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Water quality — Radium 226 and Radium 228 — Test method using liquid scintillation counting

Qualité de l'eau — Radium 226 et radium 228 — Méthode d'essai par comptage des scintillations en milieu liquide

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Foreword

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

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.*

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

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

- Natural radionuclides, including ^{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 and ^{210}Pb, can be found in water for natural reasons (e.g. desorption from the soil and washoff 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).
- Human-made radionuclides such as transuranium elements (americium, plutonium, neptunium, curium), ^{3}H, ^{14}C, ^{90}Sr, and gamma emitting radionuclides can also be found in natural waters. Small quantities of these radionuclides are discharged from nuclear fuel cycle facilities into the environment as a result of authorized routine releases. Some of these radionuclides used for medical and industrial applications are also released into the environment after use. Anthropogenic radionuclides are also found in waters as a result of past fallout contaminations resulting from the explosion in the atmosphere 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 waters are monitored for their radioactivity as recommended by the World Health Organization (WHO)[3] so that proper actions can be taken to ensure that there is no adverse health effect to the public. Following these international recommendations, national regulations usually specify radionuclide authorized concentration limits for liquid effluent discharged to the environment and radionuclide guidance levels for waterbodies and drinking waters for planned, existing, and emergency exposure situations. Compliance with these limits can be assessed using measurement results with their associated uncertainties as specified by ISO/IEC Guide 98-3 and ISO 5667-20[4].

Depending on the exposure situation, there are different limits and guidance levels that would result in an action to reduce health risk. As an example, during a planned or existing situation, the WHO guidelines for guidance level in drinking water are 1 Bq/l and 0,1 Bq/l, for ^{226}Ra and ^{228}Ra activity concentrations, respectively.

NOTE 1 The guidance level is the activity concentration with an intake of 2 l/d of drinking water for one year that results in an effective dose of 0,1 mSv/a for members of the public. This is an effective dose that represents a very low level of risk and which is not expected to give rise to any detectable adverse health effects[3].

In the event of a nuclear emergency, the WHO Codex Guideline Levels[5] mentioned that the activity concentrations might be greater.

NOTE 2 The Codex guidelines levels (GLs) apply to radionuclides contained in food destined for human consumption and traded internationally, which have been contaminated following a nuclear or radiological emergency. These GLs apply to food after reconstitution or as prepared for consumption, i.e. not to dried or concentrated foods, and are based on an intervention exemption level of 1 mSv in a year for members of the public (infant and adult)[5].

Thus, the test method can be adapted so that the characteristic limits, decision threshold, detection limit and uncertainties ensure that the radionuclide activity concentrations test results can be verified to be below the guidance levels required by a national authority for either planned/existing situations or for an emergency situation[6][7].

Usually, the test methods can be adjusted to measure the 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 verify that, before their discharge, wastewaters/liquid effluent radioactive activity concentrations do not exceed 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 relevant part of the ISO 5667 series).

This document has been developed to support the need of test laboratories carrying out these measurements, that are sometimes required by national authorities, as they may have to obtain a specific accreditation for radionuclide measurement in 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.

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WARNING — Persons using this document should be familiar with normal laboratory practices. 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 determine the applicability of any other restrictions.

IMPORTANT — It is absolutely essential that tests conducted according to this document be carried out by suitably trained staff.

1 Scope

This document specifies the determination of radium-226 (^{226}Ra) and radium-228 (^{228}Ra) activity concentrations in drinking water samples by chemical separation of radium and its measurement using liquid scintillation counting.

Massic activity concentrations of ^{226}Ra and ^{228}Ra which can be measured by this test method utilizing currently available liquid scintillation counters go down to 0,01 Bq/kg for ^{226}Ra and 0,06 Bq/kg for ^{228}Ra for a 0,5 kg sample mass and a 1 h counting time in a low background liquid scintillation counter[8].

The test method can be used for the fast detection of contamination of drinking water by radium in emergency situations.

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, *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/IEC 17025:2017, *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, *Uncertainty of measurement — Part 3: Guide to the expression of uncertainty in measurement (GUM:1995)*

3 Terms, definitions, symbols and units

3.1 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:

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

3.2 Symbols, definitions and units

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

Symbol	Unit	Definition
A_x	Bq/kg	Certified massic activity of the analyte in the certified standard solution at the reference date
A_x^t	Bq/kg	Massic activity of the analyte in the quality control sample at the reference date
a_x	Bq/kg	Massic activity of the analyte in the test sample at the sampling date
a^*	Bq/kg	Decision threshold of the analyte
$a^\#$	Bq/kg	Detection limit of the analyte
$a^{\triangleleft}$, $a^{\triangleright}$	Bq/kg	Lower and upper limits of the confidence interval
c_a	Bq/l	Activity concentration of the analyte in the test sample at the sampling date
C_x	Bq/kg	Target massic activity of the analyte in the quality control sample prepared for the validation of the procedure
$m_{s\text{-}x}$	kg	Mass of the certified standard solution taken for the analysis of the analyte
$m_{t\text{-}x}$	kg	Mass of the quality control sample taken for the analysis of the analyte
m_s	kg	Mass of the test sample
n_x^s	1/s	Net count rate of the analyte in the certified standard solution
n_x^t	1/s	Net count rate of the analyte in the quality control sample
n_x	1/s	Net count rate of the analyte in the test sample
PI	%	Precision index
R_L	Bq/kg	Reproducibility limit
r_L	Bq/kg	Repeatability limit
r_{g-x}	1/s	Gross count rate of the analyte in the test sample
$r_{0\text{-}x}$	1/s	Gross count rate of the analyte in the blank sample
S_r	Bq/kg	Standard deviation of repeatability
S_R	Bq/kg	Standard deviation of reproducibility
$T_{s\text{-}x}$	s	Counting time of the analyte in the test sample
$t_{0\text{-}x}$	s	Counting time of the analyte in the blank
$t_{s\text{-}x}$	s	Time interval between measurement date and reference date of the analyte in the certified standard solution
$t_{t\text{-}x}$	s	Time interval between measurement date and reference date of the analyte in the quality control sample
t_x	s	Time interval between measurement date and sampling date of the analyte in the test sample
$u(a)$	Bq/kg	Standard uncertainty associated with the measurement result
$u(x)$	Bq/kg	Uncertainty in quantity x
U	Bq/kg	Expanded uncertainty, calculated using $U = ku(a)$, with $k = 1, 2,$…
w	1/kg	Factor equal to $1/\varepsilon_x m_s$
ε_x	—	Counting efficiency of the analyte
ε_x^c	—	Overall efficiency of the analyte in the quality control sample
λ_x	1/s	Decay constant of the analyte
$\overline{X}_x$	Bq/kg	Mean of all measured values of the analyte in the quality control sample for the validation of the procedure
δ	%	Relative bias of the method
ρ	kg/l	Density

4 Principle

Barium co-precipitation is used as a method of separation for radium due to the very similar chemical properties of barium and radium. The exploitation of the ability of barium to react with an excess of sulfate ions to produce a precipitate allows the quantitative analysis of environmental activity concentrations of radium in water. The inclusion of a lead hold-back carrier allows the removal of ^{210}Pb from solution, which increases the accuracy of ^{228}Ra measurement, as ^{210}Pb can produce a spectral interference. The removal of ^{210}Pb is achieved by lowering the pH of the solution to re-precipitate barium sulfate using acetic acid in which lead sulfate is soluble. This allows ^{210}Pb to remain in solution and therefore be removed.

The source preparation is achieved by suspending the barium sulfate precipitate in the EDTA solution. Barium sulfate is insoluble in water, alkalis and acids, but EDTA increases the solubility due to the complexation of barium and the speciation effect. The EDTA molecule inhibits barium sulfate nucleation. This enables the use of a naphthalene-based scintillation cocktail to gain better spectral resolution than with the use of a gel-forming cocktail.

The flow chart of the procedure is given in Annex A.

Massic activities of ^{226}Ra and ^{228}Ra in the sample are calculated from net count rates of the sample source, sample amount and the overall efficiency that can be obtained from spiked sample with known activities of ^{226}Ra and ^{228}Ra, and that shows the ability of the method to extract radium (chemical recovery) as well as the ability (counting efficiency) of the instrument to detect it.

The test method applies to the analysis of a test sample of drinking water containing less than 100 mg/kg barium. If the barium concentration is higher than 100 mg/kg, it is recommended to reduce the volume of the test sample to be analysed so that the total content of barium in the sample does not exceed 50 mg.

NOTE Adjustment of the test sample mass and counting time can lead to lower detection limits. As an example, a limit of detection of 0,04 Bq/kg can be achieved for ^{228}Ra using a 0,5 kg test sample and a 2 h counting time; similarly a limit of detection of 0,02 Bq/kg can be achieved for ^{228}Ra using a 1 kg test sample and a 2 h counting time.

5 Reagents and equipment

5.1 Reagents

All reagents shall be of recognized analytical grade and, except for 5.1.12, 5.1.13 and 5.1.14, shall not contain any detectable alpha- and beta-activity.

5.1.1 Laboratory water, distilled or deionized, in conformance with ISO 3696, grade 3.

5.1.2 Lead carrier solution prepared using 2,397 g lead nitrate, 0,5 ml nitric acid solution (5.1.4) and made up to 100 ml with laboratory water (5.1.1).

5.1.3 Barium carrier solution prepared using 2,836 g barium chloride, 0,5 ml nitric acid solution (5.1.4) and made up to 100 ml laboratory water (5.1.1).

5.1.4 Nitric acid solution, $c(HNO_3)$ = 15,8 mol/l, ρ = 1,42 g/ml, $w(HNO_3)$ = 700 g/kg.

5.1.5 Hydrochloric acid solution, $c(HCl)$ = 10,2 mol/l, ρ = 1,16 g/ml, $w(HCl)$ = 320 g/kg.

5.1.6 Sulfuric acid solution, $c(H_2SO_4)$ =9,2 mol/l, ρ = 1,84 g/ml, $w(H_2SO_4)$ = 980 g/kg.

5.1.7 Ammonia solution, $c(NH_3)$ = 13,4 mol/l, ρ = 0,91 g/ml, $w(NH_3)$ = 250 g/kg.

5.1.8 Glacial acetic acid solution, $c(\mathrm{CH_3COOH}) = 16{,}8$ mol/l, $\rho = 1{,}05$ g/ml, $w(\mathrm{CH_3COOH}) = 960$ g/kg.

5.1.9 Ethylenediaminetetraacetic acid (EDTA), $M(\mathrm{EDTA}) = 292{,}2$ g/mol.

NOTE For the purposes of this document, an EDTA solution warmed up within the 60 °C–80 °C temperature range is considered as a hot EDTA solution.

5.1.10 Analytical grade ammonium sulfate, $M((\mathrm{NH_4})_2\mathrm{SO_4}) = 132{,}1$ g/mol.

5.1.11 Scintillation cocktail, commercially available scintillation cocktail, water immiscible and suitable for alpha and beta discrimination (e.g. diisopropylnaphthalene-based cocktails).

5.1.12 ^{226}Ra and ^{228}Ra standard solutions

Radium-226 and ^{228}Ra standard solutions shall be provided with calibration certificates containing at least the activity concentration, measurement uncertainty and statement of compliance with an identified metrological specification.

5.1.13 Alpha emitter standard solution (^{241}Am or ^{210}Po or ^{242}Pu)

The alpha emitter standard solution shall be provided with calibration certificate containing at least the activity concentration, measurement uncertainty and statement of compliance with an identified metrological specification.

5.1.14 Beta emitter standard solution (^{90}Sr/^{90}Y or ^{36}Cl)

The beta emitter standard solution shall be provided with calibration certificate containing at least the activity concentration, measurement uncertainty and statement of compliance with an identified metrological specification.

5.2 Equipment

5.2.1 Standard laboratory equipment.

5.2.2 Analytical balance with accuracy of 0,1 mg.

5.2.3 Hotplate with a magnetic stirrer and a stirring bar.

5.2.4 Centrifuge, with a revolution rate of 3 500 r/min.

5.2.5 pH-meter or pH papers.

5.2.6 Water bath with temperature controller.

5.2.7 Vortex mixer.

5.2.8 Wide-mouth HDPE sample bottles, volumes between 500 ml and 1 l.

5.2.9 Glass beaker, volume of 600 ml.

5.2.10 Centrifuge tubes, volume of 50 ml, made of HDPE or PP.

5.2.11 Precision pipettes, volumes of 50 µl, 5 ml and 10 ml.

5.2.12 Elemental analysis technique for barium and calcium determination.

5.2.13 Liquid scintillation counter, with alpha and beta discrimination option, with thermostated counting chamber and preferably an ultra-low level counter to achieve better detection limits.

5.2.14 Polyethylene scintillation vials, PTFE coated, 20 ml.

PTFE-coated polyethylene vials are recommended because they prevent the diffusion of the cocktail into the wall of the vial. Glass vials exhibit a considerably higher background and generally degrade the achievable alpha and beta discrimination.

5.2.15 Transfer pipette

6 Sampling

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

Collect the sample in accordance with ISO 5667-1. Store the water sample in a plastic bottle (5.2.8) according to ISO 5667-3. If necessary, carry out filtration immediately on collection and before acidification.

Acidification of the water sample minimizes the loss of radioactive material from solution by plating on the wall of the sample container. If filtration of the sample is required, the acidification is performed afterwards, otherwise radioactive material already adsorbed on the particulate material can be desorbed.

If the sample is not acidified, the sample preparation should start as soon as possible and always less than 1 month after the sampling date (ISO 5667-3).

NOTE ^{226}Ra and ^{228}Ra are present in the environment as radionuclides from the ^{238}U and ^{232}Th decay series, as shown in Annex B. Massic activity concentrations of ^{226}Ra and ^{228}Ra can vary widely according to local geological and climatic characteristics[9]. ^{226}Ra massic activity concentration ranges from some mBq/kg in surface waters up to several tens of Bq/kg in some natural groundwaters[10]. ^{228}Ra massic activity concentration ranges from a few mBq/kg in surface waters up to several Bq/kg in some natural groundwaters[10].

7 Instrument set-up and calibration

7.1 Optimization of counting conditions

7.1.1 Preparation of sources

Add 2 ml of barium carrier solution (5.1.3) to two 50 ml volume HDPE or PP centrifuge tubes (5.2.10) using a precision pipette (5.2.11).

Add 3 ml of 100 g/kg ammonium sulfate solution (5.1.10) and 1 ml of ammonia solution (5.1.7) to each solution using precision pipettes (5.2.11) to obtain the barium sulfate precipitates. Separate the precipitates by centrifuging for 5 minutes at 3 500 r/min (5.2.4).

Dissolve the precipitates in 4 ml of hot 0,25 mol/l EDTA solution (5.1.9) using a precision pipette (5.2.11) and agitate the solutions carefully to dissolve and suspend the precipitates into solution. This may require the use of a vortex mixer (5.2.7).

Quantitatively transfer the solutions including partially dissolved barium sulfate precipitate to two 20 ml plastic liquid scintillation vials (5.2.14) using transfer pipettes.

Rinse the HDPE or PP centrifuge tubes with another 1 ml of hot 0,25 mol/l EDTA solution (5.1.9) to ensure that no analyte remains in the tubes.

Add 14 ml of liquid scintillation cocktail (5.1.11) to each plastic liquid scintillation vial (5.2.14) and vortex or shake well until each solution appears homogenous. The addition of the cocktail should be done all at once or in large portions to avoid any reaction with the source solution that could cause a cloudy, inhomogeneous mixture.

Add (10 to 100) Bq of alpha emitter (5.1.13) in the first vial and add (10 to 100) Bq of beta emitter (5.1.14) in the second vial in 50 µl volume solutions using a precision pipette (5.2.11).

Seal and shake the LSC sources until the suspensions appear homogenous.

Clean the vials with an alcohol wipe to remove any static interference.

7.1.2 Optimization process

Select the full range of the instrument from channel 0 to channel 1024.

Count the calibration sources in alpha and beta-discrimination mode (see the manufacturer's instructions) for an appropriate period, at different discrimination factors.

Calculate the number of alpha counts in the beta counting mode and the number of beta counts in the alpha counting mode.

Make a graph of the correlation between spillover and discrimination factor.

The best discrimination factor (working point) is chosen by visual inspection of the graph in order to obtain a beta-spectrum free of alpha counts (see Annex C).

NOTE The determination of an optimum discrimination factor requires two standards, one pure alpha and one pure beta emitter, ^{241}Am or ^{210}Po or ^{242}Pu and ^{90}Sr/^{90}Y or ^{36}Cl, respectively. These radionuclides are used rather than ^{226}Ra and ^{228}Ra, as the latter are accompanied by progeny in-growth, which creates uncertainty in the determination of a discrimination factor.

Select the best discrimination factor to carry out the test method.

Set the lower and upper limits of the analysis windows region using the known emission energies of ^{226}Ra and ^{228}Ra.

7.2 Counting efficiencies of ^{226}Ra and ^{228}Ra

7.2.1 Preparation of ^{226}Ra and ^{228}Ra standard sources

Prepare two blank samples, consisting of barium sulfate precipitates in laboratory water, by the same method as in 7.1.1.

Spike the first blank sample with the ^{226}Ra standard solution (5.1.12).

Spike the second blank sample with the ^{228}Ra standard solution (5.1.12).

Count each spiked sample a sufficient number of times to provide a reasonable data set for counting efficiencies' calculations.

NOTE Spiking of the samples after preparation eliminates the chemical recovery variable.

7.2.2 Determination of counting efficiencies

Calculate the counting efficiencies of ^{226}Ra and ^{228}Ra (see Annex C) using Formulae (1) and (2):

$$\varepsilon_{226Ra} = \frac{n^{S}_{226Ra}}{A_{226Ra} \times m_{s-226Ra} \times e^{-\lambda_{226Ra} \times t_{s-226Ra}}} \qquad (1)$$