INTERNATIONAL
STANDARD

ISO
19361

First edition
2017-08

Measurement of radioactivity — Determination of beta emitters activities — Test method using liquid scintillation counting

Mesurage de la radioactivité — Détermination de l'activité des radionucléides émetteurs bêta — Méthode d'essai par comptage des scintillations en milieu liquide

Reference number
ISO 19361:2017(E)

ISO copyright office
Ch. de Blandonnet 8 • CP 401
CH-1214 Vernier, Geneva, Switzerland
Tel. +41 22 749 01 11
Fax +41 22 749 09 47
copyright@iso.org
www.iso.org

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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.

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

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

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For an explanation on the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see the following URL: www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 85, N*uclear energy, nuclear technologies, and radiological protection*, Subcommittee SC 2, *Radiological protection*.

Introduction

Everyone is exposed to natural radiation. The natural sources of radiation are cosmic rays and naturally occurring radioactive substances which exist in the earth and within the human body. Human activities involving the use of radiation and radioactive substances add to the radiation exposure from this natural exposure. Some of those activities, such as the mining and use of ores containing naturally-occurring radioactive materials (NORM) and the production of energy by burning coal that contains such substances, simply enhance the exposure from natural radiation sources. Nuclear power plants and other nuclear installations use radioactive materials and produce radioactive effluent and waste during operation and on their decommissioning. The use of radioactive materials in industry, agriculture and research is expanding around the globe.

All these human activities give rise to radiation exposures that are only a small fraction of the global average level of natural exposure. The medical use of radiation is the largest and a growing man-made source of radiation exposure in developed countries. It includes diagnostic radiology, radiotherapy, nuclear medicine and interventional radiology.

Radiation exposure also occurs as a result of occupational activities. It is incurred by workers in industry, medicine and research using radiation or radioactive substances, as well as by passengers and crew during air travel and for astronauts. The average level of occupational exposures is generally below the global average level of natural radiation exposure[13].

As uses of radiation increase, so do the potential health risk and the public's concerns. Thus, all these exposures are regularly assessed in order to: (1) improve the understanding of global levels and temporal trends of public and worker exposure; (2) to evaluate the components of exposure so as to provide a measure of their relative importance, and; (3) to identify emerging issues that may warrant more attention and study. While doses to workers are mostly directly measured, doses to the public are usually assessed by indirect methods using radioactivity measurements performed on various sources: waste, effluent and/or environmental samples.

To ensure that the data obtained from radioactivity monitoring programs support their intended use, it is essential that the stakeholders (for example, nuclear site operators, regulatory and local authorities) agree on appropriate methods and procedures for obtaining representative samples and then handling, storing, preparing and measuring the test samples. An assessment of the overall measurement uncertainty need also to be carried out systematically. As reliable, comparable and 'fit for purpose' data are an essential requirement for any public health decision based on radioactivity measurements, international standards of tested and validated radionuclide test methods are an important tool for the production of such measurement results. The application of standards serves also to guarantee comparability over time of the test results and between different testing laboratories. Laboratories apply them to demonstrate their technical qualifications and to successfully complete proficiency tests during interlaboratory comparison, two prerequisites for obtaining national accreditation. Today, over a hundred international standards, prepared by Technical Committees of the International Standardization Organization, including those produced by ISO/TC 85, and the International Electrotechnical Commission (IEC), are available for application by testing laboratories to measure the main radionuclides.

Generic standards help testing laboratories to manage the measurement process by setting out the general requirements and methods to calibrate and validate techniques. These standards underpin specific standards which describe the test methods to be performed by staff, for example, for different types of sample. The specific standards cover test methods for:

- Naturally-occurring radionuclides (including ^{40}K, ^{3}H, ^{14}C and those originating from the thorium and uranium decay series, in particular ^{226}Ra, ^{228}Ra, ^{234}U, ^{238}U, ^{210}Pb) which can be found in materials from natural sources 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, and curium), ^{3}H, ^{14}C, ^{90}Sr and gamma emitting radionuclides found in waste, liquid and gaseous

effluent, in environmental matrices (water, air, soil, biota) and food and feed as a result of authorized releases into the environment and of fallout resulting from the explosion in the atmosphere of nuclear devices and accidents, such as those that occurred in Chernobyl and Fukushima.

Many of these radionuclides are beta emitters that can be measured by liquid scintillation counting, following appropriate sample preparation.

A generic international standard on liquid scintillation counting is justified for test laboratories carrying out beta emitter measurements in fulfilment of national authority requirements. For example, testing laboratories need to obtain a specific accreditation for radionuclide measurement for the monitoring of drinking water, food, the environment or the discharges, as well as for biological samples for medical purpose.

This document describes (after appropriate sampling, sample handling and test sample preparation) the generic requirements to quantify the activity concentration of beta emitters using liquid scintillation counting. In the absence of a specific pre-treatment of the test sample (such as distillation for ^{3}H measurement, or after benzene synthesis for ^{14}C measurement), this document is to be used as a screening method unless the interference of beta emitters, others than those to be quantified, is considered negligible in the test portion.

This document is one of a set of generic International Standards on measurement of radioactivity.

Measurement of radioactivity — Determination of beta emitters activities — Test method using liquid scintillation counting

1 Scope

This document applies to liquid scintillation counters and requires the preparation of a scintillation source obtained by mixing the test sample and a scintillation cocktail. The test sample can be liquid (aqueous or organic), or solid (particles or filter or planchet).

This document describes the conditions for measuring the activity of beta emitter radionuclides by liquid scintillation counting[14][15].

The choice of the test method using liquid scintillation counting involves the consideration of the potential presence of other beta emitter radionuclides in the test sample. In this case, a specific sample treatment by separation or extraction is implemented to isolate the radionuclide of interest in order to avoid any interference with other beta-, alpha- and gamma-emitting radionuclides during the counting phase.

This document is applicable to all types of liquid samples having an activity concentration ranging from a few $\text{Bq}\cdot\text{l}^{-1}$ to 10^6 $\text{Bq}\cdot\text{l}^{-1}$. For a liquid test sample, it is possible to dilute liquid test samples in order to obtain a solution having an activity compatible with the measuring instrument. For solid samples, the activity of the prepared scintillation source shall be compatible with the measuring instrument.

The measurement range is related to the test method used: nature of test portion, preparation of the scintillator - test portion mixture, measuring assembly as well as to the presence of the co-existing activities due to interfering radionuclides.

Test portion preparations (such as distillation for ^{3}H measurement, or benzene synthesis for ^{14}C measurement, etc.) are outside the scope of this document and are described in specific test methods using liquid scintillation[2][3][4][5][6][7][8][9].

2 Normatives references

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

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

ISO 5667-3, *Water quality — Sampling — Part 3: Preservation and handling of water samples*

ISO 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 18589-2, *Measurement of radioactivity in the environment — Soil — Part 2: Guidance for the selection of the sampling strategy, sampling and pre-treatment of samples*

3 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

- IEC Electropedia: available at http://www.electropedia.org/
- ISO Online browsing platform: available at https://www.iso.org/obp

4 Symbols, abbreviations and units

For the purposes of this document, the symbols and abbreviations defined in ISO 80000-10[10], ISO/IEC Guide 98-3[11], ISO/IEC Guide 99[12] and the following apply.

$\beta_{\max}$	Maximum energy for the beta emission, in keV
V	Volume of test portion, in litre
m	Mass of test portion, in kilogram
ρ	Density of the sample, in kilogram per litre
ε_P	Preparation efficiency
a	Activity per unit of mass, in becquerel per kilogram
c_A	Activity concentration, in becquerel per litre
A	Activity of the calibration source, in becquerel
t_0	Background counting time, in second
t_g	Portion counting time, in second
t_s	Calibration counting time, in second
r_0	Background count rate, per second
r_g	Portion count rate, per second
r_s	Calibration count rate, per second
ε	Detection efficiency
ε_q	Quenched efficiency
f_q	Quench factor
$u(c_A)$	Standard uncertainty associated with the measurement result; in becquerel per litre
U	Expanded uncertainty, calculated by $U = k \cdot u(c_A)$ with $k = 1, 2, \ldots$, in becquerel per litre
c_A^*	Decision threshold, in becquerel per litre
$c_A^\#$	Detection limit, in becquerel per litre
$c_A^<$, $c_A^>$	Lower and upper limits of the confidence interval, in becquerel per litre

5 Principle

The aqueous, organic or particles portion is mixed with the scintillation cocktail in a counting vial to obtain a homogeneous medium (scintillation source). Electrons emitted from beta disintegration transfer their energy to the scintillation cocktail molecules that are excited by this process before returning to their ground state by emitting photons that are detected by photoelectron multiplier tubes (phototubes).

The electronic pulses emitted by the phototubes are amplified. The peak pulse amplitude is converted to a digital value by an analogue-to-digital convertor (ADC) and the pulse height stored using a multichannel analyser (MCA). The pulses are analysed (in order to remove random events) by the electronic systems and the data analysis software. The count rate of these photons allows the determination of the activity in the test portion, after correcting for the background count rate and detection efficiency, taking account of the quench correction. The requirements of the specific test method for specific beta emitting radionuclides, including test portion preparation and scintillation source preparation, shall be determined according to the intended use of the measurement results and the associated data quality objectives.

In order to determine the background count rate, a blank portion shall be prepared in the same way as the test portion.

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

- same scintillation cocktail;
- same type of counting vial;
- same filling geometry;
- same ratio between test portion and scintillation cocktail;
- same preparation conditions, minimizing photoluminescence and static electricity effects;

In addition, the quench indicating parameter should be within the range of the quench calibration curve. An alternative method using the Cerenkov effect[16][17] is treated in Annex C.

6 Reagents and equipment

Use only reagents of recognized analytical grade.

6.1 Reagents

6.1.1 Blank material

Blank material is used to prepare the blank portion. For direct counting of test portion, it shall be as free as possible of chemical impurities to avoid quenching, and with radioactive impurities negligible in comparison with the test portion activities to be measured.

If some preparation is required for the test portion, the blank portion shall be prepared with a reference material of the lowest activity available.

This blank sample shall be kept physically remote from any radioactive material to avoid cross-contamination.

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 a controlled temperature (see ISO 5667-3). 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 remain stable for years, although it is advisable to determine these activity concentrations at predetermined intervals (e.g. every year).

6.1.2 Calibration source solutions

To avoid cross-contamination, preparation of samples and calibration source solution shall be segregated.

The standardized solution used to prepare the calibration source solution shall be provided with a calibration certificate confirming traceability to a national or international standard of radioactivity.

Weigh and pour into a weighed volumetric flask (for example 100 ml) the required quantity of a standardized solution of the radionuclide to be measured, so that the activity concentration generates sufficient counts to reach the required measurement uncertainty after dilution with the blank solution and thorough mixing. Calculate the activity concentrations of the resulting calibration source solution (A). Note the date at which the standard solution was made up ($t = 0$).

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

6.1.3 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[18][19].

For the measurement of usual environmental and drinking water sample or for test sample prepared as an aqueous solution, it is recommended to use a hydrophilic scintillation cocktail.

For the direct measurement of particles in suspension, it is recommended to use a scintillation cocktail that leads to a gel type mixture.

In all cases, the characteristics of the scintillation cocktail when mixed with the sample shall result in a scintillation source with the form of a homogeneous and stable medium.

It is recommended to:

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

6.1.4 Quenching agent

Water, as well as dissolved oxygen, is a quenching agent for the scintillation cocktail.

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

Some quenching agents are dangerous or toxic and shall be handled and disposed properly.

6.2 Equipment

6.2.1 General

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

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

6.2.2 Liquid scintillation counter

Liquid scintillation counter with an automatic sample transfer is preferable. Operation at constant temperature is recommended following the manufacturer's instructions.

The generic method specified in this document 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.

It is recommended to use a liquid scintillation counter using an external source, so that the level of quench can be determined. Otherwise, an LSC-counter with three photomultipliers and appropriate software[20][21] may enable the activity to be determined directly (see Annex B).

For low activity measurements, a counter with low background photomultipliers, electronic equipment with the option of background correction and suitable shielding is recommended.

6.2.3 Counting vials

Different types of scintillation vials exist, manufactured using a large 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 scintillation source.

Other types of vials exist:

— glass vials with low level of ^{40}K, exhibit a lower background than 'normal' glass vials;

— for the determination of very low concentration of low energy beta emitters (for example, tritium), the use of polytetrafluoroethylene vials (PTFE) or polyethylene vials with an inner layer of PTFE on inside vial wall is 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 vials are 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 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.

7 Sampling and samples

7.1 Sampling

It is important that the laboratory receives a representative sample, unmodified during the transport or storage and in an undamaged container.

For example, for water and soil, conditions of sampling shall comply with ISO 5667-1 and ISO 18589-2 respectively.

If carbonated species are to be measured, water sample shall not be acidified in order to avoid changing the equilibrium of carbonated species.

For water, 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.

7.2 Sample storage

If storage of samples is required, the sample shall be stored to avoid oxidation, fermentation or any modification of its properties.

For water, if storage is required, the sample shall be stored in accordance 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.

8 Procedure

8.1 Determination of background

In order to determine the background count rate, a blank sample is prepared in the same way as the test sample.

For aqueous test sample, the blank sample is prepared using a reference water of the lowest activity available, also sometimes called “dead water”. For other matrices, the blank solution is prepared using a reference material, as close as possible to the matrix to be measured, of the lowest activity available.

8.2 Determination of detection efficiency

In order to determine the detection efficiencies, it is necessary to measure a sample having a known activity under conditions that are identical to those used for the sample. This sample shall be a mixture of certified radioactive source (standardized solution) or a dilution of this mixture produced with the prepared reference material.

8.3 Quench correction

The quench correction shall be considered, as mixing the organic liquid scintillation cocktail with the sample test portion can affect the emission properties of the cocktail.

If the quenching is the same for the blank sample vial, the test sample vial and the calibration source vial, the counting efficiency can be determined without requiring a quench correction.

Alternatively, an internal standard method can be used (see Annex A).

If chemical quenching affects the measurement results, it is recommended to determine a quench curve. It is important to choose the chemical quenching agent according to the expected type of quenching observed in the prepared test sample. An acid quenching agent, however, shall not be used if the chemical form of the carbon 14 in the standardized solution is carbonates.

It is useful to plot a quench curve for each matrix/radionuclide. These curves are only valid for:

- a given instrument;
- a given type of counting vial;
- a given type of scintillation cocktail;
- given quantities of scintillation cocktail and test portions;
- a given counting window.

The quench curve is obtained from a series of working standards (e.g. around 10) having variable quench of which the matrix is similar or close to that of the samples to be measured (same scintillation cocktail, same quantities of scintillation cocktail and test portion).

These working standards can be produced in the following manner:

- a similar quantity of standardized solution is dispensed into each vial. Its activity shall be sufficient so that the count rate of the working standard can be determined with a known statistical accuracy, even at high quench levels;
- a reference solution is added until the desired test portion is obtained;
- the scintillation cocktail is then added in order to obtain the desired proportions;
- at least one working standard is used without adding any quenching agent. Increasing quantities of a quenching agent, with a very low volume (e.g. less than 1 or 2 % of the total volume of the working standard), are added to the other working standards. This gives rise to a quench similar to that of the samples to be measured.

The quench curve relating $\varepsilon \cdot f_q$ with the quenching is used to determine f_q:

$$f_q = \frac{\varepsilon_q}{\varepsilon} \tag{1}$$

This method is not applicable to colour quenched samples.

8.4 Sample preparation

The test sample is prepared to obtain a scintillation source, aqueous or organic, which contains the radionuclide to be measured. The efficiency of the preparation, ε_p, (conservation of the radionuclide to be analysed through the transformation of the test sample, radiochemical yield) is to be determined.

8.5 Preparation of the scintillation sources to be measured

Known quantities of the sample and scintillation cocktail shall be dispensed into the counting vial.

For liquid and particulate samples, after closing the vial, it shall be thoroughly shaken to homogenize the mixture.

For filter and planchet samples, great care shall be used to obtain the proper counting geometry, with the filter or planchet materials not blocking the photons from reaching the phototubes. The active surface of the filter or planchet shall be positioned with the activity facing into the scintillation cocktail.

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 should take place in dimmed light, preferably light from an incandescent source or UV-free LED or red light. Direct sunlight or fluorescent light should be avoided.

8.6 Counting procedure

8.6.1 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 7870-2[1]. Usually, these references are sealed, unquenched scintillation sources: blank, tritium and carbon 14.

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 (see Clause 5).

8.6.2 Measurement conditions

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

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

The measurement is performed using an energy channel A that is between the detector noise threshold and the β_{max} of the radionuclide to be measured. It is recommended to choose the width of the energy window for the counting of the radionuclide to be measured in order to optimize the figure of merit $\left(\varepsilon^2 / r_0 \right)$.

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

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, intermittent or cyclic (night and day alternation for example) associated with the measurement equipment environment.

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

8.6.3 Interference control

8.6.3.1 General

The measurement can be influenced by chemiluminescence or spectrum attenuation phenomena due to the presence of chemical entities, as well as by the presence of radionuclides other than the nuclide to be measured. It is therefore advisable to take into account the characteristics of the prepared test sample and to specify them in the presentation of the result.

A possible method of verification of the chosen conditions is the measurement of a known mixture prepared with certified solutions or dilutions of these solutions.

8.6.3.2 Interference arising from luminescence

Serious interferences in the measurement of low energy beta-emitters (e.g. tritium) determinations can occur due to a variety of luminescent processes (e.g. chemiluminescence, phosphorescence, treboluminescence, and static electricity). It is advisable to use a liquid scintillation counter capable of identifying these single photon events and correcting automatically for these interferences.

8.6.3.3 Interference from other radionuclides

The following method can be used to identify possible interferences from other radionuclides in the test portion. Two additional measurement channels (B and C) may be set: (1) channel B has the same lower threshold as measurement channel A, but an upper threshold adjusted so that the counting efficiency is about two thirds of the counting efficiency of channel A; (2) channel C has the same lower threshold as measurement channel A, but an upper threshold adjusted to the $\beta_{\max}$ of the radionuclide to be measured.

In the absence of an interfering radionuclide, calculation should yield the same activity concentration in the test portion for channels A, B and C, using appropriate efficiencies for each channel. If significant differences are observed, further chemical separation steps may be needed in the sample preparation process.

However, some low energy beta emitters and electron capture emitters (e.g. ^{241}Pu, ^{210}Pb, ^{228}Ra, ^{227}Ac, ^{63}Ni and ^{55}Fe) cannot be distinguished from the energy spectrum of ^{3}H and from the lower energy part of the spectrum of ^{14}C by liquid scintillation counting.

8.6.3.4 Equipment stability

If the equipment is not stable for the measurement of low beta spectrum energies (e.g. tritium), it is not suitable for the measurement of lower parts of the test sample beta spectrum or for quenched test samples. For example, once the measurement channels A and B have been adjusted for tritium, 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 is then easily detected.

For control purposes, the use of control charts[1] is advisable.

9 Expression of results

9.1 General

In the case of the measurement of radionuclides, without a preparation, by liquid scintillation, the main components of the uncertainty are:

- — raw counts and backgrounds;
- — detection efficiencies in the windows of the relevant energy ranges for a given quench indicating parameter;
- — quench factor, if a correction is applied;
- — volume or mass of the test portion.

The other uncertainties can, to first order, be ignored (volume or mass of scintillation cocktail, counting time, etc.).

In the case of a preparation of the sample, the uncertainty in the radiochemical yield shall be included.

9.2 Calculation of activity concentration, without preparation

The symbols used are defined in Clause 4.

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

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

where $w = \dfrac{1}{V \cdot \varepsilon \cdot f_{\mathrm{q}}}$ and $\varepsilon = \dfrac{r_s - r_0}{A}$

The combined uncertainty is calculated using Formula (3):

$$u(c_{\mathrm{A}}) = \sqrt{w^2 \cdot \left(u^2(r_{\mathrm{g}}) + u^2(r_0)\right) + c_{\mathrm{A}}^2 \cdot u_{\mathrm{rel}}^2(w)} = \sqrt{w^2 \cdot \left(r_{\mathrm{g}} / t_{\mathrm{g}} + r_0 / t_0\right) + c_{\mathrm{A}}^2 \cdot u_{\mathrm{rel}}^2(w)} \qquad (3)$$

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

and the relative standard uncertainty of ε, $u_{\mathrm{rel}}^2\left(f_{\mathrm{q}}\right)$, for each quenching value is calculated using Formula (5):

$$u_{\mathrm{rel}}^2(\varepsilon) = u_{\mathrm{rel}}^2(r_{\mathrm{s}} - r_0) + u_{\mathrm{rel}}^2(A) = (r_{\mathrm{s}} / t_{\mathrm{s}} + r_0 / t_0) / (r_{\mathrm{s}} - r_0)^2 + u_{\mathrm{rel}}^2(A) \qquad (5)$$

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

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

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

$$\tilde{u}(\tilde{c}_\mathrm{A}) = \sqrt{w^2 \cdot ((\tilde{c}_\mathrm{A} / w + r_0) / t_\mathrm{g} + r_0 / t_0) + \tilde{c}_\mathrm{A}^2 \cdot u_\mathrm{rel}^2(w)} \tag{6}$$

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 a may also be expressed as the activity per unit of mass (m replacing V in preceding formula).

9.3 Decision threshold, without preparation

The decision threshold, c_A^*, is obtained from the above Formula (6) for $\tilde{c}_\mathrm{A} = 0$ (see ISO 11929). This yields:

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

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

9.4 Detection limit, without preparation

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

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

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

The detection limit can be calculated by solving Formula (9) for $c_\mathrm{A}^\#$ or, more simply, by iteration with a starting approximation $c_\mathrm{A}^\# = 2 \cdot c_\mathrm{A}^*$.

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

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

9.5 Confidence interval limits, without preparation

The lower, $c_\mathrm{A}^<$, and upper, $c_\mathrm{A}^>$, confidence limits are calculated using the Formulae (10) and (11) (see ISO 11929):

$$c_\mathrm{A}^\triangleleft = c_\mathrm{A} - k_\mathrm{p} \cdot u\left(c_\mathrm{A}\right);\ p = \omega \cdot (1 - \gamma/2) \tag{10}$$

$$c_\mathrm{A}^\triangleright = c_\mathrm{A} + k_\mathrm{q} \cdot u\left(c_\mathrm{A}\right);\ q = 1 - \omega \cdot \gamma/2 \tag{11}$$

where

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

1- γ, the probability for the confidence interval of the measurand, and

$\omega = 1$ may be set if $c_A \geq 4 \cdot u(c_A)$. In this case:

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

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

9.6 Calculations using the activity per unit of mass, without preparation

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

$$c_A = \frac{r_g - r_0}{m} \cdot \frac{\rho}{\varepsilon \cdot f_q} = (r_g - r_0) \cdot w \text{ and } w = \frac{\rho}{m \cdot \varepsilon \cdot f_q} \tag{13}$$

$$u_{\text{rel}}^2(w) = u_{\text{rel}}^2(\varepsilon) + u_{\text{rel}}^2(m) + u_{\text{rel}}^2(\rho) + u_{\text{rel}}^2(f_q) \tag{14}$$

The uncertainty, the characteristics limits and the limits of the confidence interval may be calculated using the previous expression (Formulae (3), (7), (8) and (9) with the two last equations.

10 Test report

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

a) a reference to this document with the mention of the sample pre-treatment 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:

- as recommended by ISO 11929, the test result should be compared with the decision threshold. When the activity concentration c_A is below or equal to the decision threshold, a contribution from the sample has not been observed and the result of the measurement should be expressed as ≤ c_A^* ;
- if the customer requests that the activity concentration c_A is to be compared with the detection limit, then the result of the measurement can be expressed as ≤ $c_A^\#$ 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 explaining the results.

Annex A
(informative)

Internal standard method

A.1 Sample preparation

For each test sample fill 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 the test sample. Mark the cap of the two counting vials so that they can be clearly identified (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 solution. 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.

A.2 Counting procedure

After shaking the scintillation source in the counting vials, wipe them 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, background, sample 2, etc.

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.

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 a better control of stability of the samples and the possibility of undetected erroneous counts is reduced.

A.3 Expression of results

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

$$\varepsilon = \frac{r_s - r_g}{A_s} \quad \text{(A.1)}$$

where

r_s is the count rate, in pulses per second, of the sample with the internal standard solution (see 6.1.2) 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.

For estimating the uncertainty, the uncertainty in the volume or mass of the internal reference solution and the certificated activity shall be taken into account.

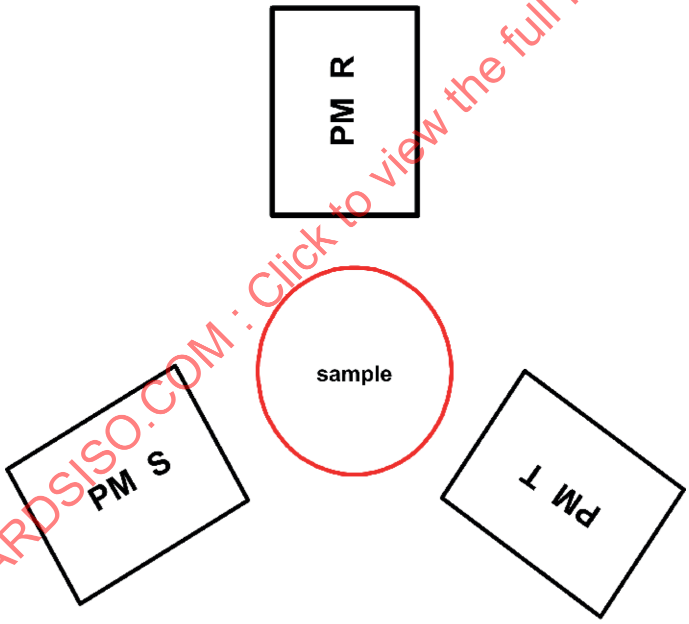
Annex B
(informative)

TDCR Liquid Scintillation Counting

B.1 General

The Triple to Double Coincidence Ratio method (TDCR) is a primary measurement method allowing the standardization of radionuclides by Liquid Scintillation Counting (LSC).[20][21] The TDCR method allows calculation of the detection efficiency from the experimental ratio of double and triple coincidence counting rates. The underlying theory is based on a statistical distribution law of the number of photons emitted by the scintillation process, the Poisson law, which is well suited to most measurement conditions.

The TDCR method allows obtaining the sample counting efficiency and activity (DPM, Bq) without known-activity standards. It requires a liquid scintillation counter with three photomultiplier tubes (PMT), as shown in Figure B.1, and utilizes the fact that scintillations are multi-photon events, i.e. each decay produces a flash of several photons within a few tens of nanoseconds.



Key
1 sample

Figure B.1 — Sample/detector geometry for TDCR counting

A valid pulse is recorded if the counter detects a triple coincidence (triple, simultaneous detection from all 3 PMT’s) or a double coincidence (double, simultaneous detection from 2 PMT’s). The sum of triples + doubles is called the logical sum of doubles and it represents all accepted coincidence pulses from counting.

The core parameter is the Triple to Double Coincidence Ratio (TDCR) which is given by:

$$\mathrm{TDCR} = \frac{t}{t+d} = \frac{t}{D}$$

where

t is the number of obtained triples;

d is the number of obtained doubles;

D Is the number of logical sum of doubles = all obtained coincidences.

Thus, TDCR is the ratio of triple coincidences to all coincidences.

One advantage of the technique is that the TDCR can be used as a quench parameter. With many simple beta emitters, e.g. ^{3}H, ^{14}C, ^{35}S, ^{63}Ni, ^{32}P, ^{33}P, it approximates counting efficiency of D, usually with a few percent bias. As the bias of TDCR is relatively small in most applications, a calibration may not necessarily be required for some analysis.

The TDCR method is in use as a primary standardization method in national and international measurement institutes. Metrologists have developed specialist software to calculate the detection efficiency. The software include factors such as the Poisson model for PMT photoelectron distribution, the energy spectrum of the beta particles and ionization quenching function for beta particle energy. The programs calculate the detection efficiency that corresponds to the measured TDCR. Furthermore, specialist TDCR counters at measurement institutes can take into account differences between phototubes.

Modern LSC counters with three photomultiplier tubes can be used for all the different methods utilizing liquid scintillation counting, either by applying the TDCR counting technique or by calibration with reference standards.

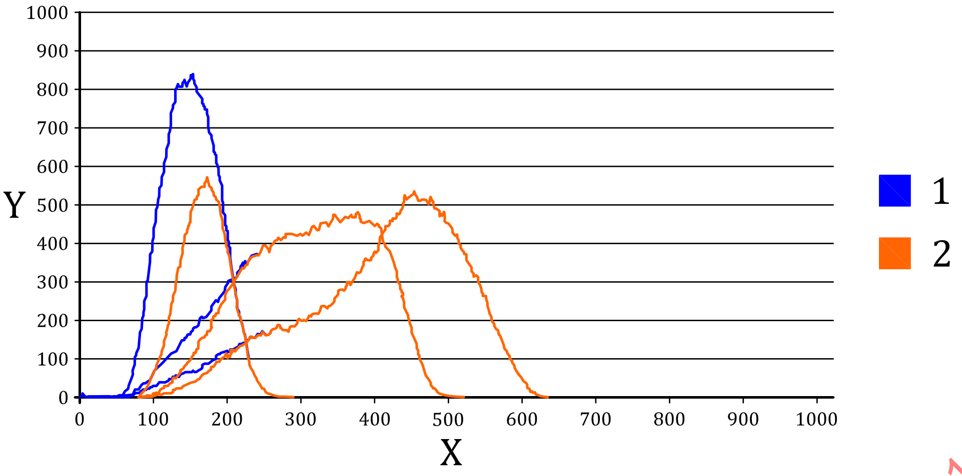
The TDCR method can also be applied to Cerenkov counting (see Annex C). High-energy beta particles (e.g. ^{32}P, ^{89}Sr, ^{90}Y, ^{40}K...) can elicit light emission directly in water, without a liquid scintillation cocktail, via the Cerenkov phenomenon. Models have been developed to obtain Cerenkov counting efficiency from the observed TDCR. For example, the TDCR-Cerenkov counting technique in combination with TDCR-LSC can be applied for a rapid analysis of ^{89}Sr and ^{90}Sr in case of a nuclear incident or in routine analysis (e.g. ^{90}Sr, ^{90}Y).

The TDCR technique requires a minimum amount of activity, usually more than some Bq·l^{-1}, in order to establish accurately the t/D ratio[22].

B.2 Efficiency and quenching

When calculating the counting efficiency, the quench effect plays a dominant role. In TDCR counting 3 identical phototubes are used, and the detection efficiency is calculated for double coincidences and for triple coincidences.

Increasing quench reduces the number of scintillation photons. This reduces the probability for triple coincidences (cubic dependence) more than in relation to probability for double coincidences (quadratic dependence), as it is shown in Figure B.2.



Key

X energy (channel)

Y counts

Figure B.2 — Various 14C spectra for different quench level

Therefore, the triple-to-double coincidence ratio (TDCR) is a convenient quantity for quench and efficiency.

The ratio of the triple to double counts/coincidences can be calculated by using the Poisson distribution, using the calculated counting efficiencies for double and triple coincidences, using Birk's parameter, and by using the calculated transferred energy spectrum. The ratio of the triple to double counting efficiency converges for high numbers of decays against the overall efficiency. Hence, the measured TDCR-value under these circumstances approximates well the counting efficiency of the system.

The technique of TDCR-method enables an automatic quench correction without using external standards. The TDCR method is therefore an absolute activity measurement method for detection of pure beta- (e.g. ^{3}H, ^{14}C, ^{32}P, ^{33}P, ^{35}S, ^{63}Ni, ^{89}Sr, ^{90}Sr) and pure EC-emitters (e.g. ^{55}Fe) activity.

Chemical and colour quench correction is inherently incorporated in this method.

An external standard is needed if there is more than one radionuclide in the sample or to reduce the uncertainty of the result.

For most environmental levels, an external source is recommended for the determination of the quench level.