INTERNATIONAL STANDARD

ISO 13165-1

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Water quality — Radium-226 —

Part 1: Test method using liquid scintillation counting

Qualité de l'eau — Radium 226 —

Partie 1: Méthode d'essai par comptage des scintillations en milieu liquide

Reference number
ISO 13165-1:2013(E)

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Foreword

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

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

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.

ISO 13165-1 was prepared by Technical Committee ISO/TC 147, *Water quality*, Subcommittee SC 3, *Radioactivity measurements*.

ISO 13165 consists of the following parts, under the general title *Water quality — Radium-226*:

— *Part 1: Test method using liquid scintillation counting*

— *Part 2: Test method using emanometry*

The following part is under preparation:

— *Part 3: Test method using coprecipitation and gamma-spectrometry*

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Introduction

Radioactivity from several naturally occurring and human-made sources is present throughout the environment. Thus, water bodies (surface waters, groundwaters, sea waters) can contain radionuclides of natural and artificial origin (i.e. human-made).

a) Natural radionuclides, including potassium-40, and those of the thorium and uranium decay series, in particular radium-226, radium-228, uranium-234, uranium-238, lead-210, can be found in water for natural reasons (e.g. desorption from the soil and wash-off by rain water) or release from technological processes involving naturally occurring radioactive materials (e.g. the mining and processing of mineral sands or phosphate fertilizer production and use).

b) Human-made radionuclides such as transuranium elements (americium, plutonium, neptunium, curium), tritium, carbon-14, strontium-90 and gamma-emitting radionuclides can also be found in natural waters as they can be authorized to be routinely released into the environment in small quantities in the effluent discharged from nuclear fuel cycle facilities and following their use in unsealed form in medicine or industry. They are also found in water due to fallout from past explosions in the atmosphere of nuclear devices and the accidents at Chernobyl and Fukushima.

Drinking water can thus contain radionuclides at activity concentrations which 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).

An International Standard on a test method of radium-226 activity concentrations in water samples is justified for test laboratories carrying out these measurements, which are sometimes required by national authorities, as laboratories may have to obtain a specific accreditation for radionuclide measurement in drinking water samples.

Radium-226 activity concentration can vary widely according to local geological and climatic characteristics and ranges from 0,001 Bq l^{-1} in surface waters up to 50 Bq l^{-1} in natural groundwaters; the guidance level for radium-226 in drinking water as recommended by WHO is 1 Bq l^{-1} (Reference [7]).

NOTE The guidance level is the activity concentration with an intake of 2 l day^{-1} of drinking water for 1 year that results in an effective dose of 0,1 mSv $year^{-1}$ for members of the public, an effective dose that represents a very low level of risk that is not expected to give rise to any detectable adverse health effect.

This International Standard is one of a series on determination of the activity concentration of radionuclides in water samples.

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Water quality — Radium-226 —

Part 1: Test method using liquid scintillation counting

WARNING — Persons using this part of ISO 13165 should be familiar with normal laboratory practice. This part of ISO 13165 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 ensure compliance with any national regulatory conditions.

IMPORTANT — It is absolutely essential that tests conducted in accordance with this part of ISO 13165 be carried out by suitably qualified staff.

1 Scope

This part of ISO 13165 specifies the determination of radium-226 (^{226}Ra) activity concentration in non-saline water samples by extraction of its daughter radon-222 (^{222}Rn) and its measurement using liquid scintillation counting.

Radium-226 activity concentrations which can be measured by this test method utilizing currently available liquid scintillation counters goes down to 50 mBq l^{-1}. This method is not applicable to the measurement of other radium isotopes.

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

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

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

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

ISO/IEC Guide 98-3:2008, *Uncertainty of measurement — Part 3: Guide to the expression of uncertainty in measurement (GUM:1995)*

3 Symbols, definitions and units

For the purposes of this document, the definitions, symbols and abbreviations given in ISO 80000-10, ISO/IEC Guide 98-3, and the following apply.

a massic activity of the sample at the measuring time, in becquerels per gram

a_S massic activity of the ^{226}Ra standard solution at the measuring time, in becquerels per gram

a^* decision threshold for the massic alpha-activity, in becquerels per gram

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$a^{\#}$ detection limit for the massic alpha-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_1 mass of initial sample subject to heating or possibly concentration, in grams

m_2 mass of heated or concentrated sample, in grams

m_3 mass of heated or concentrated sample transferred in the vial, in grams

m_S mass of ^{226}Ra standard solution used for the preparation of the calibration sample, in grams

r_0 blank sample count rate in the alpha-window, in reciprocal seconds

r_g sample gross count rate in the alpha-window, in reciprocal seconds

r_S count rate of the calibration sample in the alpha-window, in reciprocal seconds

t_0 blank sample counting time, in seconds

t_g 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 $k = 1, 2, \ldots$ in becquerels per gram

w factor equal to $1/\varepsilon m$

ε alpha-efficiency

ρ density, in grams per litre

4 Principle

^{226}Ra massic activity is determined by liquid scintillation counting of daughter ^{222}Rn at isotopic equilibrium (99,56 %) reached 30 d after the preparation of the sample. The ^{222}Rn is extracted from aqueous solution by means of a scintillation cocktail immiscible with water inside the scintillation vial (References [1]–[4]).

The aqueous sample is acidified, heated and, if possible, concentrated by slow evaporation in order to desorb ^{222}Rn and to achieve a better detection limit. The concentrated aqueous sample is transferred into a radon-tight scintillation vial and a water-immiscible scintillation cocktail is added.

After 30 d, the sample is measured by liquid scintillation counting (LSC) applying alpha and beta discrimination: only alpha-emission of ^{222}Rn and that of its short lived progeny (^{218}Po, ^{214}Po) are considered, as this counting condition ensures a better detection limit.

5 Reagents and equipment

5.1 Reagents

All reagents shall be of recognized analytical grade and, except for 5.1.3 and 5.1.4, shall not contain any detectable alpha- and beta-activity.

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5.1.1 Laboratory 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, flux it with nitrogen for about 1 h for 2 l.

5.1.2 Nitric acid, $c(HNO_3)$ = 15,8 mol l^{-1}, ρ = 1,42 g ml^{-1}, mass fraction $w(HNO_3)$ = 70 %.

5.1.3 Scintillation cocktail, commercially available scintillation cocktails, water immiscible and suitable for alpha and beta discrimination (e.g. diisopropylnaphthalene-based cocktails).

5.1.4 ^{226}Ra 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 Equipment

5.2.1 Balance.

5.2.2 Hotplate with **magnetic stirrer** and **stirring bar**.

5.2.3 pH-meter.

5.2.4 Wide-mouth HDPE sample bottles, volumes between 100 ml and 500 ml.

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

5.2.6 Polyethylene scintillation vials, PTFE coated, 20 ml.

PTFE-coated polyethylene vials are the best choice, since they prevent both the diffusion of the cocktail into the wall of the vial and the absorption of radon from the environment. Glass vials exhibit a considerably higher background and generally degrade the achievable alpha and beta discrimination.

6 Sampling

It is the responsibility of the laboratory to ensure the suitability of this test method for the water samples tested.

Collect the sample in accordance with ISO 5667-1. Store the water sample (from 0,1 l to 1 l) in a plastic bottle (5.2.4) according to ISO 5667-3. When preconcentration is desired, acidify the sample to pH 1 to pH 3 with HNO_3 (5.1.2). If necessary, carry out filtration immediately on collection and before acidification.

Acidification of the water sample minimizes the loss of radioactive material from solution by plating on the wall of the sample container. If filtration of the sample is required, the acidification is performed afterwards, otherwise radioactive material already adsorbed on the particulate material can be desorbed.

If the sample is not acidified, the sample preparation should start as soon as possible and always less than 1 month after the sampling date (ISO 5667-3).

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7 Instrument set-up and calibration

7.1 Preparation of calibration sources

Transfer an accurately known mass, m_S, of the ^{226}Ra standard solution (5.1.4) into a scintillation vial (5.2.6). Let the massic activity at the measuring time be a. Dilute with water (5.1.1) to the previously chosen volume, e.g. 10 ml. Add the scintillation cocktail (5.1.3), e.g. 10 ml.

Store the sample for at least 30 d to allow the achievement of secular equilibrium.

Ensure that the diluted standard solutions are between pH 0 and pH 2.

Store samples so as to ensure optimum preservation. Storage in the dark is recommended. Select a single generally applicable temperature in order not to affect distribution coefficients. This temperature shall be consistent with the characteristics of the scintillation cocktail (5.1.3, see manufacturer's instructions). Generally, if possible, storage in the scintillation chamber at around 15 °C is suitable.

7.2 Optimization of counting conditions

Set the alpha-counting window so that the energies of all the three alpha-emitters present in the cocktail phase: ^{222}Rn (5,49 MeV); ^{218}Po (6,00 MeV); and ^{214}Po (7,69 MeV); are covered.

Count the ^{226}Ra calibration sample in alpha and beta-discrimination mode (see manufacturer instructions) for an appropriate period, under different discriminator settings.

The best discriminator setting (working point) is chosen by visual inspection of the spectra in order to obtain an alpha-spectrum free of beta counts (see Annex A).

NOTE Since no water is present in the scintillation cocktail phase, the quenching is low and constant, while the alpha and beta discrimination is quite sharp.

7.3 Detection efficiency

Let the counting rate be r_S for the counts of the ^{226}Ra calibration sample in the alpha-window, as measured with the previously defined best discriminator setting.

Determine the alpha-efficiency:

$$\varepsilon = \frac{r_S - r_0}{a\, m_S} \tag{1}$$

Acceptance limits for efficiency should be defined.

NOTE The alpha-efficiency includes both counting and extraction efficiency. Usual values are in the range 200 % to 300 % (^{222}Rn, ^{218}Po, ^{214}Po alpha-emissions).

It is advisable to check the linearity of the method. Assess the efficiency using calibration samples whose activities cover the whole working range.

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

Verify efficiencies at a periodicity established by the laboratory and whenever changes in materials (e.g. scintillation cocktail) or when maintenance operations are performed on the scintillation counter (5.2.5). A verification or a recalibration is necessary when instrument quality control requirements (see Clause 9) are not met.

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7.4 Blank sample preparation and measurement

Acidify a laboratory water sample to between pH 0 and pH 2. Transfer the chosen quantity, e.g. 10 ml, into the scintillation vial (5.2.6). Add the scintillation cocktail (5.1.3), e.g. 10 ml, and mix thoroughly.

Store the blank sample for 30 d and then count it using the chosen optimum counting conditions. Let the measured counting rate in the alpha-window be r_0. If a preconcentration procedure is normally employed, prepare blank samples by the same method.

Acceptance limits for blank samples should also be defined on the basis of the sensitivity desired. The use of control charts (see ISO 8258[5]) is advisable for this purpose.

It is recommended that blank samples be counted for the same period of time as the test portions.

Perform blank measurements at a periodicity established by the laboratory (e.g. monthly) and whenever changes in materials (e.g. scintillation cocktail batch) or when maintenance operations are made on the scintillation counter (5.2.5). Verification or a recalibration is necessary when instrument quality control requirements (see Clause 9) are not met.

8 Procedure

8.1 Direct counting

Transfer a weighed (5.2.1) aliquot (m_1) of the initial water sample (approximately 50 g) into a beaker. If the sample has not yet been acidified, adjust to pH 0 and pH 2 using nitric acid (5.1.2) and verify with a pH-meter (5.2.3).

Heat to approximately 80 °C under stirring for 30 min in a covered flask, to allow degassing of dissolved ^{222}Rn. Allow the sample to cool and reweigh it to account for losses due to evaporation (m_2).

8.2 Thermal preconcentration

Thermal preconcentration can be used when soft waters are examined (e.g. dry residue <500 mg l^{-1}, as in most drinking waters) in order to decrease the detection limit of the method. Hard waters can give rise to salt precipitations which are difficult to dissolve completely.

Transfer a weighed (5.2.1) aliquot (m_1) of the initial water sample (about 200 g) into a beaker. If the sample has not yet been acidified, adjust to between pH 1 and pH 3 with nitric acid (5.1.2) and verify with a pH-meter (5.2.3).

Slowly evaporate the sample on a hotplate (5.2.2) down to about 20 g. Allow the sample to cool to room temperature and weigh the concentrated sample (m_2). Adjust the concentrated sample to between pH 0 and pH 2.

No precipitation should be observable, otherwise direct counting (8.1) or smaller preconcentration factors are to be applied.

If unknown, only a rough evaluation of the dry residue is needed. Any commonly used technique can be adopted.

NOTE The volume of acid required is small (normally about 0,1 ml of concentrated HNO_3 in 200 g sample when preconcentration is adopted) and its mass can be neglected.

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8.3 Sample preparation

Transfer a weighed (5.2.1) amount (m_3) of the heated or concentrated sample (e.g. 10 ml) into a scintillation vial (5.2.6). Add the scintillation cocktail (5.1.3), e.g. 10 ml, clean the outside vial surface with ethanol and store for 30 d (see 7.1, paragraph 2). Calculate the exact mass, m, of test sample analysed:

$$m = \frac{m_1\, m_3}{m_2} \tag{2}$$

8.4 Sample measurement

Count the sample after at least 30 d from its preparation using the chosen optimum counting conditions. Let the count rate in the alpha-window be r_g.

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

Avoid delays considerably longer than 30 d, since chemical degradation of the scintillation cocktail can occur.

9 Quality control

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

Maintain confidence in the measurement results by regular use of certified reference materials and participation in interlaboratory comparisons and proficiency testing in accordance with ISO/IEC 17025.

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

10 Expression of results

10.1 Calculation of massic activity

Calculate the ^{226}Ra massic activity, a, of the test water sample by:

$$a = \frac{r_g - r_0}{\varepsilon\, m} = \left(r_g - r_0\right) w$$
$$w = \frac{1}{\varepsilon\, m} \tag{3}$$

To express the result as an activity concentration, c_A, in becquerels per litre, multiply the initial result expressed in becquerels per gram by the density, ρ, in gram per litre, of the water sample, i.e. $c_A = \rho a$.

10.2 Standard uncertainty

According to ISO/IEC Guide 98-3, the standard uncertainty of a is calculated by Formula (4):

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

where the uncertainty of the counting time is neglected.

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The relative standard uncertainty of w is calculated by Formula (5):

$$u_{\mathrm{rel}}^2(w) = u_{\mathrm{rel}}^2(\varepsilon) + u_{\mathrm{rel}}^2(m) \tag{5}$$

The relative standard uncertainty of ε is calculated by Formula (6):

$$u_{\mathrm{rel}}^2(\varepsilon) = u_{\mathrm{rel}}^2(r_{\mathrm{S}} - r_0) + u_{\mathrm{rel}}^2(a) + u_{\mathrm{rel}}^2(m_{\mathrm{S}}) = \frac{(r_{\mathrm{S}}/t_{\mathrm{S}} + r_0/t_0)}{(r_{\mathrm{S}} - r_0)^2} + u_{\mathrm{rel}}^2(a) + u_{\mathrm{rel}}^2(m_{\mathrm{S}}) \tag{6}$$

If replicate efficiency determinations are available, average efficiency and its uncertainty should be accordingly calculated.

The relative standard uncertainty of m is calculated using Formula (7):

$$u_{\mathrm{rel}}^2(m) = u_{\mathrm{rel}}^2(m_1) + u_{\mathrm{rel}}^2(m_2) + u_{\mathrm{rel}}^2(m_3) \tag{7}$$

Mass uncertainties $u_{\mathrm{rel}}(m_1)$, $u_{\mathrm{rel}}(m_2)$ and $u_{\mathrm{rel}}(m_3)$ should be estimated based on laboratory experience and can be greater than balance uncertainty since they also take into account also the occurrence of phenomena like sample evaporation.

For the calculation of the characteristic limits according to ISO 11929,[6] $\tilde{u}(\tilde{a})$, i.e the standard uncertainty of a as a function of its true value, is required from Formula (8):

$$\tilde{u}(\tilde{a}) = \sqrt{w^2\left[\frac{(\tilde{a}/w + r_0)}{t_{\mathrm{g}}} + \frac{r_0}{t_0}\right] + \tilde{a}^2\, u_{\mathrm{rel}}^2(w)} \tag{8}$$

10.3 Decision threshold

The decision threshold, a^*, is obtained from Formula (8) for $\tilde{a} = 0$. This yields:

$$a^* = k_{1-\alpha}\, \tilde{u}(0) = k_{1-\alpha} w \sqrt{\frac{r_0}{t_{\mathrm{g}}} + \frac{r_0}{t_0}} \tag{9}$$

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

10.4 Detection limit

The detection limit, $a^{\#}$, is calculated using Formula (10):

$$a^{\#} = a^* + k_{1-\beta}\, \tilde{u}\left(a^{\#}\right) = a^* + k_{1-\beta} \sqrt{w^2\left[\frac{\left(a^{\#}/w + r_0\right)}{t_{\mathrm{g}}} + \frac{r_0}{t_0}\right] + a^{\#2} u_{\mathrm{rel}}^2(w)} \tag{10}$$

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

The detection limit can be calculated by solving Formula (10) for $a^{\#}$ or, more simply, by iteration with a starting approximation $a^{\#} = 2a^*$.

When taking $\alpha = \beta$, then $k_{1-\alpha} = k_{1-\beta} = k'$, the solution of Formula (10) is given by Formula (11):

$$a^{\#} = \frac{2a^* + \left(k'^2 w\right)/t_{\mathrm{g}}}{1 - k'^2 u_{\mathrm{rel}}^2(w)} \tag{11}$$

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10.5 Confidence limits

In accordance with ISO 11929,[6] the lower, $a^{\triangleleft}$, and upper, $a^{\triangleright}$, limits of the confidence interval are calculated using Formulae (12) and (13):

$$a^{\triangleleft} = a - k_p\, u(a); \quad p = \omega(1-\gamma/2) \tag{12}$$

$$a^{\triangleright} = a + k_q\, u(a); \quad q = 1-\omega\gamma/2 \tag{13}$$

where

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

in which Φ is the distribution function of the standardized normal distribution.

$\omega = 1$ may be set if $a \geq 4u(a)$ and Formula (14) applies:

$$a^{\triangleleft,\triangleright} = a \pm k_{1-\gamma/2}\, u(a) \tag{14}$$

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

10.6 Calculations using the activity concentration

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

$$c_A = \frac{r_g - r_0}{\varepsilon\, m}\,\rho = (r_g - r_0)\,w$$
$$w = \frac{\rho}{\varepsilon\ m} \tag{15}$$

$$u_{rel}^2(w) = u_{rel}^2(\varepsilon) + u_{rel}^2(m) + u_{rel}^2(\rho) \tag{16}$$

The uncertainty, the characteristic limits, and the limits of the confidence interval may be calculated using the previous expression [Formulae (1), (2), (4), (9) and (10)] with Formulae (15) and (16).

11 Interference control

In ground waters, concentrations of ^{222}Rn can be some orders of magnitude higher than those of ^{226}Ra. Insufficient removal of ^{222}Rn can lead to an overestimate of ^{226}Ra.

If a relevant amount of ^{224}Ra is present, ^{220}Rn can be absorbed in the scintillation cocktail phase and interfere with ^{226}Ra assessment. Interference due to ^{220}Rn and its daughters is indicated by the detection of the ^{212}Po alpha-peak (8,78 MeV), whose energy is higher than any other alpha-particle involved. When ^{212}Po is present, the peak is clearly visible on the right side of the alpha-spectrum. When the ^{212}Po peak is detected, this method does not produce a reliable estimate of ^{226}Ra and should not be used.

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12 Test report

The test report shall conform to requirements and shall contain at least the following information:

a) the test method used, with reference to this part of ISO 13165 (ISO 13165-1:2013);

b) all information necessary for complete 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:

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

f) decision threshold and the detection limit;

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

— when the massic activity, a, is compared with the decision threshold (see ISO 11929[6]) the result of the measurement should be expressed as $\leq a^*$ when the result is less than the decision threshold;

— when the massic activity, 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;

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

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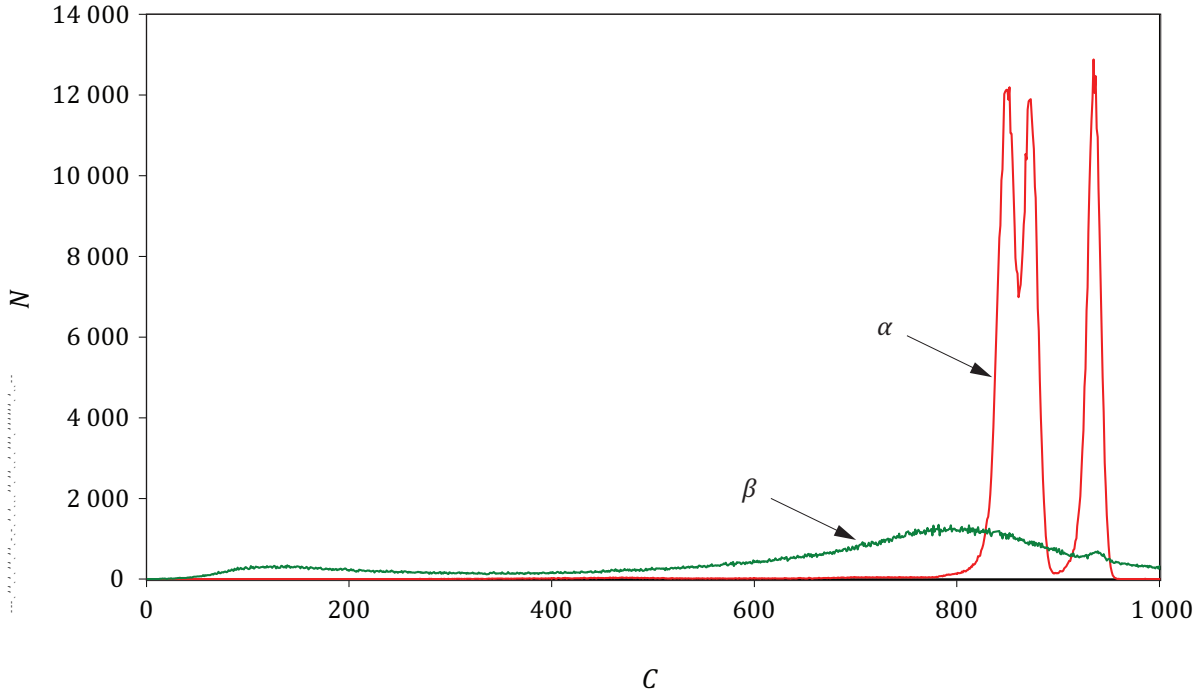
Annex A
(informative)

Set-up parameters and validation data

A.1 Instrument set-up and calibration

Measurements were performed by applying alpha and beta discrimination with the discriminator setting chosen by visual inspection of spectra (see 7.2). A spectrum appears in Figure A.1.



Key

N net counts

C channel numbers

Figure A.1 — LSC spectrum

This annex considers an alpha-counting window between channels 750 and 950.

Five replicate sources at five different massic activities, 0,000 5 Bq g^{-1}; 0,001 Bq g^{-1}; 0,005 Bq g^{-1}; 0,050 Bq g^{-1}; 0,500 Bq g^{-1} (25 calibration sources on the whole), were prepared (see 7.1) and measured. The alpha-efficiency (extraction plus counting) was determined (see Table A.1).

For preparation of blank samples, see 7.4. Results are reported in Table A.1.

Table A.1 — Calibration parameters

Parameter	Replicates	Average value	Standard deviation	Standard deviation, %
Efficiency, ε	25	227 %	0,12	5,5
Blank	25	$3{,}59 \times 10^{-4}$ counts s^{-1}	$0{,}96 \times 10^{-4}$ counts s^{-1}	26,8

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A.2 Procedure

Transfer a 200 ml aliquot of test sample into a beaker and weigh (5.2.1). Acidify the sample to pH 2,5 by adding approximately 0,1 ml of concentrated nitric acid (5.1.2) and slowly evaporate on an hotplate (5.2.2) to 20 ml. Allow to cool and weigh.

Transfer 10 ml of concentrated sample into a scintillation vial (5.2.6) and weigh.

Add 10 ml of scintillation cocktail (5.1.3).

Store the vial for 30 d and then count by liquid scintillation counter (5.2.5) using the chosen conditions. (temperature of the counting chamber 16 °C).

A.3 Expression of results

Decision threshold and detection limits calculated as in 10.3 and 10.4 are reported in Table A.2 for the conditions specified in A.2. Similar parameters for non-concentrated samples are also reported. The efficiency and blank values listed in Table A.1 are used.

Table A.2 — Characteristic limits

Procedure	Actual mass of test sample	u^2_{rel}	Counting time	Decision threshold	Detection limit
		m	s	Bq g^{-1}	Bq g^{-1}
Concentrated sample (1:10)	100 g	$7{,}7 \times 10^{-3}$	60 000	$8{,}0 \times 10^{-7}$	$2{,}0 \times 10^{-6}$

A.4 Validation data

A.4.1 Linearity

Overall efficiencies calculated (single run) for concentrations up to 0,5 Bq g^{-1} are reported in Table A.3 and Figure A.2 in order to verify the linearity.

All values fall within the 2σ interval of the average value and no definite trend is shown up to a massic activity of 500 Bq kg^{-1}.

Table A.3 — Efficiencies at different massic activity values

^{226}Ra massic activity	Alpha-efficiency	$u(\varepsilon)$	$u(\varepsilon)$
Bq g^{-1}	%		%
0,000 5	222	12	5,2
0,001	241	12	5,0
0,005	224	8	3,6
0,05	226	8	3,6
0,5	237	8	3,2
Average	230	8	3,7

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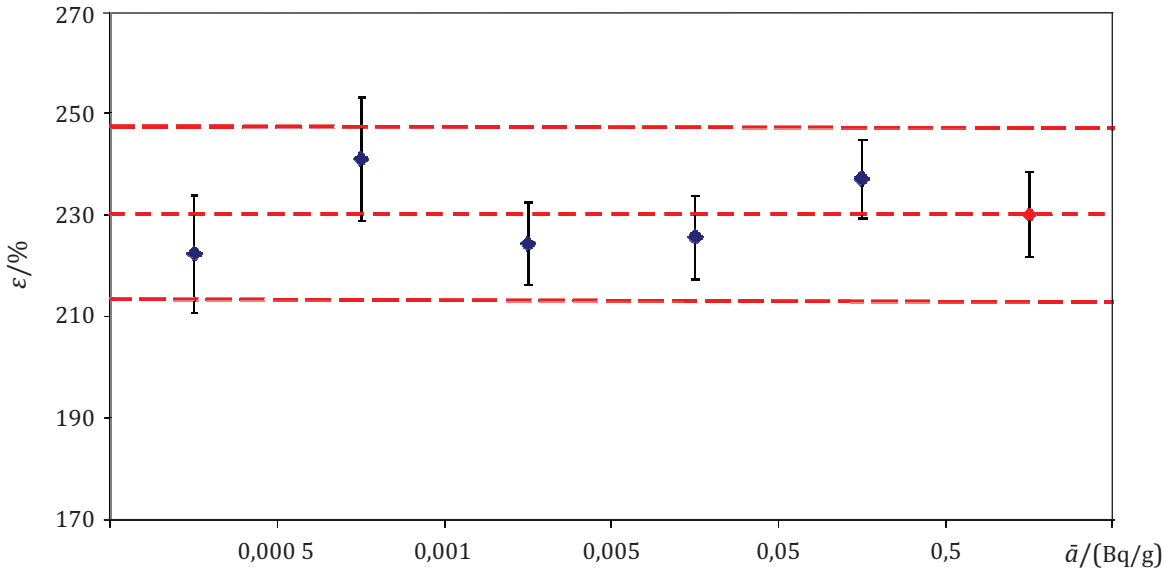

Key

ε overall efficiency

$\bar{a}$ mean massic activity

Figure A.2 — Efficiencies at different massic activity values (control chart)

A.4.2 Precision under repeatability conditions

Precision was evaluated under intermediate repeatability conditions. Two spiked tap water samples were prepared with ^{226}Ra massic activities of 0,1 Bq kg^{-1} and 50 Bq kg^{-1}, respectively. Samples were divided into 10 aliquots each and analysed following the procedure described in the preceding, including thermal concentration, over 2 months by five different technicians. Results are reported in Table A.4.

Table A.4 — Repeatability (intermediate)

^{226}Ra	Replicates	Poisson contribution	Standard deviation
Bq g^{-1}		%	%
0,000 1	9	2,6	4,3
0,050	10	0,12	3,1

A.4.3 Precision under reproducibility conditions

At the time of publication, complete reproducibility data are not available.

A.4.4 Accuracy (trueness)

Accuracy, obtained by participation in proficiency tests, provided bias values lower than 10 % and a u_{test} value always lower than 2,58. Bias values obtained are always included in the acceptability interval defined by the proficiency tests organizers.

A.4.5 Detection limits

Table A.2 shows that, with this procedure, detection limits about 2,0 × 10^{-6} Bq g^{-1} are obtained for 1 000 min measuring times and 100 g test sample.

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A.4.6 Uncertainties

Employing this procedure, a relative uncertainty of about 5 % (coverage factor $k = 1$) is obtained for a 1 000 min measuring times of a 100 g of test sample with a ^{226}Ra massic activity of $1{,}0 \times 10^{-4}$ Bq g^{-1}.

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