INTERNATIONAL STANDARD

ISO 11704

Second edition
2018-11

Water quality — Gross alpha and gross beta activity — Test method using liquid scintillation counting

Qualité de l'eau — Activités alpha globale et bêta globale — Méthode d'essai par comptage des scintillations en milieu liquide

Reference number
ISO 11704:2018(E)

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Published in Switzerland

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Foreword

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

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 147, *Water quality*, Subcommittee SC 3, *Radioactivity measurements*.

This second edition cancels and replaces the first edition (ISO 11704:2010), which has been technically revised. The main changes compared to the previous edition are as follows:

— 5.5.1 has been simplified;

— the application field of this document has been extended to emergency situations;

— slightly different counting conditions have been suggested;

— Annexes A and B have been added.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

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

— natural radionuclides, including ^{40}K, ^{3}H, ^{14}C, and those originating from the thorium and uranium decay series, in particular ^{226}Ra, ^{228}Ra, ^{234}U, ^{238}U, ^{210}Po and ^{210}Pb, can be found in water for natural reasons (e.g. desorption from the soil and washoff 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 fertilizers production and use);

— human-made radionuclides, such as transuranium elements (americium, plutonium, neptunium, curium), ^{3}H, ^{14}C, ^{90}Sr and gamma emitting radionuclides can also be found in natural waters. Small quantities of these radionuclides are discharged from nuclear fuel cycle facilities into the environment as a result of authorized routine releases. Some of these radionuclides used for medical and industrial applications are also released into the environment after use. Anthropogenic radionuclides are also found in waters as a result of past fallout contaminations resulting from the explosion in the atmosphere of nuclear devices and accidents, such as those that occurred in Chernobyl and Fukushima.

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

The radionuclides present in liquid effluents are usually controlled before being discharged into the environment[2] and water bodies. Drinking waters are monitored for their radioactivity as recommended by the World Health Organization (WHO)[3] so that proper actions can be taken to ensure that there is no adverse health effect to the public. Following these international recommendations, national regulations usually specify radionuclide authorized concentration limits for liquid effluent discharged to the environment and radionuclide guidance levels for water bodies and drinking waters for planned, existing and emergency exposure situations. Compliance with these limits can be assessed using measurement results with their associated uncertainties as specified by ISO/IEC Guide 98-3[4] and ISO 5667-20[5].

Depending on the exposure situation, there are different limits and guidance levels that would result in an action to reduce health risk. As an example, during a planned or existing situation, the WHO guidelines for guidance level in drinking water is 0,5 Bq/l for gross alpha activity and 1 Bq/l for gross beta activity.

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

Thus, the test method can be adapted so that the characteristic limits, decision threshold, detection limit and uncertainties ensure that the radionuclide activity concentrations test results can be verified to be below the guidance levels required by a national authority for either planned/existing situations or for an emergency situation[6][7][8].

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

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

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

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

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

Water quality — Gross alpha and gross beta activity — Test method using liquid scintillation counting

WARNING — Persons using this document should be familiar with normal laboratory practice. This document does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices.

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

1 Scope

This document specifies a method for the determination of gross alpha and gross beta activity concentration for alpha- and beta-emitting radionuclides using liquid scintillation counting (LSC).

The method is applicable to all types of waters with a dry residue of less than 5 g/l and when no correction for colour quenching is necessary.

Gross alpha and gross beta activity measurement is not intended to give an absolute determination of the activity concentration of all alpha- and beta-emitting radionuclides in a test sample, but is a screening analysis to ensure particular reference levels of specific alpha and beta emitters have not been exceeded. This type of determination is also known as gross alpha and beta index. Gross alpha and beta analysis is not expected to be as accurate nor as precise as specific radionuclide analysis after radiochemical separations.

The method covers non-volatile radionuclides below 80 °C, since some gaseous or volatile radionuclides (e.g. radon and radioiodine) can be lost during the source preparation.

The method is applicable to test samples of drinking water, rain water, surface and ground water as well as cooling water, industrial water, domestic and industrial waste water after proper sampling and test sample preparation (filtration when necessary and taking into account the amount of dissolved material in the water).

The method described in this document is applicable in the event of an emergency situation, because the results can be obtained in less than 4 h by directly measuring water test samples without any treatment.

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

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies

ISO 3696, *Water for analytical laboratory use — Specification and test methods*

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

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

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

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

3 Terms, definitions, symbols and abbreviated terms

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 terminological databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

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

3.2 Symbols and abbreviated terms

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

a_α, a_β	Alpha and beta activity per mass	Bq g^{-1}
a^*	Decision threshold	Bq g^{-1}
$a^\#$	Detection limit	Bq g^{-1}
$a^<$, $a^>$	Lower and upper limits of the confidence interval	Bq g^{-1}
A_α, A_β	Activity of the alpha and beta emitter certified reference solution used for the α and β calibration sources	Bq
m	Mass of the test sample	g
m_1	Mass of initial sample subject to heating or possibly concentration	g
m_2	Mass of heated or concentrated sample	g
m_3	Mass of heated or concentrated sample transferred in the vial	g
$m_{S\alpha}$, $m_{S\beta}$	Mass of alpha and beta emitters certified reference solutions, respectively	g
$r_{g\alpha}$, $r_{g\beta}$	Sample gross count rate, from the alpha and beta windows, respectively	s^{-1}
$r_{0\alpha}$, $r_{0\beta}$, r_{0T}	Blank count rate, from the alpha, beta and total windows, respectively	s^{-1}
$r_{S\alpha,\alpha}$, $r_{S\alpha,\beta}$, $r_{S\alpha,T}$	Count rate of the alpha calibration source in the alpha, beta and total window	s^{-1}
$r_{S\beta,\alpha}$, $r_{S\beta,\beta}$, $r_{S\beta,T}$	Count rate of the beta calibration source in the alpha, beta and total window	s^{-1}
t_g	Sample counting time	s
t_0	Blank counting time	s
$t_{s\alpha}$, $t_{s\beta}$	Counting time of α and β calibration sources	s
$u\,(a)$	Standard uncertainty associated with the measurement result	Bq g^{-1}
U	Expanded uncertainty, calculated from $U = ku\,(a)$, where $k = 1, 2 \ldots$	Bq g^{-1}
$\tilde{u}(\tilde{a}_\alpha)$	Standard uncertainty of a_α as a function of its true value	Bq g^{-1}

ε_α, ε_β	Counting efficiency for alpha and beta, respectively	—
$\tau_\alpha(\chi_{\alpha\,\beta})$	Alpha interference — Fraction of counts observed in the beta window with respect to the total number of counts measured by the counter when an alpha emitter is measured	—
$\tau_\beta(\chi_{\beta\,\alpha})$	Beta interference — Fraction of counts observed in the alpha window with respect to the total number of counts measured by the counter when a beta emitter is measured	—

4 Principle

Gross alpha and beta activity concentrations are determined by using liquid scintillation counting of a water sample mixed with a scintillation cocktail.

Gross alpha and beta determinations are not absolute determinations of the sample radioactive contents, but relative determinations referred to a specific alpha or beta emitter which constitutes the standard calibration sources. These types of determinations are also known as the alpha and beta index and are usually employed as screening parameters for first assessment of total radioactive content.

The aqueous sample is acidified using nitric acid and heated. Subsequently, water with low salt content can be thermally concentrated by slow evaporation to improve the method sensitivity. An aliquot of sample is transferred into a liquid scintillation vial with scintillation cocktail; scintillations from the vial are then counted by equipment with an alpha and beta discrimination device.

The counter is previously optimized with respect to an alpha and beta discriminator setting and then calibrated against alpha and beta emitter certified reference solutions. In data evaluation, no correction for chemical quenching is applied, since the procedure is designed to provide samples with a relatively constant quench level.

The method does not account for ^{222}Rn and its short lived progeny and it is not suitable for ^{3}H measurement.

When suspended matter is present in significant quantities, a filtration step is required before acidification.

5 Reagents and equipment

All reagents shall be of recognized analytical grade, except for the scintillation cocktail, and shall not contain any detectable alpha and beta activity, except for the radioactive certified reference solutions.

5.1 Nitric acid, $c(HNO_3)$ = commercially available acid with mass fraction $w(HNO_3)$ = (65 to 70) %.

5.2 Water, ISO 3696, grade 3.

Deionized water can contain detectable amounts of ^{222}Rn and short lived progeny. It is therefore strongly recommended to boil water under vigorous stirring and let it stand for one day before use. Alternatively, use nitrogen flushing for about 1 h for a 2 l sample.

5.3 Scintillation cocktail.

Commercially available scintillation cocktails suitable for alpha and beta discrimination (e.g. diisopropylnaphthalene-based cocktails), water miscible.

5.4 Volatile organic solvents.

Methanol or ethanol.

5.5 Certified reference solutions.

5.5.1 General

In general, the experimental parameters (efficiency, alpha and beta optimum discrimination) depend on alpha and beta energies, thus the choice of alpha and beta emitter certified reference solutions depends on knowledge of the type of radioactive contaminant likely to be present in the waters being tested (see ISO 9696[9] and Reference [10]).

NOTE More information on metrological traceability can be found in ISO/IEC 17025.

5.5.2 Alpha emitter certified reference solution

The alpha emitter certified reference solution shall not contain any unexpected detectable alpha and beta activity.

^{236}U is a convenient choice when waters are checked for their natural radioactivity content, as its energy is close to the most widespread natural radionuclides (e.g. uranium and thorium isotopes, ^{226}Ra) and it is commercially available without decay products of short half-life. The supplier can supply details of the absence of any decay product.

^{241}Am is commonly used when artificial radionuclide contamination is suspected. ^{239}Pu can be used as well in such circumstances.

5.5.3 Beta emitter certified reference solution

The beta emitter certified reference solution shall not contain alpha-emitting radioisotopes.

A ^{90}Sr and ^{90}Y mixture or ^{40}K are commonly used. A potassium solution for atomic absorption spectrometry has one arguable advantage, in that its specific activity can be calculated from established physical constants and isotopic abundance data which are independent of the calibration procedures of a particular organization. Other beta emitters, such as ^{137}Cs or ^{36}Cl, can also be used.

5.6 Equipment.

5.6.1 Analytical balance.

5.6.2 Hot plate with a magnetic stirrer and a stirring bar.

5.6.3 pH meter.

5.6.4 Wide-mouth HDPE sample bottles.

5.6.5 Liquid scintillation counter, with α and β discrimination option, preferably an ultra-low level counter to achieve better detection limits.

5.6.6 Polyethylene scintillation vials, capacity 20 ml, such as PET vials, low diffusion PET vials or PTFE-coated polyethylene vials.

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 outer environment. Glass vials generally degrade α and β discrimination.

6 Sampling

Collect 0,1 l to 1 l of water in a plastic bottle (5.6.4) in accordance with ISO 5667-1 and ISO 5667-3. If necessary, filter immediately on collection and before acidification. If possible, acidify immediately with nitric acid (5.1) to a value not lower than pH 1,7 ± 0,2 (7.1) or pH 2,7 ± 0,2 if thermal preconcentration is desired (7.2). Verify the acidity by using a pH meter (5.6.3).

Additional information on sampling of different types of waters can be found in the relevant other parts of the ISO 5667 series[11][12][13][14][15][16][17][18].

NOTE Acidification of the water sample minimizes the loss of radioactive material from solution by adsorption. If carried out before filtration, it desorbs radioactive material already adsorbed on to the particulate material.

The relatively low acidification of the sample does not ensure long-term preservation. Prepare the test sample preferably within seven days from collection. Underground waters are usually more stable than raw waters (see ISO 5667-3).

7 Procedure

7.1 Direct counting

Transfer a weighed (5.6.1) aliquot of the water sample of approximately 50 g, m_1, into a beaker. If the laboratory sample has not yet been acidified, acidify the aliquot using nitric acid (5.1) to pH 1,7 ± 0,2 (verify by pH meter, 5.6.3).

Cover the beaker and heat to approximately 80 °C while stirring for 30 min (5.6.2) to remove the dissolved ^{222}Rn. Allow the aliquot to cool and weigh it again to account for the losses due to evaporation. Record the mass as m_2.

The necessary amount of acid is small (normally about 0,15 g for a 50 g sample) and its mass can be neglected.

7.2 Thermal preconcentration

It is possible to apply a thermal preconcentration when soft waters are considered (e.g. dry residue less than 500 mg/l, as in most drinking waters) in order to increase the sensitivity of the method. Hard waters (dry residue more than 500 mg/l) may give rise to salt precipitations or to a difficult homogenization with the scintillation cocktail.

Transfer a weighed (5.6.1) aliquot of the water sample of approximately 200 g, m_1, into a beaker. If the laboratory sample has not yet been acidified, acidify the aliquot using nitric acid (5.1) to pH 2,7 ± 0,2 (verify by pH meter).

Slowly evaporate the aliquot on a hot plate (5.6.2) to a final quantity of approximately 20 g. Allow the aliquot to cool to room temperature and weigh the concentrated aliquot. Record the mass as m_2. The pH of the concentrated aliquot shall be 1,7 ± 0,2.

No precipitation should be observed, otherwise direct counting (7.1) or smaller preconcentration factors shall be applied.

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

7.3 Sample preparation

Transfer a weighed (5.6.1) test portion (7.1 or 7.2), m_3, of the aliquot into the vial. Add the scintillation cocktail (5.3) and shake vigorously. Clean the scintillation vial (5.6.6) with ethanol or methanol (5.4). Calculate the exact mass, m, of the sample analysed using Formula (1):

$$m = \frac{m_1\, m_3}{m_2} \tag{1}$$

The relative amounts of test portion and scintillation cocktail depend on the characteristics of the latter. Follow the manufacturer's instructions. With many commercially available cocktails, 8:12 volume ratios can be used. The sample to cocktail ratio has to be selected and shall remain consistent for all samples and used for every measurement (e.g. 8 ml test portion +12 ml scintillation cocktail). It is important to ensure homogeneity of the test portion and cocktail mix before measurement.

During emergency situations when measurement results shall be obtained rapidly, transfer the desired aliquot of sample without any treatment into the scintillation vial, close the vial and shake it vigorously to remove most of dissolved ^{222}Rn. Then, add the scintillation cocktail to the vial and shake it again. If possible, wait 3 h before performing the measurements to allow ^{222}Rn short-lived progeny to decay. Different concentration ratios can be adopted. Similarly, different sample to scintillation cocktail ratios can be chosen. It is up to the laboratory to ensure the performance of the modified procedure.

7.4 Liquid scintillation measurement

7.4.1 Preparation of alpha and beta calibration sources

Transfer an accurately known amount, $m_{S\alpha}$ (e.g. corresponding to an activity of about 10 Bq), of the chosen alpha emitter certified reference solution (5.5.2) into a scintillation vial (5.6.6). Let the activity at the time of measurement be A_α. Dilute with water (5.2) to the previously chosen mass (e.g. 8 g). Add the scintillation cocktail (5.3), e.g. 12 ml, and mix thoroughly.

In the same way, prepare the chosen beta emitter certified reference solution (5.5.3). Let the amount of the beta solution transferred into the vial be $m_{S\beta}$ and the activity at the time of measurement be A_β.

The pH of the diluted certified reference solutions shall be 1,7 ± 0,2.

7.4.2 Optimization of counting conditions

Set the alpha- and beta-counting windows of the scintillation counter (5.6.5) so that the energies of all the alpha and beta emitters of interest are covered (see the manufacturer's instructions).

Usually all alpha emitters are included in the determination. In principle, using this procedure, all beta emitter energies can be covered, as the liquid scintillation counting sensitivity is extended down to approximately 20 keV. A common choice is to set the beta-counting window so that all beta emitter energies higher than 20 keV are included in the determination. Tritium and some low beta energy emitters are not counted. In addition, chemi- and photo-luminescence signals are mostly excluded.

Count for an appropriate period the alpha and beta calibration sources in alpha and beta discrimination mode (see the manufacturer's instructions), under different discriminator settings.

Let the counting rate be $r_{S\beta,\alpha}$ and $r_{S\beta,T}$, respectively, for the counts of the alpha calibration source in beta and in the total (undiscriminated) window. Let the counting rate be $r_{S\beta.\alpha}$ and $r_{S\beta,T}$, respectively, for the counts of the beta calibration source in alpha and in the total (undiscriminated) window.

Determine the alpha (τ_α) and beta (τ_β) interference parameter for each discriminator setting (background contribution is often negligible) using Formulae (2) and (3):

$$\tau_\alpha = \frac{r_{S\alpha,\beta} - r_{0\beta}}{r_{S\alpha,T} - r_{0T}} \tag{2}$$

$$\tau_\beta = \frac{r_{S\beta,\alpha} - r_{0\alpha}}{r_{S\beta,T} - r_{0T}} \tag{3}$$

The best discriminator setting (working point) is chosen in order to minimize both τ_α and τ_β.

The selected counting conditions are used for all other subsequent counts (sample, blank and calibration sources).

NOTE 1 The term interference means the misclassification of alpha pulses in the beta-counting window, or vice versa.

NOTE 2 Examples of setting determination are given in Reference [10].

It is necessary for the values of both alpha and beta interference in the chosen working conditions to be adequately low (e.g. less than 5 %). In this situation, the uncertainty introduced in the activity determination is generally included in the range of values defined by the total uncertainty. Otherwise, it is necessary to account for interference in the calculations of sample activity, decision threshold and detection limit (see ASTM D7283[19] and Reference [10]).

It is known that quenching can affect both interference and detection efficiency (see ASTM D7283[19] and References [10] and [20] to [23]). However, the strict control of the pH of samples (as outlined above) allows quenching variability and its effects on results to be minimized. It is therefore advisable to determine an acceptability range for quench values of any measured vial (sample, blank or calibration source), e.g. on the basis of repeated measurements of replicate samples. When measuring samples, blank or calibration source vials, their quenching should be checked (as monitored by the instrument, see the manufacturer's instructions) and compared with the acceptability range.

NOTE 3 Optical quench or colour quench cannot be pointed out by the parameter given by the instrument (this is a general problem of LSC counting). The presence of optical quench can be determined by considering the external source spectrum (see the manufacturer's instructions). Optical quench can lead to underestimation of results, in which the extent is unpredictable.

7.4.3 Blank sample preparation and measurement

Acidify water (5.2) to pH 1,7 ± 0,2. Transfer the chosen quantity (e.g. 8 ml) into the scintillation vial (5.6.6) and weigh the vial. Add the scintillation cocktail (5.3), e.g. 12 ml, and mix thoroughly.

Count (5.6.5) the blank sample using the chosen optimum counting conditions. Let the measured counting rates be $r_{0\alpha}$ and $r_{0\beta}$, respectively, for the counts in the alpha and beta windows.

Repeated counts allow for a confirmation of the stability of the blank count rate. The use of an appropriate control chart is recommended.

7.4.4 Alpha and beta efficiencies

Let the counting rates be $r_{S\alpha,\alpha}$ and $r_{S\beta,\beta}$, respectively, for the counts of the alpha calibration source in the alpha window and for the counts of the beta calibration source in the beta window, as measured with the previously defined best discriminator setting.

Determine the alpha- and beta-counting efficiencies using Formulae (4) and (5):

$$\varepsilon_\alpha = \frac{r_{S\alpha,\alpha} - r_{0\alpha}}{A_\alpha} \tag{4}$$

$$\varepsilon_{\beta} = \frac{r_{S\beta,\beta} - r_{0\beta}}{A_{\beta}} \tag{5}$$

7.4.5 Sample measurement

Count the sample using the chosen optimum counting conditions. Let the measured counting rates be $r_{g\alpha}$ and $r_{g\beta}$, respectively, for the counts in the alpha and beta windows.

Samples should be counted immediately after preparation, to minimize undesirable ingrowth of ^{222}Rn and other decay products from ^{226}Ra (see ISO 9696[9] and ASTM D7283[19]). Nevertheless, if direct counting procedure is adopted and no pretreatment is performed, wait 3 h before performing the sample measurements to allow ^{222}Rn short lived progeny to decay.

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

8 Expression of results

8.1 Calculation of activity per mass

When the beta interference is negligible, calculate the alpha activity per mass, a_{α}, of the water sample using Formula (6):

$$a_{\alpha} = \frac{r_{g\alpha} - r_{0\alpha}}{m\ \varepsilon_{\alpha}} = \left(r_{g\alpha} - r_{0\alpha}\right) w_{\alpha} \tag{6}$$

where

$$w_{\alpha} = \frac{1}{m\ \varepsilon_{\alpha}}$$

When the alpha interference is negligible, calculate the beta activity per mass, a_{β}, of the water sample using Formula (7):

$$a_{\beta} = \frac{r_{g\beta} - r_{0\beta}}{m\ \varepsilon_{\beta}} = \left(r_{g\beta} - r_{0\beta}\right) w_{\beta} \tag{7}$$

where

$$w_{\beta} = \frac{1}{m\ \varepsilon_{\beta}}$$

If the result has to be expressed in becquerels per volume, then multiply the initial result expressed in becquerels per mass by the density of the water sample.

8.2 Standard uncertainty

As specified in ISO/IEC Guide 98-3:2008[4], the standard uncertainty of a_α is calculated using Formula (8):

$$u(a_\alpha) = \sqrt{w_\alpha^2\left[u^2(r_{g\alpha})+u^2(r_{0\alpha})\right]+(r_{g\alpha}-r_{0\alpha})^2\,u_{rel}^2(w_\alpha)} = \sqrt{w_\alpha^2\left(\frac{r_{g\alpha}}{t_g}+\frac{r_{0\alpha}}{t_0}\right)+a_\alpha^2\;u_{rel}^2(w_\alpha)} \tag{8}$$

where the uncertainty of the counting time is neglected and the relative standard uncertainty of w is calculated using Formula (9):

$$u_{rel}^2(w_\alpha)=u_{rel}^2(\varepsilon_\alpha)+u_{rel}^2(m) \tag{9}$$

The relative standard uncertainty of m is calculated using Formula (10):

$$u_{rel}^2(m)=u_{rel}^2(m_1)+u_{rel}^2(m_2)+u_{rel}^2(m_3) \tag{10}$$

and the relative standard uncertainty of ε_α is calculated using Formula (11):

$$u_{rel}^2(\varepsilon_\alpha)=u_{rel}^2(r_{S\alpha,\alpha}-r_{0\alpha})+u_{rel}^2(A_\alpha)=\frac{(r_{S\alpha,\alpha}/t_{S\alpha})+(r_{0\alpha}/t_0)}{(r_{S\alpha,\alpha}-r_{0\alpha})^2}+u_{rel}^2(A_\alpha) \tag{11}$$

$u_{rel}^2(A_\alpha)$ includes all the uncertainties related to the calibration source, i.e. in the certified reference solution and the preparation of the calibration source.

For the calculation of the characteristic limits, one needs $\tilde{u}(\tilde{a}_\alpha)$ (see ISO 11929[24]), i.e. the standard uncertainty of a_α as a function of its true value, calculated using Formula (12):

$$\tilde{u}(\tilde{a}_\alpha)=\sqrt{w_\alpha^2\left[\frac{(\tilde{a}_\alpha/w_\alpha+r_{0\alpha})}{t_g}+\frac{r_{0\alpha}}{t_0}\right]+\tilde{a}_\alpha^2\;u_{rel}^2(w_\alpha)} \tag{12}$$

In the same way, the standard uncertainty of the beta activity per mass is calculated using Formula (13):

$$u(a_\beta)=\sqrt{w_\beta^2\left[u^2(r_{g\beta})+u^2(r_{0\beta})\right]+a_\beta^2\;u_{rel}^2(w_\beta)}=\sqrt{w_\beta^2\left(\frac{r_{g\beta}}{t_g}+\frac{r_{0\beta}}{t_0}\right)+a_\beta^2\;u_{rel}^2(w_\beta)} \tag{13}$$

and the standard uncertainty of a_β as a function of its true value using Formula (14):

$$\tilde{u}(\tilde{a}_\beta)=\sqrt{w_\beta^2\left[\frac{(\tilde{a}_\beta/w_\beta+r_{0\beta})}{t_g}+\frac{r_{0\beta}}{t_0}\right]+\tilde{a}_\beta^2\;u_{rel}^2(w_\beta)} \tag{14}$$

NOTE If an analytical balance is used, the mass uncertainty contribution to the total uncertainty can be neglected.

8.3 Decision threshold

The decision threshold, a_α^*, is obtained from Formula (12) for $\tilde{a}_\alpha = 0$ (see ISO 11929[24]). This yields Formula (15):

$$a_\alpha^* = k_{1-\alpha}\,\tilde{u}(0) = k_{1-\alpha}\,w_\alpha \sqrt{\frac{r_{0\alpha}}{t_g} + \frac{r_{0\alpha}}{t_0}} \tag{15}$$

and, in the same way, the decision threshold, a_β^*, is shown by Formula (16):

$$a_\beta^* = k_{1-\alpha}\,\tilde{u}(0) = k_{1-\alpha}\,w_\beta \sqrt{\frac{r_{0\beta}}{t_g} + \frac{r_{0\beta}}{t_0}} \tag{16}$$

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

8.4 Detection limit

The detection limit, $a_\alpha^\#$, is calculated using Formula (17) (see ISO 11929[24]):

$$a_\alpha^\# = a_\alpha^* + k_{1-\beta}\,\tilde{u}\left(a_\alpha^\#\right) = a_\alpha^* + k_{1-\beta}\sqrt{w_\alpha^2\left[\frac{\left(a_\alpha^\#/w_\alpha + r_{0\alpha}\right)}{t_g} + \frac{r_{0\alpha}}{t_0}\right] + \left(a_\alpha^\#\right)^2 u_{\mathrm{rel}}^2\left(w_\alpha\right)} \tag{17}$$

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

The detection limit can be calculated by solving Formula (17) for $a_\alpha^\#$ or, more simply, by iteration with an initial approximation $a_\alpha^\# = 2a_\alpha^*$.

When taking $\alpha = \beta$, then $k_{1-\alpha} = k_{1-\beta} = k$ and the solution of Formula (17) is given by Formula (18):

$$a_\alpha^\# = \frac{2a_\alpha^* + \left(k^2 w_\alpha\right)/t_g}{1 - k^2\,u_{\mathrm{rel}}^2\left(w_\alpha\right)} \tag{18}$$

In the same way, the detection limit of the beta activity per mass is given by Formula (19):

$$a_\beta^\# = \frac{2a_\beta^* + \left(k^2 w_\beta\right)/t_g}{1 - k^2\,u_{\mathrm{rel}}^2\left(w_\beta\right)} \tag{19}$$

8.5 Confidence limits

The lower, $a^<$, and upper, $a^>$, confidence limits are calculated using Formulae (20) and (21) (see ISO 11929[24]):

$$a^< = a - k_p\,u(a) \quad \text{with} \quad p = \omega\left(1 - \gamma/2\right) \tag{20}$$

$$a^> = a + k_q\,u(a) \quad \text{with} \quad q = 1 - \omega\,\gamma/2 \tag{21}$$

where

$$\omega = \Phi\left[y/u(y)\right]$$

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

If $a \geq 4\,u(a)$, ω may be set to 1. In this case, Formula (22):

$$a^{<,>} = a \pm k_{1-\gamma/2}\,u(a) \tag{22}$$

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

8.6 Quality control

Precision, sensitivity and bias are dependent on the characteristics of the detector, the radionuclides present, and the certified reference solution selected both for the discriminator setting and for counting efficiency. The radionuclides used for the calibration shall be carefully chosen in order to minimize the bias. Relevant validation and performance data of the method are reported in Annexes A and B.

The repeatability of this method has been determined and is reported in Reference [10].

9 Interference control

9.1 Contamination

Check the contamination of reagents by processing blank measurements using appropriate aliquots of distilled water. If a significant contribution of the reagents to the gross alpha or beta activity is found, select reagents with lower content of radioactivity. Run contamination checks with every new reagent batch.

The contamination of the counting system should be controlled by passing appropriate background samples (e.g. background vials supplied by the manufacturer of the counting system).

9.2 Ingrowth of radon

Radon isotopes should be volatilized during the preconcentration step. If ^{226}Ra and ^{228}Th/^{224}Ra are present, ^{222}Rn and ^{220}Rn and their alpha- and beta-emitting progeny grow in during the measurement.

9.3 Loss of polonium

Loss of polonium isotopes due to volatilization is not expected, since the samples are acidified using nitric acid and heated at temperatures far below 400 °C.

10 Test report

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

a) a reference to this document, i.e. ISO 11704:2018;

b) identification of the sample;

c) the radionuclides used for the calibration;

d) the units in which the results are expressed;

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

Complementary information can be provided, such as:

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

g) decision threshold and the detection limit;

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

   1) when the activity per mass, a, is compared with the decision threshold (see ISO 11929[24]), the result of the measurement should be expressed as $\leq a^*$ when the result is below the decision threshold;

   2) when the activity per 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;

i) all operating details not specified in this document, or regarded as optional, together with details of any incidents that could have influenced the test result(s).

Annex A
(informative)

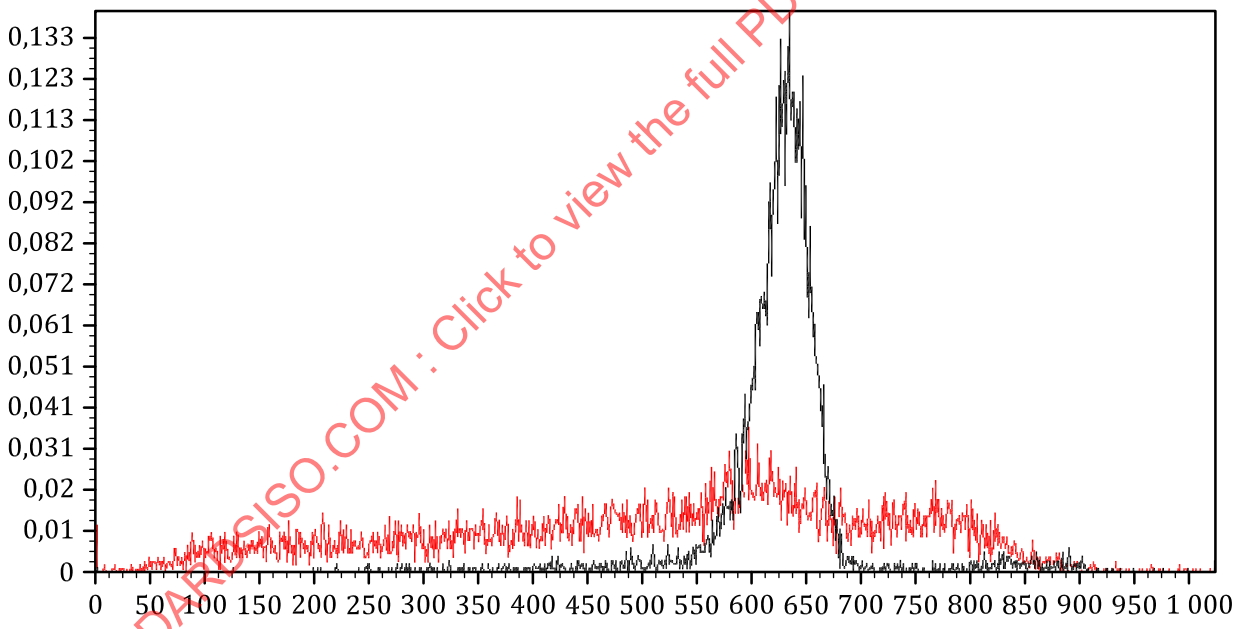
Set-up parameters and validation data

A.1 General

The following data were obtained by ARPA Lombardia, Milano (Italy). Measurements were performed by a Quantulus 1220 (PerkinElmer) liquid scintillation counter. PTFE-coated polyethylene vials (Zinsser, Polyvials SLD) and Quicksafe 400 (Zinsser) scintillation cocktail were used. Counts in 500 to 700 channel window (alpha) and in 200 to 1 000 channel window (beta) were considered.

A.2 Instrument set up and calibration

In Figure A.1, discriminated alpha and beta spectra of a natural water obtained with the above described materials and a 60 000 s counting time are shown.



Key

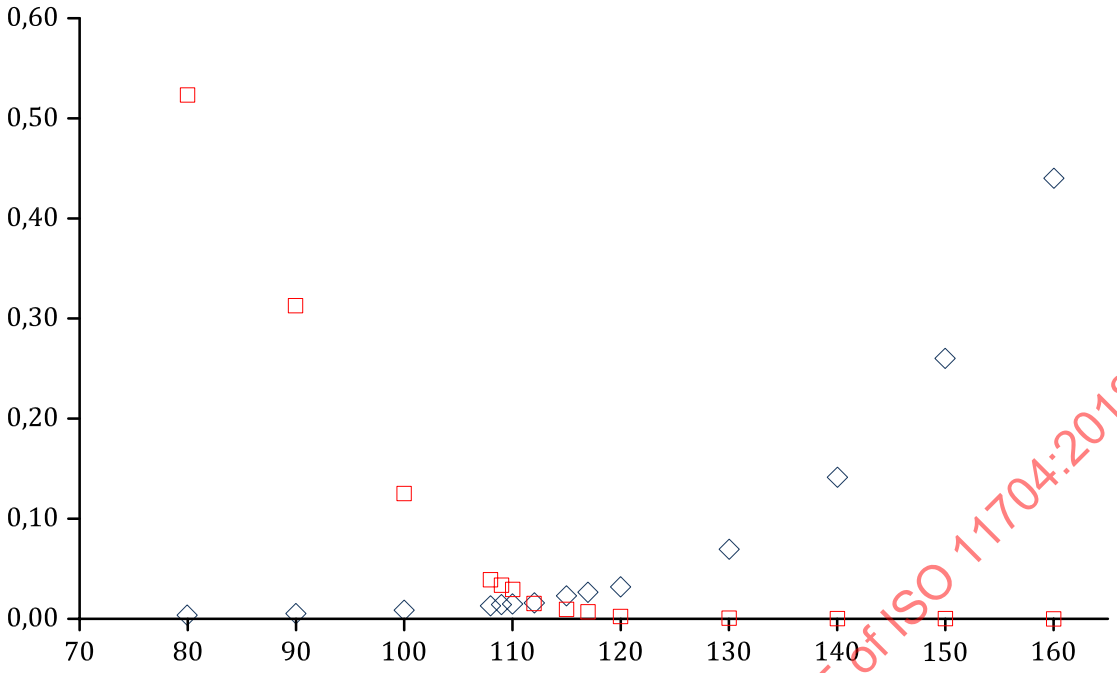
X counts

Y channels

Figure A.1 — Superposed alpha/beta spectra of a natural water sample

The spillover diagram obtained as described in 7.4.2 is reported in Figure A.2. Calibration sources of ^{236}U and ^{40}K were used.

Under the specified working conditions, the resulting best discrimination parameter (PSA) is 112 and the minimum interference value is 1,5 %. Different values can be obtained when other chemicals and/or counters are used.



Key

X discrimination parameter (PSA)

Y alpha (τ_α) and beta (τ_β) spillover

Figure A.2 — Spillover diagram

Overall efficiency was determined as described in 7.4.2. Results are reported in Table A.1.

Table A.1 — Calibration parameters

Calibration RN	Activity	Replicates	Average value ε	ε combined uncertainty[a]
^{236}U	0,48 Bq	3	0,983	0,023 (2,3 %)
^{40}K	0,54 Bq[b]	3	0,975	0,027 (2,8 %)

[a] ε combined uncertainty is the common uncertainty of efficiency values. These combined uncertainties take into account uncertainties of counting, background and standard activity.

[b] For ^{40}K, 0,54 Bq correspond to 0,48 beta/sec, taking into account the emission probability by beta decay.

The variance of replicate measurement is not considered in the calculation of efficiency uncertainty since the method repeatability contribution is evaluated.

A.3 Expression of results

Decision threshold and detection limits, calculated as in 8.3 and 8.4, are reported in Table A.2 for the chosen condition (1:10 concentrated samples). The above-reported efficiency and blank values are used. Counting times of 60 000 s were used.