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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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ISO copyright office
CP 401 • Ch. de Blandonnet 8
CH-1214 Vernier, Geneva
Phone: +41 22 749 01 11
Email: copyright@iso.org
Website: www.iso.org

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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, ^{232}Th, ^{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 $Bq \cdot l^{-1}$[4] for ^{3}H and 100 $Bq \cdot l^{-1}$ 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 $l \cdot d^{-1}$ of drinking water for one year, results in an effective dose of 0,1 $mSv \cdot a^{-1}$ 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].

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.

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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 ^{3}H and ^{14}C 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 $\text{Bq}\cdot\text{l}^{-1}$ to 10^{6} $\text{Bq}\cdot\text{l}^{-1}$ (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	kg·l^{-1}
c_{AT}	Activity concentration for ^{3}H	Bq·l^{-1}
c_{AC}	Activity concentration for ^{14}C	Bq·l^{-1}
a	Activity per unit of mass	Bq·kg^{-1}
A_T	Activity of the calibration source, in becquerel, for ^{3}H	Bq
A_C	Activity of the calibration source, in becquerel, for ^{14}C	Bq
t	Measurement time	s
t_0	Background counting time	s
t_g	Sample counting time	s
t_sT	Calibration counting time for ^{3}H	s
t_sC	Calibration counting time, for ^{14}C	s
r_0T	Mean background count rate for ^{3}H	s^{-1}
r_0C	Mean background count rate for ^{14}C	s^{-1}
r_gT	Mean sample count rate for ^{3}H	s^{-1}
r_gC	Mean sample count rate for ^{14}C	s^{-1}
r_sT	Calibration count rate for ^{3}H	s^{-1}
r_sC	Calibration count rate for ^{14}C	s^{-1}
$r_{\mathrm{sC}\rightarrow\mathrm{T}}$	Calibration count rate for ^{14}C in the ^{3}H 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 ^{3}H	—
ε_C	Detection efficiency for ^{14}C	—
$\varepsilon_{\mathrm{C}\rightarrow\mathrm{T}}$	Detection efficiency for ^{14}C in the chosen window of the ^{3}H energy range	—
χ	Correcting factor, for the interfering ^{14}C in the chosen window of the ^{3}H energy range	—

Symbol	Description	Unit
f_{qT}	Quench factor for ^{3}H	—
f_{qC}	Quench factor for ^{14}C	—
$f_{\mathrm{qC\rightarrow T}}$	Quench factor, for the interfering ^{14}C in the chosen window of the ^{3}H energy range	—
$u(c_{AT})$	Standard uncertainty associated with the measurement result for ^{3}H	$\mathrm{Bq \cdot l^{-1}}$
$u(c_{AC})$	Standard uncertainty associated with the measurement result for ^{14}C	$\mathrm{Bq \cdot l^{-1}}$
u_{rel}	Relative standard uncertainty	—
$\tilde{c}_A$	Possible or assumed true quantity values of the measurand	$\mathrm{Bq \cdot l^{-1}}$
$\tilde{u}(\tilde{c}_A)$	Standard uncertainty of the estimator c_A as a function of an assumed true value $\tilde{c}_A$ of the measurand	$\mathrm{Bq \cdot l^{-1}}$
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 $p = 1 - \alpha$, $1 - \beta$ or $1 - \gamma/2$)	—
k_{q}	Quantiles of the standardized normal distribution for the probabilities q (for instance $q = 1 - \alpha$, $1 - \beta$ or $1 - \gamma/2$)	—
λ	Decay constant of the isotope (ex: $\lambda_{^{215}\mathrm{Po}}$ is the decay constant of ^{215}Po)	—
c_{AT}^{*}	Decision threshold for ^{3}H	$\mathrm{Bq \cdot l^{-1}}$
c_{AC}^{*}	Decision threshold for ^{14}C	$\mathrm{Bq \cdot l^{-1}}$
$c_{AT}^{\#}$	Detection limit for ^{3}H	$\mathrm{Bq \cdot l^{-1}}$
$c_{AC}^{\#}$	Detection limit for ^{14}C	$\mathrm{Bq \cdot l^{-1}}$
$c_{AT}^{\triangleleft}$	Lower limit of the probabilistically symmetric coverage interval for ^{3}H	$\mathrm{Bq \cdot l^{-1}}$
$c_{AT}^{\triangleright}$	Upper limit of the probabilistically symmetric coverage interval for ^{3}H	$\mathrm{Bq \cdot l^{-1}}$
$c_{AC}^{\triangleleft}$	Lower limit of the probabilistically symmetric coverage interval for ^{14}C	$\mathrm{Bq \cdot l^{-1}}$
$c_{AC}^{\triangleright}$	Upper limit of the probabilistically symmetric coverage interval for ^{14}C	$\mathrm{Bq \cdot l^{-1}}$
$\gamma/2$	Probability of the measurand being smaller than $c_A^{\triangleleft}$ or larger than $c_A^{\triangleright}$	—
$\boldsymbol{\Phi}$	Distribution function of the standardized normal distribution	—
ω	Distribution function of the standardized normal distribution of $c_A / u(c_A)$	—
$c_{AT}^{<}$	Lower limit of the shortest coverage interval for ^{3}H	$\mathrm{Bq \cdot l^{-1}}$
$c_{AT}^{>}$	Upper limit of the shortest coverage interval for ^{3}H	$\mathrm{Bq \cdot l^{-1}}$
$c_{AC}^{<}$	Lower limit of the shortest coverage interval for ^{14}C	$\mathrm{Bq \cdot l^{-1}}$
$c_{AC}^{>}$	Upper limit of the shortest coverage interval for ^{14}C	$\mathrm{Bq \cdot l^{-1}}$
U	Expanded uncertainty, calculated by $U = k \cdot u(c_A)$ with $k = 1, 2, \ldots$	$\mathrm{Bq \cdot l^{-1}}$

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 ^{3}H measurement, chemical oxidation or combustion for ^{14}C 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 [8] to [15]. It is important that the laboratory receives a sample that is truly representative and has not been damaged nor modified during either transportation or storage. It is recommended to use a glass container for sampling and to fill up the container to its maximum 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[16]
- 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 ^{3}H (e.g. from water vapour in the air and from ^{3}H 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.

6.1.3 Scintillation solution

The scintillation cocktail is chosen according to the characteristics of the sample to be analysed and the properties of the detection equipment[17].

It is recommended to use a hydrophilic scintillation cocktail, especially for the measurement of environmental waters.

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 solution 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, could require disposal as radioactive waste.

6.1.4 Quenching agent

The chemical quenching agent shall not be acidic when ^{14}C is present as carbonated species in the standard solution. Examples of chemical quenching agents are: acetone, organochloride compounds, nitromethane.

NOTE Some quenching agents are dangerous or toxic.

6.2 Equipment

Use the equipment specified in ISO 19361.

7 Procedure

7.1 Sample preparation

If the raw sample stems from water presenting low concentrations of suspended matter, the test is generally carried out without separation. If the activity of the filtered or centrifuged sample is to be measured, it is necessary to conduct the separation as soon as possible after collection (see ISO 5667-3).

7.2 Preparation of the counting vial

A known quantity of test sample and scintillation cocktail are transferred to the counting vial.

After closing the vial, it shall be shaken thoroughly 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 operations should take place in dimmed light (preferably light from an incandescent source, 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

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

7.4 Control and calibration

Statistical control of the detection system shall be monitored by measurement of reference vials (e.g. a set of flame-sealed vials for background count rate, ^{3}H efficiency and ^{14}C efficiency monitoring). These are usually provided by the equipment supplier. Control charts can be created in accordance with ISO 7870-2[18].

The measurement of the blank reference water is performed before each test or each series of sample tests under conditions representative of each type of measurement (Clause 4).

It is essential to generate a quench curve for each type of matrix measured. The quench curve is valid only for a given:

- type of measurement apparatus;
- type of scintillation cocktail;
- type of counting vial,
- ratio of scintillation cocktail and test sample;
- energy window;
- matrix, for example water, precipitate, absorbed CO_2, Na_2CO_3 solution.

The standards are counted by liquid scintillation counting to determine the net count rate from ^{14}C in the counting window to be used for test samples. The counting efficiency, ε_Q, at quench parameter Q for each vial is calculated. The quench parameter, Q, is generated by the spectrometer. Calculate f_q for each quenched standard with the Formula (1):

$$f_q = \frac{\varepsilon_Q}{\varepsilon} \tag{1}$$

where ε is the counting efficiency in the unquenched vial.

The quench curve is prepared by plotting a graph relating Q and f_q with a polynomial regression curve. The quench factor f_q of the test sample can then be found by interpolation from its quench parameter.

Two separate sets of quenching curves, one for ^{3}H and another for ^{14}C, shall be used.

The quench curve is obtained from a series of working standards (e.g., 10 or so) having variable quench of which the matrix is similar or close to that of the samples to be measured (same scintillation cocktail, same respective quantities of scintillation cocktail and test portion). These working standards can be produced in the following manner:

- a similar quantity of standard solution is introduced into each vial. Its activity shall be sufficient so that the count rate of the working standard can be determined with a known statistical accuracy, even in presence of a high quench;
- reference water is added until the desired test portion is obtained;
- the scintillation cocktail is then added in order to obtain the desired proportions;

- at least one working standard is used as such. Increasing quantities of a quenching agent are added to the other working standards. This gives rise to a range of quench values similar to that of the samples to be measured.

From the two quench curves, the efficiencies are determined

- for ^{3}H, in the window of the energy range characteristic of the beta emission of ^{3}H,
- for ^{14}C, in the window of the energy range characteristic of the beta emission of ^{3}H,
- for ^{14}C, in the window of the energy range characteristic of the beta emission of ^{14}C, and
- for ^{3}H, in the window of the energy range characteristic of the beta emission of ^{14}C.

A simple method for setting counting windows consists in selecting as lower limit of ^{14}C window the end point of the spectrum of the tritium working standard having the lowest quench (the less "quenched") of ^{3}H range. The upper limit of ^{3}H window can be equal to or less than this value. The upper limit of ^{14}C window can be the end point of the spectrum of the less "quenched" working standard of ^{14}C range. Under these conditions, it is considered that there is not any contribution of ^{3}H in the ^{14}C window.

Another method would be to select the ^{3}H and ^{14}C counting windows in order to obtain optimised efficiencies. This method requires a more complex mathematical processing.

7.5 Measurement conditions

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

For the measurement of low activities, it is recommended to make repeated counting cycles: all test samples are counted once, then the counting starts for a second cycle and so on.

These divisions of the count time allow the detection of random or transitory interfering effects (luminescence, static) that are not auto-corrected by the measurement equipment. It also allows taking into account any perturbations, punctual or cyclic (e.g. night and day alternation) associated to the measurement equipment environment.

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.

7.6 Interference control

The measurement can be influenced by chemiluminescence or spectrum attenuation phenomena due to the presence of chemical entities, as well as by the presence of radionuclides other than the nuclide to be measured. It is therefore advisable to take into account the characteristics of the water being measured and to specify them in the presentation of the result.

A possible means of verification of the chosen conditions is the measurement of a known mixture prepared with certified solutions or dilutions of these solutions.

Some low energy beta emitters and electron capture emitters (e.g. ^{241}Pu, ^{210}Pb, ^{228}Ra, ^{227}Ac, ^{63}Ni and ^{55}Fe) cannot be distinguished from the energy spectrum of ^{3}H and from the lower energy part of the spectrum of ^{14}C by liquid scintillation counting. An examination of the full spectrum of the counted vials may reveal the presence of high energy beta emitters.

The absence of other high-energy radionuclides is verified by checking the count rate above the maximum energy $\beta_{\max}$ of ^{14}C.

The activity measured for ^{3}H can be verified according to ISO 9698[19].

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.

No matter 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 be ignored (volume or mass of scintillation cocktail, counting time, etc.).

The covering of the energy ranges of ^{3}H and ^{14}C leads to separating the energy ranges into at least two windows. The simple method proposed in 7.4 consists in minimizing the contribution of ^{3}H in ^{14}C energy window.

The symbols used are defined in Clause 3.

The variables specific to the chosen window of ^{3}H energy range are indexed (T).

The variables specific to the chosen window of ^{14}C energy range are indexed (C).

Examples are given in Annex A.

8.2 Activity concentration of tritium

The activity concentration c_{AT} of ^{3}H in the sample is calculated according to the Formula (2):

$$c_{AT} = \frac{r_{gT} - r_{0T} - \chi \cdot \left(r_{gC} - r_{0C}\right)}{V \cdot \varepsilon_{T} \cdot f_{qT}} = \left[r_{gT} - r_{0T} - \chi \cdot \left(r_{gC} - r_{0C}\right)\right] \cdot w_{T} \qquad (2)$$

where

$$w_{T} = \frac{1}{V \cdot \varepsilon_{T} \cdot f_{qT}}$$

The interfering ^{14}C in the chosen window of ^{3}H energy range shall be taken in account, in order to obtain the counting rate of ^{3}H. The correcting factor χ is calculated according to Formula (3):

$$\chi = \varepsilon_{C \to T} \cdot f_{q_{C \to T}} = \left(r_{sC \to T} / r_{sC}\right) \cdot f_{q_{C \to T}} \qquad (3)$$

8.3 Activity concentration of carbon 14

The activity concentration c_{AC} of ^{14}C in the sample is calculated according to the Formula (4):

$$c_{AC} = \frac{r_{gC} - r_{0C}}{V \cdot \varepsilon_C \cdot f_{qC}} = \left[r_{gC} - r_{0C} \right] \cdot w_C \qquad (4)$$

where

$$w_C = \frac{1}{V \cdot \varepsilon_C \cdot f_{qC}}$$

8.4 Combined standard uncertainty for tritium

The combined standard uncertainty for ^{3}H is calculated according to the Formula (5):

$$u(c_{AT}) = \sqrt{{w_T}^2 \cdot \left[u^2(r_{gT}) + u^2(r_{0T}) + T(\chi) \right] + {c_{AT}}^2 \cdot u_{rel}^2(w_T)} = \sqrt{{w_T}^2 \cdot \left[r_{gT}/t_g + r_{0T}/t_0 + T(\chi) \right] + {c_{AT}}^2 \cdot u_{rel}^2(w_T)} \qquad (5)$$

where

$$T(\chi) = (r_{gC} - r_{0C})^2 \cdot u^2(\chi) + \chi^2 \cdot (r_{gC}/t_g + r_{0C}/t_0)$$

and

$$u(\chi) = \sqrt{\chi \cdot (\chi + 1)/(r_{sC} \cdot t_{sC})}$$

As the uncertainty on the counting time is very small against the uncertainty of the other parameters, it is ignored, and the relative uncertainty of *w* is calculated according to the Formula (6):

$$u_{rel}^2(w_T) = u_{rel}^2(\varepsilon_T) + u_{rel}^2(f_{qT}) + u_{rel}^2(V) \qquad (6)$$

If the mass is used instead of the volume, the mass of the test sample, *m*, is expressed in kilograms. The intermediate calculations are done with similar equations. The activity concentration can also be expressed as the activity per unit of mass (*m* replacing *V* in Formula (6)).

The relative uncertainty of ε_T is calculated according to the Formula (7):

$$u_{rel}^2(\varepsilon_T) = u_{rel}^2(r_{sT} - r_{0T}) + u_{rel}^2(A_T) = (r_{sT}/t_s + r_{0T}/t_0)/(r_{sT} - r_{0T})^2 + u_{rel}^2(A_T) \qquad (7)$$

where

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

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

For the calculation of the characteristic limits, $\tilde{u}(\tilde{c}_{AT})$ is needed (see ISO 11929-1[20]), i.e., the standard uncertainty of c_{AT} as a function of its true value, calculated by using Formula (8):

$$\tilde{u}(\tilde{c}_{AT}) = \sqrt{w_\mathrm{T}^2 \cdot \left\{\left[\tilde{c}_{AT}/w_\mathrm{T} + \chi \cdot \left(r_\mathrm{gC} - r_\mathrm{0C}\right) + r_\mathrm{0T}\right]/t_\mathrm{g} + r_\mathrm{0T}/t_0 + T(\chi)\right\} + \tilde{c}_{A\mathrm{T}}^2 \cdot u_\mathrm{rel}^2(w_\mathrm{T})} \tag{8}$$

It is agreed to ignore the covariance term between $\varepsilon_{\mathrm{C}\to\mathrm{T}}$ and ε_T which would result in a decrease of $T(\chi)$.

8.5 Combined standard uncertainty for carbon 14

The combined standard uncertainty for ^{14}C is calculated according to the Formula (9):

$$u(c_{AC}) = \sqrt{{w_\mathrm{C}}^2 \cdot \left[u^2(r_\mathrm{gC}) + u^2(r_\mathrm{0C})\right] + {c_{AC}}^2 \cdot u_\mathrm{rel}^2(w_\mathrm{C})} = \sqrt{{w_\mathrm{C}}^2 \cdot (r_\mathrm{gC}/t_\mathrm{g} + r_\mathrm{0C}/t_0) + {c_{AC}}^2 \cdot u_\mathrm{rel}^2(w_\mathrm{C})} \tag{9}$$

As the uncertainty on the counting time is very small against the uncertainty of the other parameters, it is ignored, and the relative uncertainty of w is calculated according to the Formula (10):

$$u_\mathrm{rel}^2(w_\mathrm{C}) = u_\mathrm{rel}^2(\varepsilon_\mathrm{C}) + u_\mathrm{rel}^2(f_\mathrm{qC}) + u_\mathrm{rel}^2(V) \tag{10}$$

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

The relative uncertainty of ε_C is calculated according to the Formula (11):

$$u_\mathrm{rel}^2(\varepsilon_\mathrm{C}) = u_\mathrm{rel}^2(r_\mathrm{sC} - r_\mathrm{0C}) + u_\mathrm{rel}^2(A_\mathrm{C}) = (r_\mathrm{sC}/t_s + r_\mathrm{0C}/t_0)/(r_\mathrm{sC} - r_\mathrm{0C})^2 + u_\mathrm{rel}^2(A_\mathrm{C}) \tag{11}$$

where

$u_\mathrm{rel}^2(A_\mathrm{C})$	includes all the uncertainties related to the calibration source: that is in the standard solution and the preparation of the calibration source.
$u_\mathrm{rel}^2(f_\mathrm{qC})$	depends on the mathematical model used to fit the quench curve.

For the calculation of the characteristic limits, $\tilde{u}(\tilde{c}_\mathrm{A})$ is needed (see ISO 11929-1), i.e. the standard uncertainty of c_{AC} as a function of its true value, calculated by using Formula (12):

$$\tilde{u}(\tilde{c}_{AC}) = \sqrt{w_\mathrm{C}^2 \cdot \left[(\tilde{c}_{AC}/w_\mathrm{C} + r_\mathrm{0C})/t_\mathrm{g} + r_\mathrm{0C}/t_0\right] + \tilde{c}_{A\mathrm{C}}^2 \cdot u_\mathrm{rel}^2(w_\mathrm{c})} \tag{12}$$

8.6 Decision threshold for tritium

The decision threshold c_{AT}^* is obtained from the Formula (13) for $\tilde{c}_{AT} = 0$ (see ISO 11929-1). This yields

$$c_{AT}^* = k_{1-\alpha} \cdot \tilde{u}(0) = k_{1-\alpha} \cdot w_\mathrm{T} \cdot \sqrt{\left[\chi\left(r_\mathrm{gC} - r_\mathrm{0C}\right) + r_\mathrm{0T}\right]/t_\mathrm{g} + r_\mathrm{0T}/t_0 + T(\chi)} \tag{13}$$

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

8.7 Decision threshold for carbon 14

The decision threshold c^*_{AC} is obtained from the Formula (14) for $\tilde{c}_{AT} = 0$ (see ISO 11929-1). This yields

$$c^*_{AC} = k_{1-\alpha} \times u^{\%}(0) = k_{1-\alpha} \times w_C \sqrt{r_{0C}\left(\frac{1}{t_g} + \frac{1}{t_0}\right)} \tag{14}$$

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

8.8 Detection limit for tritium

The detection limit $c^\#_{AT}$ is calculated by using Formula (15) (ISO 11929-1):

$$c^\#_{AT} = c^*_{AT} + k_{1-\beta} \cdot \tilde{u}\left(c^\#_{AT}\right) =$$

$$c^*_{AT} + k_{1-\beta} \cdot \sqrt{w_T^2 \cdot \left\{\left[c^\#_{AT} / w_T + \chi \cdot \left(r_{gC} - r_{0C}\right) + r_{0T}\right] / t_g + r_{0T} / t_0 + T(\chi)\right\} + c^{\#2}_{AT} \cdot u^2_{rel}(w_T)} \tag{15}$$

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

The detection limit can be calculated by solving Formula (15) for $c^\#_{AT}$ or, more simply, by iteration with a starting approximation $c^\#_{AT} = 2 \cdot c^*_{AT}$.

When taking $\alpha = \beta$ then $k_{1-\alpha} = k_{1-\beta} = k$ and the solution of Formula (15) is given by the following Formula (16):

$$c^\#_{AT} = \frac{2 \cdot c^*_{AT} + \left(k^2 \cdot w_T\right) / t_g}{1 - k^2 \cdot u^2_{rel}(w_T)} \tag{16}$$

8.9 Detection limit for carbon 14

The detection limit $c^\#_{AC}$ is calculated by using Formula (17) (ISO 11929-1):

$$c^\#_{AC} = c^*_{AC} + k_{1-\beta} \cdot \tilde{u}\left(c^\#_{AC}\right) = c^*_{AC} + k_{1-\beta} \cdot \sqrt{w_C^2 \cdot \left[\left(c^\#_{AC} / w_C + r_{0C}\right) / t_g + r_{0C} / t_0\right] + c^{\#2}_{AC} \cdot u^2_{rel}(w_C)} \tag{17}$$

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

The detection limit can be calculated by solving Formula (17) for $c^\#_{AC}$ or, more simply, by iteration with a starting approximation $c^\#_{AC} = 2 \cdot c^*_{AC}$.

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

$$c^\#_{AC} = \frac{2 \cdot c^*_{AC} + \left(k^2 \cdot w_C\right) / t_g}{1 - k^2 \cdot u^2_{rel}(w_C)} \tag{18}$$

8.10 Limits of the coverage intervals

8.10.1 Limits of the probabilistically symmetric coverage interval

The lower, $c_A^{\triangleleft}$ and upper $c_A^{\triangleright}$, coverage limits are calculated using Formulae (19) and (20) (see ISO 11929-1):

$$c_A^{\triangleleft} = c_A - k_{\mathrm{p}} \cdot u(c_A)\,;\; p = \omega \cdot (1 - \gamma/2) \tag{19}$$

$$c_A^{\triangleright} = c_A + k_{\mathrm{q}} \cdot u(c_A)\,;\; q = 1 - \omega \cdot \gamma/2 \tag{20}$$

where

$\omega = \Phi\left[\dfrac{y}{u(y)}\right]$ Φ being the distribution function of the standardized normal distribution

$\omega = 1$ may be set if $c_A > 4 \cdot u(c_A)$

In this case the following approximations using Formula (21) for a symmetric uncertainty apply:

$$c_A^{\triangleleft} = c_A - k_{1-\gamma/2} \cdot u(c_A)\text{, and } c_A^{\triangleright} = c_A + k_{1-\gamma/2} \cdot u(c_A) \tag{21}$$

The result should be given by using Formula (22)

$$c_A \pm k_{1-\gamma/2} \cdot u(c_A) \tag{22}$$

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

8.10.2 Limits of the shortest coverage interval

As specified in detail in ISO 11929-1, the lower limit of the shortest coverage interval, $c_A^{<}$ and the upper limit of the shortest coverage interval, $c_{AC}^{>}$, are calculated from a primary measurement result, c_A, of the measurand and the standard uncertainty, $u(c_A)$, associated with c_A, either Formula (23):

$$c_A^{<},\, c_A^{>} = c_A \pm k_{\mathrm{p}} \cdot u(c_A)\,;\; p = \omega\left(1 - \frac{\gamma}{2}\right) \tag{23}$$

or if $c_A^{<} < 0$, by Formula (24):

$$c_A^{<} = 0;\; c_A^{>} = c_A \pm k_{\mathrm{q}} \cdot u(c_A)\,;\; q = 1 - \omega \cdot \gamma/2 \tag{24}$$

The relation $0 \le c_A^{<} < c_A^{>}$ applies and the approximation of Formula (21) is valid.

8.11 Calculations using the activity per unit of mass

The activity concentration can be calculated by multiplying the activity per unit of mass by the density ρ in kilogram per litre, as given in Formula (25):

$$V = \frac{m}{\rho} \tag{25}$$

with

$$u_{\mathrm{rel}}^2(V) = u_{\mathrm{rel}}^2(m) + u_{\mathrm{rel}}^2(\rho)$$

The uncertainty, the characteristic limits and the limits of the coverage interval can be calculated using the previous expression [see Formulae (2), (4), (6) and (10)] with Formula (25).

9 Test report

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

a) reference to this document i.e. ISO 13168:2023;

b) identification of the sample;

c) units in which the results are expressed;

d) the test result:

1) when the activity concentration, c_A, is compared with the decision threshold (see ISO 11929 series[20][21][22]);

— if the result is less than the decision threshold, the result of the measurement is expressed as; $\leq c_A^*$

— if the result is greater than the decision threshold, the result of the measurement is expressed as $c_A \pm u(c_A)$ or $c_A \pm U$ with the associated k value;

2) when the activity concentration, c_A, is compared with the detection limit;

— if the result is less than the detection limit, the result of the measurement is expressed as $\leq c_A^{\#}$;

— if the result is greater than the detection limit, the result of the measurement is expressed as $c_A \pm u(c_A)$ or $c_A \pm U$ with the associated k value.

Complementary information can be provided such as:

e) the uncertainty can also be expressed as the limits of the probabilistically symmetric coverage interval $c_A^{\triangleleft}, c_A^{\triangleright}$ and/or the limits of the shortest coverage interval $c_A^{<}$, $c_A^{>}$;

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

g) decision threshold and the detection limit;

h) if the detection limit exceeds the guideline value, it shall be documented that the method is not suitable for the measurement purpose;

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