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Water quality — Simultaneous determination of tritium and carbon 14 activities — Test method using liquid scintillation counting

Qualité de l'eau — Détermination simultanée des activités volumiques du tritium et du carbone 14 — Méthode par comptage des scintillations en milieu liquide

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Foreword

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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 document 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).

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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 13168:2015), which has been technically revised. The main changes compared to the previous edition are as follows:

- Introduction developed;
- Normative references updated;
- Bibliography updated.

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

Radionuclides are present throughout the environment; thus, water bodies (e.g. surface waters, ground waters, sea waters) contain radionuclides, which can be of either natural or anthropogenic origin:

- naturally occurring radionuclides, including ^{3}H, ^{14}C, ^{40}K and those originating from the thorium and uranium decay series, in particular ^{210}Pb, ^{210}Po, ^{222}Rn, ^{226}Ra, ^{228}Ra, ^{227}Ac, ^{231}Pa, ^{234}U, and ^{238}U can be found in water bodies due to either natural processes (e.g., desorption from the soil, runoff by rain water) or released from technological processes involving naturally occurring radioactive materials (e.g. mining, mineral processing, oil, gas and production, water treatment and the production and the use of phosphate fertilisers);

- anthropogenic radionuclides such as ^{55}Fe, ^{59}Ni, ^{63}Ni, ^{90}Sr, ^{99}Tc, transuranic elements (Np, Pu, Am, and Cm)and some gamma emitting radionuclides such as ^{60}Co and ^{137}Cs can also be found in natural waters. Small quantities of anthropogenic radionuclides can be discharged from nuclear facilities to the environment as a result of authorized routine releases. The radionuclides present in liquid effluents are usually controlled before being discharged to the environment[1] and water bodies. Anthropogenic radionuclides used in medical and industrial applications can be released to the environment after use. Anthropogenic radionuclides are also found in waters due to the contamination from fallout resulting above-ground nuclear detonations and accidents such as those that occurred at the Chornobyl and Fukushima nuclear facilities.

Radionuclide activity concentrations in water bodies can vary according to local geological characteristics and climatic conditions and can be locally and temporally enhanced by releases from nuclear facilities during planned, existing, and emergency exposure situations[2][3]. Some drinking water sources can thus contain radionuclides at activity concentrations that could present a human health risk. The World Health Organization (WHO) recommends to routinely monitor radioactivity in drinking waters[4] and to take proper actions when needed to minimize the health risk.

National regulations usually specify the activity concentration limits that are authorized in drinking waters, water bodies, and liquid effluents to be discharged to the environment. These limits can vary for planned, existing, and emergency exposure situations. As an example, during either a planned or existing situation, the WHO guidance level is 10 000 Bq·l^{-1}[3] for ^{3}H and 100 Bq·l^{-1} for ^{14}C in drinking water, see NOTE 1 and 2. Compliance with these limits is assessed by measuring radioactivity in water samples and by comparing the results obtained with their associated uncertainties as specified by ISO/IEC Guide 98-3 and ISO 5667-20 [5].

NOTE 1 If the value is not specified in Annex 6 of Reference [4], the value has been calculated using the formula provided in Reference [4] and the dose coefficient data from References [6] and [7].

NOTE 2 The guidance level calculated in Reference [4] is the activity concentration with an intake of 2 l·d^{-1} of drinking water for one year, results in an effective dose of 0,1 mSv·a^{-1} to members of the public. This is an effective dose that represents a very low level of risk to human health and which is not expected to give rise to any detectable adverse health effects[4].

In the event of a nuclear emergency, the WHO Codex Guideline Levels[8] mentioned that the activity concentration might not be greater than 1 000 Bq·l^{-1} for ^{3}H in infant food and 10 000 Bq·l^{-1} for ^{3}H in food, including organically bound tritium, and 10 000 Bq·l^{-1} for ^{14}C in food other than for infant food.

This document contains method to support laboratories which need to determine ^{3}H and ^{14}C in water samples.

The method described in this document can be used for various types of waters (see Clause 1). Minor modifications such as sample volume and counting time can be made if needed to ensure that the characteristic limit, decision threshold, detection limit, and uncertainties are below the required limits. This can be done for several reasons such as emergency situations, lower national guidance limits, and operational requirements.

Water quality — Simultaneous determination of tritium and carbon 14 activities — 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 essential that tests conducted according to this document be carried out by suitably trained staff.

1 Scope

This document specifies a method for the simultaneous measurement of ^{3}H and ^{14}C in water samples by liquid scintillation counting of a source obtained by mixing the water sample with a hydrophilic scintillation cocktail.

The method presented in this document is considered a screening method because of the potential presence of interfering radionuclides in the test sample. However, if the sample is known to be free of interfering radionuclides then 3H and 14C can be measured quantitatively

The method can be used for any type of environmental study or monitoring.

This method is applicable to test samples of supply/drinking water, rainwater, surface and ground water, marine water, as well as cooling water, industrial water, domestic, and industrial wastewater having an activity concentration ranging from 5 Bq·l^{-1} to 10^{6} Bq·l^{-1} (upper limit of the liquid scintillation counters for direct counting). For higher activity concentrations, the sample can be diluted to obtain a test sample within this range.

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

ISO/IEC Guide 99:2007, *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 5667-10, *Water quality — Sampling — Part 10: Guidance on sampling of waste water*

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

ISO 19361, *Measurement of radioactivity — Determination of beta emitters activities — Test method using liquid scintillation counting*

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 terms and definitions given in ISO/IEC Guide 98-3:2008, ISO/IEC Guide 99:2007, ISO 80000-10 apply.

ISO and IEC maintain terminology databases for use in standardization at the following addresses:

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

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

3.2 Symbols

For the purposes of this document, the symbols and abbreviations given in ISO/IEC Guide 99:2007, ISO/IEC Guide 98-3:2008, ISO 80000-10 and the following shall apply.

Symbol	Description	Unit
V	Sample volume	l
m	Sample mass	kg
ρ	Density of the sample	$\text{kg}\cdot\text{l}^{-1}$
$C_{A\text{T}}$	Activity concentration for tritium	$\text{Bq}\cdot\text{l}^{-1}$
$C_{A\text{C}}$	Activity concentration for carbon 14	$\text{Bq}\cdot\text{l}^{-1}$
a	Activity per unit of mass	$\text{Bq}\cdot\text{kg}^{-1}$
A_T	Activity of the calibration source, in becquerel, for tritium	Bq
A_C	Activity of the calibration source, in becquerel, for carbon 14	Bq
t	Measurement time	s
t_o	Background counting time	s
t_g	Sample counting time	s
t_sT	Calibration counting time for tritium	s
t_sC	Calibration counting time, for carbon 14	s
r_oT	Mean background count rate for tritium	s^{-1}
r_oC	Mean background count rate for carbon 14	s^{-1}
r_gT	Mean sample count rate for tritium	s^{-1}
r_gC	Mean sample count rate for carbon 14	s^{-1}
r_sT	Calibration count rate for tritium	s^{-1}
r_sC	Calibration count rate for carbon 14	s^{-1}
$r_{\text{sC}\rightarrow\text{T}}$	Calibration count rate for carbon 14 in the tritium window	s^{-1}
ε	Counting efficiency for the lowest value of the quenching parameter	—
Q	Quenching parameter	—
f_q	Quench factor	—
ε	Counting efficiency in the unquenched vial	—
ε_Q	Counting efficiency for the quenching parameter, Q	—
ε_T	Detection efficiency for tritium	—
ε_C	Detection efficiency for carbon 14	—
$\varepsilon_{\text{C}\rightarrow\text{T}}$	Detection efficiency for carbon 14 in the chosen window of the tritium energy range	—

Symbol	Description	Unit
χ	Correcting factor, for the interfering carbon 14 in the chosen window of the tritium energy range	—
f_{qT}	Quench factor for tritium	—
f_{qC}	Quench factor for carbon 14	—
$f_{\mathrm{qC \to T}}$	Quench factor, for the interfering carbon 14 in the chosen window of the tritium energy range	—
$u(c_{A\mathrm{T}})$	Standard uncertainty associated with the measurement result for tritium	Bq·l^{-1}
$u(c_{A\mathrm{C}})$	Standard uncertainty associated with the measurement result for carbon 14	Bq·l^{-1}
u_{rel}	Relative standard uncertainty	—
$\tilde{c}_A$	Possible or assumed true quantity values of the measurand	Bq·l^{-1}
$\tilde{u}(\tilde{c}_A)$	Standard uncertainty of the estimator c_A as a function of an assumed true value c_A of the measurand	Bq·l^{-1}
α	Probability of a false positive decision	—
β	Probability of a false negative decision	—
β_{max}	Maximum energy for the beta emission	keV
$1 - \gamma$	Probability for the coverage interval of the measurand	—
k_{p}	Quantiles of the standardized normal distribution for the probabilities p (for instance p = 1−α, 1− β or 1−γ/ 2)	—
k_{q}	Quantiles of the standardized normal distribution for the probabilities q (for instance q = 1−α, 1− β or 1−γ/ 2)	—
λ	Decay constant of the isotope (ex: $\lambda_{215_{Po}}$ is the decay constant of ^{215}Po)	—
$C_{A\mathrm{T}}^{*}$	Decision threshold for tritium	Bq·l^{-1}
$C_{A\mathrm{C}}^{*}$	Decision threshold for carbon 14	Bq·l^{-1}
$C_{A\mathrm{T}}^{\#}$	Detection limit for tritium	Bq·l^{-1}
$C_{A\mathrm{C}}^{\#}$	Detection limit for carbon 14	Bq·l^{-1}
$C_{A\mathrm{T}}^{\triangleleft}$	Lower limit of the probabilistically symmetric coverage interval for tritium	Bq·l^{-1}
$C_{A\mathrm{T}}^{\triangleright}$	Upper limit of the probabilistically symmetric coverage interval for tritium	Bq·l^{-1}
$C_{A\mathrm{C}}^{\triangleleft}$	Lower limit of the probabilistically symmetric coverage interval for carbon 14	Bq·l^{-1}
$C_{A\mathrm{C}}^{\triangleright}$	Upper limit of the probabilistically symmetric coverage interval for carbon 14	Bq·l^{-1}
$\gamma/2$	Probability of the measurand being smaller than $c_{\mathrm{A}}^{\triangleleft}$ or larger than $c_{\mathrm{A}}^{\triangleright}$	—
$\boldsymbol{\Phi}$	Distribution function of the standardized normal distribution	—
ω	Distribution function of the standardized normal distribution of $c_{\mathrm{A}} / u(c_{\mathrm{A}})$	—
$C_{AT}^{<}$	Lower limit of the shortest coverage interval for tritium	Bq·l^{-1}
$C_{AT}^{>}$	Upper limit of the shortest coverage interval for tritium	Bq·l^{-1}
$C_{AC}^{<}$	Lower limit of the shortest coverage interval for carbon 14	Bq·l^{-1}
$C_{AC}^{>}$	Upper limit of the shortest coverage interval for carbon 14	Bq·l^{-1}
U	Expanded uncertainty, calculated by $U = k \cdot u(c_{\mathrm{A}})$ with k = 1, 2,…	Bq·l^{-1}

4 Principle

The method is for the measurement of ^{3}H and^{14}C in water samples by direct liquid scintillation counting. The general principles for the measurement of beta emitters by liquid scintillation counting are described in ISO 19361..

This direct determination is applicable to the analysis of water samples that can produce a homogeneous mixture between the test portion and a suitable scintillation cocktail.

The direct LSC method does not apply to waters containing micelles or large organic molecules (e.g. lipids, fulvic acid, humic acid) that do not form homogeneous mixtures with scintillation cocktails. In these cases, there is a risk that the beta radiation could be attenuated. This reduces the counting efficiency of the system and hence the results can be underestimated. For these samples, the determination of ^{3}H and ^{14}C requires additional chemical processing (such as distillation for tritium measurement, chemical oxidation or combustion for 14C measurement).

A prerequisite for the direct determination of ^{3}H and ^{14}C in a water sample is the absence of, or a negligible contribution from, other beta-emitting radionuclides, such as ^{90}Sr and some Ra isotopes decay progeny. When the radionuclide content of the sample is unknown, the method specified in this document only provides a ^{14}C equivalent activity for the sample.

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

In order to determine the detection efficiencies, it is necessary to measure a water sample having known ^{3}H and ^{14}C activities under conditions that are identical to those used for the test sample. This water shall be a mixture of certified radioactive sources or a dilution of this mixture produced with the reference water.

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

- same type of counting vial;
- same filling geometry;
- same ratio between test sample and scintillation cocktail;
- temperature stability of the detection equipment;
- value of the quench indicating parameter lies on the calibration curve.

Where chemical quenching can affect the measurement results, it is necessary to correct the counting data using a quench curve (see 7.4).

5 Sampling and storage

5.1 Sampling

Sampling, handling and storage of the water shall be done as specified in ISO 5667-1, ISO 5667-3 and ISO 5667-10 and guidance is given for the different types of water in References [9] to [16]. It is important that the laboratory receives a sample that is truly representative and has not been damaged or modified during transportation or storage. It is recommended to use a glass container for sampling and to fill up the container to its maximum is used to minimize ^{3}H and ^{14}C exchange with atmospheric moisture and CO_2.

The samples shall not be acidified to avoid the destruction of the carbonic equilibrium (CO_3^{2-}, HCO_3^-, H_2CO_3), as specified in ISO 5667-3. Basification of the sample is recommended, for example between pH 8 and pH 9. If NaOH is used to adjust the pH of the sample, the NaOH solution shall not contain carbonates, ^{14}C and ^{3}H. The volume added is needed to correct for dilution.

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

5.2 Sample storage

If required, the sample shall be stored in compliance with ISO 5667-3. If the storage duration exceeds that specified in ISO 5667-3, it is advisable to store the samples in glass containers.

6 Reagents and equipment

Use only reagents of recognized analytical grade.

6.1 Reagents

6.1.1 Water for blank sample

The water used for the blank sample shall be:

- as free as possible of chemical impurities to avoid quenching of radioactive impurities[17]
- with an activity concentration of ^{3}H and ^{14}C negligible in comparison with the activities to be measured.

For example, a water sample with a low ^{3}H and ^{14}C 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 ^{3}H and ^{14}C 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) and ^{14}C (air CO_2) or other radioactive species should be avoided.

Determine ^{3}H and ^{14}C activity concentration of this water and note the date.

For sample activities around 1 $Bq \cdot l^{-1}$, it is necessary to verify that the activity concentration of ^{3}H and ^{14}C in the blank water is less than 0,5 $Bq \cdot l^{-1}$.

When the volume of blank water is sufficiently large, for example 10 l to 20 l, and well-sealed, ^{3}H and ^{14}C activity concentrations should remain stable for years, although it is advisable to determine these activity concentrations at predetermined intervals, for example, every year.

6.1.2 Calibration source solutions

In order to avoid cross-contamination, prepare the solution in a suitable location which is remote from the area where the analyses are to be carried out.

Weigh and pour into a weighed volumetric container (e.g. 100 ml) the requisite quantity of a concentrated tritium ($[^{3}H]H_2O$) standard solution and of a concentrated ^{14}C standard solution, so that ^{3}H and ^{14}C activity concentrations generate sufficient counts to reach the required measurement uncertainty after dilution with blank water and thorough mixing. Calculate the activity concentrations of the resulting calibration source solution ($t = 0$). Note the date at which the standard solution was made up ($t = 0$).

The ^{3}H activity concentration of the calibration source solution at the measurement time t of the samples shall be corrected for radioactive decay.

When using a radiocarbon labelled organic molecule (e.g. glucose) in a standard solution, the absence of biological degradation shall be periodically verified.