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

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

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2. www.iso.org/directives

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The committee responsible for this document is ISO/TC 147, *Water quality*, Subcommittee SC3 *Radioactivity measurements.*

This corrected version of ISO 13168:2015 incorporates the following correction:

—8.2, Formula (3): r_{sT} has been replaced by r_{sC}.

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 potassium 40, tritium, carbon 14, and those originating from the thorium and uranium decay series, in particular radium 226, radium 228, uranium 234, uranium 238, lead 210, can be found in water for natural reasons (e.g. desorption from the soil and wash-off 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 fertilizer production and use);

— human-made radionuclides, such as transuranium elements (americium, plutonium, neptunium, curium), tritium, carbon 14, strontium 90 and gamma emitting radionuclides can also be found in natural waters as a result of authorized routine releases into the environment in small quantities in the effluent discharged from nuclear fuel cycle facilities. They are also released into the environment following their use in unsealed form for medical and industrial applications. They are also found in the water as a result of past fallout contamination resulting from the explosion in the atmosphere of nuclear devices and accidents such as those that occurred in Chernobyl and Fukushima.

Drinking-water may thus contain radionuclides at activity concentrations which could present a risk to human health. In order to assess the quality of drinking-water (including mineral waters and spring waters) with respect to its radionuclide content and to provide guidance on reducing health risks by taking measures to decrease radionuclide activity concentrations, water resources (groundwater, river, lake, sea, etc.) and drinking water are monitored for their radioactivity content as recommended by the World Health Organization [WHO] and may be required by some national authorities.

An international standard on a test method of simultaneous measurement of tritium and carbon 14 concentrations in water samples is justified for test laboratory carrying out these measurements, required sometimes by national authorities, as laboratories may have to obtain a specific accreditation for radionuclide measurement in drinking water samples. Such standard is to be used as a screening method, until the interference of other beta emitters in the test portion is considered negligible.

Tritium and carbon 14 natural activity concentration can vary according to local geological and climatic characteristics, at a level below 5 Bq/l and below 0,1 Bq/l respectively. These radioactivity levels can be locally enhanced by nuclear installation authorized discharges of low level radioactive effluent into the environment. The guidance level for tritium and carbon 14 in drinking water as recommended by WHO is 10 000 and 100 Bq/l respectively.[4]

NOTE The guidance level is the activity concentration with an intake of 2 l/day of drinking water for 1 year, that results in an effective dose of 0,1 mSv/year for members of the Public, an effective dose that represents a very low level of risk that is not expected to give rise to any detectable adverse health effect.

This International Standard is one of a set of International Standards on test methods dealing with the measurement of the activity concentration of radionuclides in water samples.

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WARNING — Persons using this International Standard should be familiar with normal laboratory practice. This standard does not purport to address all of the safety issues, 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 describes a test method for the simultaneous measurement of tritium and carbon-14 in water samples by liquid scintillation counting of a source obtained by mixing the water sample with a hydrophilic scintillation cocktail.

This is considered a screening method because of the potential presence of interfering nuclides in the test sample.

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

This International Standard is applicable to all types of waters having an activity concentration ranging from 5 Bq/l to 10^6 Bq/l (upper limit of the liquid scintillation counters for direct counting). For higher activity concentrations, the sample can be diluted to obtain a test sample within this range.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. 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 9698, *Water quality — Determination of tritium activity concentration — Liquid scintillation counting method*

ISO 80000-10, *Quantities and units — Part 10: Atomic and nuclear physics*

ISO 11929, *Determination of the characteristic limits (decision threshold, detection limit and limits of the confidence interval) for measurements of ionizing radiation — Fundamentals and application*

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 abbreviations defined in ISO 80000-10, ISO/IEC Guide 98-3 and ISO/IEC Guide 99, and the following apply.

$\beta\mathrm{max}$	Maximum energy for the beta emission, in keV
V	Volume of test sample, in litre
m	Mass of test sample, in kilogram
ρ	Density of the sample, in kilogram per litre
$c_{\mathrm{AT}}, c_{\mathrm{AC}}$	Activity concentration, in becquerel per litre, respectively for tritium and carbon 14
a	Activity per unit of mass, in becquerel per kilogram
$A_{\mathrm{T}}, A_{\mathrm{C}}$	Activity of the calibration source, in becquerel, respectively for tritium and carbon 14
t_0	Background counting time, in second
t_{g}	Sample counting time, in second
$t_{\mathrm{sT}}, t_{\mathrm{sC}}$	Calibration counting time, in second, respectively for tritium and carbon 14
$r_{0\mathrm{T}}, r_{0\mathrm{C}}$	Mean background count rate, per second, respectively for tritium and carbon 14
$r_{\mathrm{gT}}, r_{\mathrm{gC}}$	Mean sample count rate, per second, respectively for tritium and carbon 14
$r_{\mathrm{sT}}, r_{\mathrm{sC}}$	Calibration count rate, per second, respectively for tritium and carbon 14
$r_{\mathrm{sC}\rightarrow\mathrm{T}}$	Calibration count rate, per second, for the interfering carbon 14 in the chosen window of the tritium energy range
ε_{q}	Detection efficiency for the quenching parameter q
ε	Detection efficiency for the lowest value of the quenching parameter
$\varepsilon_{\mathrm{T}}, \varepsilon_{\mathrm{C}}$	Detection efficiency, respectively for tritium and carbon 14
$\varepsilon_{\mathrm{C}\rightarrow\mathrm{T}}$	Detection efficiency for carbon 14 in the chosen window of the tritium energy range
χ	Correcting factor, for the interfering carbon 14 in the chosen window of the tritium energy range
$f_{\mathrm{qT}}, f_{\mathrm{qC}}$	Quench factor, respectively for tritium and carbon 14
$f_{\mathrm{qC}\rightarrow\mathrm{T}}$	Quench factor, for the interfering carbon 14 in the chosen window of the tritium energy range
$u(c_{\mathrm{AT}})$ $u(c_{\mathrm{AC}})$	Standard uncertainty associated with the measurement result, in becquerel per litre, respectively for tritium and carbon 14
U	Expanded uncertainty, calculated by $U = k \cdot u(c_A)$ with $k = 1, 2, \ldots$, in becquerel per litre
$c^{*}_{\mathrm{AT}}, c^{*}_{\mathrm{AC}}$	Decision threshold, in becquerel per litre, respectively for tritium and carbon 14
$c^{\#}_{\mathrm{AT}}, c^{\#}_{\mathrm{AC}}$	Detection limit, in becquerel per litre, respectively for tritium and carbon 14
$c^{\triangleleft}_{\mathrm{A}}, c^{\triangleright}_{\mathrm{A}}$ $c^{\triangleleft}_{\mathrm{AT}}, c^{\triangleright}_{\mathrm{AT}}$ $c^{\triangleleft}_{\mathrm{AC}}, c^{\triangleright}_{\mathrm{AC}}$	Lower and upper limits of the confidence interval, in becquerel per litre, respectively for tritium and carbon 14

4 Principle

The test sample is mixed with the scintillation cocktail in a counting vial to obtain a homogeneous medium. Electrons emitted by the radionuclide 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 sample 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 sample. The blank sample is prepared using a reference water of the lowest activity available, also sometimes called “dead water”.

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

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

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

If particular conditions of chemical quenching affect the measurement results, it is recommended to correct the counting data using a quench curve. It is important to choose the chemical quenching agent according to the supposed type of quenching observed in the sample. It shall not be acid when carbon 14 is present as carbonated species in the standard solution. This method is not applicable to colour quenched samples.

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[5] and with an activity concentration of tritium and carbon 14 negligible in comparison with the activities to be measured.

For example, a water sample with a low tritium and carbon 14 activity concentration can be obtained from (deep) subterranean water kept in a well-sealed borosilicate glass bottle in the dark at controlled temperature (ISO 5667-3). This blank water sample shall be kept physically remote from any tritium and carbon 14 containing material .

It is advisable to keep an adequate quantity of blank water in stock and to make small working amounts from it for immediate use as required. Contamination with tritium (e.g. from water vapour in the air and from tritium sources such as luminous watches and gas chromatographs) and carbon 14 (air CO_2) or other radioactive species should be avoided.

Determine the tritium and carbon 14 activity concentration (t = 0), in Bq/l, of this water and note the date (t = 0) of this determination.

As the activity is becoming non-negligible for activities around 1 Bq/l, it is necessary to use a blank water measured to ensure the “absence” of tritium and carbon 14. 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. The carbon 14 activity concentration in the blank water can be determined by techniques such as the synthesis of benzene or by accelerator mass spectrometry.

When the volume of blank water is sufficiently large, e.g. 10 l to 20 l, and well-sealed, tritium and carbon 14 activity concentrations should remain stable for years, although it is advisable to determine these activity concentrations at predetermined intervals, e.g. every year.

5.1.2 Calibration source solutions

In order to avoid cross-contamination prepare, in a suitable location which is remote from the area where the analyses are to be carried out, weigh and pour into a weighed volumetric flask (for example, 100 ml) the requisite quantity of a concentrated tritium ($[^3H]H_2O$) standard solution and of a concentrated carbon 14 standard solution, so that the tritium and carbon 14 activity concentrations generate sufficient counts to reach the required measurement uncertainty after dilution with blank water and thorough mixing. Calculate the activity concentrations of the resulting calibration source solution ($t = 0$). Note the date at which the standard solution was made up ($t = 0$).

The tritium activity concentration of the calibration source solution at the measurement time t of the samples shall be corrected for radioactive decay.

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

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.[6]

It is recommended to use a hydrophilic scintillation cocktail, especially for the measurement of environmental 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 solution in the dark and, particularly just before counting, avoid exposure to direct sunlight or fluorescent light in order to prevent interfering luminescence, and
- comply with storage conditions specified by the scintillation cocktail supplier.

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

5.1.4 Quenching agent

Examples of chemical quenching agents: acetone, organochloride compounds, nitromethane, etc.

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. 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 that exist are the following:

- glass vials with low level of ^{40}K, exhibit a lower background than 'normal' glass vials;
- for the determination of very low tritium concentration, the use of polytetrafluoroethylene vials (PTFE) or polyethylene vials with an inner layer of PTFE on 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 re-used, 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 counting.

NOTE 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 be in accordance with ISO 5667-1. Samples shall not be acidified because of the shifting of the equilibrium of carbonated species.

It is important that the laboratory receives 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.

When NaOH is added in the sample, the solution shall not contain carbonates, carbon 14 and tritium. The volume added is needed to correct for dilution. For low level activity measurements, it is important to avoid any contact between sample and atmosphere during the sampling.