BS EN ISO 13162:2015

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Water quality — Determination of carbon 14 activity — Liquid scintillation counting method (ISO 13162:2011)

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National foreword

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A list of organizations represented on this committee can be obtained on request to its secretary.

This publication does not purport to include all the necessary provisions of a contract. Users are responsible for its correct application.

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Qualité de l'eau - Détermination de l'activité volumique du carbone 14 - Méthode par comptage des scintillations en milieu liquide (ISO 13162:2011)

Wasserbeschaffenheit - Bestimmung der Aktivität von Kohlenstoff-14 - Verfahren mit dem Flüssigszintillationszähler (ISO 13162:2011)

This European Standard was approved by CEN on 30 July 2015.

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European foreword

The text of ISO 13162:2011 has been prepared by Technical Committee ISO/TC 147 “Water quality” of the International Organization for Standardization (ISO) and has been taken over as EN ISO 13162:2015 by Technical Committee CEN/TC 230 “Water analysis” the secretariat of which is held by DIN.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by February 2016, and conflicting national standards shall be withdrawn at the latest by February 2016.

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Endorsement notice

The text of ISO 13162:2011 has been approved by CEN as EN ISO 13162:2015 without any modification.

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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.

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ISO 13162 was prepared by Technical Committee ISO/TC 147, *Water quality*.

Introduction

The carbon 14 (^{14}C) 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 ^{14}C have been released into the environment. Due to the substantial proportion of ^{14}C in the human internal dose contribution, monitoring of ^{14}C activity concentrations in the environment is necessary in order to follow its circulation in the hydrosphere and biosphere. ^{14}C is the second radionuclide (~3 500 Bq) to contribute to the human body natural radioactivity, behind ^{40}K (~6 000 Bq).

INTERNATIONAL STANDARD ISO 13162:2011(E)

Water quality — Determination of carbon 14 activity — Liquid scintillation counting method

WARNING — Persons using this International Standard should be familiar with normal laboratory practice. This 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 ^{14}C activity concentration in samples of environmental water or of ^{14}C-containing water using liquid scintillation counting.

The method is applicable to the analysis of any organic molecule soluble in water that is well mixed with the scintillation cocktail. It does not apply to micelles or "large" particles (lipids, fulvic acid, humic acid, etc.) that are inadequately mixed with the scintillation cocktail and the water. Some beta energy is lost without any excitation of the scintillation cocktail and the results are underestimated. The method is not applicable to the analysis of organically bound ^{14}C, whose determination requires additional chemical processing (such as chemical oxidation, combustion).

It is possible to determine ^{14}C activity concentrations below 10^6 Bq l^{-1} without any sample dilution.

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: Preservation and handling of water samples*

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

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

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

3 Symbols, definitions, units, and abbreviations

For the purposes of this document, the symbols, definitions, units, and abbreviations defined in ISO 80000-10, ISO 11929, ISO/IEC Guide 98-3 and the following apply.

A	Activity of the calibration source, in becquerels
c_A	Activity concentration, 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
f_q	Quench factor
m	Mass of test sample, in kilograms
r_0	Background count rate, in reciprocal seconds
r_g	Sample count rate, in reciprocal seconds
r_s	Count rate of the calibration sample, in reciprocal seconds
t_0	Background counting time, in seconds
t_g	Sample counting time, in seconds
t_s	Counting time of the calibration sample, in seconds
U	Expanded uncertainty, calculated by $U = k\,u(c_A)$ with $k = 1, 2, \ldots$, in becquerels per litre
$u(c_A)$	Standard uncertainty associated with the measurement result, in becquerels per litre
V	Volume of test sample, in litres
α	Activity per mass, in becquerels per kilogram
β_max	Maximum energy for the beta emission, in kiloelectronvolts
ε	Detection efficiency
ρ	Mass density of the sample, in kilograms per litre

4 Principle

The scintillation phenomenon results from interaction of ionizing radiation with solvents and compounds exhibiting fluorescence (scintillators). Both solvents and scintillators constitute the scintillation cocktail. The scintillation mixture is achieved by adding the scintillation cocktail to the test sample in order to obtain a homogeneous mixture.

The test sample is mixed with the scintillation cocktail in a counting vial to obtain a homogeneous medium. Electrons emitted by ^{14}C 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 electric pulses allows the determination of the test sample activity, after correcting for the background count rate and detection efficiency.

In order to determine the background, 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, in accordance with the activities to be measured.

The detection efficiency is determined with a calibration sample that is prepared with a standard of aqueous ^{14}C, or a dilution of this standard with reference water, measured under the same conditions as the test sample.

The sample (blank, test, calibration) and the measurement conditions shall be:

— same type of counting vial;

— same filling geometry;

— same scintillation cocktail;

— same ratio between test sample and scintillation cocktail;

— temperature stability of the detection apparatus;

— value of quench-indicating parameter included in calibration curve.

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 International Standard only provides a ^{14}C equivalent activity for the sample.

Examples of methods of sample pretreatment are described in Annexes C and D.

Concerning quench correction, if particular conditions of chemical quenching affect the measurement results, it is recommended that a quench curve be established. It is important to choose the chemical quenching agent in accordance with the supposed type of quenching observed in the sample.

5 Reagents and equipment

5.1 Reagents

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

5.1.1 Reference water for the blank

The reference water for the blank should be as free as possible of chemical or radioactive impurities.

The reference water may have a low ^{14}C activity concentration, in becquerels per litre, at the time t at which 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 next paragraph). Determine (see final paragraph) the ^{14}C activity concentration ($t = 0$), in becquerels per litre, of this water and note the date ($t = 0$) 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 l^{-1}, water with a very low activity concentration is necessary as reference water.

5.1.2 Calibration source solution

In order to avoid cross-contamination, prepare the calibration source solution in a suitable location which is remote from the area where the ^{14}C analyses are to be carried out. Weigh and pour the requisite quantity of a ^{14}C aqueous standard solution into a weighed volumetric flask (e.g. of capacity 100 ml), so that the ^{14}C activity concentration generates sufficient counts to reach the required measurement uncertainty after dilution with water for the blank and thorough mixing. Calculate the ^{14}C activity concentration of the resulting internal standard solution ($t = 0$), in becquerels per litre. Note the date at which the standard solution was made up ($t = 0$).

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 apparatus.

It is recommended that a good hydrophilic scintillation cocktail be used, especially for the measurement of low activity levels.

The scintillation cocktail shall be homogeneous and stable.

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

It is recommended that the scintillation solution be:

— stored in the dark and, particularly just before use, exposure to direct sunlight or fluorescent light avoided in order to prevent interfering luminescence;

— compliant 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

Examples of chemical quenching agents (non acid): organochloride compounds, nitromethane.

NOTE Some quenching agents are dangerous or toxic.

5.2 Equipment

Usual laboratory equipment and in particular the following.

5.2.1 Liquid scintillation counter, preferably with an automatic sample transfer and ability to measure or correct for sample quench.

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 (LSCs) with vials that hold about 20 ml. When other vials are used with appropriate counters, the method specified shall be adapted accordingly.

5.2.2 Pipette, suitable for

— accurate transfer of the standard solution (e.g. a micropipette of capacity 100 µl);

— accurate transfer of the test sample.

5.2.3 Balance, e.g. capable of being read to the nearest 0,1 mg.

5.2.4 Counting vials.

Different types of scintillation vials exist, manufactured using a range of materials. The most common are glass vials and polyethylene (PE) 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 PE, accelerating the degradation of the mixture.

There are other types of vials.

— Glass vials with low level of ^{40}K, which exhibit a lower background than “normal” glass vials.

— Polytetrafluoroethylene vials (PTFE) or PE vials with a layer of PTFE on the inside wall, which are strongly recommended for the determination of very low ^{14}C concentrations. Diffusion of organic solvents is slower through PTFE than through PE. These vials are used for long counting times when very low-level activity is to be measured.

Generally, the vials are single use. If the vial is re-used, efficient cleaning is essential.

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

NOTE Toluene-based scintillation solutions can physically distort PE and counting vials made of that polymer are unsuitable for use with them. Diffusion of organic solvents into and through the walls is also a serious drawback of PE vials.

6 Sampling and samples

6.1 Sampling

Conditions of sampling shall conform to ISO 5667-1 and ISO 5667-3.

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.

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 flask filled to the maximum be used to minimize ^{14}C exchange with atmospheric CO_2.

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 for carbon dioxide. 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

On a raw sample, measurement of the test sample is generally performed without removal of 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.

7.2 Preparation of the sources to be measured

Known quantities 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 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 defined 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 the reference vials (background, tritium and ^{14}C) usually provided by the equipment supplier, e.g. in compliance with ISO 8258 [1].

The measurement of the blank sample 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) a given type of measurement apparatus;

b) a given type of scintillation cocktail;

c) a given ratio of scintillation cocktail and test sample;

d) a given energy window;

e) a given analyte radionuclide, e.g. ^{14}C.

The quench curve is obtained with a series (e.g. 10) of working standards, 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 ^{14}C standard water solution in each vial. The activity of the certified standard shall 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;

— one working standard at least is used as it is. In the other working standards, increasing quantities of quenching agent are added to simulate the expected range of quench values encountered in the samples to be measured.

The quench curve relating ε and f_q with the quenching is used to determine the f_q of the test sample, e.g. by fitting a polynomial regression curve.

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 detector tritium threshold up to the β_{max} of ^{14}C (156 keV). It is recommended that the size of the energy window be chosen in order to optimize the figure of merit (ε^2/r_0).

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

In order to verify the statistical distribution of counting data, it is recommended that the counting be done one sample at a time: 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

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

a) raw counting and blank sample;

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

c) quench parameter, if a correction is applied;

d) volume or mass of test sample.

To a first approximation, other uncertainties (in scintillation liquid volume or mass, counting time, etc.) can be neglected. An example of the computation is given in Annex A.

8.2 Calculation of activity concentration

The symbols used are defined in Clause 3.

The sample activity concentration of the radionuclide present in the sample is calculated according to Equation (1):

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

where

$$w = \frac{1}{V\, \varepsilon\, f_q}$$

and

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

The combined uncertainty is calculated as follows:

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

$$u_{\text{rel}}^2(w) = u_{\text{rel}}^2(\varepsilon) + u_{\text{rel}}^2(V) + u_{\text{rel}}^2\left(f_{\text{q}}\right) \tag{3}$$

and the relative standard uncertainty of ε for each quenching value is calculated using Equation (4):

$$u_{\text{rel}}^2\left(\varepsilon\right) = u_{\text{rel}}^2\left(r_{\text{s}} - r_0\right) + u_{\text{rel}}^2(A) = \frac{\left(r_{\text{s}} / t_{\text{s}}\right) + \left(r_0 / t_0\right)}{\left(r_{\text{s}} - r_0\right)^2} + u_{\text{rel}}^2\,(A) \tag{4}$$

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

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

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

$$\tilde{u}(\tilde{c}_A) = \sqrt{w^2\left[\frac{\left(\tilde{c}_A / w\right) + r_0}{t_{\text{g}}} + \frac{r_0}{t_0}\right] + \tilde{c}_A^2\; u_{\text{rel}}^2(w)} \tag{5}$$

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 mass (m replacing V in the preceding equations).

If the transformation of the activity per mass is done by multiplying the specific activity by the density ρ in grams per litre, a parameter associated with the determination of the density shall appear in the expression of the activity and its associated uncertainty.

8.3 Decision threshold

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

$$c_A^* = k_{1-\alpha}\;\tilde{u}(0) = k_{1-\alpha}\;w\sqrt{\frac{r_0}{t_{\text{g}}} + \frac{r_0}{t_0}} \tag{6}$$

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

8.4 Detection limit

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

$$c_A^{\#} = c_A^* + k_{1-\beta}\;\tilde{u}(c_A^{\#}) = c_A^* + k_{1-\beta}\sqrt{w^2\left[\frac{\left(c_A^{\#} / w\right) + r_0}{t_{\text{g}}} + \frac{r_0}{t_0}\right] + c_A^{\#2}\; u_{\text{rel}}^2(w)} \tag{7}$$

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

The detection limit can be calculated by solving Equation (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 Equation (7) is given by Equation (8):

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

8.5 Confidence limits

In accordance with ISO 11929, the lower, $c_A^{\triangleleft}$, and upper, $c_A^{\triangleright}$, confidence limits are calculated using Equations (9) and (10):

$$c_A^{\triangleleft} = c_A - k_{\mathrm{p}}\, u\left(c_A\right); \quad p = \omega\left(1-\frac{\gamma}{2}\right) \tag{9}$$

$$c_A^{\triangleright} = c_A + k_{\mathrm{q}}\, u\left(c_A\right); \quad q = 1-\omega\,\frac{\gamma}{2} \tag{10}$$

where

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

$1 - \gamma/2$ is the probability for the confidence interval of the measurand;

$\omega = 1$ may be set if $c_A \geq 4\ u_{\mathrm{c}}(c_A)$.

In this case,

$$c_A^{\triangleleft}, c_A^{\triangleright} = c_A \pm k_{1-\gamma/2}\, u_{\mathrm{c}}(c_A) \tag{11}$$

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

8.6 Calculations using the activity per mass

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

$$c_A = \frac{r_{\mathrm{g}} - r_0}{m \times 10^3}\,\frac{\rho}{\varepsilon\ f_{\mathrm{q}}} = (r_{\mathrm{g}} - r_0)\ w \tag{12}$$

where

$$w = \frac{\rho}{m \times 10^3 \times \varepsilon\ f_{\mathrm{q}}}$$

$$u_{\mathrm{rel}}^2(w) = u_{\mathrm{rel}}^2(\varepsilon) + u_{\mathrm{rel}}^2(m) + u_{\mathrm{rel}}^2(\rho) + u_{\mathrm{rel}}^2\left(f_{\mathrm{q}}\right) \tag{13}$$

The uncertainty, the characteristic limits and the limits of the confidence interval may be calculated using the previous expression [Equations (2), (6), (7) and (8)] with Equations (12) and (13).

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 International Standard (ISO 13162:2011);

b) the evaluation procedure used;

c) identification of the sample;

d) units in which the results are expressed;

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

Complementary information can be provided such as:

f) probabilities α, β, and (1 – γ);

g) decision threshold and the detection limit;

h) 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, in agreement with ISO 11929, the result of the measurement should be expressed as $\leq c_A^*$ when the result is below the decision threshold,

— when the activity concentration c_A is compared with the detection limit, the result of the measurement can be expressed as $\leq c_A^\#$ when the result is below the detection limit — if the detection limit exceeds the guideline value, it shall be documented that the method is not suitable for the purpose of measurement;

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

Annex A
(informative)

Numerical applications

Table A.1 presents the parameter values for three situations of activity concentration. Table A.1 may be used to verify any computation of the different formulae.

Table A.1 — Parameter values

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
$u_{rel}(\varepsilon)$	—	0,035	0,035	0,035
α, β, γ	%	5	5	5
w	l^{-1}	400	400	400
$u_{rel}(w)$	—	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	Bq l^{-1}	3,33	5,00	23,33
$u(c_A)$	Bq l^{-1}	2,35	2,57	6,46
c_A^*	Bq l^{-1}	3,47	3,47	3,47
$c_A^\#$	Bq l^{-1}	8,74	8,74	8,74
$c_A^\triangleleft$	Bq l^{-1}	0,34	0,78	10,69
$c_A^\triangleright$	Bq l^{-1}	8,02	10,06	36,00

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

For example, to calculate in Excel®[1)]:

1) Excel is the trade name of a product supplied by Microsoft. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of the product named. Equivalent products may be used if they can be shown to lead to the same results.

ω = NORMSDIST [$u(c_A)/c_A$];

k_p = NORMSINV (p);

k_q = NORMSINV (q).

Annex B
(informative)

Internal standard method

B.1 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, e.g. N and S. Add, using a pipette (e.g. of capacity 100 µl), a known quantity of internal 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 with the designations N_1, S_1, N_2, S_2, N_3, S_3, etc. Shake the counting vials thoroughly and uniformly, e.g. 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, little difference may be observed in the counting efficiency between samples. In this case, it is acceptable to determine a mean counting efficiency from the addition of internal standard to 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 PE counting vials are used. When using an external standard in PE counting vials, interference can occur 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 % volume fraction of water, in this case V_1 = 10 ml.

B.2 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 LSC: background, sample 1, sample 1 with internal standard solution added, 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 LSC for light and temperature adaptation, e.g. overnight, thus reducing the chance of interfering luminescence occurring during counting.

B.3 Expression of results

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

$$\varepsilon = \frac{r_s - r_g}{A_s} \tag{B.1}$$

where

r_s is the count rate, in pulses per second, of the sample with the internal standard solution (5.1.2) added;

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

A_s is the added activity.

Annex C
(informative)

Extraction of total carbon: precipitate counting

C.1 Principle

The total carbon is determined in the water sample (US EPA method 9060A[2]). 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 precipitated as $CaCO_3$ in traps (References [3][4][5]). The $CaCO_3$ is transferred as a solution into a previously weighed counting glass vial. The solution is evaporated until dryness and the vial is 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 may 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 may be 0,030 Bq l^{-1}.

The main point is to avoid any mixing of the carbon contained in the sample with the ^{14}C in laboratory air and in the reagents used.

C.2 Reagents

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

C.2.1 Sodium persulfate.

C.2.2 Silver nitrate solution, 40 g l^{-1} of silver nitrate.

C.2.3 Sodium carbonate, anhydrous.

C.2.4 Hydrochloric acid, 0,6 mol l^{-1}.

C.2.5 Ammonium hydroxide, concentrated at 250 g l^{-1}.

C.2.6 Ammonium hydroxide, 0,1 mol l^{-1}.

C.2.7 Calcium chloride, 1,5 mol l^{-1}.

C.2.8 Methanol.

C.2.9 Inert gas.

C.2.10 Distilled water.

C.2.11 Calcium carbonate.

C.2.12 Sodium hydroxide.

C.2.13 CO_2 absorber, e.g. Carbo-Sorb® E[2)].

C.2.14 Scintillation cocktail, e.g. Permafluor® E^+ [3)].

C.3 Equipment

Usual laboratory equipment and in particular the following.

C.3.1 Analytical balance.

C.3.2 Water bath.

C.3.3 Ultrasonic bath.

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

C.3.5 Flow meters, two.

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

C.4 Extraction

C.4.1 General

The extraction procedure is designed to avoid carbonation of the precipitation solution and contamination of the sample with laboratory air.

C.4.2 Preparation of the precipitation solution

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

C.4.3 Preparation of the traps

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

C.4.4 Chemical separation

Fill a reservoir with the sample water (25 ml), with some drops of concentrated NH_4OH (C.2.5) to obtain a pH of 10. Fill another reservoir with 5 ml of the silver nitrate solution (C.2.2). In the round-bottomed flask, add 5 g of $Na_2S_2O_8$ (C.2.1). If necessary, add the anhydrous Na_2CO_3 (C.2.3) as a carrier to obtain a total of 80 mg to 105 mg of $CaCO_3$. Use the inert gas (C.2.9) to clean all the assembly (reservoirs, balloon, traps), verifying with the flow meters (C.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.

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2) 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.

3) 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.

C.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 (C.3.3), transfer the content of the traps into a centrifuge tube, rinsing the traps with NH_4OH, 0,1 mol l^{-1} (C.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. Extraction yield can then be determined.

C.5 Preparation of the sources to be measured

C.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 (C.2.10), and 0,5 ml of a solution of 50 g l^{-1} NaOH (C.2.12) and 10 g l^{-1} Na_2CO_3. Mix vigorously and place the vial in the ultrasonic bath (C.3.3) for 10 min. Verify that the solution is homogeneous.

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

C.5.2 Test sample preparation

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

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

C.6 Counting procedures

See 7.3 and following.

Annex D
(informative)

Extraction of total carbon: absorption counting

D.1 Principle

The total carbon is determined in the water sample (US EPA method 9060A[2]). 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 a quantity of water containing about 0,01 g of carbon.

The main point is to avoid any mixing of the carbon contained in the sample with the ^{14}C in laboratory air and in the reagents used.

D.2 Reagents

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

D.2.1 Potassium permanganate, 100 g l^{-1}.

D.2.2 Sulfuric acid, 4 mol l^{-1}.

D.2.3 Oxalic acid, 80 g l^{-1}.

D.2.4 Inert gas.

D.2.5 Distilled water.

D.2.6 Silica drying, grain size 1 mm to 3 mm with colour indicator.

D.2.7 CO_2 absorber, e.g. Carbo-Sorb® E[4)].

D.2.8 Scintillation cocktail, e.g. Permafluor® E^{+}[5)].

D.3 Equipment

Usual laboratory equipment and in particular the following.

D.3.1 Analytical balance.

D.3.2 Liquid cooler.

D.3.3 Heating mantle.

4) 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.

5) 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.

D.3.4 Standard laboratory PVC tubing, to connect the reflux cooler, the silica cartridge and the LSC vial.

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

D.3.6 Flow meter.

D.3.7 Stopper with a rubber septum, rubber bung or silicone bung.

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

D.3.9 LSC vials.

D.3.10 Cap for the LSC vials, with a small hole drilled in, which is a little larger than the diameter of the Pasteur pipette.

D.4 Extraction

D.4.1 General

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

D.4.2 Preparation

Transfer a known volume (50 ml to 200 ml) of the aqueous sample into the three-necked flask (D.3.5). Add distilled water (D.2.5) to a total volume of 250 ml and add glass beads to facilitate boiling.

Fill the silica drying cartridge (D.3.5) with fresh and dry silica.

Fill the LSC counting vial (D.3.9) with a known quantity of CO_2 absorber (D.2.7) and cap (D.3.10).

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

Start mild inert gas (D.2.4) 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.

D.4.3 Chemical separation

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

Heat (D.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.

D.5 Preparation of the sources to be measured

D.5.1 Blank sample preparation

Fill an LSC vial with the same proportion of CO_2 absorber (D.2.7) and scintillation cocktail (D.2.8) as the vials containing the sample.

D.5.2 Test sample preparation

Add the scintillation cocktail (D.2.8) to each of the vials and shake well.

Carefully wipe the vials.

D.6 Counting procedures

See 7.3 and following.

D.7 Verification

Determine whether the oxidation is complete from the LSC results. As all organic molecules in the sample consume $KMnO_4$, it is hard 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.

Bibliography

[1] ISO 8258, *Shewhart control charts*

[2] US EPA method 9060A, *Total organic carbon*, 2004. (*US EPA test methods for evaluating solid waste, physical/chemical methods*.) Available (viewed 2011-10-11) at: http://www.epa.gov/wastes/hazard/testmethods/sw846/pdfs/9060a.pdf

[3] KNOWLES, G.K. ^{14}C in reactor plant water. In: LYON, W.S., editor. *Radioelement analysis: Progress and problems*, pp. 87-94. Ann Arbor, MI: Ann Arbor Science Publishers,1980

[4] KRIEGER, H.L., GOLD, S. *Procedure for radiochemical analysis of nuclear reactor aqueous solutions.* Washington, DC: Environmental Protection Agency, 1973. (EPA-R4-73-014.)

[5] CARNACHO, A., VALLÉS, I., ORTEGA, X. Determination of C-14 in water: Liquid scintillation counting method. *29th meeting of the SNE*, Zaragoza, 2003-10-01/03

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