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Water quality — Determination of tritium activity concentration — Liquid scintillation counting method

Qualité de l'eau — Détermination de l'activité volumique du tritium — Méthode par comptage des scintillations en milieu liquide

Reference number
ISO 9698:2010(E)

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

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.

ISO 9698 was prepared by Technical Committee ISO/TC 147, *Water quality*.

This second edition cancels and replaces the first edition (ISO 9698:1989), which has been technically revised.

Introduction

The tritium present in the environment is of natural origin and man made. As a result of atmospheric nuclear weapon testing, emissions from nuclear engineering installations, and the application and processing of isotopes, relatively large amounts of tritium have been released to the environment. Despite the low dose factor associated to tritium, monitoring of tritium activity concentrations in the environment is necessary in order to follow its circulation in the hydrosphere and biosphere.

INTERNATIONAL STANDARD **ISO 9698:2010(E)**

Water quality — Determination of tritium activity concentration — Liquid scintillation counting method

WARNING — This International Standard 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 ensure compliance with any national regulatory conditions.

IMPORTANT — It is absolutely essential that tests conducted according to this International Standard be carried out by suitably trained staff.

1 Scope

This International Standard specifies the conditions for the determination of tritium activity concentration in samples of environmental water or of tritiated water ($[^3H]H_2O$) using liquid scintillation counting.

The choice of the analytical procedure, either with or without distillation of the water sample prior to determination, depends on the aim of the measurement and the sample characteristics (see References [1], [2], [3]).

Direct measurement of a raw water sample using liquid scintillation counting has to consider the potential presence of other beta emitter radionuclides. To avoid interference with these radionuclides when they are detected, the quantification of tritium will be performed following the sample treatment by distillation (see References [4], [5], [6], [7]). Three distillation procedures are described in Annexes B, D and E.

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

With suitable technical conditions, the detection limit may be as low as 1 Bq l^{-1}. Tritium activity concentrations below 10^6 Bq l^{-1} can be determined without any sample dilution. A prior enrichment step can significantly lower the limit of detection (see References [8], [9]).

2 Normative references

The following referenced documents are indispensable for the application 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: Guidance on the preservation and handling of water samples*

ISO 5667-14, *Water quality — Sampling — Part 14: Guidance on quality assurance of environmental water sampling and handling*

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)*

ISO/IEC Guide 99:2007, *International vocabulary of metrology — Basic and general concepts and associated terms (VIM)*

3 Symbols, definitions and units

For the purposes of this document, the definitions, symbols and units defined in ISO 80000-10, ISO/IEC Guide 98-3 and ISO/IEC Guide 99, as well as the following symbols, apply.

β_{max}	Maximum energy for the beta emission, in kilo-electronvolts
V	Volume of test sample, in litres
m	Mass of test sample, in kilograms
ρ	Mass density of the sample, in grams per litre
c_A	Activity concentration, in becquerels per litre
a	Activity per unit of mass, in becquerels per kilogram
A	Activity of the calibration source, in becquerels
t_0	Background counting time, in seconds
t_{g}	Sample counting time, in seconds
t_{s}	Calibration counting time, in seconds
n	Number of repetitions
r_{0i}	Background count rate in the repetition i, per second
r_0	Mean background count rate for i repetitions, per second
$r_{\mathrm{g}i}$	Sample count rate in the repetition i, per second
r_{g}	Mean sample count rate for i repetitions, per second
r_{s}	Calibration count rate, per second
ε	Detection efficiency
ε_{q}	Efficiency measured for each of the working standards to elaborate the quench curve
f_{q}	Quench factor
$u(c_A)$	Standard uncertainty associated with the measurement result, in becquerels per litre
U	Expanded uncertainty, calculated by $U = k \cdot u(c_A)$ with $k = 1, 2, \ldots$, in becquerels per litre
c_A^*	Decision threshold, in becquerels per litre
$c_A^\#$	Detection limit, in becquerels per litre
$c_A^\triangleleft, c_A^\triangleright$	Lower and upper limits of the confidence interval, in becquerels per litre

4 Principle

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

The electric pulses emitted by the photodetectors are amplified, sorted (in order to remove random events) and analysed by the electronic systems and the data analysis software. The count rate of these photons allows the determination of the test portion activity, after correcting for the background count rate and detection efficiency.

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

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

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

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

IMPORTANT — Quench correction: If the measurement results are affected by particular conditions of chemical quenching, it is recommended that a quench curve be established. It is important to choose a suitable chemical quenching agent for the type of quenching suspected in the sample.

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

5 Reagents and equipment

Use only reagents of recognized analytical grade.

5.1 Reagents

5.1.1 Water for the blank

The water used for the blank shall be as free as possible of chemical impurities to avoid quenching, of radioactive impurities (see Reference [10]) and with an activity concentration of tritium negligible in comparison with the activities to be measured.

For example, a water sample with a low tritium activity concentration can be obtained from (deep) subterranean water kept in a well-sealed borosilicate glass bottle in the dark at a controlled temperature (ISO 5667-3). This blank water sample shall be kept physically remote from any tritium-containing material (see Clause 4, important notice). Determine the tritium activity concentration ($t = 0$), in Bq l^{-1}, of this water and note the date ($t = 0$) of this determination (see Clause 4, Note).

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

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

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

5.1.2 Calibration source solution

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

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

5.1.3 Scintillation solution

The scintillation cocktail is chosen according to the characteristics of the sample to be analysed and according to the properties of the detection equipment (see Reference [11]).

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

The characteristics of the scintillation cocktail must allow the mixture to be homogeneous and stable.

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

It is recommended to:

- store in the dark and, particularly just before use, avoid exposure to direct sunlight or fluorescent light in order to prevent interfering luminescence;

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

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

5.1.4 Quenching agent

The following are examples of chemical quenching agents: nitric acid, acetone, organochloride compounds, nitromethane.

NOTE Some quenching agents are dangerous or toxic.

5.2 Equipment

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

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

5.2.1 Liquid scintillation counter

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

5.2.2 Counting vials

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

Other types of vials exist:

- glass vials with low level of ^{40}K, will exhibit a lower background than “normal” glass vials;
- for the determination of very low tritium concentration, the use of polytetrafluoroethylene (PTFE) vials or polyethylene vials with an inner layer of PTFE on the inside vial wall is strongly recommended. Diffusion of organic solvents is then slower through PTFE than through polyethylene. These vials are used for long counting times with very low-level activity to be measured.

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

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

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

6 Sampling and samples

6.1 Sampling

Conditions of sampling shall conform to ISO 5667-1.

It is not advised to acidify the sample due to the high chemical quench caused by acids, and the potential presence of tritium in the acid, as specified in ISO 5667-3.

It is important that the laboratory receive a representative sample, unmodified during the transport or storage and in an undamaged container. It is recommended to use a glass flask and to fill it to the maximum, to minimize tritium exchange with the atmospheric moisture.

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

6.2 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 flasks.

7 Procedure

7.1 Sample preparation

7.1.1 Direct procedure

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

7.1.2 Distillation

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

Distillation shall avoid isotopic fractionation (see Reference [12]).

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

7.2 Preparation of the sources to be measured

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

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

The vial identification shall be written on the top of the vial stopper. 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, e.g. after 12 h.

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

7.3 Counting procedure

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

7.3.1 Control and calibration

Statistical control of the detection system shall be monitored by measurement of suitable reference background and reference sources usually provided by the equipment supplier, for example in compliance with ISO 8258 [13].

The measurement of the blank sample is performed before each analysis or each series of sample measurement in representative conditions of each type of measurement (Clause 4).

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

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

- a given type of measurement equipment;
- a given type of scintillation cocktail;
- a given ratio of scintillation cocktail and test sample.

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

- similar quantity of certified standard tritiated water solution in each vial; the activity of the certified standard must be sufficient for the counting ratio to be defined with a known statistical precision, even in the case of a strong quench;
- the standard is completed with reference water until the volume of test sample is reached;
- the scintillation cocktail is added to obtain the desired ratio;
- at least one working standard is used as it is; in the other working standards, increasing quantities of quenching agent are added to simulate the quench encountered in the samples to be measured.

The quench curve relating ε_q and the quenching parameter provided by the equipment are used to determine f_q as follows:

$$f_\mathrm{q} = \frac{\varepsilon_\mathrm{q}}{\varepsilon} \tag{1}$$

7.3.2 Measurement conditions

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

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

The absence of other radionuclides is verified by checking the counting rate above the maximum energy β_max of the tritium.

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

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

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

7.3.3 Interference control

7.3.3.1 Interference arising from luminescence

Serious interference of tritium determinations can occur due to a variety of luminescent processes, e.g. chemiluminescence, phosphorescence, triboluminescence, and static electricity. It is advisable to use a liquid scintillation counter capable of identifying these single photon events and current LSC equipment can even automatically correct for these interferences. In the absence of such an automatic correction the tritium is measured in parallel in another measurement, channel B having the same lower threshold as measurement channel A, but an upper threshold adjusted so that the tritium counting efficiency is about two-thirds of the tritium counting efficiency of channel A.

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

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

7.3.3.2 Equipment stability

Once the measurement channels A and B have been adjusted, it is advisable to check that the setting is maintained by measuring in each sequence two hermetically sealed unquenched vials, one containing tritium standard solution and the other containing blank water. Drift of the equipment from its initial setting will then be easily detected. For control purposes, the use of control charts (see ISO 8258) is advisable.

8 Expression of results

8.1 General

In the particular case of the measurement of radionuclides by liquid scintillation, only the elementary uncertainties of the following parameters are retained:

- test and blank samples counts;

- detection efficiency in the considered energy window for a given quench indicator parameter;

- volume or mass of test sample.

The other uncertainties may be neglected in first approximation (scintillation liquid volume or mass, counting time, etc.).

For symbols not defined in Clause 3, see also Annex A.

8.2 Calculation of activity concentration

The sample activity concentration of the radionuclide present in the sample is calculated using Equation (2):

$$c_A = \frac{r_\text{g} - r_0}{V} \cdot \frac{1}{\varepsilon \cdot f_\text{q}} = (r_\text{g} - r_0) \cdot w \qquad (2)$$

where $w = \frac{1}{V \cdot \varepsilon \cdot f_\text{q}}$ and $\varepsilon = \frac{r_\text{s} - r_0}{A}$

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

The combined uncertainty is calculated using Equation (3):

$$u\left(c_A\right) = \sqrt{w^2 \cdot \left[u^2(r_{\text{g}}) + u^2(r_0)\right] + c_A{}^2 \cdot u_{\text{rel}}^2\left(w\right)} = \sqrt{(w^2/n) \cdot \left(r_{\text{g}}/t_{\text{g}} + r_0/t_0\right) + c_A{}^2 \cdot u_{\text{rel}}^2\left(w\right)} \tag{3}$$

$$u_{\text{rel}}^2(w) = u_{\text{rel}}^2(\varepsilon) + u_{\text{rel}}^2(V) + u_{\text{rel}}^2\left(f_{\text{q}}\right) \tag{4}$$

and the relative standard uncertainty of ε for each quenching value is calculated using Equation (5):

$$u_{\text{rel}}^2(\varepsilon) = u_{\text{rel}}^2(r_{\text{s}} - r_0) + u_{\text{rel}}^2(A) = \left(r_{\text{s}}/t_{\text{s}} + r_0/t_0\right) / \left(r_{\text{s}} - r_0\right)^2 + u_{\text{rel}}^2\left(A\right) \tag{5}$$

considering that in this case r_{s} as well as r_0 come from one single measurement.

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

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

For the calculation of the characteristic limits, $\tilde{u}(\tilde{c}_A)$ is needed (see ISO 11929), i.e. the standard uncertainty of c_A as a function of its true value, calculated by using Equation (6):

$$\tilde{u}(\tilde{c}_A) = \sqrt{(w^2/n) \cdot \left[(\tilde{c}_A/w + r_0)/t_{\text{g}} + r_0/t_0\right] + \tilde{c}_A^2 \cdot u_{\text{rel}}^2(w)} \tag{6}$$

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

8.3 Decision threshold

The decision threshold, c_A^*, is obtained from Equation (6) for $\tilde{c}_A = 0$ (see ISO 11929).This yields:

$$c_A^* = k_{1-\alpha} \cdot \tilde{u}(0) = k_{1-\alpha} \cdot w \cdot \sqrt{(r_0/n) \cdot (1/t_{\text{g}} + 1/t_0)} \tag{7}$$

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

8.4 Detection limit

The detection limit, $c_A^\#$, is calculated by using Equation (8) (see ISO 11929):

$$c_A^\# = c_A^* + k_{1-\beta} \cdot \tilde{u}(c_A^\#) = c_A^* + k_{1-\beta} \cdot \sqrt{(w^2/n) \cdot \left[(c_A^\#/w + r_0)/t_{\text{g}} + r_0/t_0)\right] + c_A^{\#2} \cdot u_{\text{rel}}^2(w)} \tag{8}$$

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

The detection limit can be calculated by solving Equation (8) for $c_A^\#$ or, more simply, by iteration with a starting approximation $c_A^\# = 2 \cdot c_A^*$.

When taking $\alpha = \beta$, then $k_{1-\alpha} = k_{1-\beta} = k$ and the solution of Equation (8) is given by Equation (9):

$$c_A^{\#} = \frac{2 \cdot c_A^{\ *} + \left(k^2 \cdot w\right) / n \cdot t_{\mathrm{g}}}{1 - k^2 \cdot u_{\mathrm{rel}}^2\left(w\right)} \qquad (9)$$

8.5 Confidence interval limits

The lower, $c_A^{\triangleleft}$, and upper, $c_A^{\triangleright}$, confidence limits are calculated using Equations (10) and (11) (see ISO 11929):

$$c_A^{\triangleleft} = c_A - k_p \cdot u(c_A);\ p = \omega \cdot (1 - \gamma/2) \qquad (10)$$

$$c_A^{\triangleright} = c_A + k_q \cdot u(c_A);\ q = 1 - (\omega \cdot \gamma/2) \qquad (11)$$

where

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

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

$\omega = 1$ may be set if $c_A \geqslant 4 \cdot u\left(c_A\right)$.

In this case,

$$c_A^{\triangleleft}, c_A^{\triangleright} = c_A \pm k_{1-\gamma/2} \cdot u(c_A) \qquad (12)$$

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

8.6 Calculations using the activity per unit of mass

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

$$c_A = \frac{r_{\mathrm{g}} - r_0}{m \cdot 10^3} \cdot \frac{\rho}{\varepsilon \cdot f_{\mathrm{q}}} = (r_{\mathrm{g}} - r_0) \cdot w \text{ and } w = \frac{\rho}{m \cdot 10^3 \varepsilon \cdot f_{\mathrm{q}}} \qquad (13)$$

$$u_{\mathrm{rel}}^2(w) = u_{\mathrm{rel}}^2(\varepsilon) + u_{\mathrm{rel}}^2(m) + u_{\mathrm{rel}}^2(\rho) + u_{\mathrm{rel}}^2\left(f_{\mathrm{q}}\right) \qquad (14)$$

The uncertainty, the characteristics limits and the limits of the confidence interval may be calculated using the previous expression [Equations (3), (7), (8) and (9)] with Equations (13) and (14).

9 Test report

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

a) a reference to this International Standard (ISO 9698:2010) with the mention of the sample pretreatment with or without distillation;

b) identification of the sample;

c) units in which the results are expressed;

d) test result, $c_A \pm u(c_A)$ or $c_A \pm U$ with the associated k value.

Complementary information can be provided, such as:

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

f) decision threshold and the detection limit;

g) depending on the customer request, there are different ways to present the result:

  - when the activity concentration c_A is compared with the decision threshold (see ISO 11929), the result of the measurement should be expressed as $\leqslant c_A^*$ when the result is below or equal to the decision threshold;
  - when the activity concentration c_A is compared with the detection limit, the result of the measurement can be expressed as $\leqslant c_A^\#$ when the result is below or equal to the detection limit. If the detection limit exceeds the guideline value, it shall be documented that the method is not suitable for the measurement purpose;

h) mention of any relevant information likely to affect and/or explain the results.

Annex A
(informative)

Numerical applications

Table A.1 presents the parameter values for three situations of activity concentration. This table may be used to verify any computation of the different formulae. The repetition number, n, is taken to be = 1.

Table A.1

Symbol	Unit	$c_A < c_A^*$	$c_A^* < c_A < c_A^\#$	$c_A > c_A^\#$
N_g		210	225	390
t_g	s	3 600	3 600	3 600
r_g	s^{-1}	0,058 3	0,062 5	0,108 3
N_0		180	180	180
t_0	s	3 600	3 600	3 600
r_0	s^{-1}	0,050	0,050	0,050
V	l	0,010	0,010	0,010
$u(V)$	l	0,002 5	0,002 5	0,002 5
ε		0,25	0,25	0,25
$u_\mathrm{rel}(\varepsilon)$		0,035	0,035	0,035
α, β, γ	%	5	5	5
w	l^{-1}	400	400	400
$u_\mathrm{rel}(w)$		0,252	0,252	0,252
ω	—	0,922 0	0,974 2	0,999 8
p	—	0,898 9	0,949 9	0,974 9
q	—	0,977 0	0,975 6	0,975 0
k_p	—	1,275	1,644	1,957
k_q	—	1,994	1,971	1,960
c_A	$\mathrm{Bq\ l}^{-1}$	3,33	5,00	23,33
$u(c_A)$	$\mathrm{Bq\ l}^{-1}$	2,35	2,57	6,46
c_A^*	$\mathrm{Bq\ l}^{-1}$	3,47	3,47	3,47
$c_A^\#$	$\mathrm{Bq\ l}^{-1}$	8,74	8,74	8,74
$c_A^\triangleleft$	$\mathrm{Bq\ l}^{-1}$	0,34	0,78	10,69
$c_A^\triangleright$	$\mathrm{Bq\ l}^{-1}$	8,02	10,06	36,00

N_g and N_0 are the number of the counted impulsions for the sample and for the background, respectively.

For example, functions to calculate ω, k_p, k_q, in Excel®[1] are:

$\omega =$ NORMSDIST ($u\left(c_A\right)/c_A$)

$k_p =$ NORMSINV (p)

$k_q =$ NORMSINV (q)

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

Annex B
(informative)

Distillation of large volume sample

B.1 Principle

Samples of volume from 100 ml to 500 ml are considered as large volume samples. Before the distillation of the water sample, oxidizing and suitable alkaline agents are added to degrade organic matter and transform iodine into iodide. An aliquot of the distillate is then mixed with the scintillation solution in a counting vial (see Reference [14]).

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

B.2 Reagents and equipment

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

B.2.1 Reagents

For the oxidant/alkaline medium use either of those given in B.2.1.1.

B.2.1.1 **Sodium thiosulfate**, anhydrous, $Na_2S_2O_3$, and **sodium carbonate**, anhydrous, Na_2CO_3, or

potassium permanganate, $KMnO_4$ and **sodium hydroxide**, NaOH.

The sodium hydroxide shall be free of tritium.

B.2.1.2 **Tritium standard solution**.

B.2.1.3 **Scintillation solution**.

B.2.1.4 **Blank water**.

B.2.1.5 **Carborundum** or **glass beads**.

B.2.2 Equipment

Use usual laboratory equipment and the following.

B.2.2.1 **Cooling system**, consisting of

- cooler, circulating bath (5 °C);
- Dewar flask, adapted to the receiver flask.

B.2.2.2 **Heating system**, consisting of

- heater, adapted to the distillation flask;
- air gun heater.

B.2.2.3 Distillation equipment, consisting of the following.

B.2.2.3.1 Distillation flask, with a capacity of 500 ml.

B.2.2.3.2 Splash head.

B.2.2.3.3 Distillation column, length 40 cm.

B.2.2.3.4 Condenser.

B.2.2.3.5 Adapter, bent type.

The equipment shall be dried before use.

B.2.2.3.6 Borosilicate glass or **polyethylene bottles**, of capacity about 100 ml.

B.3 Distillation

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

Assemble the distillation equipment and start the distillation process.

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

B.3.1 Sample preparation

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

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

All the employed material has to be well dried.

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

B.3.1.1 Oxidation in alkaline medium

Add the necessary reagents to obtain an adequate medium for the oxidation. The following can be used:

a) 0,1 g of potassium permanganate and 0,5 g of sodium hydroxide; or

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

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

B.3.1.2 Homogenization

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

B.3.2 Discard

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

B.3.3 Collection

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

B.3.4 Control

The pH value or the conductivity of the intermediate distillation fraction has to be controlled. The pH value must be neutral and the conductivity lower than 100 µS cm^{-2}. When these pH or conductivity conditions are not satisfied, the distillation shall be performed again.

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

B.4 Measurement

The measurement steps shall be performed as described in 7.2 and 7.3.

Annex C
(informative)

Internal standard methods

C.1 Principle

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

C.2 Sample preparation

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

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

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

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

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

C.3 Counting procedure

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

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

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

A counting time of 100 min per vial is generally sufficient. It is preferable to count the vial series during repeated short counting times rather than one long counting time, e.g. instead of one 100 min count, count five times for 20 min; for this purpose, an automatic sample presentation unit is necessary. This provides for a better control of stability of the samples and the possibility of undetected erroneous counts is reduced.

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

C.4 Expression of results

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

$$\varepsilon = \frac{r_\mathrm{s} - r_\mathrm{g}}{A_\mathrm{s}} \tag{C.1}$$

where

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

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

A_s is the added activity.

Annex D
(informative)

Distillation of small volume sample

D.1 Principle

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

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

If necessary, the addition of sodium thiosulfate or potassium permanganate oxidizes the water sample, which is then made alkaline and distilled.

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

D.2 Reagents and equipment

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

D.2.1 Reagents

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

D.2.1.2 **Sodium thiosulfate**, anhydrous, $Na_2S_2O_3$, and **sodium carbonate**, anhydrous, Na_2CO_3, or

potassium permanganate, $KMnO_4$, and **sodium hydroxide**, NaOH.

The sodium hydroxide shall be free of tritium.

D.2.1.3 **Working tritium standard solution**.

D.2.1.4 **Scintillation solution**.

D.2.1.5 **Blank water**.

D.2.1.6 **Carborundum** or **glass beads**.

D.2.2 Equipment

Use usual laboratory equipment and the following.

D.2.2.1 **Cooling system**, consisting of

- cooler, circulating bath (5 °C);
- Dewar flask, adapted to the receiver flask.

D.2.2.2 **Heating system**, consisting of

- heater, adapted to the distillation flask;
- air gun heater.

D.2.2.3 **Distillation equipment**, dried before use, consisting of the following.

D.2.2.3.1 **Distillation flask**, with a capacity of 25 ml.

D.2.2.3.2 **Distillation column**, Vigreux type, length 15 cm.

D.2.2.3.3 **Condenser**, length circa 10 cm.

D.2.2.3.4 **Adapter**, bent type, with a tube,

D.2.2.3.5 **Receiver flask**, with a capacity of 25 ml, with stopper.

D.3 Distillation

Weigh the test sample in the distillation flask. Add some beads to prevent bumping. Assemble the distillation equipment. Distil to dryness. Dry the tubing with the heater. Weigh the distillate.

D.4 Sample preparation

If necessary, the water sample is chemically prepared.

D.4.1 Oxidation in alkaline medium

Add the necessary reagents to obtain an adequate medium for the oxidation. The following can be used for 10 ml of water sample:

a) 0,01 g of potassium permanganate and 0,05 g of sodium hydroxide, or

b) 0,025 g of sodium thiosulfate and 0,050 g of sodium carbonate.

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

D.4.2 Neutralization

If the pH of the water sample is acid (water from combustion, for example), add enough calcium carbonate to obtain a neutral pH.

Place an aliquot of the water sample (up to 12 g) in the distillation flask.

Weigh the test sample in the distillation flask. Add the beads. Weigh again.

Weigh the receiver flask, with stopper.

D.4.3 Collect

Weigh the receiver flask with stopper. Weigh the distillation flask.

D.4.4 Control

The recovery of the test sample must be above 95 %.

D.5 Preparation of the sources to be measured

Measure the usual fraction analysed as a sample test portion for a direct determination and mix it with the scintillation cocktail, as described in 7.2 and 7.3.

Annex E
(informative)

Screening method for wet matrices

E.1 Principle

The evaporation, in a relatively small free volume, of a small quantity of water from different matrices, is enhanced by the use of a heating plate, and the condensation by the use of dry ice.

It is important to evaluate the yield of this distillation procedure by analysing a tritium certified standard solution in the same way as the portion test sample.

E.2 Reagents and equipment

E.2.1 Reagents

E.2.1.1 Cooling agents

- Dry ice;
- propan-2-ol (isopropanol).

E.2.1.2 Working tritium standard solution.

E.2.1.3 Scintillation solution.

E.2.1.4 Blank water.

E.2.2 Equipment

Use usual laboratory equipment and the following.

E.2.2.1 Extracting hood.

E.2.2.2 Heating plate.

E.2.2.3 Distillation equipment, dried before use, consisting of the following.

E.2.2.3.1 Petri dish, with cover.

E.2.2.3.2 Glass plate.

E.2.2.3.3 Beaker, 600 ml for example.

E.3 Distillation

E.3.1 Preparation

Switch on the heating plate and set to about 60 °C (temperature of the plate).

Get flaked dry ice in sufficient quantity.

Prepare the ice bath by filling a 600 ml beaker with 200 ml of propan-2-ol (isopropyl alcohol) and dry ice up to the top of the beaker.

Take, for example, a small aliquot, 14 ml, from the portion test sample to be analysed, and pour it into a Petri dish; close with its cover.

E.3.2 Formation of the lens ice and collection of the distilled water

Put the Petri dish on the heating plate, and place the beaker containing the ice bath on top of it.

As the water evaporates, a convex lens of ice forms under the cover.

Add more dry ice during evaporation if necessary.

The evaporation of 14 ml of water needs about 1 h 30 min.

At the end of the operation, take off the ice bath, turn over the cover of the dish, place a glass plate on it and put it on the working surface.

Melt the ice lens quickly (without using a heating plate or heat gun), until room temperature.

Homogenize and measure the corresponding volume.

E.4 Preparation of the sources to be measured

Measure the usual fraction analysed as a sample test portion for a direct determination (10 ml for example) and mix it with the scintillation cocktail, as described in 7.2 and 7.3.

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