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BSI Standards Publication

Water quality — Radon-222

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

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National foreword

This British Standard is the UK implementation of ISO 13164-4:2015.

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A list of organizations represented on this committee can be obtained on request to its secretary.

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Part 4:
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Contents

Page

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO 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 on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the WTO principles in the Technical Barriers to Trade (TBT), see the following URL: Foreword — Supplementary information.

The committee responsible for this document is ISO/TC 147, *Water quality*, Subcommittee SC 3, *Radioactivity measurements*.

ISO 13164 consists of the following parts, under the general title *Water quality — Radon-222*:

- *Part 1: General principles*
- *Part 2: Test method using gamma-ray spectrometry*
- *Part 3: Test method using emanometry*
- *Part 4: Test method using two-phase liquid scintillation counting*

Introduction

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

- Natural radionuclides, including potassium-40, and those originating from the thorium and uranium decay series, in particular radium-226, radium-228, uranium-234, uranium-238, and lead-210, 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), tritium, carbon-14, strontium-90, and some gamma-emitting radionuclides can also be found in natural waters as a result of authorized routine releases into the environment in small quantities in the effluent discharged from nuclear fuel cycle facilities. They are also released into the environment following their use in unsealed form in medicine or industrial applications. They are also found in the water as a result of past fallout resulting from explosion in the atmosphere of nuclear devices and accidents such as those that occurred in Chernobyl and Fukushima.

Drinking water can, thus, contain radionuclides at activity concentration which could present a risk to human health. In order to assess the quality of drinking water (including mineral waters and spring waters) with respect to its radionuclide content and to provide guidance on reducing health risks by taking measures to decrease radionuclide activity concentrations, water resources (groundwater, river, lake, sea, etc.) and drinking water are monitored for their radioactivity content as recommended by the World Health Organization (WHO) and may be required by some national authorities.

Standard test methods for radon-222 activity concentrations in water samples are needed by test laboratories carrying out such measurements in fulfilment of national authority requirements.

Laboratories may have to obtain a specific accreditation for radionuclide measurement in drinking water samples.

The radon activity concentration in surface water is very low, usually below 1 Bq l^{-1}. In groundwater, the activity concentration varies from 1 Bq l^{-1} up to 50 Bq l^{-1} in sedimentary rock aquifers, from 10 Bq l^{-1} up to 300 Bq l^{-1} in wells, and from 100 Bq l^{-1} up to 1 000 Bq l^{-1} in crystalline rocks. The highest activity concentrations are normally measured in rocks with high concentration of uranium (see Reference [9]).

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 greatly higher than the average value for the same region. Significant seasonal variations have also been recorded (see ISO 13164-1:2013, Annex A).

Water can dissolve chemical substances as it passes from the soil surface to an aquifer or spring waters. The water can pass through or remain for some time in rock, some formations of which can contain a high concentration of natural radionuclides. Under favourable geochemical conditions, the water can selectively dissolve some of these natural radionuclides.

Guidance on radon in drinking water supplies provided by WHO in 2008 suggests that controls should be implemented if the radon concentration of drinking water for public water supplies exceeds 100 Bq l^{-1}. It is also recommended that any new, especially public, drinking water supply using groundwater should be tested prior to being used for general consumption and that if the radon concentration exceeds 100 Bq l^{-1}, treatment of the water source should be undertaken to reduce the radon levels to well below that level (see Reference [10]).

This part of ISO 13164 is one of the series dealing with the measurement of the activity concentration of radionuclides in water samples.

The origin of radon-222 and its short-lived decay products in water and other measurement methods are described generally in ISO 13164-1.

Water quality — Radon-222 —

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

WARNING — Persons using this part of ISO 13164 should be familiar with normal laboratory practice. This part of ISO 13164 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 absolutely essential that tests conducted in accordance with this part of ISO 13164 be carried out by suitably qualified staff.

1 Scope

This part of ISO 13164 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 radon-222 activity concentrations, which can be measured by this test method utilizing currently available instruments, are at least above 0,5 Bq l^{-1} for a 10 ml test sample and a measuring time of 1 h.

This test method can be used successfully with drinking water samples and 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, in whole or in part, are normatively referenced in this document and are indispensable for its application. 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 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 and definitions and symbols

3.1 Terms and definitions

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

3.2 Symbols and abbreviated terms

For the purposes of this document, symbols and abbreviations defined in ISO 80000-10, as well as the following symbols, apply.

a	massic activity of the sample, in becquerels per gram

a_S	massic activity of the standard solution at the measuring time, in becquerels per gram
a^*	decision threshold for the total massic activity, in becquerels per gram
$a^\#$	detection limit for the total massic activity, in becquerels per gram
$a^{\triangleleft}$, $a^{\triangleright}$	lower and upper limits of the confidence interval, in becquerels per gram
c_A	activity concentration, in becquerels per litre
m	mass of the test sample, in grams
m_S	mass of standard solution used for the preparation of the counting standard, in grams
r_0	blank sample count rate, in reciprocal seconds
r_g	sample gross count rate, in reciprocal seconds
r_S	count rate of the standard in the counting window (alpha + beta), in reciprocal seconds
t_0	blank sample counting time, in seconds
t_g	test sample counting time, in seconds
t_S	calibration sample counting time, in seconds
$u(a)$	standard uncertainty associated with the measurement result; in becquerels per gram
U	expanded uncertainty, calculated using $U = ku(a)$, with $k = 2$, in becquerels per gram
w	coefficient equal to $1/(\varepsilon\ m)$, in reciprocal gram
ε	total efficiency
ρ	density, in grams per litre

4 Principle

^{222}Rn is extracted from aqueous solution by means of a scintillation cocktail not miscible with water (without emulsifier) inside the scintillation vial and counted as the equilibrium with its short lived decay products is reached.[1] [2] [3] [4]

The aqueous sample is drawn by the mean of 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 only counts are considered. In these conditions ^{222}Rn and its short lived progeny (^{218}Po, ^{214}Pb, ^{214}Bi, and ^{214}Po) are measured.

5 Reagents and apparatus

5.1 Reagents

All reagents shall be of recognized analytical grade and, except for 5.1.4, shall not contain any detectable alpha and beta activity.

5.1.1 Water, distilled or deionized, complying with ISO 3696, grade 3.

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

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

5.1.3 Ethanol, 95 %.

5.1.4 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.

5.2 Apparatus

5.2.1 Balance.

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

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

5.2.4 Gas-tight syringe.

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

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

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

NOTE PTFE coated polyethylene vials are the best 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 exhibit a considerably higher background due to potassium-40 content.

6 Sampling

6.1 General

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

6.2 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 Erlenmeyer flask (5.2.3). Allow a steady water stream to get out and overflow the flask for approximately 2 min. Adjust the flux 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 (5.2.4) inserting the needle well below the surface.

6.3 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 borosilicate bottle (5.2.2). Allow a steady water stream to flow out and overflow the bottle for approximately 2 min. Adjust flux 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 one-litre bottle is generally suitable for the sampling.

The sample should be transported into laboratory and analysed possibly within 48 h. The sample should neither be frozen nor overheated. Its preservation at temperature not higher than that of the sampled water is recommended.

7 Instrument set up and calibration

7.1 Preparation of calibration sources

Transfer an accurately known amount m_S of the ^{226}Ra standard solution (5.1.4) into a 20 ml scintillation vial (5.2.6 or 5.2.7). Let the massic activity at the measuring time be a_S. Dilute with laboratory water (5.1.1) (see ISO 3696) to the previously chosen mass (e.g. 10 g). Add the scintillation cocktail (5.1.2). Store the sample for at least 30 days to allow the achievement of secular equilibrium.

A standard solution of ^{222}Rn can also be used if available. In this case, it can be counted 3 h after its preparation. Since Ra-226 is not extracted into the organic phase, its alpha emission would not affect detection efficiency calibration for Rn-222.

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:

$$\varepsilon = \frac{r_S - r_0}{a_S \cdot m_S} \quad (1)$$

Acceptance limits for efficiency should be defined.

NOTE ε includes both counting and extraction efficiency. Usual values are in the range of 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 ($\leq$ 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 sufficient number of calibration sources.

Efficiencies should be verified with a periodicity established by the laboratory and whenever changes in materials [e.g. scintillation cocktail (5.1.2)] or when maintenance operations are performed on the scintillation counter (5.2.5). A verification or a recalibration is necessary when requisites 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 (5.1.1) into the scintillation vial (5.2.6 or 5.2.7). Add the scintillation cocktail (5.1.2) and shake.

After phase separation, a waiting time of at least 3 h shall be used 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.[5]

It is recommended to count blank samples for the same counting time as the usual 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 (5.1.2)] or when maintenance operations are performed on the scintillation counter (5.2.5). Verification or a recalibration is necessary when requisites of instrument quality control (see Clause 11) are not met.

8 Sample preparation and measurement

Transfer into the scintillation vial (5.2.6 or 5.2.7) the chosen amount of the scintillation cocktail (5.1.2) (e.g. 10 ml). Weigh the vial.

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

Withdraw slowly a sample aliquot from the bulk sample contained in the flask (5.2.2 or 5.2.3) (see 6.1 or 6.2) by a gas-tight syringe (5.2.4). The tip of the needle should be placed around 3 cm under the surface of the water in the flask.

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

Withdraw one last time 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. Remove carefully the needle and firmly replace the cap.

Shake the vial for some seconds and take note of the sampling time. Weigh again the vial 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 on 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 is 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.

9 Expression of results

9.1 Calculation of activity per unit of mass

Calculate the massic activity, a, of the water sample by:

$$a = \frac{r_\mathrm{g} - r_0}{\varepsilon \cdot m} = \left(r_\mathrm{g} - r_0\right) \cdot w \text{ with } w = \frac{1}{\varepsilon \cdot m} \qquad (2)$$

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.

9.2 Standard uncertainty

According to ISO/IEC Guide 98-3,[6] the standard uncertainty of a is calculated by Formula (3).

$$u(a) = \sqrt{w^2 \cdot \left(u^2\left(r_g\right) + u^2\left(r_0\right)\right) + a^2 \cdot u_{rel}^2(w)} = \sqrt{w^2 \cdot \left(r_g / t_g + r_0 / t_0\right) + a^2 \cdot u_{rel}^2(w)} \qquad (3)$$

where the uncertainty of the counting time is neglected.

The relative standard uncertainty of w is calculated by Formula (4).

$$u_{rel}^2(w) = u_{rel}^2(\varepsilon) + u_{rel}^2(m) \qquad (4)$$

The relative standard uncertainty of ε is calculated by Formula (5).

$$u_{rel}^2(\varepsilon) = u_{rel}^2\left(r_s - r_0\right) + u_{rel}^2\left(a_s\right) + u_{rel}^2\left(m_s\right) = \left(r_s / t_s + r_0 / t_0\right) / \left(r_s - r_0\right)^2 + u_{rel}^2\left(a_s\right) + u_{rel}^2\left(m_s\right) \qquad (5)$$

If replicate efficiency determinations are performed (see 7.3, NOTE 3), the efficiency uncertainty should be accordingly calculated (see A.2).

Mass uncertainty, $u_\mathrm{rel}(m)$, 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, one needs $\tilde{u}\left(\tilde{a}\right)$, i.e. the standard uncertainty of a as a function of its true value, calculated by Formula (6).

$$\tilde{u}\left(\tilde{a}\right) = \sqrt{w^2 \cdot \left(\left(\tilde{a} / w + r_0\right) / t_g + r_0 / t_0\right) + \tilde{a}^2 \cdot u_{rel}^2(w)} \qquad (6)$$

9.3 Decision threshold

The decision threshold, a^*, is obtained from Formula (6) for $\tilde{a} = 0$. This yields:

$$a^* = k_{1-\alpha} \cdot \tilde{u}(0) = k_{1-\alpha} \cdot w \cdot \sqrt{r_0 / t_g + r_0 / t_0} \qquad (7)$$

where

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

9.4 Detection limit

The detection limit, $a^{\#}$, is calculated using Formula (8):

$$a^{\#} = a^{*} + k_{1-\beta} \cdot \tilde{u}\,(a^{\#})$$

$$= a^{*} + k_{1-\beta} \cdot \sqrt{w^{2} \cdot \left(\left(a^{\#} / w + r_{0}\right) / t_{g} + r_{0} / t_{0}\right) + a^{\#2} \cdot u_{rel}^{2}\left(w\right)} \tag{8}$$

where

β is equivalent to 0,05 with $k_{1-\beta} = 1{,}65$ are often chosen by default.

The detection limit can be calculated by solving Formula (8) for $a^{\#}$ or, more simply, by iteration with a starting approximation $a^{\#} = 2 \cdot a^{*}$.

When taking $\alpha = \beta$ then $k_{1-a} = k_{1-\beta} = k$, the solution of Formula (8) is given by Formula (9).

$$a^{\#} = \frac{2 \cdot a^{*} + \left(k^{2} \cdot w\right) / t_{g}}{1 - k^{2} \cdot u_{rel}^{2}\left(w\right)} \tag{9}$$

9.5 Confidence limits

In accordance with ISO 11929, the lower, $a^{\triangleleft}$, and upper, $a^{\triangleright}$, limits of the confidence interval are calculated using Formulae (10) and (11).

$$a^{\triangleleft} = a - k_{p} \cdot u(a)\ ;\ p = \omega \cdot (1 - \gamma / 2) \tag{10}$$

$$a^{\triangleright} = a + k_{q} \cdot u(a)\ ;\ q = 1 - \omega \cdot (\gamma / 2) \tag{11}$$

where

ω is equivalent to $\phi(y/u(y))$, being ϕ the distribution function of the standardized normal distribution;

ω is equivalent to 1; may be set if $a \geq 4 \cdot u(a)$ and Formula (12) applies.

$$a^{\triangleleft\triangleright} = a \pm k_{1-\gamma/2} \cdot u\left(a\right) \tag{12}$$

where

γ is equivalent to 0,05 with $\mathrm{k}_{1-\gamma/2} = 1{,}96$ is often chosen by default.

9.6 Calculations using the activity concentration

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

$$c_{A} = \frac{r_{g} - r_{0}}{\varepsilon \cdot m} \cdot \rho = \left(r_{g} - r_{0}\right) w \text{ with } w = \frac{\rho}{\varepsilon \cdot m} \tag{13}$$

$$u_{rel}^{2}\left(w\right) = u_{rel}^{2}\left(\varepsilon\right) + u_{rel}^{2}\left(m\right) + u_{rel}^{2}\left(\rho\right) \tag{14}$$

The uncertainty, the characteristics limits and the limits of the confidence interval may be calculated using the previous expression [Formulae (1), (2), (4), (9), and (10)] with Formulae (13) and (14).

10 Interference control

Other radionuclides soluble in the scintillation cocktail (e.g. radionuclides bound to organic molecules) can interfere. Water contaminated with high energy beta or gamma emitters can exhibit interferences as well. These conditions are seldom observed in drinking waters.

Nonetheless a careful spectrum examination should always be performed.

11 Quality control

Measurement methods shall be selected and associated procedures performed by suitably skilled staff under a quality assurance and control program.

Confidence in the measurement results is maintained by regular use of certified reference materials and the participation in interlaboratory comparisons and proficiency testing (see ISO/IEC 17025).

Laboratory procedures shall ensure that laboratory and equipment contamination as well as cross sample contamination is avoided.

12 Test report

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

a) the test method used, together with a reference to this part of ISO 13164, i.e. ISO 13164-4;

b) identification of the sample;

c) units in which the results are expressed;

d) test result, $a \pm u(a)$ or $a \pm U$, with the associated k value.

Complementary information can be provided such as:

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

b) decision threshold and the detection limit;

c) depending on the customer request there are different ways to present the result:

   — When the activity per unit of mass, a, is compared with the decision threshold (see ISO 11929) the result of the measurement should be expressed as $\leq a^*$ when the result is below the decision threshold.

   — When the activity per unit of mass, a, is compared with the detection limit, the result of the measurement can be expressed as $\leq a^\#$ when the result is below 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.

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

Annex A
(informative)

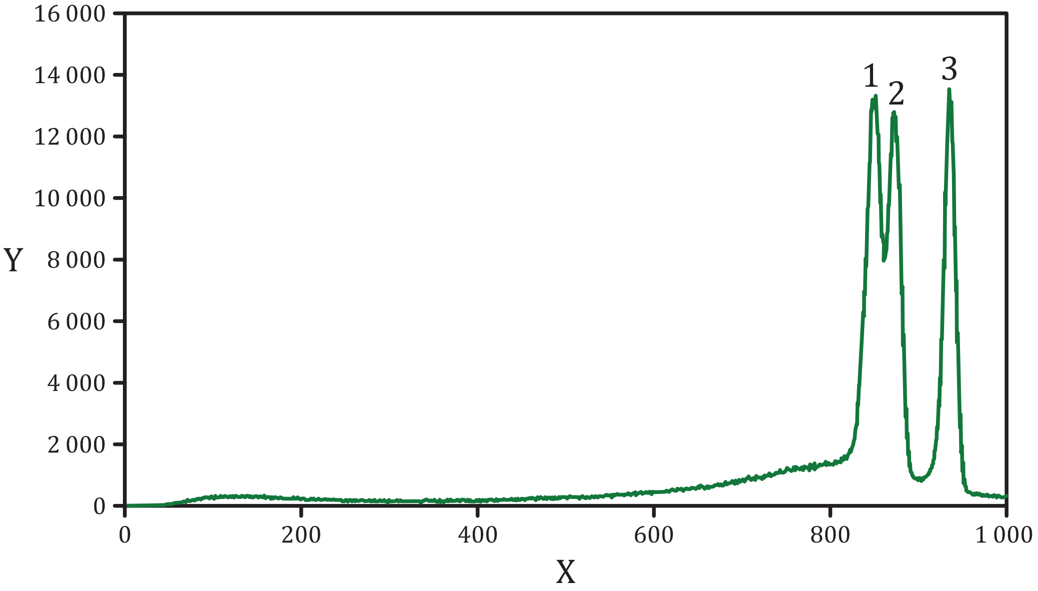
Set-up parameters and validation data

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

Measures 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).

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

Figure A.1 — LSC spectrum

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[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.

Total (alpha + beta) spectrum counting window between channels 100 and 1 000 is considered.

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; 310 Bq/kg; 610 Bq/kg; 910 Bq/kg; 1 210 Bq/kg; 1 510 Bq/kg) 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) have been prepared and measured.

In “Calibration 3”, 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	**Replicates/ measurements**	**Scintillation cocktail**	**Average value** ε %	**Stand. dev.** $s(\varepsilon)$ Bq/kg	**Rel. stand. dev.** $s_{rel}(\varepsilon)$
1	^{226}Ra	0,2 to 1 510[a]	6 measures[a]	Ultima Gold™ F[b]	394	7	0,02
2	^{226}Ra	1 500	10 replicates	Ultima Gold™ F[b]	392	5	0,01
3	^{222}Rn	6 400	10 replicates	Optiscint[b]	407	10	0,02

[a] Measurements at six concentration levels (0,2 Bq/kg; 310 Bq/kg; 610 Bq/kg; 910 Bq/kg; 1 210 Bq/kg; 1 510 Bq/kg).

[b] Ultima Gold™ F and Optiscint are examples of suitable products 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.

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 9.3 and 9.4 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_{rel}^2 m	**Decision threshold** Bq/kg	**Detection limit** Bq/kg
0,010	3 600	170 ± 15	2,5 10^{-5}	2,1 10^{-1}	4,5 10^{-1}

A.4 Validation data

A.4.1 Linearity

Mandel test has been used to check linearity in the range 0,2 Bq/kg to 1 210 Bq/kg. Values of activity (x values) vs CPS (y values) are reported in Table A.3. Mandel test applied to this set of data showed a linear relationship between x and y values. No anomalous residue is present.

Table A.3 — CPS (counts per second) at different activity concentration values

^{226}Ra standard activity a Bq/kg	CPS counts/s	CPS u counts/s	CPS u_{rel}
0,2	0,008 3	0,001 3	0,15
310	12,186	0,050	0,004 1
610	23,698	0,099	0,004 2
910	35,02	0,15	0,004 2
1 210	46,85	0,20	0,004 2
1 510	57,93	0,25	0,004 3

A.4.2 Precision under intermediate repeatability conditions

Precision was evaluated under intermediate repeatability conditions (or intralaboratory reproducibility). Three tap water samples were prepared and measured by different technicians. Results are reported in Table A.4. The standard deviations of the three sets are never significantly higher than the uncertainties of individual measurements.

Table A.4 — Repeatability (intermediate)

^{222}Rn average concentration a Bq/kg	Activity concentration uncertainty (average) u_a Bq/kg	Activity concentration relative uncertainty (average) u_a	Replicates	Standard deviation of measured activity concentrations $s(a)$ Bq/kg	Relative standard deviation of measured activity concentrations $s_{rel}(a)$
4,05	0,34	0,084	10	0,39	0,097
5,34[a]	0,43	0,081	5	0,37	0,069
13,49[a]	0,96	0,071	5	0,34	0,025

[a] Optiscint scintillation cocktail has been used. Optiscint 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 Repeatability contribution should be taken into account in uncertainty determination.[8]

A.4.3 Accuracy (trueness)

Accuracy, obtained by participation in a PT, provided bias values lower than 10 % and an E_n value lower than 1. Obtained bias values were included in the acceptability interval defined by the PT organizers.

A.4.4 Detection limit

As is shown in Table A.2, with this procedure, a detection limit about 0,5 Bq/kg is obtained for 1 h counting time and 0,01 kg of sample.

A.4.5 Uncertainty

Employing this procedure, a relative uncertainty of about 7 % (coverage factor $k = 1$) is obtained for a 1 h counting time of a 0,01 kg sample with a ^{222}Rn activity concentration of about 10 Bq/kg.

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