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**9698**

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

**iTeh STANDARD PREVIEW**  
*Qualité de l'eau — Détermination de l'activité volumique du tritium —  
Méthode par comptage des scintillations en milieu liquide*  
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## Foreword

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

Draft International Standards adopted by the technical committees are circulated to the member bodies for approval before their acceptance as International Standards by the ISO Council. They are approved in accordance with ISO procedures requiring at least 75 % approval by the member bodies voting.

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

Annex A of this International Standard is for information only.

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## Introduction

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

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

## 1 Scope

This International Standard specifies a method for the determination of tritiated water ( $[^3\text{H}]\text{H}_2\text{O}$ ) activity concentration in water by liquid scintillation counting.

The method is applicable to all types of water including seawater with tritium activity concentrations of up to  $10^6$  Bq/m<sup>3</sup> when using 20 ml counting vials.

### NOTES

1 Below tritium activity concentrations of about  $5 \times 10^4$  Bq/m<sup>3</sup><sup>[8]</sup>, a prior enrichment step and/or the measurement of larger sample volumes can significantly improve the accuracy of the determination and lower the limit of detection (see clause 9 for calculation of the minimum detectable activity concentration).

However, enrichment means an extra step in the analytical procedure and thus an extra source of error, quite apart from the greater analytical effort involved. A scatter of about 1 % occurs as a result of the inherent variability of the enrichment cells. Direct scintillation counting with commonly used liquid scintillation counters<sup>[5]</sup> is therefore preferable for tritium activity concentrations higher than about  $5 \cdot 10^4$  Bq/m<sup>3</sup>, and, depending on the required accuracy of the measurements, is also applicable to much lower activity concentrations.

2 Tritium activity concentrations higher than  $10^6$  Bq/m<sup>3</sup> may be determined after appropriate dilution with distilled water of proven low tritium content. An alternative method for the determination of these higher activities involves increasing the tritium activity concentrations of the internal standard solution (4.4).

3 The method is not applicable to the analysis of organically bound tritium; its determination requires an oxidative digestion.

## 2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the editions indicated were valid. All stand-

ards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 5667-1:1980, *Water quality — Sampling — Part 1: Guidance on the design of sampling programmes*.

ISO 5667-2:1982, *Water quality — Sampling — Part 2: Guidance on sampling techniques*.

## 3 Principle

Addition of thiosulfate to a water sample which is then made alkaline and distilled. Mixing of an aliquot of the distillate with the scintillation solution in a counting vial. Partial conversion of the kinetic energy of the tritium beta particles in the resulting mixture (usually an emulsion) into photons. Counting of these photons as pulses. The counting rate is a measure of the tritium activity concentration.

### NOTES

4 Tritium decays to helium by emitting beta radiation with a maximum energy of 18,6 keV. Its half-life is 4540 days (12,43 years)<sup>[7]</sup>.

5 The majority of the interfering compounds which act, for example, by quenching of the scintillation process, remain in the residue of the distillation together with any radioactive iodide and bicarbonate that might be present.

6 For counting, certain boundary conditions should be satisfied, e.g. simultaneous detection by two or more photomultiplier tubes connected in series; discrimination of pulses by preset measurement channels.

## 4 Reagents

During the analysis use only reagents of recognized analytical grade.

**4.1 Sodium carbonate**, anhydrous ( $\text{Na}_2\text{CO}_3$ ) .

**4.2 Sodium thiosulfate**, anhydrous ( $\text{Na}_2\text{S}_2\text{O}_3$ ) .

**4.3 Blank water**, with a tritium activity concentration  $c_o(t)$ , in becquerels per cubic metre, at the time  $t$  at which the samples are measured.

Obtain water with a tritium activity concentration as low as possible, e.g. (deep) subterranean water. Distil the water according to 7.1. Keep the distillate in a well-stoppered borosilicate glass bottle in the dark at a temperature as constant as possible. Determine (see note 8) the tritium activity concentration  $c_o(t=0)$ , in becquerels per cubic metre, of this water and note the date ( $t=0$ ) of this determination.

NOTES

7 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.

8 The tritium activity concentration in the blank water can be determined by enrichment, followed by, for example, liquid scintillation counting.

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

9 Preferably use blank water with a tritium activity concentration of less than  $500 \text{ Bq/m}^3$ . In case the tritium activity concentration of the blank water is greater than  $500 \text{ Bq/m}^3$ , a correction must be made using the calculation procedure given in 8.1.2. The tritium activity concentration at the time  $t$  at which the samples are measured (7.3), corrected for radioactive decay, is given by the equation

$$c_o(t) = c_o(t=0)e^{-\lambda t} \quad \dots (1)$$

where

- $c_o(t)$  is the tritium activity concentration, in becquerels per cubic metre, of the blank water at the time  $t$  at which the samples are measured;
- $c_o(t=0)$  is the tritium activity concentration, in becquerels per cubic metre, of the blank water at the time of its preparation;
- $\lambda$  is the decay constant, in reciprocal years ( $\lambda = 0,05576$ );
- $t$  is the time, in years, between the preparation of the blank water and the measurement of the samples.

For blank water with a tritium activity concentration of up to  $500 \text{ Bq/m}^3$ , correction for radioactive decay is not necessary.

**4.4 Internal standard solution**, tritium activity concentration  $c_s(t)$ .

In a location which is remote from the area where the tritium analyses are to be carried out, weigh and pour into a weighed 100 ml volumetric flask the requisite quantity of a concentrated tritium ( $[^3\text{H}]\text{H}_2\text{O}$ ) standard solution (tritium activity concentration  $10^{10} \text{ Bq/m}^3$  to  $10^{11} \text{ Bq/m}^3$ , total inaccuracy less than about 1 %), so that the tritium activity concentration will be about  $170 \text{ Bq/m}^3$  after making up to the mark with blank water (4.3) and mixing. Calculate the tritium activity concentration of the resulting internal standard solution  $c_s(t=0)$  in becquerels per cubic metre. Note the date at which the standard solution was made up ( $t=0$ ).

NOTES

10 The tritium activity concentration of the internal standard solution at time  $t$  at which the samples are measured (7.3), corrected for radioactive decay, is given by the equation

$$c_s(t) = c_s(t=0)e^{-\lambda t} \quad \dots (2)$$

where

- $c_s(t)$  is the tritium activity concentration, in becquerels per cubic metre, of the internal standard solution at the time  $t$  at which the samples are measured;
- $c_s(t=0)$  is the tritium activity concentration, in becquerels per cubic metre, of the internal standard solution at the time of its preparation;
- $\lambda$  is the decay constant, in reciprocal years ( $\lambda = 0,05576$ );
- $t$  is the time, in years, between the preparation of the internal standard solution and the measurement of the samples.

11 Instead of a concentrated tritium ( $[^3\text{H}]\text{H}_2\text{O}$ ) standard solution, alternatively soluble aqueous tritium standard capsules may be used. However, commercially available standard capsules have a total inaccuracy much greater than 1 %.

**4.5 Scintillation solution.**

Scintillation solutions with one or more emulsifiers in which relatively large quantities of water samples can be incorporated, usually in an emulsion or gel, are commonly used. Commercially available cocktails are found to be the most satisfactory in practice (see also 9.1).

Pseudocoumene (1,2,4-trimethylbenzene) based cocktails are preferable because of their lower toxicity, higher flash point, better stability and lack

of distortion of plastic vials. Dioxane based cocktails are to be avoided.

Store in the dark and, particularly just before use (see 7.2, note 15), avoid exposure to direct sunlight or fluorescent light in order to prevent interfering luminescence.

#### 4.6 Carborundum or glass beads.

### 5 Apparatus

Usual laboratory apparatus and

**5.1 Liquid scintillation counter**, preferably with an automatic sample presentation unit (see 7.3, note 19). Operation at constant temperature is recommended. Follow the manufacturer's instructions.

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 must be modified.

**5.2 Distillation apparatus**, dried before use, consisting of:

- round bottom flask, of capacity 500 ml [a larger flask may be used for preparation of the blank water (4.3)],
- splash head,
- Vigreux distillation column, length 40 cm,
- condenser,
- adapter, bent type.

**5.3 Pipette**, suitable for the accurate transfer of 100  $\mu$ l of internal standard solution (4.4) with a total inaccuracy less than or equal to 1 %.

**5.4 Counting vials**, made from polyethylene or equivalent material, that will hold at least 20 ml and will fit the counting chamber of the liquid scintillation counter (5.1). Diffusion of organic solvents into and through the counting vials and distortion should be acceptably small after being filled (see 7.2).

Plastic counting vials are in general preferable to glass counting vials as they generally give a lower background counting rate than glass vials.

#### NOTES

12 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 (see 7.2, note 15).

13 Toluene-based scintillation solutions may distort 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.

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

### 6 Sampling and samples

Obtain samples in accordance with ISO 5667-1 and ISO 5667-2. Take a laboratory sample of about 250 ml for the sample preparation (see 7.1).

### 7 Procedure

#### 7.1 Sample preparation

Place the laboratory sample (clause 6) in the distillation apparatus (5.2). Add about 250 mg of sodium thiosulfate (4.2) to convert iodine into iodide, about 0.5 g of sodium carbonate (4.1) to make the sample alkaline, and finally some carborundum beads (4.6) to prevent bumping. Assemble the distillation apparatus (5.2). Distill, discard the first 50 ml to 75 ml of distillate, then collect about 100 ml of the middle fraction in a bottle (5.5). Discard the residue in the flask.

NOTE 14 With this procedure there is no significant isotopic fractionation in the distillation.

#### 7.2 Filling the counting vials

For each water sample fill, preferably in dimmed light, three counting vials (5.4) with a volume  $V_1$ , in millilitres (see note 18) of scintillation solution (4.5) followed by a volume  $V_2 = 20 - V_1$ , in millilitres, of distillate (7.1). This mixture will be further referred to as scintillation emulsion. Add, using a pipette (5.3), 100  $\mu$ l of internal standard solution (4.4) to one of these counting vials. Mark the lids of the three counting vials, for example with the designations 1a, 1\* and 1b for sample 1; 2a, 2\* and 2b for sample 2 etc. (The asterisk indicates the vial with internal standard solution added.) Fill, in the same way, the appropriate number, as required by the counting procedure (7.3), of background counting vials (5.4) with a volume  $V_1$ , in millilitres, of scintillation solution (4.5) followed by a volume  $V_2 = 20 - V_1$ , in millilitres, of blank water (4.3). 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 B<sub>1</sub>, B<sub>2</sub>, B<sub>3</sub>, etc. Shake the counting vials thoroughly and uniformly, for example by using a shaking machine.

#### NOTES

15 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.

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

17 The use of an internal standard is recommended when polyethylene counting vials (5.4) 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 (4.5) 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).

18 Under optimal counting conditions (clause 9), many liquid scintillation solutions (4.5) can incorporate up to about 40 % of water, in this case  $V_1 = 12$  ml.

### 7.3 Counting procedure

After shaking (see 7.2), wipe the counting vials with a damp cloth that does not leave any deposit to remove any electrostatic charge; hereafter, avoid any contact with the light-transmitting parts of the counting vials.

Place the counting vials in a fixed sequence in the liquid scintillation counter (5.1), as follows: background, sample 1, sample 1 with internal standard solution (4.4) added, sample 1, background, sample 2, etc. [B<sub>1</sub>, 1a, 1\*, 1b, B<sub>2</sub>, 2a, 2\*, 2b, B<sub>3</sub>, 3a, 3\*, 3b, B<sub>4</sub>, 4a, 4\*, 4b, etc. (see 7.2)].

Count the vials for a preset time period using one or more measurement channels (see clause 9) or, for the vials with internal standard solution, until a preset count is reached.

#### NOTES

19 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 erroneous counts passing undetected is reduced.

Low tritium activity concentrations may necessitate longer counting times depending on the desired counting accuracy (see 8.1.3).

20 Before counting it is advisable to equilibrate the counting vials in the liquid scintillation counter (5.1) for light and temperature adaptation, for example overnight,

thus reducing the chance of interfering luminescence occurring during counting.

21 For samples containing relatively high tritium activity concentrations a preset count may be used. In this case the formula given in 8.1.3 is not applicable (see 8.1.3, note 25).

## 8 Expression of results

### 8.1 Method of calculation

#### 8.1.1 Counting efficiency

Calculate the counting efficiency from equation

$$\varepsilon = \frac{\bar{R}^* - \bar{R}}{A_s(t)} \quad \dots (3)$$

where

$\varepsilon$  is the counting efficiency, a dimensionless entity, representing the number of pulses per second counted per becquerel;

$\bar{R}^*$  is the counting rate, in pulses per second, of the sample with the internal standard solution (4.4) added;

$\bar{R}$  is the mean counting rate, in pulses per second, of the duplicate samples without internal standard solution added;

$A_s(t)$  is the activity, in becquerels, of the added internal standard solution at the time the sample is measured; calculate it from the equation  $A_s(t) = Vc_s(t)$ , where  $c_s(t)$  is defined in 4.4, and  $V = 10^{-7}$  m<sup>3</sup>, as follows from 7.2.

#### 8.1.2 Tritium activity concentration of the sample

Calculate the tritium activity concentration of the sample from the equation

$$c = \left[ \frac{R - R_0}{\varepsilon V_2} + c_0(t) \right] e^{\lambda \Delta t} \quad \dots (4)$$

where

$c$  is the tritium activity concentration of the sample, in becquerels per cubic metre, at the time of sampling;

$\bar{R}$  is the mean counting rate, in pulses per second, of the duplicate samples without internal standard solution;

$\bar{R}_0$  is the mean counting rate, in pulses per second, of both adjacent duplicate blank water samples;

$\varepsilon$  is the counting efficiency (8.1.1);

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- $V_2$  is the volume, in cubic metres, of sample or blank water (see 7.2) in the counting vial;
- $\lambda$  is the decay constant, in reciprocal years ( $\lambda = 0,055\ 76$ );
- $\Delta t$  is the interval, in years, between sampling (clause 6) and counting (7.3);
- $c_o(t)$  is the tritium activity concentration, in becquerels per cubic metre, of the blank water (4.3) at the time  $t$  at which the sample is measured.

NOTES

22 When using blank water with a low tritium activity concentration compared to the tritium activity concentration of the sample, there is no need to correct the result for the decay of the tritium activity concentration of the blank water (see also 4.3, note 9).

23 If  $\Delta t < 0,5$  year, the last factor of the equation can be deleted.

8.1.3 Inaccuracy due to the statistical nature of radioactive decay and background radiation

Calculate the standard deviation  $c$  (8.1.2) due to the statistical nature of radioactive decay and background radiation from the equation

$$s_c = \left\{ \frac{\sqrt{(R_o + \bar{R}_s)/t_o}}{\varepsilon V_2} \right\} e^{\lambda \Delta t} \dots (5)$$

where

- $s_c$  is the standard deviation of  $c$  (8.1.2), in becquerels per cubic metre;
- $t_o$  is the summed counting time, in seconds, of the blank counting vials (equal to the summed counting time of the sample counting vials);

$\bar{R}_o, \bar{R}, \varepsilon, V_2, \lambda$  and  $\Delta t$  are as defined in 8.1.2.

NOTES

24 In samples with a low tritium activity concentration, the statistical nature of radioactive decay and background radiation is the predominant source of inaccuracy, usually designated as "statistical counting error". At tritium activity concentrations higher than about  $10^5$  Bq/m<sup>3</sup>, other sources of error become noticeable (see [5] and [8]).

25 When a preset count is used, calculate the standard deviation of  $c$  (8.1.2) due to the statistical nature of radioactive decay and background radiation from the more general equation

$$s_c = \frac{\sqrt{\bar{R}_o/t_o + \bar{R}/t_s}}{\varepsilon V_2} e^{\lambda \Delta t} \dots (6)$$

where

- $t_o$  is the summed counting time, in seconds, of the blank counting vials;
- $t_s$  is the summed counting time, in seconds, of the sample counting vials;

$\bar{R}_o, \bar{R}, \varepsilon, V_2, \lambda$  and  $\Delta t$  are as defined in 8.1.2 and 8.1.3.

8.2 Repeatability and reproducibility

Figures on reproducibility, as derived from the results of an interlaboratory test in Germany, F. R., according to a method based on the same principle as described in this International Standard, are as follows:

Sample number	1	2	3	
Number of participating laboratories	37	37	41	
Number of single values	158	157	165	
Mean values of the laboratories, without outliers (Grubbs test, $P_z = 90\%$ ):				
$c_{min}$ Bq/l	0,00	15,4	65,5	
$c_{max}$ Bq/l	10,07	26,4	82,2	
Mean values of the mean laboratory values, without outliers				
Bq/l	5,72	20,8	75,3	
Reference values	Bq/l	6,11	21,1	77,2
Deviation of the mean values				
Bq/l	0,39	0,30	1,86	
from the reference values	%	6,3	1,4	2,4

9 Optimization of the determination

9.1 Minimum detectable activity concentration  $c_{min}$

The minimum detectable activity concentration can be calculated from the equation

$$c_{min} = \frac{3\sqrt{\bar{R}_o/t_s \cdot (1 + t_s/t_o)}}{\varepsilon V_2} e^{\lambda \Delta t} \dots (7)$$

where

- $c_{min}$  is the minimum detectable activity concentration, in becquerels per cubic metre;
- 3 is the confidence coefficient;

$\bar{R}_o, t_o, t_s, \varepsilon, V_2, \lambda$  and  $\Delta t$  are as defined in 8.1.2 and 8.1.3.