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Second edition
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# Water quality — Carbon 14 — Test method using liquid scintillation counting

*Qualité de l'eau — Carbone 14 — Méthode d'essai 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 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).

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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*, in collaboration with the European Committee for Standardization (CEN) Technical Committee CEN/TC 230, *Water analysis*, in accordance with the Agreement on technical cooperation between ISO and CEN (Vienna Agreement).

This second edition cancels and replaces the first edition (ISO 13162:2011), which has been technically revised. The main changes compared to the previous edition are as follows:

— Introduction developed;

— Scope updated;

— References updated;

— Sample preparation revised.

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



 

# Introduction

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

— natural radionuclides, including $^{40}K$, $^{3}H$, $^{14}C$, and those originating from the thorium and uranium decay series, in particular $^{226}Ra$, $^{228}Ra$, $^{234}U$, $^{238}U$, $^{210}Po$ and $^{210}Pb$ can be found in water for natural reasons (e.g. desorption from the soil and washoff by rain water) or can be released from technological processes involving naturally occurring radioactive materials (e.g. the mining and processing of mineral sands or phosphate fertilizers production and use);

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

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

The radionuclides present in liquid effluents are usually controlled before being discharged into the environment[2] and water bodies. Drinking waters are monitored for their radioactivity as recommended by the World Health Organization (WHO)[3] so that proper actions can be taken to ensure that there is no adverse health effect to the public. Following these international recommendations, national regulations usually specify radionuclide authorized concentration limits for liquid effluent discharged to the environment and radionuclide guidance levels for waterbodies 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 100 $Bq \cdot l^{-1}$ for $^{14}C$ 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 10 000 $Bq \cdot l^{-1}$ for $^{14}C$ in foods other than for infant foods.

NOTE 2 The Codex guidelines levels (GLs) apply to radionuclides contained in foods 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 foods, 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 being discharged 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(s) 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(s) may be used for water samples after proper sampling, sample handling, and test sample preparation (see the relevant part of the ISO 5667 series).

This document has been developed to support 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 — Carbon 14 — 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 for the measurement of $^{14}C$ activity concentration in all types of water samples by liquid scintillation counting (LSC) either directly on the test sample or following a chemical separation.

The 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.

The detection limit depends on the sample volume, the instrument used, the sample counting time, the background count rate, the detection efficiency and the chemical recovery. The method described in this document, using currently available liquid scintillation counters and suitable technical conditions, has a detection limit as low as 1 $Bq \cdot l^{-1}$, which is lower than the WHO criteria for safe consumption of drinking water (100 $Bq \cdot l^{-1}$). $^{14}C$ activity concentrations can be measured up to $10^6$ $Bq \cdot l^{-1}$ without any sample dilution.

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

## 2 Normative references

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

ISO 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 11929-1, *Determination of the characteristic limits (decision threshold, detection limit and limits of the coverage interval) for measurements of ionizing radiation — Fundamentals and application — Part 1: Elementary applications*

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*

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

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

## 3 Terms, definitions, symbols and abbreviations

For the purposes of this document, the definitions, symbols and abbreviations given in ISO/IEC Guide 99:2007, ISO/IEC Guide 98-3:2008, 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/

| | | |
|---|---|---|
| $\beta_{max}$ | Maximum energy for the beta emission | keV |
| $V$ | Volume of laboratory sample | l |
| $m$ | Mass of laboratory sample | kg |
| $\rho$ | Density of the sample | $kg \cdot l^{-1}$ |
| $c_A$ | Activity concentration | $Bq \cdot l^{-1}$ |
| $a$ | Activity per unit of mass | $Bq \cdot kg^{-1}$ |
| $A$ | Activity of the calibration source | Bq |
| $A_s$ | Activity of the internal standard solution | Bq |
| $n$ | Number of counting | - |
| $N_o$ | Number of the counted pulses for the background | - |
| $t_0$ | Background counting time, in second | s |
| $N_g$ | Number of the counted pulses for the sample | - |
| $t_g$ | Sample counting time | s |
| $t_s$ | Calibration counting time | s |
| $r_0$ | Background count rate | $s^{-1}$ |
| $r_g$ | Test sample count rate | $s^{-1}$ |
| $r_s$ | Calibration count rate | $s^{-1}$ |
| $\varepsilon$ | Detection efficiency | - |
| Q | Quench parameter | - |
| $f_q$ | Quench factor | - |
| $\varepsilon_q$ | Counting efficiency at quench parameter Q | - |
| $R_c$ | Chemical recovery | - |
| $m_{TC}$ | Mass of total carbon in the sample | kg |
| $m_{PC}$ | Mass of carbon in the precipitate | kg |
| $m_{CC}$ | Mass of carbon in the carrier | kg |
| $m_{SC}$ | Mass of sample carbon in the precipitate | kg |
| $u(c_A)$ | Standard uncertainty associated with the measurement result | $Bq \cdot l^{-1}$ |
| $u_{rel}$ | Relative standard uncertainty | - |
| $\tilde{c}_A$ | Possible or assumed true quantity values of the measurand | $Bq \cdot l^{-1}$ |
| $\tilde{u}(\tilde{c}_A)$ | Standard uncertainty of $\tilde{c}_A$ | $Bq \cdot l^{-1}$ |
| $\alpha, \beta$ | Probability of a false positive and false negative decision, respectively | - |

| | | |
|---|---|---|
| $k_{1-\alpha}$ | Quantile of the standardized normal distribution for the probability 1- $\alpha$ | - |
| $k_{1-\beta}$ | Quantile of the standardized normal distribution for the probability 1- $\beta$ | - |
| $c_A^*$ | 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 probabilistically symmetric coverage interval | $Bq \cdot l^{-1}$ |
| $c_A^<, c_A^>$ | Lower and upper limits of the shortest coverage interval | $Bq \cdot l^{-1}$ |
| $\gamma/2$ | Probability of the measurand being smaller than $c_A^\triangleleft$ or larger than $c_A^\triangleright$ | - |
| $1-\gamma$ | Probability for the coverage interval of the measurand | - |
| $\Phi$ | Distribution function of the standardized normal distribution | - |
| $\omega$ | Distribution function of the standardized normal distribution of $c_A / u(c_A)$ | - |
| $k_p, k_q$ | Quantiles of the standardized normal distribution for the probabilities $p$ and $q$, respectively | - |
| $U$ | Expanded uncertainty, calculated by $U = k \cdot u(c_A)$ with $k = 1, 2, ...$ | $Bq \cdot l^{-1}$ |

## 4 Principle

The method described is for measurement of $^{14}C$ in water samples by direct liquid scintillation counting. The general principles of this method 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, etc.) that do not form homogeneous mixtures with scintillation cocktails. In these cases, there is a risk that the beta particles could be attenuated. This reduces the counting efficiency of the system and hence the results can be underestimated. For these samples, the determination of $^{14}C$ requires additional chemical processing (such as chemical oxidation or combustion). Examples of methods of chemical preparation are described in Annexes A and B.

The choice of the analytical procedure (either with or without chemical preparation of the water sample prior to determination) depends on the aim of the measurement and the sample characteristics [17][18][19][20].

A prerequisite for the direct determination of $^{14}C$ in a water sample is the absence of, or a negligible contribution from, other beta-emitting radionuclides, such as $^{90}Sr$ and Ra isotopes. 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.

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”.

To determine the detection efficiency, it is necessary to measure a water sample having a known $^{14}C$ 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 $^{14}C$ activity usable without dilution.

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

Conditions of sampling and handling shall conform to ISO 5667-1, ISO 5667-3 and ISO 5667-10. Guidance is given for the different types of water in References [8] to [15].

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 9.

It is important that the laboratory receives a representative sample, unmodified during transport or storage and in an undamaged container. It is recommended that a glass container filled to the maximum is used to minimize $^{14}C$ exchange with atmospheric $CO_2$.

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 accordance with ISO 5667-3 for carbon dioxide. 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

During the analysis, unless otherwise stated, use only reagents of recognized analytical grade.

## 6.1 Reagents

### 6.1.1 Reference water for the blank

The reference water for the blank should be as free as possible of chemical or radioactive impurities, although it may have a low $^{14}C$ activity concentration, at the time the samples are measured.

For example, obtain water with a $^{14}C$ activity concentration as low as possible, e.g. (deep) subterranean water. Distil the water. Keep the distillate in a well-sealed borosilicate glass bottle in the dark at a temperature as constant as possible. This reference water shall be kept physically remote from any $^{14}C$-containing material (see 6.1.2). Determine (7.4) the $^{14}C$ activity concentration of this water, in becquerel per litre, and note the date of this determination.

It is advisable to keep an adequate quantity of reference water in stock and to draw off small working volumes from it for immediate use, as required. Contamination with $^{14}C$ (e.g. from $CO_2$ in the air) or other radioactive species should be avoided.

For measurement of activity concentrations close to 1 $Bq \cdot l^{-1}$, water with a very low activity concentration is necessary as reference water.

### 6.1.2 Calibration source solution

In order to avoid cross-contamination, prepare the calibration source solution in a suitable location which is well removed from the area where the $^{14}C$ analyses are to be carried out. Transfer a known amount of $^{14}C$ aqueous standard solution into a volumetric flask (e.g. of capacity 100 ml). Make up to the mark with blank reference water and mix well. The calibration source solution shall have sufficient $^{14}C$ activity such that, when used to prepare counting sources, a suitable count rate to reach the required measurement uncertainty is obtained. Calculate the $^{14}C$ activity concentration of the resulting calibration source solution, in becquerel per litre. Note the date at which the standard solution was made up, to monitor the ageing of the solution.

It is recommended to select the standard source container size so as to minimize the volume of air above the solution and therefore minimize the exchange of $^{14}C$ with the atmosphere, when opening the container.

### 6.1.3 Scintillation solution

Chose the scintillation cocktail according to the characteristics of the test sample to be analysed (e.g. precipitate or alkaline) and according to the properties of the detection equipment [21][22].

It is recommended to use a hydrophilic scintillation cocktail for the direct 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 of scintillation cocktail and test sample taken for testing should be disposed of as chemical waste, and, depending on the levels of radioactivity, may require disposal as radioactive waste.

### 6.1.4 Quenching agent

Examples of chemical quenching agents (non-acid): 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

For the direct determination of $^{14}C$ in a raw sample, measurement of the test sample is generally performed without removal of any suspended matter if the sample has low levels of such material. 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 sampling.

For the measurement of high alkaline samples (pH above 9) with a low-level activity of $^{14}C$, extract the carbon from the sample (for example, see Annex A).

## 7.2 Preparation of the counting vial

Known quantities of test sample and scintillation cocktail are transferred into a counting vial.

After closing the vial, shake thoroughly to homogenize the mixture.

The sample identification shall be written on the top of the vial lid. The sample may require storage before counting to allow photoluminescence or static electricity effects to decay. The storage

time depends upon the scintillation mixture, the mixture stability and the nature of the sample. It is recommended that the measurement be performed as soon as any photoluminescence or static electricity effects have become negligible (e.g. 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 red light). In addition, exposure of the vial to direct sunlight or fluorescent light should be avoided.

### 7.3 Counting procedure

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

### 7.4 Calibration and verification

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 [16].

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;

— a given type of scintillation cocktail;

— a given ratio of scintillation cocktail and test sample;

— a given energy window;

— a given matrix, e.g. water, precipitate, absorbed $CO_2$, $Na_2CO_3$ solution, etc.

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

— add a similar quantity of $^{14}C$ standard (e.g. water solution, precipitate, $Na_2CO_3$ solution, etc.) to each vial. The activity of the standard shall be sufficient for the counting rate to achieve a known statistical precision, even in the case of a strong quench;

— add blank reference water until the desired volume is reached;

— the scintillation cocktail is added to obtain the desired ratio;

— at least one working standard is used without addition of quenching agent. Increasing quantities of quenching agent are added to the other working standards, to simulate the expected range of quench values encountered in the samples to be measured.

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 ($\varepsilon_q$) 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

$$f_q = \frac{\varepsilon_q}{\varepsilon}$$

where $\varepsilon$ 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.

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

### 7.5 Measurement conditions

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

The measurement is performed using an energy window that is above the upper limit in energy where the tritium is detected up to the $\beta_{max}$ of $^{14}C$ (156 keV). It is recommended that the energy window discriminators are set to optimize the figure of merit ($\varepsilon^2/r_0$).

The presence of other radionuclides can be monitored by observation of the counting rate in the full energy window, e.g. 0 keV to 2 000 keV.

To verify the statistical distribution of counting data, it is recommended that, for high activity samples, the first sample is counted several times in a row (number of repetitions), then the second sample is counted likewise, and so on.

For measurement of low activities, it is recommended that the counting be done on each sample in sequence: all samples are counted once, then the counting starts for the second cycle, and so on.

Sequential counting allows the detection of random or transitory interfering effects (luminescence, static electricity) that are not auto-corrected by the measurement apparatus. It also allows any disturbances, either one-off or cyclic (e.g. night and day alternation) associated with the measurement apparatus environment to be taken into account.

## 8 Expression of results

### 8.1 General

For the measurement of $^{14}C$, the uncertainties of only the following parameters need to be considered:

a) counting uncertainties for the sample and background vials;

b) counting efficiency in the energy window considered for a given quench indicator parameter;

c) quench parameter;

d) volume or mass of test sample;

e) chemical recovery.

As a first approximation, other uncertainties (volume or mass of scintillation cocktail, counting time, etc.) can be neglected. An example of the calculation is given in Annex D.

### 8.2 Calculation of activity concentration without sample preparation

The calculation of activity concentration by direct liquid scintillation counting is specified in ISO 19361.

## 8.3 Calculation of activity concentration with sample preparation

The symbols used are defined in Clause 3.

The activity concentration of $^{14}C$ in the sample is calculated according to Formula (1):

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

where

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

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

The combined uncertainty is calculated as Formula (2), Formula (3):

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

$$u_{rel}^2(w) = u_{rel}^2(\varepsilon) + u_{rel}^2(V) + u_{rel}^2(f_q) + u_{rel}^2(R_c) \tag{3}$$

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

$$u_{rel}^2(\varepsilon) = u_{rel}^2(r_s - r_0) + u_{rel}^2(A) = \frac{(r_s / t_s) + (r_0 / t_0)}{(r_s - r_0)^2} + u_{rel}^2(A) \tag{4}$$

All uncertainties related to the calibration source, i.e. in the standard solution and the preparation of the calibration source, are included in $u_{rel}^2(A)$.

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

The term $u_{rel}^2(R_c)$ depends on the type of preparation used to make the material to be counted.

For the calculation of the characteristic limits according to ISO 11929-1, $\tilde{u}(\tilde{c}_A)$ is needed, i.e. the standard uncertainty of $c_A$ as a function of its true value, calculated by Formula (5):

$$\tilde{u}(\tilde{c}_A) = \sqrt{w^2 \cdot \left( \left( (\tilde{c}_A \cdot w + r_0) / t_g \right) + r_0 / t_0 \right) + \tilde{c}_A^2 \cdot u_{rel}^2(w)} \tag{5}$$

If the calculation of the activity per unit mass is done by multiplying the specific activity by the density $\rho$ in kilogram per litre, a parameter associated with the determination of the density shall appear in the expression of the activity and its associated uncertainty.

## 8.4 Decision threshold

In accordance with ISO 11929-1, the decision threshold, $c_A^*$, is obtained from Formula (5) for $\tilde{c}_A = 0$. This yields:

$$c_A^* = k_{1-\alpha} \cdot \tilde{u}(0) = k_{1-\alpha} \cdot w \cdot \sqrt{r_0 / t_g + r_0 / t_0} \tag{6}$$

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

## 8.5 Detection limit

In accordance with ISO 11929-1, the detection limit, $c_A^{\#}$, is calculated by

$$c_A^{\#} = c_A^{*} + k_{1-\beta} \cdot \tilde{u}\left(c_A^{\#}\right) = c_A^{*} + k_{1-\beta} \cdot \sqrt{w^2 \cdot \left(\left(c_A^{\#}/w + r_0\right)/t_g + r_0/t_0\right) + c_A^{\#2} \cdot u_{rel}^2(w)} \tag{7}$$

$\beta = 0{,}05$ with $k_{1-\beta} = 1{,}65$ are 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 $c_A^{\#} = 2\,c_A^{*}$.

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

$$c_A^{\#} = \frac{2\,c_A^{*} + \left(k^2\,w\right)/t_g}{1 - k^2\,u_{rel}^2(w)} \tag{8}$$

## 8.6 Limits of the coverage intervals

### 8.6.1 Limits of the probabilistically symmetric coverage interval

The lower, $c_A^{\triangleleft}$ and upper $c_A^{\triangleright}$, coverage limits are calculated using Formulae (9) and (10) (see ISO 11929-1):

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

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

where

$\omega = \Phi[y/u(y)]$, $\Phi$ being the distribution function of the standardized normal distribution;

$1-\gamma$ is the probability for the coverage interval of the measurand;

$\omega = 1$ may be set if $c_A > 4 \cdot u\left(c_A\right)$ and in this case the following approximations for a symmetric uncertainty apply:

$$c_A^{\triangleleft} = c_A - k_{1-\gamma/2} \cdot u\left(c_A\right), \text{ and } c_A^{\triangleright} = c_A + k_{1-\gamma/2} \cdot u\left(c_A\right) \tag{11}$$

and the result should be given by $c_A \pm k_{1-\gamma/2} \cdot u\left(c_A\right)$ (12)

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

### 8.6.2 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, $c_A^{>}$, are calculated from a primary measurement result, $c_A$, of the measurand and the standard uncertainty, $u\left(c_A\right)$, associated with $c_A$, either Formula (13):

$$c_A^{<}, c_A^{>} = c_A \pm k_p \cdot u\left(c_A\right);\ p = \omega \cdot (1 + \omega(1 - \gamma))/2 \tag{13}$$

or if $c_A^{<} < 0$, by Formula (14):

$$c_A^{<} = 0;\ c_A^{>} = c_A \pm k_q \cdot u\left(c_A\right);\ q = 1 - \omega \cdot \gamma/2 \tag{14}$$

$\Phi$ being the distribution function of the standardized normal distribution;

The relation $0 \leq c_A^{\lhd} < c_A^{\rhd}$ apply and the approximation of Formula (12) is valid.

### 8.7 Calculations using the activity per mass

The activity concentration may be calculated multiplying the activity per unit of mass by the density $\rho$ in kilogram per litre, as given in Formula (15):

$$c_A = \frac{r_g - r_0}{m} \frac{\rho}{\varepsilon f_q R_c} = (r_g - r_0) w \tag{15}$$

where

$$w = \frac{\rho}{m \varepsilon R_c f_q}$$

$$u_{rel}^2(w) = u_{rel}^2(\varepsilon) + u_{rel}^2(m) + u_{rel}^2(\rho) + u_{rel}^2(f_q) + u_{rel}^2(R_c) \tag{16}$$

The uncertainty, the characteristic limits and the limits of the coverage interval may be calculated using the previous expression [Formulae (2), (6), (7) and (8)] with Formulae (15) and (16).

## 9 Test report

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

a) the test method used, with reference to this document i.e. ISO 13162:2021;

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);

      — 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 $c_A^{\lhd}$, $c_A^{\rhd}$ and/or the limits of the shortest coverage interval $c_A^{<}$, $c_A^{>}$;

f) probabilities $\alpha$, $\beta$ 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.

NOTE Occasionally, it is requested by the customer or regulator to compare the primary measurement result, $c_A$, with the detection limit, $c_A^{\#}$, in order to decide whether the physical effect is recognized or not. Such stipulations are not in accordance with the ISO 11929 series. They have the consequence that it is decided too frequently that the physical effect is absent when in fact it is not absent.

# Annex A
(informative)

# Extraction of total carbon by precipitation of calcium carbonate

## A.1 Principle

The total carbon content in the water sample is determined[17]. The carbon-containing products in the water sample are hydrolysed and oxidized to $CO_2$ under a flow of inert gas (e.g. nitrogen or argon), and the $CO_2$ is trapped then precipitated as $CaCO_3$[18][19][20]. The $CaCO_3$ is transferred as a solution into a weighed glass counting vial. The solution is evaporated until dryness and the vial is re-weighed. The calcium carbonate is then dissolved before counting.

The method described applies to a water sample of volume 0,25 l, for quantities of $CaCO_3$ as precipitate of 80 mg to 105 mg. It can be necessary to use a carbonate carrier (anhydrous sodium carbonate), with a known $^{14}C$ content. For a counting time of 180 min and a sample volume of 0,25 l, the detection limit can be 0,030 $Bq \cdot l^{-1}$.

It is important to avoid any mixing of the carbon contained in the sample with the $^{14}C$ in laboratory air and in the reagents used.

## A.2 Reagents

Unless otherwise stated, use only reagents of recognized analytical grade.

**A.2.1 Sodium peroxodisulfate ($Na_2S_2O_8$)**

**A.2.2 Silver nitrate solution ($AgNO_3$),** 40 $g \cdot l^{-1}$ of silver nitrate.

**A.2.3 Sodium carbonate ($Na_2CO_3$),** anhydrous.

**A.2.4 Hydrochloric acid (HCl),** 0,6 $mol \cdot l^{-1}$.

**A.2.5 Ammonium hydroxide ($NH_4OH$),** concentrated at 250 $g \cdot l^{-1}$.

**A.2.6 Ammonium hydroxide ($NH_4OH$),** 0,1 $mol \cdot l^{-1}$.

**A.2.7 Calcium chloride ($CaCl_2$),** 1,5 $mol \cdot l^{-1}$.

**A.2.8 Methanol ($CH_3OH$).**

**A.2.9 Inert gas.**

**A.2.10 Distilled water.**

**A.2.11 Calcium carbonate ($Na_2CO_3$).**

**A.2.12 Sodium hydroxide (NaOH).**

**A.2.13 $CO_2$ absorber**, e.g. Carbo-Sorb® E[1].

**A.2.14 Scintillation cocktail,** e.g. Insta Gel Plus[2].

## A.3 Equipment

Standard laboratory equipment is required, and in particular the following.

**A.3.1 Analytical balance.**

**A.3.2 Water bath.**

**A.3.3 Ultrasonic bath.**

**A.3.4 Glass equipment**, three-necked round-bottomed flask, two reservoirs, tubing, four traps.

**A.3.5 Flow meters,** two.

**A.3.6 Pipettes**, e.g. one- or two-mark pipettes, or e.g. fixed volume pipette, adjusted to the volume needed.

## A.4 Extraction

### A.4.1 General

The extraction procedure is designed to avoid contamination of the sample with laboratory air.

### A.4.2 Preparation of the precipitation solution

To 400 ml of $NH_4OH$, 0,1 mol·l$^{-1}$ (A.2.6), add 100 ml of $CH_3OH$ (A.2.8). Mix. Then add 4 ml of $CaCl_2$, 1,5 mol·l$^{-1}$ (A.2.7).

### A.4.3 Preparation of the traps

In trap 1 (A.3.4), put 70 ml of HCl, 0,6 mol·l$^{-1}$ (A.2.4). In traps 2 to 4, distribute the precipitation solution (A.4.2, e.g. 125 ml in each). It can be useful to cool the traps with ice.

### A.4.4 Chemical separation

Fill a reservoir with the sample water (25 ml), with some drops of concentrated $NH_4OH$ (A.2.5) to obtain a pH of 10. Fill another reservoir with 5 ml of the silver nitrate solution (A.2.2). In the round-bottomed flask, add 5 g of $Na_2S_2O_8$ (A.2.1). If necessary, add the anhydrous $Na_2CO_3$ (A.2.3) as a carrier to obtain a total of 80 mg to 105 mg of $CaCO_3$. Use the inert gas (A.2.9) to clean all the assembly (reservoirs, balloon, traps), verifying with the flow meters (A.3.5) that there is no leak. Introduce half of the sample into the flask, then the $AgNO_3$ solution, then the remainder of the sample. The extraction is achieved in 2 h. Warming the flask helps to completely outgas the liquid.



1) Carbo-Sorb® E 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.

2) Insta Gel Plus 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.

### A.4.5 Recovery of calcium carbonate

Protecting the traps from air, remove solution in traps 2 to 4, leaving about 40 ml. After 10 min in the ultrasonic bath (A.3.3), transfer the content of the traps into a centrifuge tube, rinsing the traps with $NH_4OH$, 0,1 mol·l$^{-1}$ (A.2.6).

After centrifugation (e.g. 10 min at 3 000 r·min$^{-1}$), discard the solution, and add 10 ml of $NH_4OH$, 0,1 mol·l$^{-1}$. Place the tube in the ultrasonic bath for 10 min. Transfer the solution into a previously weighed counting vial, which is called the test sample vial. Evaporate to dryness. Store the vial in a desiccator and allow to cool to room temperature. Weigh the vial and its contents. Chemical recovery can then be determined.

### A.4.6 Chemical recovery

The total carbon $m_{TC}$ is determined in the water sample with an uncertainty $u(m_{TC})$. The carbon in the precipitate $m_{PC}$ is the sum of the carbon in the carrier $m_{CC}$ and of the carbon in the sample, $m_{SC}$.

The chemical recovery is determined using the Formula (A.1):

$$R_c = \frac{m_{PC} - m_{CC}}{m_{TC}} \tag{A.1}$$

and the relative standard uncertainty of $R_c$ is calculated using Formula (A.2):

$$u_{rel}^2(R_c) = u_{rel}^2(m_{PC} - m_{CC}) + u_{rel}^2(m_{TC}) = \left( \frac{u(m_{PC}) + u(m_{CC})}{m_{PC} - m_{CC}} \right)^2 + u_{rel}^2(m_{TC}) \tag{A.2}$$

## A.5 Preparation of the sources to be measured

### A.5.1 Blank sample preparation

In a counting vial, add 80 mg to 105 mg of $CaCO_3$ (the same as in the test sample), 4,4 ml of distilled water (A.2.10), and 0,5 ml of a solution of 50 g·l$^{-1}$ NaOH (A.2.12) and 10 g·l$^{-1}$ $Na_2CO_3$. Mix vigorously and place the vial in the ultrasonic bath (A.3.3) for 10 min. Verify that the solution is homogeneous.

Add 0,1 ml of $CO_2$ absorber (A.2.13) and 5 ml of the scintillation cocktail (A.2.14) to the vial. Mix vigorously and place the vial in the ultrasonic bath for 10 min. Verify that the solution is homogeneous.

### A.5.2 Test sample preparation

In the test sample vial, add 4,4 ml of distilled water (A.2.10) and 0,5 ml of a solution of 50 g·l$^{-1}$ NaOH (A.2.12) and 10 g·l$^{-1}$ $Na_2CO_3$. Mix the content of the vial vigorously and place it in the ultrasonic bath (A.3.3) for 10 min. Verify that the solution is homogeneous.

Add 0,1 ml of $CO_2$ absorber (A.2.13) and 5 ml of the scintillation cocktail (A.2.14) to the vial. Mix vigorously and place in the ultrasonic bath for about 10 min. Verify that the solution is homogeneous.

## A.6 Counting procedures

See 7.3 and Annex B.

# Annex B
(informative)

# Extraction of total carbon: absorption counting

## B.1 Principle

The total carbon is determined in the water sample[17]. The carbon-containing products in the water sample are hydrolysed and oxidized in $CO_2$ under a current of inert gas (e.g. nitrogen or argon), and the $CO_2$ is absorbed in an LSC vial.

The method described applies to analysis of water containing about 0,01 g of carbon in the test sample.

It is important to avoid any mixing of the carbon contained in the sample with the $^{14}C$ in laboratory air and in the reagents used.

## B.2 Reagents

Unless otherwise stated, use only reagents of recognized analytical grade.

**B.2.1 Potassium permanganate ($KMnO_4$),** 100 g·l$^{-1}$.

**B.2.2 Sulfuric acid ($H_2SO_4$),** 4 mol·l$^{-1}$.

**B.2.3 Inert gas**, for example $N_2$.

**B.2.4 Distilled water.**

**B.2.5 Silica drying**, grain size 1 mm to 3 mm with colour indicator.

**B.2.6 $CO_2$ absorber**, e.g. Carbo-Sorb® E[3].

**B.2.7 Scintillation cocktail,** e.g. Permafluor® E $^{+}$ [4].

## B.3 Equipment

Standard laboratory equipment is required, and in particular the following.

**B.3.1 Analytical balance.**

**B.3.2 Liquid cooler.**

**B.3.3 Heating mantle.**

3) Carbo-Sorb® E 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.

4) Permafluor® E$^{+}$ 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.

**B.3.4 Standard laboratory tubing** (e.g. PVC Vinyl tubing), to connect the reflux cooler, the silica cartridge and the LSC vial.

**B.3.5 Glass equipment**, three-necked round-bottomed flask of capacity 500 ml, reflux cooler, silica drying cartridge.

**B.3.6 Flow meter.**

**B.3.7 Stopper with a rubber septum,** rubber bung or silicone bung.

**B.3.8 Glass tubing of small diameter,** e.g. Pasteur pipettes.

**B.3.9 LSC vials.**

**B.3.10 Cap for the LSC vials**, with two small holes drilled in, which are a little larger than the diameter of the Pasteur pipette.

## B.4 Extraction

### B.4.1 General

The extraction procedure is designed to avoid contamination of the sample with laboratory air.

### B.4.2 Preparation

Transfer a known volume (50 ml to 200 ml) of the aqueous sample into the three-necked flask (B.3.5). Add distilled water (B.2.4) to a total volume of 250 ml and add glass beads to facilitate boiling.

Fill the silica drying cartridge (B.3.5) with fresh, dry silica.

Fill the LSC counting vial (B.3.9) with a known quantity of $CO_2$ absorber (B.2.7), for example 8 ml of Carbo-Sorb® E, and cap (B.3.10).

Place this vial in a small beaker with ice (in order to prevent evaporation losses).

Start mild inert gas (B.2.3) purging (1 bubble $s^{-1}$ to 2 bubbles $s^{-1}$) and make sure that the bubble speed in the LSC vial containing the $CO_2$ absorber is about the same volume rate.

### B.4.3 Chemical separation

Start the oxidation by adding 50 ml $KMnO_4$ solution (B.2.1) and 40 ml 4 $mol \cdot l^{-1}$ $H_2SO_4$ (B.2.2) by injection through the septum or bung (B.3.7). A 10 ml or 20 ml plastic syringe can be used conveniently to add the oxidant and acid in portions.

Heat (B.3.3) the sample to simmering point.

**IMPORTANT — — For safety reasons, when boiling, monitor the experimental setup for at least 15 min and ensure that the oxidation is proceeding well.**

Check the condition of the LSC vial containing the $CO_2$ absorber regularly and refresh the cooling ice if necessary.

After 5 h of boiling and oxidation, remove the LSC vial (vial 1) and replace it directly with a new LSC vial (vial 2), filled exactly as vial 1.

Add 20 ml extra $KMnO_4$ solution and continue the oxidation for 1 h longer.

First remove vial 2 from the heat source. Shut off the $N_2$ purging system and allow the equipment to cool to room temperature.

Do not change the order of steps in the procedure. Otherwise, the reduction in vapour pressure can cause the $CO_2$ absorber to be drawn into the tubing and possibly into the silica cartridge.

## B.5 Preparation of the sources to be measured

### B.5.1 Blank sample preparation

Fill an LSC vial with the same proportion of $CO_2$ absorber (B.2.6) and scintillation cocktail (B.2.7) as the vials containing the sample.

### B.5.2 Test sample preparation

Add the scintillation cocktail (B.2.7), for example 12 ml of Permafluor® E + to each of the vials and shake well.

Carefully wipe the vials.

## B.6 Counting procedures

See 7.3.

## B.7 Verification

Determine whether the oxidation is complete from the LSC results. As all organic molecules in the sample consume $KMnO_4$, it is difficult to establish the true endpoint of the oxidation. From a practical point of view, it is not recommended to leave a boiling, strongly oxidative and acidic solution unattended overnight. Therefore, a practical approximation of the oxidation endpoint can be carried out as follows: the $^{14}C$ activity in vial 2 relative to vial 1 is used to determine whether the oxidation is finished. If the $^{14}C$ activity in vial 2 is less than 3 % of the $^{14}C$ activity in vial 1, the oxidation is considered to be complete.

# Annex C
(informative)

# Internal standard method

## C.1 Sample preparation

For each water sample, prepare two counting vials with identical volume of sample ($V_1$) and scintillation cocktail in each. The volumes of sample and scintillation cocktail are determined by the capacity of the scintillation cocktail for aqueous samples but a total volume of about 20 ml is recommended. To one of the two vials, add accurately a known quantity, with activity $A_s$, of the internal standard solution. The volume should be kept as small as possible (e.g. use a 100 µl pipette) with an uncertainty of less than 1 %. Label the samples in such a way that the spiked and unspiked vials can be differentiated from each other, and from other samples in the same analytical batch. Shake all vials in the batch thoroughly.

Background counting vials are prepared similarly, using the same volume ($V_1$) of blank water plus scintillation cocktail.

Counting source preparation 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.

The use of an internal standard is recommended when polyethylene counting vials are used. When using an external standard in polyethylene counting vials, errors can occur because the counting rate of the external standard changes as a function of time, due to 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).

## C.2 Counting procedure

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

Place the counting vials in the LSC, noting the sequence, e.g. background, sample 1, sample 1 with internal standard solution added, background, sample 2, etc.

Count the vials for a pre-set time or, until a pre-set count is reached.

A counting time of 100 min per vial is generally sufficient, although the laboratory shall determine whether this meets the required limit of detection and adjust accordingly. It is preferable to count the vial series for repeated short counting times rather than one long counting time, e.g. instead of one 100 min count, count five times for 20 min. This can only be done where an automatic sample changer is available. 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 stand the counting vials in the LSC instrument overnight to allow light and temperature adaptation, thus reducing the chance of interfering luminescence occurring during counting.