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Water quality — Gross alpha activity — Test method using thick source

Qualité de l'eau — Activité alpha globale — Méthode d'essai par source concentrée

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Foreword

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

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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 147, *Water quality*, Subcommittee SC 3, *Radioactivity measurements*.

This third edition cancels and replaces the second edition (ISO 9696:2007), which has been technically revised.

Introduction

Radioactivity from several naturally occurring and anthropogenic sources is present throughout the environment. Thus, water bodies (e.g. surface waters, ground waters, sea waters) can contain radionuclides of natural, human-made or of both origins:

- natural 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}Po and ^{210}Pb, can be found in water for natural reasons (e.g. desorption from the soil and runoff by rain water) or can be released from technological processes involving naturally occurring radioactive materials (e.g. the mining and processing of mineral sands or phosphate fertilizers production and use);
- anthropogenic radionuclides, such as the transuranium elements (e.g. americium, plutonium, neptunium and curium), ^{3}H, ^{14}C, ^{90}Sr, and some gamma-emitting radionuclides can also be found in natural waters. Small quantities of these radionuclides may be discharged from nuclear fuel cycle facilities into the environment as the result of authorized routine releases. Some of these radionuclides used for medical and industrial applications may also be released into the environment after use. Anthropogenic radionuclides are also found in waters as the result of past fallout contamination resulting from the above ground detonation of nuclear devices and accidents such as those that occurred in Chernobyl and Fukushima.

Radionuclide activity concentration in water bodies can vary according to local geological characteristics and climatic conditions and can be locally and temporally enhanced by releases from nuclear installation during planned, existing and emergency exposure situations[1]. Drinking water may thus contain radionuclides at activity concentrations which could present a risk to human health.

The radionuclides present in liquid effluents are usually controlled before being discharged into the environment[2] and water bodies. Drinking water may be monitored for their radioactivity as recommended by the World Health Organization (WHO)[3]. Such control and monitoring can enable to take proper actions to ensure that there is no adverse health effects to the public. Following these international recommendations, radionuclide authorized concentration limits for liquid effluent discharged to the environment and radionuclide guidance levels for water bodies and drinking water are usually specified by national regulations for planned, existing and emergency exposure situations. Compliance with these limits can be assessed using measurement results with their associated uncertainties as requested by ISO/IEC Guide 98-3 and ISO 5667-20.

Depending on the exposure situation, the limits and guidance levels that would result in an action to reduce health risk differ. As an example, during planned or existing situation, the WHO guidance for screening levels in drinking water is 0,5 $Bq\cdot l^{-1}$ for gross alpha activity and 1 $Bq\cdot l^{-1}$ for gross beta activity.

NOTE The guidance level is the activity concentration with an intake of 2 $l\cdot d^{-1}$ of drinking water for 1 year that results in an effective dose of 0,1 $mSv\cdot a^{-1}$ for members of the public, an effective dose that represents a very low level of risk that is not expected to give rise to any detectable adverse health effect[3].

Thus, the test method may need to be adjusted depending if it is applied for either a planned-existing or an emergency situation since during emergency situations, a large number of samples needs to be rapidly characterized. The test methods could be adapted so that its performance in term of characteristic limits, decision threshold and detection limit, and the uncertainties ensure that the gross activity concentration test results permit the verification that they are below the guidance levels required by national authority for either planned-existing situations or an emergency situation[5][6][7].

Usually, the test methods can be adjusted to measure the gross activity concentration of the radionuclide(s) in either wastewaters before storage or in liquid effluents before being discharged to the environment. The test results will enable the plant/installation operator to comply with national regulations in verifying that before their discharge, wastewaters/liquid effluent radioactive activity concentrations are lower than the authorized limits.

The test method(s) described in this document may be used during planned, existing and emergency exposure situations, as well as for wastewaters and liquid effluents with specific modifications that could increase the overall uncertainty, detection limit and threshold.

The test method(s) may be used for water samples after proper sampling, sample handling and test sample preparation (see the ad hoc part of ISO 5667).

An international standard on a test method of gross alpha and gross beta activity concentrations in water samples is justified for test laboratories carrying out these measurements and may be required by national authorities, as laboratories may have to obtain a specific accreditation for radionuclide measurement of drinking water samples.

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

Water quality — Gross alpha activity — Test method using thick source

WARNING — Persons using this document should be familiar with normal laboratory practice. This document 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 in accordance with this document be carried out by suitably trained staff.

1 Scope

This document specifies a method for the determination of gross alpha activity in non-saline waters for alpha-emitting radionuclides which are not volatile up to 350 °C.

The method is applicable to raw and potable waters.

The range of application depends on the amount of total soluble salts in the water and on the performance characteristics (background count rate and counting efficiency) of the counter.

It is the laboratory's responsibility to ensure the suitability of this method for the water samples tested.

2 Normative 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 3696:1987, *Water for analytical laboratory use — Specification and test methods*

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

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

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

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

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

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 11929, ISO 80000-10, ISO/IEC Guide 98-3 and ISO/IEC Guide 99 apply.

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

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

4 Symbols

V_t	volume of the water sample, in litres
V	volume of test sample, in litres, equivalent to the mass of solid on the planchet
m	mass, in milligrams, of ignited residue from volume, V
m_r	mass of the sample residue deposited on the planchet, in milligrams
A	alpha activity of the calibration source, in becquerels
c_A	alpha activity concentration, in becquerels per litre
t_0	background counting time, in seconds
t_g	sample counting time, in seconds
r_0	background count rate, per second
t_s	calibration count time of the alpha source, in seconds
r_g	sample gross count rate, per second
r_s	calibration count rate, per second
ε	counting efficiency of the specified calibration source
S	area of the planchet, in square millimetres
ρ_s	source thickness, in milligrams per square millimetres, of the sample residue deposited on the planchet
$u(c_A)$	standard uncertainty associated with the measurement result, in becquerels per litre
U	expanded uncertainty calculated by $U = k \cdot u(a)$ with k = 1, 2.., 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

5 Principle

Gross alpha activity is determined by using a gas-flow proportional counter or a solid scintillation counter [e.g. ZnS(Ag) detector] on water residue deposited on a planchet. The method requires a uniform thickness and homogenous layer of residue deposit on the planchet as the sample positioning in the detector could seriously influence the counting efficiency due to self-absorption of alpha particles within the residue material.

Alpha activity shall be counted using either a silver-activated zinc sulfide scintillation screen, a silicon charged-particle detector [ion-implanted silicon or surface barrier detector (SSB)] or a gas-flow proportional counter (windowless or with a window of <100 µg·cm^{-2}).

Gross alpha measurement is not intended to give an absolute determination of total alpha activity in the sample, but rather a screening analysis to ensure particular action levels of specific alpha emitters have not been exceeded. This type of determination is also known as gross alpha index. Gross alpha analysis is not expected to be as accurate nor as precise as specific radionuclide analysis after radiochemical separations.

The sample is acidified for stabilization, evaporated to near dryness, converted to the sulfate form and ignited at 350 °C. After transferring a portion of the residue to a planchet, the alpha activity is measured in an alpha-particle detector or counting system previously calibrated against specific alpha-emitting standards and the alpha activity concentration calculated. It should be noted that this method may not allow the determination of some volatile species such as gaseous ^{222}Rn and polonium halides. The short-lived radionuclides (e.g. ^{224}Ra) may also not be detected due to the time period between sampling and analysis.

6 Reagents and equipment

6.1 Reagents

Except for the certified reference solution, all reagents shall be of recognized analytical grade and shall not contain any measurable alpha activity.

A method for preparing reagent blanks to check for endemic radioactivity or contamination is given in Clause 8.

6.1.1 Water, complying with ISO 3696:1987, grade 3.

6.1.2 Certified reference solution.

A calibration laboratory establishes traceability of its own measurement standards and measuring instruments to the International System of Units (SI) by means of an unbroken chain of calibrations or comparisons linking them to relevant primary standards of the SI units of measurement. The link to SI units may be achieved by reference to national measurement standards. National measurement standards may be primary standards, which are primary realizations of the SI units or agreed representations of SI units based on fundamental physical constants, or they may be secondary standards which are standards calibrated by another national metrology institute. When using external calibration services, traceability of measurement shall be ensured by the use of calibration services from laboratories that can demonstrate competence, measurement capability and traceability. The calibration certificates issued by these laboratories shall contain the measurement results, including the measurement uncertainty and/or a statement of compliance with an identified metrological specification.

The choice of alpha standard depends on knowledge of the type of radioactive contaminant likely to be present in the waters being tested. In general, this amounts to a choice between naturally occurring and manmade alpha emitters.

Among standard solutions of artificial alpha-emitting radionuclides, ^{241}Am and ^{239}Pu are commonly used. The presence of other impurities in the chosen alpha standard, which may emit alpha particles or decay to an alpha-emitting progenies, shall be taken into account. When ^{241}Am is used, the potential interferences of its gamma emission or alpha-beta crosstalk shall be taken into account (see Reference [8]).

NOTE 1 A uranium compound of certified natural or known isotopic composition has one arguable advantage, as its specific activity can be calculated from established physical constants and isotopic abundance data which are independent of the calibration procedures of a particular organization.

NOTE 2 Furthermore, since the energies of the alpha emissions from uranium isotopes are less than those from the artificial transuranic nuclides, the use of a uranium standard tends to give a high result for transuranics. When the true composition is unknown, some authorities prefer to overestimate the results as a conservative approach.

6.1.3 **Nitric acid**, $c(\mathrm{HNO_3}) = 8\ \mathrm{mol{\cdot}l^{-1}}$.

6.1.4 **Sulfuric acid**, $c(\mathrm{H_2SO_4}) = 18\ \mathrm{mol{\cdot}l^{-1}}$, $\rho = 1{,}84\ \mathrm{g{\cdot}ml^{-1}}$, mass fraction $w(\mathrm{H_2SO_4}) = 95\ \%$.

6.1.5 **Volatile organic solvents**.

Methanol or acetone.

6.1.6 **Poly vinyl acetate (PVA)**.

6.1.7 **Calcium sulfate, $\mathrm{CaSO_4}$**.

As calcium salts may contain trace amounts of ^{226}Ra and/or ^{210}Pb, checks for the presence of these nuclides shall be made.

6.2 Equipment

6.2.1 **Usual laboratory equipment**.

6.2.2 **Alpha counter**.

Alpha activity shall be counted using either a silver-activated zinc sulfide scintillation screen, a silicon charged-particle detector [ion-implanted silicon or surface barrier detector (SSB)] or a gas-flow proportional counter (windowless or with a window of <100 µg·cm^{-2}).

If a gas-flow proportional counter is used, it is advisable to choose the alpha window so that the beta-alpha cross-talk is minimal.

If a windowless gas-flow proportional counter is used, regular checks for possible contamination of the counting system shall be carried out by counting blank samples.

NOTE The particulate nature of the source to be counted can give rise to contamination problems if operated in a vacuum (as in the case of an SSB) or gas flow systems (as used in a proportional counter).

6.2.3 **Planchets**, of surface density of at least 2,5 mg·mm^{-2} (250 mg·cm^{-2}) to avoid any deformation of the planchet during the drying step, lipped and made of stainless steel.

NOTE The diameter of the planchet to be used is determined by the counter requirements, i.e. the detector diameter and source holder dimensions.

An evenly spread source is required and some workers find it easier to produce this on a polished metal surface, whereas others prefer to use an etched or roughened planchet (sand blasting and chemical etching has been applied for this purpose).

6.2.4 **Muffle furnace**, capable of maintaining a temperature of (350 ± 10) °C.

6.2.5 **Crucible**, in silica or glazed porcelain, volume of 30 ml to 50 ml.

7 Procedure

WARNING — The use of this document may involve hazardous materials, operations and equipment. This document does not purport to address all the safety problems associated with

its use. It is the responsibility of the user of this document to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use. All steps in this clause, except 7.1, should be carried out in a safety cabinet.

7.1 Sampling

Sampling, handling and storage of the water samples shall be done as specified in ISO 5667-1, ISO 5667-3 and ISO 5667-14.

If the measurement of the activity in the filtered water sample is required, carry out filtration immediately on collection and before acidification.

NOTE Acidification of the water sample minimizes the loss of radioactivity from solution by adsorption. If carried out before filtration, it desorbs radioactive material already adsorbed on the particulate material.

7.2 Pretreatment

The determination of the total solids content of the water may be performed to determine the smallest volume of water needed for the measurement. Making due allowance for changes in composition due to ignition at 350 °C and sulfation of the residue, calculate the sample volume required to produce a mass of solid residue slightly in excess of ρ_S (mg·mm^{-2}) given by Formula (1):

$$\rho_S = \frac{m_{\mathrm{r}}}{S} \geq 0{,}1 \qquad (1)$$

Use this as a guide to determine the sample volume required for the concentration stage.

The analysis should be carried out in an area with no risk of radioactive contamination.

7.3 Concentration stage

Transfer to a beaker a measured volume, V, in litres, (±1 %) of the sample chosen such that after ignition, the value for ρ_S exceeds 0,1 mg·mm^{-2}.

With very soft water samples, it is possible that the volume required to produce $\rho_S > 0{,}1$ mg·mm^{-2} is impractically large. In these circumstances, the largest practicable volume should be used or calcium salts should be added.

Evaporate the sample carefully on a hot-plate until the volume is reduced to about 50 ml.

After cooling, transfer the concentrated solution to a weighed silica (or glazed porcelain) dish (6.2.5), which has been previously ignited at 350 °C. Rinse the beaker carefully with a minimum quantity of distilled water and transfer the rinses to the dish (6.2.5).

If the beaker is large, it may be more convenient to transfer the rinses to a smaller beaker. The rinses can then be evaporated to a smaller volume to facilitate transfer to the silica dish.

7.4 Sulfation stage

Ensure that the sample in the dish (6.2.5) is cooled and add 1 ml of concentrated sulfuric acid (6.1.4).

After drying and ignition, some water residue may be hygroscopic or difficult to disperse, which is unsuitable for the measurement of alpha activity. The sulfation process is a suitable treatment for many such samples. The volume of sulfuric acid (6.1.4) chosen (1 ml) is sufficient for sulfating about 1,8 g of calcium carbonate. To allow for an excess of acid, the initial volume of sample should be chosen such that the total solids content does not exceed 1 g (experience with some waters may show this step to be unnecessary).

Carefully evaporate the sample in the dish to dryness.