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Water quality — Radon-222 —

Part 4: Test method using two-phase liquid scintillation counting

Qualité de l'eau — Radon 222 —

Partie 4: Méthode d'essai par comptage des scintillations en milieu liquide à deux phases

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Contents

Page

Foreword ..... **iv**
Introduction ..... **v**
1 Scope **1**
2 Normative references **1**
3 Terms, definitions and symbols **1**
3.1 Terms and definitions 1
3.2 Symbols 2
4 Principle **3**
5 Sampling **3**
5.1 General 3
5.2 Sampling with source preparation “on site” 3
5.3 Sampling without “on site” source preparation 3
6 Reagents and apparatus **3**
6.1 Reagents 3
6.2 Apparatus 4
7 Procedure **4**
7.1 Preparation of calibration sources 4
7.2 Optimization of counting conditions 4
7.3 Detection efficiency 5
7.4 Blank sample preparation and measurement 5
7.5 Sample preparation and measurement 5
8 Quality assurance and quality control program **6**
8.1 General 6
8.2 Variables that could influence the measurement 6
8.3 Instrument verification 6
8.4 Contamination 6
8.5 Interference control 7
8.6 Method verification 7
8.7 Demonstration of analyst capability 7
9 Expression of results **7**
9.1 General 7
9.2 Count rate 7
9.3 Calculation of activity concentration per unit of mass 8
9.4 Combined uncertainty 8
9.5 Decision threshold 8
9.6 Detection limit 9
9.7 Probabilistically symmetric coverage interval 9
9.7.1 Limits of the probabilistically symmetric coverage interval 9
9.7.2 The shortest coverage interval 10
9.8 Calculations using the activity concentration 10
10 Test report **10**
Annex A (informative) **Set-up parameters and validation data** **12**
Bibliography **16**

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, *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 13164-4:2015), which has been technically revised.

The main changes are as follows:

— 3.2: index has been modified according to more recent standards;

— Clause 8: a note has been added;

— A.4.2: efficiency and repeatability data have been revised and updated;

— A.4.2: subclause on reproducibility has been added.

A list of all the parts in the ISO 13164 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 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, 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 could 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 ^{222}Rn 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].

The ^{222}Rn activity concentration in surface water is very low, usually below 1 $Bq{\cdot}l^{-1}$. In groundwater, the activity concentration varies from 1 $Bq{\cdot}l^{-1}$ up to 50 $Bq{\cdot}l^{-1}$ in sedimentary rock aquifers, from 10 $Bq{\cdot}l^{-1}$ up to 300 $Bq{\cdot}l^{-1}$ in wells, and from 100 $Bq{\cdot}l^{-1}$ up to 1 000 $Bq{\cdot}l^{-1}$ in crystalline rocks. The highest activity concentrations are normally measured in rocks with a high concentration of uranium[7].

High variations in the activity concentrations of radon in aquifers have been observed. Even in a region with relatively uniform rock types, some well water can exhibit radon activity concentration much higher than the average value for the same region. Significant seasonal variations have also been recorded (see ISO 13164-1:2013, Annex A[8]).

In circumstances where high radon concentrations might be expected in drinking-water, it is prudent to measure for radon and, if high concentrations are identified, consider whether measures to reduce the concentrations present are justified[2].

This document contains method(s) to determine ^{222}Rn in water samples. It has been developed to support laboratories that need either a certification or accreditation to determine ^{222}Rn in water samples. A certification or accreditation are sometimes required by local and national authorities as well as some customers. The certification and accreditation are provided by an independent body.

The method(s) 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 — Radon-222 —

Part 4:
Test method using two-phase liquid scintillation counting

WARNING — This document does not purport to address all of the safety issues, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to ensure compliance with any national regulatory conditions.

IMPORTANT — It is essential that tests conducted in accordance with this document be carried out by suitably qualified staff.

1 Scope

This document describes a test method for the determination of radon-222 (^{222}Rn) activity concentration in non-saline waters by extraction and liquid scintillation counting.

The ^{222}Rn activity concentrations, which can be measured by this test method utilizing currently available instruments, are above 0,5 Bq·l^{-1} which is the typical detection limit for a 10 ml test sample and a measuring time of 1 h.

It is the responsibility of the laboratory to ensure the validity of this test method for water samples of untested matrices.

Annex A gives indication on the necessary counting conditions to meet the required detection limits for drinking water monitoring.

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 5667-1, *Water quality — Sampling — Part 1: Guidance on the design of sampling programmes*

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

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

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

3 Terms, definitions and symbols

3.1 Terms and definitions

For the purposes of this document, the terms and definitions given in 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

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

a	Massic activity of sample	$Bq \cdot g^{-1}$
a_S	Massic activity of standard solution at the measuring time	$Bq \cdot g^{-1}$
$\tilde{a}$	Possible or assumed true quantity values of the measurand	$Bq \cdot g^{-1}$
a^*	Decision threshold for the total massic activity	$Bq \cdot g^{-1}$
$a^\#$	Detection limit for the total massic activity	$Bq \cdot g^{-1}$
$a^\lhd$, $a^\rhd$	Lower and upper limits of the probabilistically symmetric coverage interval of the measurand, respectively	$Bq \cdot g^{-1}$
$a^<$, $a^>$	Lower and upper limits of the shortest coverage interval of the measurand, respectively	$Bq \cdot g^{-1}$
c_A	Activity concentration	$Bq \cdot l^{-1}$
m	Mass of the test sample	g
m_S	Mass of standard solution used for the preparation of the counting standard	g
N_0	Number of background counts measured from the LSC spectrum for a given time in the region of interest of the measurand.	
N_g	Number of counts measured from the LSC spectrum for a given time in the region of interest of the measurand.	
r_0	Blank sample count rate	s^{-1}
r_g	Sample gross count rate	s^{-1}
r_S	Count rate of the standard in the counting window (alpha + beta)	s^{-1}
t_0	Blank sample counting time	s
r_{net}	Net count rate	s^{-1}
t_g	Test sample counting time	s
$t_{1/2}$	Radioactive half-life of an isotope	
$u(a)$	Standard uncertainty associated with the measurement result	$Bq \cdot g^{-1}$
U	Expanded uncertainty, calculated using $U = ku(a)$, with $k = 2$	$Bq \cdot g^{-1}$
w	Coefficient equal to $1/(\varepsilon m)$	g^{-1}
ε	Total efficiency	
ρ	Density	$g \cdot l^{-1}$
u_{rel}^2	Relative uncertainty	
$\tilde{u}(\tilde{a})$	Standard uncertainty of a as a function of its true value	$Bq \cdot g^{-1}$
$\tilde{u}\left(a^\#\right)$	Standard uncertainty of an estimate of the measurand when the true value is equivalent to the detection limit	
k_p	Quantile of the standardized normal distribution for the probability p (for instance $p = 1 - \alpha$, $1 - \beta$ or $1 - \gamma/2$)	
λ	Decay constant of the isotope	
ω	Auxiliary quantity	
y	Primary measurement result of measurand	
Φ	Distribution function of the standardized normal distribution	
α	Probability of the false positive decision	
β	Probability of the false negative decision	

4 Principle

Radon is extracted from an aqueous solution by means of a scintillation cocktail not miscible with water (without emulsifier) inside the scintillation vial and counted after the equilibrium is reached with its short-lived decay products [9][10][11][12].

The aqueous sample is drawn with a gas-tight syringe from inside the water volume (i.e., well below surface) to avoid radon losses during sampling and transferred into a scintillation vial containing the desired amount of scintillation cocktail. For the same reason, the water sample is injected below the cocktail surface. The vial is tightly capped, shaken and kept for 3 h, preferably in the dark and at controlled temperature. The sample is then counted by a liquid scintillation counter. Either total counts (alpha + beta) or alpha counts only can be considered. In these conditions ^{222}Rn and its short-lived progeny (^{218}Po, ^{214}Pb, ^{214}Bi, and ^{214}Po) are measured.

5 Sampling

5.1 General

Sampling, handling and storage of the water samples shall be done as specified in ISO 5667-1 and ISO 5667-3. It is important that the laboratory receives a sample that is truly representative and has not been damaged or modified during transportation or storage.

Since radon is easily desorbed from water sample, care should be taken to avoid analyte losses during the sampling.

5.2 Sampling with source preparation "on site"

Attach a plastic tube to a faucet with a proper fitting. Insert the other end of the tube in a wide-mouth flask (6.2.3). Allow a steady water stream to fill and the volume of water should be overflowed in terms of volume, such as twice or three times. Adjust the flow rate to avoid turbulence, bubbles, and empty volumes both in the tube and in the flask.

Draw the water sample aliquot with a gas-tight syringe (6.2.4) inserting the needle well below the surface. Sampling time shall be recorded to calculate decay correction.

Prepare the counting source following the method described in 7.5.

5.3 Sampling without "on site" source preparation

Attach a plastic tube to a faucet with a proper fitting. Insert the other end of the tube in a wide-mouth glass bottle (6.2.2). Allow a steady water stream to flow out and overflow the bottle for approximately 2 min. Adjust flow rate to avoid turbulence, bubbles, and empty volumes both in the tube and in the bottle. Gently extract the tube and screw tightly the cap avoiding any air head space. A 1 l bottle is generally suitable for the sampling. Sampling time shall be recorded to calculate decay correction.

The sample should be transported into the laboratory and analysed ideally within 48 h. The sample should not be frozen to prevent breaking of the container. If the bottle is completely filled without bubbles and tightly capped, then normal road transport can deliver sample without significant radon loss even if the samples are exposed to elevated ambient temperatures.

6 Reagents and apparatus

6.1 Reagents

All reagents shall be of recognized analytical grade and, except for 6.1.4, shall not contain any detectable alpha and beta activity.

6.1.1 Water, distilled or deionized.

Deionized water can contain detectable amounts of ^{222}Rn and short-lived progeny. It is, therefore, strongly recommended that water be boiled with vigorous stirring and allowed to stand for 1 day before use. Otherwise, purge it with nitrogen for about 1 h for 2 l water.

6.1.2 Scintillation cocktail, commercially available scintillation cocktails, not water miscible.

6.1.3 Ethanol, 95 %.

6.1.4 Radium standard solution.

^{226}Ra standard solutions shall be provided with calibration certificates containing at least the activity concentration, measurement uncertainty and/or statement of compliance with an identified metrological specification.

6.2 Apparatus

6.2.1 Balance.

6.2.2 Wide-mouth glass sample bottles, volume from 500 ml to 1 l.

6.2.3 Wide-mouth flask, volume from 500 ml to 1 l.

6.2.4 Gas-tight syringe.

6.2.5 Liquid scintillation counter, preferably with thermostated counting chamber and preferably ultra-low level counter to achieve better detection limits.

6.2.6 Polyethylene scintillation vials, PTFE coated, volume 20 ml.

6.2.7 Glass scintillation vials, low potassium glass, volume 20 ml.

NOTE PTFE coated polyethylene vials are the better choice since they prevent both the diffusion of the cocktail into the wall of the vial, radon loss and the absorption of radon from the external environment. Glass vials have similar advantages but exhibit a considerably higher background due to ^{40}K content.

7 Procedure

7.1 Preparation of calibration sources

Transfer an accurately known amount, m_S, of the ^{226}Ra standard solution (6.1.4) into a 20 ml scintillation vial (6.2.6 or 6.2.7). Dilute with laboratory water (6.1.1) (see ISO 3696) to the previously chosen mass (e.g. 10 g). Add the scintillation cocktail (6.1.2). Store the sample for at least 25 days until secular equilibrium is reached. A standard solution of ^{222}Rn can also be used if available.

Vigorously shake the vial for a few seconds. A vortex mixer could also be used for shaking. After phase separation, a waiting time of at least 3 h shall be used before starting counting. Since ^{226}Ra is not extracted into the organic phase, its alpha emission would not affect the detection efficiency calibration for ^{222}Rn.

7.2 Optimization of counting conditions

Both alpha + beta counting or alpha counting using alpha-beta discrimination can be used (see manufacturer instructions).

When using alpha-beta discrimination, both alpha background and efficiency are usually lower; in practice it is found that a much lower detection limit can be achieved.

Set the counting window so that the channels affected by photo- and chemo-luminescence are excluded.

NOTE Since no water is present in the scintillation cocktail phase, the quenching is low and constant, thus no quenching correction is needed.

7.3 Detection efficiency

Let the counting rate be r_S for the counts of the calibration source in the counting window (alpha + beta).

Determine the detection efficiency according to Formula (1):

$$\varepsilon = \frac{r_S - r_0}{a_S \cdot m_S} \tag{1}$$

Acceptance limits for efficiency should be defined.

NOTE ε includes both counting and extraction efficiency. Usual values are in the range of approximately 400 % to 500 % (^{222}Rn, ^{218}Po, ^{214}Po alpha emissions and ^{214}Pb, ^{214}Bi beta emissions). If using alpha-only counting, a lower ε value (≤300 %) is to be expected.

It is advisable to check the method linearity. The efficiency should be assessed using calibration sources whose activities should cover the whole working range.

A more accurate estimate of efficiency can be obtained by preparing and measuring a number of calibration sources.

Efficiencies should be verified with a periodicity established by the laboratory and whenever changes in materials (e.g., scintillation cocktail (6.1.2)) or when maintenance operations are performed on the scintillation counter (6.2.5). A verification or a recalibration is necessary when requirements of instrument quality control are not met.

7.4 Blank sample preparation and measurement

Transfer the chosen quantity (e.g., 10 g) of degassed laboratory water (6.1.1) into the scintillation vial (6.2.6 or 6.2.7). Add the scintillation cocktail (6.1.2) and shake vigorously the vial for a few seconds. A vortex mixer could also be used for shaking.

After phase separation, wait at least 3 h before starting counting. Count the blank sample using the chosen conditions. Let the measured counting rate in the counting window be r_0.

Acceptance limits for blank samples should be defined, also on the basis of the desired detection limit. For this purpose, the use of control charts is advisable.[13]

It is recommended to count blank samples for the same counting time as the test samples.

Blank measurements should be performed with a periodicity established by the laboratory (e.g., monthly) and whenever changes in materials (e.g., scintillation cocktail batch (6.1.2)) or when maintenance operations are performed on the scintillation counter (6.2.5). Verification or a recalibration is necessary when requirements of instrument quality control (see Clause 8) are not met.

7.5 Sample preparation and measurement

Transfer into the scintillation vial (6.2.6 or 6.2.7) the chosen amount of the scintillation cocktail (6.1.2) (e.g., 10 ml). Weigh the vial.

This operation should be done in the laboratory. The weighed, capped vial, containing the scintillation cocktail, can be transported to perform “on site” sampling.

Withdraw slowly a sample aliquot from the bulk sample contained in the bottle/flask (6.2.2 or 6.2.3) (see 7.1 or 7.2) by a gas-tight syringe (6.2.4). The tip of the needle should be placed around 3 cm under the surface of the water in the bottle/flask.

Invert the syringe and slowly eject the water. Repeat this rinsing operation two or more times. Bubbles inside the syringe should be avoided.

Withdraw a sample aliquot, invert the syringe, and slowly eject any remaining small air bubble. Retain the desired quantity of sample.

Remove the cap from the vial and carefully place the tip of the needle at the bottom of the vial. Slowly eject the sample water under the scintillation cocktail. Carefully remove the needle and firmly replace the cap.

Vigorously shake the vial for at least 30 seconds. A vortex mixer could also be used for shaking. Weigh the vial again and calculate the mass, m, of sampled water.

The water is injected under the liquid scintillation solution to prevent loss of radon from the sample. The operation should be carried out slowly to avoid turbulence in the solution which might cause loss of radon.

Count the sample after at least 3 h from its preparation using the chosen optimum counting conditions in order to allow the equilibrium with short-lived radon progeny to be reached. Let the measured counting rate in the chosen window be r_g.

The duration of counting depends on the sample count rate and also on precision and detection limit required.

Before starting the counting, it is recommended to ensure that the two immiscible liquid phases are clearly separated (absence of third phase). In case of persistence of a third phase for a few hours, 0,1 g of NaCl is added to scintillation cocktail before the water is added to prevent the emulsion [14]. Shake vigorously the vial for a few tens of seconds and wait for the total disappearance of the third phase (scintillation cocktail-in-water emulsion).

8 Quality assurance and quality control program

8.1 General

Quality control operations shall meet the requirements of ISO/IEC 17025. Measurement methods shall be performed by suitably skilled staff under a quality assurance program.

8.2 Variables that could influence the measurement

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

8.3 Instrument verification

Major instrumental parameters (detection efficiency, background signal) shall be periodically verified within a quality assurance program established by the laboratory and in accordance with the manufacturer's instructions.

8.4 Contamination

Verify the absence of reagent contamination through the periodic performance of reagent blank analysis. Laboratory procedures shall ensure that laboratory and equipment contamination as well as sample cross contamination is avoided.

8.5 Interference control

It is the user's responsibility to ensure that all potential interferences have been removed. The removal of potential interferences is limited by the decontamination factor of the method.

8.6 Method verification

A periodic verification of the method accuracy should be performed. This may be accomplished by:

— participating in intercomparison exercises;

— analysing reference materials;

— analysing spiked samples.

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

The chemical recovery (R_c) should be monitored for quality control.

8.7 Demonstration of analyst capability

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

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

9 Expression of results

9.1 General

Measurement results are expressed as activity concentrations in $Bq \cdot l^{-1}$ or $Bq \cdot kg^{-1}$ with associated uncertainties, presented in a test report. The coverage factor for the expanded uncertainty is specified in the presentation of results.

9.2 Count rate

The count rates are calculated using Formulae (2) to (3):

$$r_g = N_g / t_g \tag{2}$$

$$r_0 = N_0 / t_0 \tag{3}$$

It is recommended to count the background at least the same amount of time as for the sample.

The net count rate of the sample (r_{net}) is calculated using Formula (4).

$$r_{net} = r_g - r_0 \tag{4}$$

9.3 Calculation of activity concentration per unit of mass

Calculate the massic activity, a, of the water sample using Formula (5):

$$a = r_{net} / (m \cdot \varepsilon) = w \cdot r_{net} \tag{5}$$

The term w in Formula (5) is isolated (Formula (6)) to calculate the decision threshold, the detection limit, and the probabilistic symmetric coverage interval.

$$w = 1 / (\varepsilon \cdot m) \tag{6}$$

If the result has to be expressed in Bq per unit volume, then the initial result expressed in Bq per unit of mass shall be multiplied by the density of the water sample. In this case, the uncertainty contribution of density is negligible and can be ignored.

9.4 Combined uncertainty

This subclause contains the Formulae needed to calculate the uncertainty on a. The uncertainties on the liquid scintillation volume or mass, λ, $t_{1/2}$, t_g and t_0 are considered negligible for the calculation of $u(a)$. According to ISO/IEC Guide 98-3, the combined uncertainty of a is calculated using Formula (7):

$$u(a) = \sqrt{w^2 \cdot \left(r_g / t_g + r_0 / t_0\right) + a^2 \cdot u_{rel}^2(w)} \tag{7}$$

The relative standard uncertainty of w is calculated by Formula (8).

$$u_{rel}^2(w) = u_{rel}^2(\varepsilon) + u_{rel}^2(m) \tag{8}$$

The relative standard uncertainty of ε is calculated by Formula (9).

$$u_{rel}^2(\varepsilon) = u_{rel}^2(r_s - r_0) + u_{rel}^2(a_s) + u_{rel}^2(m_s) = (r_s / t_s + r_0 / t_0) / (r_s - r_0)^2 + u_{rel}^2(a_s) + u_{rel}^2(m_s) \tag{9}$$

If replicate efficiency determinations are performed (see NOTE in 7.3), the efficiency uncertainty should be calculated accordingly (see A.2).

Mass uncertainty, $u_{rel}(m)$, should be estimated based on laboratory experience and can be greater than balance uncertainty.

For the calculation of the characteristic limits according to ISO 11929-1,[15] $\tilde{u}(\tilde{a})$ is needed, i.e., the standard uncertainty of a as a function of its true value, calculated by Formula (10).

$$\tilde{u}(\tilde{a}) = \sqrt{w^2 \cdot \left(\tilde{a} / w + r_0\right) / t_g + r_0 / t_0\right) + \tilde{a}^2 \cdot u_{rel}^2(w)} \tag{10}$$

9.5 Decision threshold

The decision threshold a^* is obtained from Formula (11) (see ISO 11929-1).

This yields:

$$a^* = k_{1-\alpha} \cdot w \cdot \sqrt{(r_0 / t_g) + (r_0 / t_0)} \tag{11}$$

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

When $t_g = t_0 = t$, a* is calculated using Formula (12):

$$a^* = k_{1-\alpha} \cdot w \cdot \sqrt{2N_0} / t \tag{12}$$

When the background is very low, or when $N_0 = 0$, a^* is calculated with Formula (13) according to ISO 11929-2:

$$a^* = k_{1-\alpha} \cdot w \cdot \sqrt{2(N_0 + 1)} / t \tag{13}$$

9.6 Detection limit

The detection limit, $a^{\#}$, is calculated using the implicit Formula (14) according to ISO 11929-1:

$$a^{\#} = a^* + k_{1-\beta} \cdot \tilde{u}\left(a^{\#}\right) = a^* + k_{1-\beta} \sqrt{w^2 \left[\left(a^{\#} / w + r_g / t_g\right) / t_g + u^2\left(r_g\right) / t_g^2\right] + a^{\#2} \cdot u_{rel}^2(w)} \tag{14}$$

$\beta = 0{,}05$ and then, $k_{1-\beta} = 1{,}65$ is often chosen by default.

The detection limit can be calculated by solving Formula (14) for $a^{\#}$ or, more simply, by iteration with a starting approximation $a^{\#} = 2 \cdot a^*$.

When taking $k_{1-\alpha} = k_{1-\beta} = k$, the solution of Formula (14) is given by Formula (15):

$$a^{\#} = \left(2a^* + \left(w \cdot k_{1-\alpha}^2\right) / t_g\right) / \left(1 - k_{1-\alpha}^2 \cdot u_{rel}^2(w)\right) \tag{15}$$

where α = 0,05 with $k_{1\text{-a}}$ = 1,65, are values often chosen by default.

9.7 Probabilistically symmetric coverage interval

9.7.1 Limits of the probabilistically symmetric coverage interval

The lower, $a^{\triangleleft}$ and upper, $a^{\triangleright}$ coverage limits are calculated using Formulae (16) and (17) according to ISO 11929-1[15]:

$$a^{\triangleleft} = a - k_p \cdot u(a),\ p = \omega \cdot (1 - \gamma/2) \tag{16}$$

$$a^{\triangleright} = a + k_q \cdot u(a),\ q = 1 - \omega \cdot \gamma/2 \tag{17}$$

where

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

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

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

$$a^{\triangleleft}, a^{\triangleright} = a \pm k_{1-\gamma/2} \cdot u(a) \tag{18}$$

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

9.7.2 The shortest coverage interval

As described in detail in ISO 11929-1,[15] the lower limit of the shortest coverage interval, $a^{<}$, and the upper limit of the shortest coverage interval, $a^{>}$, are calculated from a primary measurement result, a, of the measurand and the standard uncertainty, $u(a)$, associated with a, either by:

$$a^{<}, a^{>} = a \pm k_p \cdot u(a); p = [1 + \omega \cdot (1 - \gamma)] / 2 \tag{19}$$

or if $a^{<} < 0$, were the result by:

$$a^{<} = 0; a^{>} = a \pm k_q \cdot u(a); q = 1 - \omega \cdot \gamma \tag{20}$$

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

The relations $0 \leq a^{<} < a^{>}$ apply and the approximation of Formula (18) is valid.

9.8 Calculations using the activity concentration

The activity concentration can be calculated multiplying the activity per unit of mass by the density, ρ, in gram per litre, as follows:

$$c_A = \frac{r_g - r_0}{\varepsilon \cdot m} \cdot \rho = (r_g - r_0) w \text{ with } w = \frac{\rho}{\varepsilon \cdot m} \tag{21}$$

$$u_{rel}^2(w) = u_{rel}^2(\varepsilon) + u_{rel}^2(m) + u_{rel}^2(\rho) \tag{22}$$

The uncertainty of the density $u_{rel}(\rho)$ is usually negligible (see 9.3). The uncertainty, the characteristics limits and the limits of the confidence interval can be calculated using the previous expression by replacing symbol a by c_A.

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 13164-4;

b) identification of the sample;

c) units in which the results are expressed;

d) the test result:

   1) when the massic activity, 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 $\leq a^{*}$,

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

   2) when the massic activity, a, is compared with the detection limit;

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

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

Complementary information can be provided such as:

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

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

g) decision threshold and the detection limit;

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

i) 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, a, with the detection limit, $a^{\#}$, in order to decide whether the physical effect is recognized or not. Such stipulations are not in accordance with ISO 11929-1. They have the consequence that if is decided too frequently that the physical effect is absent when in fact it is not absent.

Annex A
(informative)

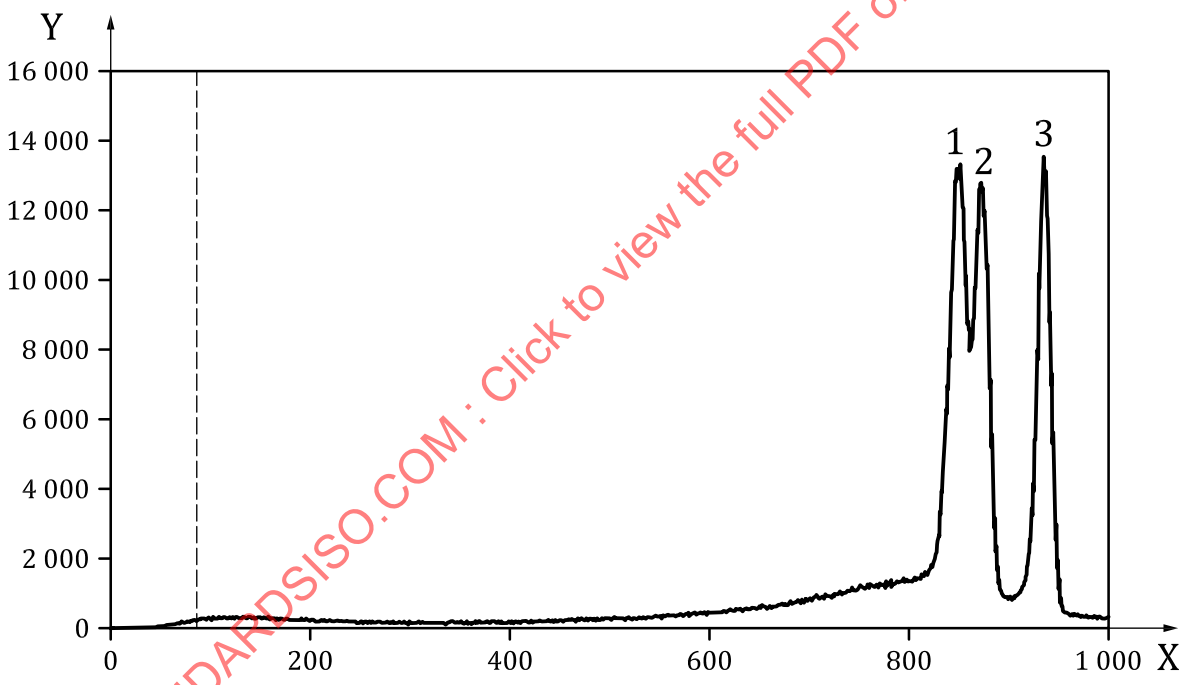
Set-up parameters and validation data

A.1 General

The following measurements have been performed by a 1220 Quantulus™[1] liquid scintillation counter. PTFE coated polyethylene vials [Polyvials® SLD[2]] and Ultima Gold™ F[3] scintillation cocktail have been used (except if otherwise specified).

A.2 Instrument set up and calibration

Measurements are performed without applying alpha/beta discrimination. A spectrum is reported below (see Figure A.1).



Key

X channels

Y counts

NOTE 1 Peak 1: ^{222}Rn (5,489 MeV).

NOTE 2 Peak 2: ^{218}Po (6,002 MeV).

1) 1220 Quantulus™ is an example of a suitable product available commercially from PerkinElmer. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of this product.

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

3) Ultima Gold™ F is an example of a suitable product available commercially from PerkinElmer. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of this product.

NOTE 3 Peak 3: ^{214}Po (7,687 MeV).

Figure A.1 — LSC spectrum

Total (alpha + beta) spectrum counting window between channels 100 and 1 000 is considered (dotted lines in Figure A.1).

In Table A.1, results obtained with different calibrations procedures are reported. In “Calibration 1”, single sources of ^{226}Ra (see 7.1) at six different concentrations levels (0,2 Bq·kg^{-1}; 310 Bq·kg^{-1}; 610 Bq kg^{-1}; 910 Bq·kg^{-1}; 1 210 Bq·kg^{-1}; 1 510 Bq·kg^{-1}) have been prepared and measured. The overall efficiency (extraction + counting) has been determined (see Table A.1, first line).

In “Calibration 2”, 10 sources of ^{226}Ra (1 500 Bq·kg^{-1}) have been prepared and measured. For calibrations 1 and 2, the standard solution of ^{226}Ra was in secular equilibrium with ^{222}Rn when the analysis began.

"Calibration 3" employed a water sample containing radon supplied and certified by JRC-Geel (EU) in the framework of the radon-in-water pilot PT-2017.

In “Calibration 4”, a set of 10 calibration sources was prepared from a national standard of ^{222}Rn in water (provided by ENEA INMRI, Rome-Italy). Sources were prepared on-site and then transported to the measuring laboratory.

Table A.1 — Calibration parameters

Calibration	Calibration radionuclide	Activity Bq·kg^{-1}	Replicates/ measure-ments	Scintillation cocktail	Average value ε %	Stand. dev. $s(\varepsilon)$ Bq·kg^{-1}	Rel. stand. dev. $s_{rel}(\varepsilon)$
1	^{222}Rn (+^{226}Ra)	0,2 to 1 510[a]	6 measures[a]	Ultima Gold™ F[b]	394	7	0,02
2	^{222}Rn (+^{226}Ra)	1 500	10 replicates	Ultima Gold™ F[b]	392	5	0,01
3	^{222}Rn	2 288	4 replicates	Ultima Gold™ F[b]	410	3	0,007
4	^{222}Rn	6 400	10 replicates	Optiscint[b]	407	10	0,02

[a] Measurements at six concentration levels (0,2 Bq·kg^{-1}; 310 Bq·kg^{-1}; 610 Bq·kg^{-1}; 910 Bq·kg^{-1}; 1 210 Bq·kg^{-1}; 1 510 Bq·kg^{-1}).

[b] Ultima Gold™ F is an example of suitable products available commercially from PerkinElmer. Optiscint cocktail is no longer available, values are still reported for exemplification purpose. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of this product.

The three calibration procedures give comparable result if measurement uncertainty is considered.

A.3 Expression of results

Decision threshold and detection limits calculated as in 9.5 and 9.6 are reported in Table A.2 for the above reported conditions. The same parameters for non-concentrated samples are reported too. Above reported efficiency and blank values are used.

Table A.2 — Characteristic limits

Actual mass of test sample kg	Counting time s	Background counts	u^2_{rel} m	Decision threshold Bq·kg^{-1}	Detection limit Bq·kg^{-1}
0,010	3 600	170 ± 15	2,5 10^{-5}	2,2 10^{-1}	4,5 10^{-1}