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Water quality — Tritium — Test method using liquid scintillation counting

Qualité de l'eau — Tritium — Méthode d'essai par comptage des scintillations en milieu liquide

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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 third edition cancels and replaces the second edition (ISO 9698:2010), which has been technically revised. The main changes compared to the previous edition are as follows:

— the Introduction has been developed;

— the Scope has been updated;

— the sample preparation has been revised;

— the Bibliography has been enhanced.

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, 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 fertilizer 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 the 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]. Water bodies and drinking waters are monitored for their radioactivity content 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 and ISO 5667-20[4].

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 10 000 $Bq \cdot l^{-1}$ for ^{3}H activity concentration.

NOTE 1 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].

In the event of a nuclear emergency, the WHO Codex guideline levels[5] mentioned that the activity concentration might not be greater than 1 000 $Bq \cdot l^{-1}$ for infant food and 10 000 $Bq \cdot l^{-1}$ for food other than infant food, including organically bound tritium.

NOTE 2 The Codex guidelines levels (GLs) apply to radionuclides contained in food destined for human consumption and traded internationally, which have been contaminated following a nuclear or radiological emergency. These GLs apply to food after reconstitution or as prepared for consumption, i.e. not to dried or concentrated food, and are based on an intervention exemption level of 1 mSv in a year for members of the public (infant and adult)[5].

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].

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

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

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

This document has been developed to answer the need of test laboratories carrying out these measurements, that are sometimes required by national authorities, as they 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 — Tritium — 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 and to determine the applicability of any other restrictions.

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 by liquid scintillation counting for the determination of tritium activity concentration in samples of marine waters, surface waters, ground waters, rain waters, drinking waters or of tritiated water ($[^3H]H_2O$) in effluents.

The method is not directly applicable to the analysis of organically bound tritium; its determination requires additional chemical processing of the sample (such as chemical oxidation or combustion).

With suitable technical conditions, the detection limit may be as low as 1 $Bq \cdot l^{-1}$. Tritium activity concentrations below 10^6 $Bq \cdot l^{-1}$ can be determined without any sample dilution.

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

ISO/IEC Guide 99, *International vocabulary of metrology — Basic and general concepts and associated terms (VIM)*

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 and symbols

3.1 Terms and definitions

For the purposes of this document, the definitions, symbols and abbreviations given in ISO/IEC Guide 99, ISO/IEC Guide 98-3, ISO 80000-10 and the following 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/

3.1.1
effluent
water or wastewater discharged from a containing space such as a treatment plant, industrial process or lagoon

3.2 Symbols

For the purposes of this document, the symbols given in ISO/IEC Guide 99, ISO/IEC Guide 98-3, ISO 80000-10 and the following apply.

Symbol	Definition	Unit
β_{max}	Maximum energy for the beta emission	keV
V	Volume of test sample	l
m	Mass of test sample,	kg
ρ	Density of the sample	$kg \cdot l^{-1}$
c_A	Activity concentration, in	$Bq \cdot l^{-1}$
a	Activity per unit of mass	$Bq \cdot kg^{-1}$
A	Activity of the calibration source	Bq
n	Number of counting	
t_0	Background counting time	s
t_g	Sample counting time	s
t_s	Calibration counting time	s
r_0	Background count rate	s^{-1}
r_g	Sample count rate	s^{-1}
r_s	Calibration count rate	s^{-1}
ε	Detection efficiency	
f_q	Quench factor	
$u(c_A)$	Standard uncertainty associated with the measurement result	$Bq \cdot l^{-1}$
U	Expanded uncertainty, calculated by $U = k \cdot u(c_A)$ with k = 1, 2,...,	$Bq \cdot l^{-1}$
c_A^*	Decision threshold	$Bq \cdot l^{-1}$
$c_A^\#$	Detection limit	$Bq \cdot l^{-1}$
$c_A^\triangleleft, c_A^\triangleright$	Lower and upper limits of the confidence interval	$Bq \cdot l^{-1}$

4 Principle

The test portion is mixed with the scintillation cocktail in a counting vial to obtain a homogeneous medium. Electrons (Beta particles) emitted by tritium transfer their energy to the scintillation medium. Molecules excited by this process return to their ground state by emitting photons that are detected by photodetectors[8].

The choice of the analytical procedure (either with or without distillation of the water sample prior to determination), depends on the aim of the measurement and the sample characteristics[19][20][21].

Direct measurement of a raw water sample using liquid scintillation counting[8] shall consider the potential presence of other beta emitter radionuclides. To avoid interference with these radionuclides when they are detected, the quantification of tritium is performed following the sample treatment by distillation[22][23][24][25]. Annexes B, D and E describe three distillation procedures.

In order to determine the background count rate, a blank sample is prepared in the same way as the test portion. The blank sample is prepared using a reference water of the lowest activity available, also sometimes called “dead water”.

In order to determine the detection efficiency, it is necessary to measure a water sample having a known tritium activity under conditions that are identical to those used for the test sample. This water shall be a dilution of this mixture produced with the reference water, or a water with a traceable tritium activity usable without dilution.

The conditions to be met for the blank sample, the test portion and the calibration source are:

— same scintillation cocktail;

— same type of counting vial;

— same filling geometry;

— same ratio between test portion and scintillation cocktail;

— temperature stability of the detection equipment;

— value of quench indicating parameter included in calibration curve.

If particular conditions of chemical quenching affect the measurement results, it is recommended to correct the counting data using a quench curve (see 7.3.2).

5 Reagents and equipment

Use only reagents of recognized analytical grade.

5.1 Reagents

5.1.1 Water for the blank

The water used for the blank shall be as free as possible of chemical impurities to avoid quenching, of radioactive impurities[26][27] and with an activity concentration of tritium negligible in comparison with the activities to be measured.

For example, a water sample with a low tritium activity concentration can be obtained from (deep) subterranean water kept in a well-sealed borosilicate glass bottle in the dark at controlled temperature (see ISO 5667-3). This blank water sample shall be kept physically remote from any tritium containing material.

It is advisable to keep an adequate quantity of blank water in stock and to make small working amounts from it for immediate use as required. Contamination with tritium (e.g. from water vapour in the air and from tritium sources such as luminous watches and gas chromatographs) or other radioactive species should be avoided.

Determine the tritium activity concentration, in $Bq \cdot l^{-1}$, of this water and note the date of the determination.

As the activity is becoming non-negligible for activities around 1 $Bq \cdot l^{-1}$, it is necessary to use a blank water measured to ensure the “absence” of tritium. The tritium activity concentration in the blank water can be determined by enrichment followed by liquid scintillation counting or from the measurement of ^{3}He by mass spectrometry. Preferably use blank water with a tritium activity concentration of less than 0,5 $Bq \cdot l^{-1}$.

When the volume of blank water is sufficiently large, e.g. 10 l to 20 l, and well-sealed, tritium activity concentration should remain stable for years, although it is advisable to verify this activity concentration at predetermined intervals, e.g. every year.

5.1.2 Calibration source solution

In order to avoid cross-contamination, prepare, in a suitable location which is remote from the area where the tritium analyses are to be carried out, weigh and pour into a weighed volumetric flask (for example, 100 ml) the requisite quantity of a concentrated tritium ($[^3H]H_2O$) standard solution, so that the tritium activity concentration generates sufficient counts to reach the required measurement uncertainty after dilution with blank water and thorough mixing. Calculate the tritium activity concentration of the resulting calibration source solution (t = 0). Note the date at which the standard solution was made up (t = 0).

The tritium activity concentration of the calibration source solution at time t at which the samples are measured shall be corrected for radioactive decay.

It is recommended to adapt the flask to the standard source volume so as to not leave air above its surface, in order to minimize the exchange of tritium with the atmosphere at each opening of the flask.

5.1.3 Scintillation solution

The scintillation cocktail is chosen according to the characteristics of the sample to be analysed and according to the properties of the detection equipment[28].

It is recommended to use a hydrophilic scintillation cocktail for the measurement of environmental water or waste water.

The characteristics of the scintillation cocktail shall ensure the mixture is homogeneous and stable at the given mixing ratio and at the temperature of the counting system.

For the direct measurement of raw waters containing particles in suspension, it is recommended to use a scintillation cocktail leading to a gel type mixture.

It is recommended to

— store the scintillation cocktail in the dark and, particularly just before counting, avoid exposure to direct sunlight or fluorescent light in order to prevent interfering luminescence, and

— comply with storage conditions specified by the scintillation cocktail supplier.

The mixtures (scintillation cocktail and test sample) should be disposed of as chemical waste, and, depending on the radioactivity, may require disposal as radioactive waste.

5.1.4 Quenching agent

Examples of chemical quenching agents include nitric acid, acetone, organochloride compounds, nitromethane, etc.

NOTE Some quenching agents are dangerous or toxic.

5.2 Equipment

5.2.1 General

Laboratory equipment, such as pipettes and balances, shall be employed that enables the expected/agreed data quality objectives to be achieved, as well as the quantification of the uncertainty attached to the measurement.

Control of the quantity of liquid scintillation cocktail used in source preparation is essential to achieve consistent data quality.

5.2.2 Liquid scintillation counter

Liquid scintillation counter preferably with an automatic sample transfer. Operation at constant temperature is recommended following the manufacturer's instructions. Depending on the limit of detection to be reached, a liquid scintillation counter with a low-level-configuration may be needed. The method specified in this document relates to the widely used liquid scintillation counters with vials that hold about 20 ml. When other vials are used with appropriate counters, the described method shall be adapted accordingly.

5.2.3 Counting vials

Different types of scintillation vials exist, manufactured using a range of materials. The most common are glass vials and polyethylene vials. Glass vials allow visual inspection of the scintillation medium, but have an inherent background, due to the presence of ^{40}K. However, some organic solvents contained in scintillation cocktails diffuse through the polyethylene, accelerating the degradation of the mixture.

Other types of vials that exist are the following:

— glass vials with a low level of ^{40}K, exhibit a lower background than 'normal' glass vials;

— for the determination of very low tritium concentration, the use of polytetrafluoroethylene vials (PTFE) or polyethylene vials with an inner layer of PTFE on inside vial wall is strongly recommended. Diffusion of organic solvents is then slower through PTFE than through polyethylene. These vials are used for long counting times with very low-level activity to be measured.

Generally, the vials are single use. If the vial is re-used, it is necessary to apply an efficient cleaning procedure.

To prevent interfering luminescence, the counting vials should be kept in the dark and should not be exposed to direct sunlight or fluorescent light, particularly just before counting.

Toluene-based scintillation solutions may physically distort polyethylene and should therefore not be used in combination with polyethylene counting vials. Diffusion of organic solvents into and through the polyethylene walls is also a serious drawback of polyethylene vials.

6 Sampling and samples

6.1 Sampling and sample transportation

Conditions of sampling shall conform to ISO 5667-1. Preservation and handling of water samples shall be in accordance with ISO 5667-3. Additional information on sampling of different types of waters can be found in the relevant parts of ISO 5667[9][10][11][12][13][14][15][16]. Additional information on quality assurance of environmental water sampling and handling is given in ISO 5667-14[17].

The sample shall not be acidified due to the high chemical quench caused by acids, and the potential presence of tritium in the acid (as specified in ISO 5667-3).

It is important that the laboratory receives a representative sample, unmodified during the transport or storage and in an undamaged container. To avoid compromising the sample, it is recommended to use plastic containers for effluents and glass containers for other types of samples. The glass containers reduce the risk of cross contamination. The plastic containers limit the risk of breakage and spilling of effluents, which may contain high activity concentrations of radionuclides.

For low level activity measurements, it is important to minimize contact between the sample and the atmosphere during the sampling.

It is recommended to fill the container completely, leaving no headspace to minimize tritium exchange with the atmospheric moisture.

6.2 Sample storage

If needed, the samples shall be stored in compliance with ISO 5667-3. If the storage duration exceeds three months as recommended in ISO 5667-3, it is advisable to store the samples in glass containers.

For liquid effluents, it is recommended to store separately the samples with high, medium and low level tritium activity concentrations.

7 Procedure

7.1 Sample preparation

7.1.1 General

A monitoring program should be part of the laboratory quality system, in order to detect any potential cross contamination between samples with widely varying activity concentrations. The ambient air of the laboratory should be monitored for tritium, for example by measuring condensed humidity, free surface water from open vial, etc. or carrying out specific studies demonstrating the absence of risk of cross contamination.

A prior enrichment step can significantly lower the limit of detection[27][28][29][30].

7.1.2 Direct procedure

Measurement of the test sample is generally performed on raw water without removal of suspended matter. If the activity of a filtered or centrifuged sample is to be measured, the removal of suspended matter shall be performed as soon as possible after the sampling (see ISO 5667-3).

7.1.3 Distillation

Examples of distillation procedures are given in Annexes B, D and E.

Distillation shall avoid isotopic fractionation[31][32]. The yield of the distillation method shall be verified by analysing a tritium certified standard solution, or at least a known activity concentration water, in the same way as the portion test sample.

Distillation or any other physic-chemical treatment of water is not appropriate for simultaneous measurement of ^{3}H and ^{14}C.

7.2 Preparation of the sources to be measured

A known quantity of the test sample and the scintillation cocktail are introduced into the counting vial.

After closing the vial, it shall be thoroughly shaken to homogenize the mixture.

The vial identification shall be indicated on the top of the vial cap. The storage time depends upon the scintillation mixture, the mixture stability and the nature of the sample. It is recommended to perform the measurement as soon as any photoluminescence or static electricity effects have become negligible, for example, after 12 h.

In order to reduce photoluminescence effects, it is recommended that the above-mentioned operations take place in dimmed light (preferably light from an incandescent source or UV-free LED or red light); in addition one should avoid direct sunlight or fluorescent light.

In order to reduce static electricity effects, the vial can be sprayed with an antistatic agent or wiped with a moist tissue.

7.3 Counting procedure

7.3.1 General

The measurement conditions (measurement time, blank sample, number of cycles or repetitions) are defined according to the uncertainty and detection limit to be achieved.

7.3.2 Control and calibration

Statistical control of the detection system shall be monitored by measurement of suitable reference background and reference sources usually provided by the equipment supplier, for example in compliance with ISO 7870-2[18].

The correct operation of the counter shall be checked periodically by means of reference sources which cover the energy range to be measured.

The background is measured prior to each measurement or each series of measurements of samples, under the conditions representative of each type of measurement (Clause 4).

The detection efficiency is determined with a sample of a standard of aqueous tritium (calibration source), or a dilution of this standard with water for the blank, measured in the same conditions as the test portion.

Using direct measurement, it is essential to generate a quench curve for each type of water measured. The quench curve is valid only for:

— a given type of measurement equipment;

— a given type of scintillation cocktail;

— a given ratio of scintillation cocktail and test sample.

Particular conditions of chemical quenching affect the measurement results, thus it is recommended to correct the counting data using a quench curve. It is important to choose a chemical quenching agent similar to the quenching observed in the sample. The quench curve correction is not applicable to colour quenched samples.

The quench curve is obtained with a series of working standards (10 for example), presenting different quench. The matrix of the working standards is representative of matrix of the samples to be measured (same scintillation liquid, same ratio scintillation liquid-test sample). The working standards may be prepared as follows:

— Similar quantity of certified standard tritiated water solution in each vial. The activity of the certified standard shall be sufficient for the counting ratio to be defined with a known statistical precision, even in the case of a strong quench.

— The standard is completed with reference water until the volume of test sample is reached.

— The scintillation cocktail is added to obtain the desired ratio.

— One working standard at least is used as it is. In the other working standards, increasing quantities of quenching agent are added to simulate the quench encountered in the samples to be measured.

The quench curve relating $\varepsilon \cdot f_q$ with the quenching is used to determine f_q.

For high activity and highly quenched samples or colour quenched samples, it may be practical to use an internal standard method, as described in Annex C.

7.3.3 Measurement conditions

The counting room used shall be suitable for the measurement equipment and to the activity levels of the samples.

The measurement is performed using an energy window that is between the detector noise threshold and the β_{max} of tritium (18,6 keV). It is recommended to choose the width of the energy window in order to optimize the figure of merit $\left(\varepsilon^2/r_0\right)$.

The absence of other radionuclides is verified by checking the counting rate above the maximum energy β_{max} of the tritium.

In order to verify the statistical distribution of counting data, it is recommended to arrange the counting as repetitions: the first sample is counted several times in a row (number of repetitions), then the second sample is counted likewise, and so on.

To measure low activities, it is recommended to fractionate the counting as cycles: all samples are counted once, then the counting starts for the second cycle and so on.

These fractionations of the counting time allow the detection of random or transitory interfering effects (luminescence, static electricity) that are not auto-corrected by the measurement equipment. They also take into account any perturbations, punctual or cyclic (night and day alternation for example) associated to the measurement equipment environment.

7.3.4 Interference control

7.3.4.1 Interference arising from luminescence

Serious interference of tritium determinations can occur due to a variety of luminescent processes, e.g. chemiluminescence, phosphorescence, treboluminescence, and static electricity. It is advisable to use a liquid scintillation counter capable of identifying these single photon events and current LSC equipment can even automatically corrects for these interferences.

In the absence of such an automatic correction, for example the tritium can be measured in parallel in another measurement channel B having the same lower threshold as measurement channel A, but an upper threshold adjusted so that the tritium counting efficiency is about two thirds of the tritium counting efficiency of channel A:

— In the absence of interfering luminescent phenomena, calculation should yield the same absolute tritium activity concentration in a sample for both measuring channels A and B, using appropriate efficiencies for each channel.

— In the presence of excessive luminescence the calculation gives an apparently higher activity for channel B than for channel A, due to random coincident monophoton events which the equipment cannot distinguish from the tritium double photon pulses; these pulses lie near the lower threshold and are consequently registered by channels A and B with the same counting efficiency. The occurrence of such a discrepancy points to an interference due to luminescence and the data should be discarded.

7.3.4.2 Equipment stability

Once the measurement channels A and B have been adjusted, it is advisable to check that the setting is maintained by measuring in each sequence two hermetically sealed unquenched vials, one containing tritium standard solution and the other containing blank water. Drift of the equipment from its initial setting is then easily detected. The use of control charts ISO 7870-2[18] is advisable.

8 Expression of results

8.1 General

The results are generally expressed in activity per unit of mass or activity concentration together with their associated uncertainty. The coverage factor is specified in the presentation of the results.

Whatever the adopted form, the expression of results is an estimation of the "true" value, with which an uncertainty is associated, itself being a combination of elementary uncertainties.

In the case of the measurement of radionuclides by liquid scintillation, only the elementary uncertainties of the following parameters are taken into consideration:

— raw counts and backgrounds;

— detection efficiencies in the windows of the relevant energy ranges for a given quench indicating parameter;

— quench factor, if a correction is applied;

— volume or mass of the test portion.

The other uncertainties can, at first approximation, be ignored (volume or mass of scintillation cocktail, counting time, etc.). An example is given in Annex A.

8.2 Calculation of activity concentration

The symbols used are defined in Clause 3.

The sample activity concentration of the radionuclide present in the sample is calculated using Formula (1):

$$c_A = \frac{r_g - r_0}{V} \cdot \frac{1}{\varepsilon \cdot f_q} = (r_g - r_0) \cdot w \tag{1}$$

where

$$w = \frac{1}{V \cdot \varepsilon \cdot f_q} \quad \text{and}$$

$$\varepsilon = \frac{r_s - r_0}{A}$$

r_g and r_0 are calculated using the expressions: $r_g = \sum_{i=1}^{n} \frac{r_{gi}}{n}$ and $r_0 = \sum_{i=1}^{n} \frac{r_{0i}}{n}$, considering that the number of repetitions n is the same for the sample and for the background.

The combined uncertainty is calculated using Formula (2):

$$u(c_A) = \sqrt{w^2 \cdot \left(u^2(r_g) + u^2(r_0)\right) + c_A{}^2 \cdot u_{rel}^2(w)} = \sqrt{\frac{w^2}{n} \cdot \left(\frac{r_g}{t_g} + \frac{r_0}{t_0}\right) + c_A{}^2 \cdot u_{rel}^2(w)} \tag{2}$$

$$u_{\mathrm{rel}}^2(w) = u_{\mathrm{rel}}^2(\varepsilon) + u_{\mathrm{rel}}^2(V) + u_{\mathrm{rel}}^2(f_{\mathrm{q}}) \tag{3}$$

and the relative standard uncertainty of ε for each quenching value is calculated using Formula (4):

$$u_{\mathrm{rel}}^2(\varepsilon) = u_{\mathrm{rel}}^2(r_{\mathrm{s}} - r_0) + u_{\mathrm{rel}}^2(A) = (r_{\mathrm{s}}/t_{\mathrm{s}} + r_0/t_0)/(r_{\mathrm{s}} - r_0)^2 + u_{\mathrm{rel}}^2(A) \tag{4}$$

$u_{\mathrm{rel}}^2(A)$ includes all the uncertainties related to the calibration source: that is in the standard solution and the preparation of the calibration source.

$u_{\mathrm{rel}}^2(f_{\mathrm{q}})$ depends on the mathematical model used to fit the quench curve.

For the calculation of the characteristic limits, $\tilde{u}(\tilde{c}_A)$ is needed (see ISO 11929), i.e. the standard uncertainty of c_A as a function of its true value, calculated by using Formula (5):

$$\tilde{u}(\tilde{c}_A) = \sqrt{\frac{w^2}{n} \cdot \left[\left(\frac{\tilde{c}_A}{w} + r_0 \right) \Big/ t_{\mathrm{g}} + \left(r_0 / t_0 \right) \right] + \tilde{c}_A^2 \cdot u_{\mathrm{rel}}^2(w)} \tag{5}$$

If the mass is used instead of volume, the mass of the test sample, m, is expressed in kilogram. The intermediate calculations are done with similar equations. Activity may also be expressed as the activity per unit of mass (m replacing V in preceding formula).

8.3 Decision threshold

The decision threshold, c_A^*, is obtained from Formula (5) for $\tilde{c}_A = 0$ (see ISO 11929). This yields:

$$c_A^* = k_{1-\alpha} \cdot \tilde{u}(0) = k_{1-\alpha} \cdot w \cdot \sqrt{\left(r_0 / n \right) \cdot \left(1/t_{\mathrm{g}} + 1/t_0 \right)} \tag{6}$$

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

8.4 Detection limit

The detection limit, $c_A^\#$, is calculated by using Formula (7) (see ISO 11929):

$$c_A^\# = c_A^* + k_{1-\beta} \cdot \tilde{u}(c_A^\#) = c_A^* + k_{1-\beta} \cdot \sqrt{\frac{w^2}{n} \cdot \left[\left(\frac{c_A^\#}{w} + r_0 \right) \Big/ t_{\mathrm{g}} + \left(r_0 / t_0 \right) \right] + c_A^{\#2} \cdot u_{\mathrm{rel}}^2(w)} \tag{7}$$

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

The detection limit can be calculated by solving Formula (7) for $c_A^\#$ or, more simply, by iteration with a starting approximation $c_A^\# = 2 \cdot c_A^*$.

When taking $\alpha = \beta$ then $k_{1-\alpha} = k_{1-\beta} = k$ and the solution of Formula (7) is given by Formula (8):

$$c_A^\# = \frac{2 \cdot c_A^* + \dfrac{k^2 \cdot w}{n \cdot t_{\mathrm{g}}}}{1 - k^2 \cdot u_{\mathrm{rel}}^2(w)} \tag{8}$$

8.5 Confidence interval limits

The lower, $c_A^{\triangleleft}$, and upper, $c_A^{\triangleright}$, confidence limits are calculated using Formulae (9) and (10) (see ISO 11929):

$$c_A^{\triangleleft} = c_A - k_p \cdot u(c_A) \; ; \; p = \omega \cdot (1 - \gamma/2) \tag{9}$$

$$c_A^{\triangleright} = c_A + k_q \cdot u(c_A) \; ; \; q = 1 - (\omega \cdot \gamma/2) \tag{10}$$

where

ω = $\Phi(y/u(y))$, Φ being the distribution function of the standardized normal distribution,

$1 - \gamma$ is the probability for the confidence interval of the measurand, and $\omega = 1$ may be set if $c_A \geq 4 \cdot u(c_A)$. In this case:

$$c_A^{\triangleleft}, c_A^{\triangleright} = c_A \pm k_{1-\gamma/2} \cdot u(c_A) \tag{11}$$

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

8.6 Calculations using the activity per unit of mass

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

$$c_A = \frac{r_g - r_0}{m} \cdot \frac{\rho}{\varepsilon \cdot f_q} = (r_g - r_0) \cdot w \quad \text{and} \quad w = \frac{\rho}{m \cdot \varepsilon \cdot f_q} \tag{12}$$

$$u_{rel}^2(w) = u_{rel}^2(\varepsilon) + u_{rel}^2(m) + u_{rel}^2(\rho) + u_{rel}^2(f_q) \tag{13}$$

The uncertainty, the characteristics limits and the limits of the confidence interval may be calculated using the previous expression [Formulae (2),(6),(7) and (8) with Formulae (12) and (13)].

9 Test report

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

a) a reference to this document, i.e. ISO 9698:2019;

b) identification of the sample;

c) units in which the results are expressed;

d) test result, $c_A \pm u(c_A)$ or $c_A \pm U$ 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 activity concentration c_A is compared with the decision threshold (see ISO 11929), the result of the measurement should be expressed as ≤ c_A^* when the result is below or equal to the decision threshold;

   — when the activity concentration c_A is compared with the detection limit, the result of the measurement can be expressed as ≤ $c_A^\#$ when the result is below or equal to 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 and/or to explain the results.

Annex A
(informative)

Numerical applications

Table A.1 presents the parameter values for three situations of activity concentration. This table may be used to verify any computation of the different formulae. Example for constant quenching measurement: same quenching between reference vial, background and test vial.

Table A.1 — Examples of numerical applications

Symbol	Unit	$c_A < c_A^*$	$c_A^* < c_A < c_A^\#$	$c_A > c_A^\#$
r_g	s^{-1}	0,058 3	0,062 5	0,108 3
t_g	s	3 600	3 600	3 600
r_0	s^{-1}	0,050	0,050	0,050
t_0	s	3 600	3 600	3 600
V	l	0,010	0,010	0,010
$u(V)$	l	0,002 5	0,002 5	0,002 5
ε		0,25	0,25	0,25
$u_{rel}(\varepsilon)$		0,008 75	0,008 75	0,008 75
α, β, γ	%	5	5	5
w	l^{-1}	400	400	400
$u_{\text{rel}}^2(w)$		0,063 7	0,063 7	0,063 7
ω	—	0,922 0	0,974 2	0,999 8
p	—	0,898 9	0,949 9	0,974 9
q	—	0,977 0	0,975 6	0,975 0
k_p	—	1,275	1,644	1,957
k_q	—	1,994	1,971	1,960
c_A	$Bq \cdot l^{-1}$	3,33	5,00	23,33
$u(c_A)$	$Bq \cdot l^{-1}$	2,35	2,57	6,46
c_A^*	$Bq \cdot l^{-1}$	3,47	3,47	3,47
$c_A^\#$	$Bq \cdot l^{-1}$	8,74	8,74	8,74
$c_A^\triangleleft$	$Bq \cdot l^{-1}$	0,34	0,78	10,69
$c_A^\triangleright$	$Bq \cdot l^{-1}$	8,02	10,06	36,00

For example, to calculate in Excel©[1)]:

ω = NORMSDIST($c_A/u(c_A)$)

k_p = NORMSINV (p)

k_q = NORMSINV (q)

1) Microsoft Excel© is an example of a suitable product available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of this product.

Annex B
(informative)

Distillation of large volume sample

B.1 Principle

Samples of volume from 100 ml to 500 ml are considered as large volume samples. If the presence of iodine is suspected in the water sample, before the distillation, oxidizing and suitable alkaline agents are added to convert iodine into iodide (non-volatile iodine compounds). Some organically bound tritium (OBT) compounds present in the sample may be oxidized[22][33] and can contribute to the tritium measured in the distillate.

An aliquot of the distillate is then mixed with the scintillation solution in a counting vial.

NOTE The majority of the interfering compounds, which quench the scintillation process, remain in the residue of the distillation together with any interfering radionuclides (radioactive iodine, carbon 14, caesium 137, etc.).

B.2 Reagents and equipment

During the analysis use only reagents of recognized analytical grade.

B.2.1 Reagents

For the oxidant/alkaline medium use either

B.2.1.1 Sodium thiosulfate, anhydrous, $Na_2S_2O_3$, and

B.2.1.2 Sodium carbonate, anhydrous, Na_2CO_3, or

B.2.1.3 Potassium permanganate, $KMnO_4$ and

B.2.1.4 Sodium hydroxide, NaOH.

The sodium hydroxide shall be free of tritium.

B.2.1.5 Tritium standard solution.

B.2.1.6 Scintillation solution.

B.2.1.7 Blank water.

B.2.1.8 Carborundum or **glass beads.**

B.2.2 Equipment

Usual laboratory equipment and the following.

B.2.2.1 Distillation equipment, consisting of the following.

B.2.2.1.1 Distillation flask, with a capacity of 500 ml.

B.2.2.1.2 Splash head.

B.2.2.1.3 Distillation column, length 40 cm.

B.2.2.1.4 Condenser.

B.2.2.1.5 Adapter, bent type.

The equipment shall be dried before use.

B.2.2.1.6 Borosilicate glass or **polyethylene bottles,** of capacity about 100 ml.

B.3 Distillation

B.3.1 General

Place the test sample in the distillation equipment. Add a quantity of oxidant agent to convert iodine into iodide, enough of alkaline agent to make the sample alkaline. Add porous porcelain or carborundum or glass beads in order to facilitate a homogeneous and smooth boiling.

Assemble the distillation equipment and start the distillation process.

Distil, discard the first part of distillate, and collect about the half of the middle fraction in a clean and dry bottle. Discard the residue in the flask.

B.3.2 Sample preparation

B.3.2.1 General

Place an aliquot of the water sample (100 ml to 250 ml) in the distillation flask.

If a suspended matter is observed, it can be eliminated by filtering.

All the employed material shall be well dried.

The initial sample should not be acidified and should be kept in a hermetic glass container.

B.3.2.2 Oxidation in alkaline medium

Add the necessary reagents to obtain an adequate medium for the oxidation. For example, using an aliquot of 250 ml, the following can be used:

a) 0,1 g of potassium permanganate and 0,5 g of sodium hydroxide[22][33], or

b) 0,25 g of sodium thiosulfate and 0,50 g of sodium carbonate.

NOTE If the above reagents are not added, the possible presence of organic matter and/or volatile isotopes in the sample can affect the results.

B.3.2.3 Homogenization

Add porous porcelain or carborundum or glass beads in order to facilitate a homogeneous and smooth boiling.

B.3.3 Discard

The first millilitre of distilled water (10 % to 30 % of the initial aliquot) can be kept for isotopic control if needed.

B.3.4 Collection

Collect the intermediate fraction (about 50 % of the initial aliquot) and collect the volume that remains in the flask for any ultimate control.

B.3.5 Control

The pH-value or the conductivity of the intermediate distillation fraction shall be controlled. The pH-value shall be neutral and the conductivity lower than 0,1 $mS.cm^{-1}$. When these pH or conductivity conditions are not satisfied, the distillation shall be performed again.

The distilled sample should be kept in a hermetic glass container and in a refrigerated and darkened room, preferably.

The following measurement steps shall be performed as described in the main body of this document.

B.4 Measurement

The measurement steps shall be performed as described in Clause 7.

Annex C
(informative)

Internal standard methods

C.1 Principle

A tritium standard solution can be added in the sample. This method is recommended for sample with high chemical and/or colour quenching value to assess the counting efficiency.

C.2 Sample preparation

For each water sample fill, preferably in dimmed light, two counting vials, with a volume V_1, in millilitres (see note) of scintillation solution followed by a volume $V = 20 - V_1$, in millilitres, of sample. Identify separately the two counting vials, for example N and S. This mixture is further referred to as scintillation emulsion. Add, using a pipette (for example, 100 µl), a known quantity of a tritium standard solution to one of these counting vials, labelled S. The added activity is called A_s. Fill, in the same way, the appropriate number, as required by the counting procedure, of background counting vials with a volume V_1, in millilitres, of scintillation solution followed by a volume $V = 20 - V_1$, in millilitres, of blank water. The total inaccuracy of each addition should be less than or equal to 1 %. Mark the lids of these counting vials, for example with the designations N_1, S_1, N_2, S_2, N_3, S_3, etc. Shake the counting vials thoroughly and uniformly, for example using a shaking machine.

The above-mentioned operations should take place in dimmed light (preferably light from an incandescent source or red light). Avoid direct sunlight or fluorescent light in view of the possible interference by luminescence in some batches of counting vials.

For routine control determinations of similar samples, little difference may be experienced in the counting efficiency between samples. In this case it would be acceptable to determine a mean counting efficiency from internal standard addition to two to three samples of the group or to use the efficiency indicated by a calibrated external standard technique.

The use of an internal standard is recommended when polyethylene counting vials are used. When using an external standard in polyethylene counting vials, interference may arise because the counting rate of the external standard changes as a function of time, on account of the loss of components of the scintillation solution by diffusion into the wall of the counting vial. The effects are considerably smaller at lower temperatures (4 °C to 10 °C) than at higher temperatures (e.g. 20 °C to 25 °C).

NOTE Under optimal preparation conditions, many liquid scintillation solutions can incorporate up to about 50 % of water, in this case V_1 = 10 ml.

C.3 Counting procedure

After shaking, wipe the counting vials with a damp cloth that does not leave any deposit to remove any electrostatic charge; hereafter, avoid contact with the light-transmitting parts of the counting vials.

Place the counting vials in a fixed sequence in the liquid scintillation counter: background, sample 1, sample 1 with internal standard solution added, sample 1, background, sample 2, etc.

Count the vials for a preset time period using one or more measurement channels or, for the vials with internal standard solution, until a preset count is reached.

A counting time of 100 min per vial is generally sufficient. It is preferable to count the vial series during repeated short counting times rather than one long counting time, e.g. instead of one 100 min count,

count five times for 20 min; for this purpose, an automatic sample presentation unit is necessary. This provides for a better control of stability of the samples and the possibility of undetected erroneous counts is reduced.

Before counting it is advisable to equilibrate the counting vials in the liquid scintillation counter for light and temperature adaptation, for example overnight, thus reducing the chance of interfering luminescence occurring during counting.

C.4 Expression of results

The generic formulae are used taking into account that the counting efficiency is calculated with Formula (C.1):

$$\varepsilon = \frac{r_s - r_g}{A_s} \tag{C.1}$$

where

r_s is the counting rate, in pulses per second, of the sample with the internal standard solution added;

r_g is the counting rate, in pulses per second, of the sample without internal standard solution added;

A_s is the added activity.

Annex D
(informative)

Distillation of small volume sample

D.1 Principle

Samples of volume below 100 ml are considered as small volume sample. A dry distillation is easier to realize with a small volume of water. The almost closed system avoids an isotopic fractionation. All the distillation equipment, including the beads, shall be dried (100 °C) before use.

If necessary, the addition of dry calcium carbonate is used to neutralize the water to be distilled.

If the presence of iodine is suspected in the water sample, the addition of sodium thiosulfate or potassium permanganate oxidises the water sample, which is then made alkaline and distilled.

The OBT compounds present in the sample may be oxidized[22][33] and can contribute to the tritium measured in the distillate.

NOTE The majority of the interfering compounds, which quench the scintillation process, remain in the dry residue of the distillation together with any interfering radionuclides (radioactive iodine, carbon 14, caesium 137, etc.)

D.2 Reagents and equipment

During the analysis use only reagents of recognized analytical grade.

D.2.1 Reagents

D.2.1.1 Calcium carbonate, dry, $CaCO_3$.

D.2.1.2 Sodium thiosulfate, anhydrous, $Na_2S_2O_3$, or

D.2.1.3 Sodium carbonate, anhydrous, Na_2CO_3, or

D.2.1.4 Potassium permanganate, $KMnO_4$, or

D.2.1.5 Sodium hydroxide, NaOH.

The sodium hydroxide shall be free of tritium.

D.2.1.6 Working tritium standard solution.

D.2.1.7 Scintillation solution.

D.2.1.8 Blank water.

D.2.1.9 Carborundum or glass beads.