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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 $\mathrm{Bq \cdot l^{-1}}$ 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 $\mathrm{Bq \cdot l^{-1}}$ for infant food and 10 000 $\mathrm{Bq \cdot l^{-1}}$ 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	$\mathrm{kg \cdot l^{-1}}$
c_A	Activity concentration, in	$\mathrm{Bq \cdot l^{-1}}$
a	Activity per unit of mass	$\mathrm{Bq \cdot kg^{-1}}$
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	$\mathrm{s^{-1}}$
r_{g}	Sample count rate	$\mathrm{s^{-1}}$
r_{s}	Calibration count rate	$\mathrm{s^{-1}}$
ε	Detection efficiency	
f_{q}	Quench factor	
$u(c_A)$	Standard uncertainty associated with the measurement result	$\mathrm{Bq \cdot l^{-1}}$
U	Expanded uncertainty, calculated by $U = k \cdot u(c_A)$ with k = 1, 2,…,	$\mathrm{Bq \cdot l^{-1}}$
c_A^*	Decision threshold	$\mathrm{Bq \cdot l^{-1}}$
$c_A^\#$	Detection limit	$\mathrm{Bq \cdot l^{-1}}$
$c_A^\triangleleft, c_A^\triangleright$	Lower and upper limits of the confidence interval	$\mathrm{Bq \cdot l^{-1}}$

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 $\text{Bq}\cdot\text{l}^{-1}$, of this water and note the date of the determination.

As the activity is becoming non-negligible for activities around 1 $\text{Bq}\cdot\text{l}^{-1}$, 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 $\text{Bq}\cdot\text{l}^{-1}$.

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.