17):

$$c_A = \left(n_{\mathrm{N},E_1} - x \cdot n_{\mathrm{N},E_2} \right) \cdot \frac{w}{t_\mathrm{g}} \tag{17}$$

Neglecting the standard uncertainty of x, the standard uncertainty of c_A is calculated by Formula (18):

$$u^2(c_A) = \left(\frac{w}{t_\mathrm{g}} \right)^2 \left\{ n_{\mathrm{g},E_1} + u^2\left(n_{\mathrm{b},E_1}\right) + x^2 \cdot \left[n_{\mathrm{g},E_2} + u^2\left(n_{\mathrm{b},E_2}\right) \right] \right\} + c_A^2 \cdot u_\mathrm{rel}^2(w) \tag{18}$$

For the calculation of the characteristic limits (see ISO 11929-1), $\tilde{u}(\tilde{c}_A)$, is needed, i.e. the combined standard uncertainty of c_A as a function of its true value.

$$\tilde{u}^2(\tilde{c}_A) = \left(w / t_\mathrm{g} \right)^2 \left\{ \tilde{c}_A \cdot t_\mathrm{g} / w + n_{\mathrm{b},E_1} + u^2\left(n_{\mathrm{b},E_1}\right) + x\left(n_{\mathrm{g},E_2} - n_{\mathrm{b},E_2} \right) + x^2 \left[n_{\mathrm{g},E_2} + u^2\left(n_{\mathrm{b},E_2}\right) \right] \right\} + \tilde{c}_A^2 \cdot u_\mathrm{rel}^2(w) \tag{19}$$

The decision threshold, c_A^*, is given by Formula (20) for $\tilde{c}_A = 0$:

$$c_A^* = k_{1-\alpha} \cdot \frac{w}{t_\mathrm{g}} \cdot \sqrt{n_{\mathrm{b},E_1} + u^2\left(n_{\mathrm{b},E_1}\right) + x\left(n_{\mathrm{g},E_2} - n_{\mathrm{b},E_2} \right) + x^2 \left[n_{\mathrm{g},E_2} + u^2\left(n_{\mathrm{b},E_2}\right) \right]} \tag{20}$$

and the detection limit, $c_A^\#$, is given by Formula (21):

$$c_A^\# = c_A^* + k_{1-\beta} \cdot \sqrt{\left(\frac{w}{t_\mathrm{g}} \right)^2 \left\{ \frac{c_A^\# \cdot t_\mathrm{g}}{w} + n_{\mathrm{b},E_1} + u^2\left(n_{\mathrm{b},E_1}\right) + x\left(n_{\mathrm{g},E_2} - n_{\mathrm{b},E_2} \right) + x^2 \left[n_{\mathrm{g},E_2} + u^2\left(n_{\mathrm{b},E_2}\right) \right] \right\} + c_A^{\#2} \cdot u_\mathrm{rel}^2(w)} \tag{21}$$

The detection limit can be calculated by solving Formula (21) for $c_A^\#$ or, more simply, by iteration with a starting approximation: $c_A^\# = 2 \cdot c_A^*$.

When taking $k_{1-\alpha} = k_{1-\beta} = k$, the solution of Formula (21) is given by Formula (10).

10.7.3 Contribution from background

In this case, Formula (16) is used for the correction with $x = 1$ and $u(x) = 0$, which yields Formula (22):

$$c_A = \left(\frac{n_{\mathrm{N},E}}{t_\mathrm{g}} - \frac{n_{\mathrm{N}_0,E}}{t_0} \right) \cdot w \tag{22}$$

where

$n_{\mathrm{N}0}$ is the net peak area of the gamma-ray line in the background spectrum;

t_0 is the counting time of the background spectrum.