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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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# Contents

Page

**Foreword** ..... **iv**
**Introduction** ..... **v**
**1 Scope** ..... **1**
**2 Normative references** ..... **1**
**3 Terms, definitions, symbols and units** ..... **1**
3.1 Terms and definitions ..... 1
3.2 Symbols, definitions and units ..... 2
**4 Principle** ..... **3**
**5 Reagents and equipment** ..... **3**
5.1 Reagents ..... 3
5.2 Equipment ..... 4
**6 Sampling** ..... **5**
**7 Instrument set-up and calibration** ..... **5**
7.1 Optimization of counting conditions ..... 5
7.1.1 Preparation of sources ..... 5
7.1.2 Optimization process ..... 6
7.2 Counting efficiencies of $^{226}$Ra and $^{228}$Ra ..... 6
7.2.1 Preparation of $^{226}$Ra and $^{228}$Ra standard sources ..... 6
7.2.2 Determination of counting efficiencies ..... 6
7.3 Blank sample measurement ..... 7
**8 Procedure** ..... **7**
8.1 General ..... 7
8.2 Separation of radium by precipitation ..... 7
8.3 Purification of radium ..... 8
8.4 Test sample preparation ..... 8
8.5 Measurement ..... 9
8.6 Chemical recovery ..... 9
8.6.1 General ..... 9
8.6.2 Preparation of a QC sample with known $^{226}$Ra and $^{228}$Ra activities ..... 9
8.6.3 Determination of overall counting efficiencies ..... 9
8.6.4 Determination of chemical recovery ..... 9
**9 Quality control** ..... **10**
**10 Expression of results** ..... **10**
10.1 Calculation of massic activities of $^{226}$Ra and $^{228}$Ra at the sampling date ..... 10
10.2 Standard uncertainty ..... 10
10.3 Decision threshold ..... 12
10.4 Detection limit ..... 12
10.5 Confidence limits ..... 12
**11 Interference control** ..... **12**
**12 Test report** ..... **13**
**Annex A** (informative) **Flow chart of the procedure** ..... **14**
**Annex B** (informative) **Decay series relevant to radium isotopes** ..... **15**
**Annex C** (informative) **Set-up parameters and procedure** ..... **16**
**Annex D** (informative) **Validation data** ..... **22**
**Bibliography** ..... **28**

# 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).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

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.

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

**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 $1/\varepsilon_x m_s$ |
| $\varepsilon_x$ | — | Counting efficiency of the analyte |
| $\varepsilon_x^c$ | — | Overall efficiency of the analyte in the quality control sample |
| $\lambda_x$ | 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 |
| $\delta$ | % | Relative bias of the method |
| $\rho$ | 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, $\rho$ = 1,42 g/ml, $w(HNO_3)$ = 700 g/kg.

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

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

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

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

**5.1.9 Ethylenediaminetetraacetic acid (EDTA)**, $M$(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**, $M((NH_4)_2SO_4)$ = 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):

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



$$\varepsilon_{228Ra} = \frac{n^{s}_{228Ra}}{A_{228Ra} \times m_{s-228Ra} \times e^{-\lambda_{228Ra} \times t_{s-228Ra}}} \quad (2)$$

Acceptance limits for counting efficiencies should be defined. The use of control charts according to ISO 7870-2[11] is advisable for this purpose.

Verify counting efficiencies at a periodicity established by the laboratory and whenever changes in materials (e.g. scintillation cocktail) or when maintenance operations are performed on the liquid scintillation counter (5.2.13). A verification or a recalibration is necessary when instrument quality control requirements (see ISO/IEC 17025:2017, 6.4.7) are not met.

### 7.3 Blank sample measurement

Perform blank measurements at a periodicity established by the laboratory (e.g. for every set of samples) and whenever changes in materials (e.g. scintillation cocktail batch) or when maintenance operations are made on the liquid scintillation counter (5.2.13).

Acceptance limits for blank samples should be defined on the basis of the sensitivity desired. Control charts according to ISO 7870-2[11] should be used for this purpose.

It is recommended that blank samples be counted for the same period of time as the test portions.

## 8 Procedure

### 8.1 General

Standard laboratory equipment (5.2.1) is required to carry out the procedure. Prior to the start of the analysis of $^{226}$Ra and $^{228}$Ra in the water sample, it is recommended to determine the calcium and barium contents of the test sample using an elemental analysis technique (5.2.12) (for example, AAS, ICP-OES or ICP-MS), since the volume of EDTA solution (5.1.9) required at the first barium sulfate precipitate dissolution step (8.3 step 1) depends on the calcium and barium contents in the test sample.

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.

### 8.2 Separation of radium by precipitation

Acidify 500 ml of test sample in a glass beaker (5.2.9) to approximately pH 2 using drops of hydrochloric acid solution (5.1.5).

Add 2 ml of lead carrier solution (5.1.2) and 2 ml of barium carrier solution (5.1.3) to the acidified test sample. In case that the total content of barium in the sample solution is 50 mg or higher, it is not necessary to add the barium carrier solution to the acidified test sample.

Add 4 ml of sulfuric acid solution (5.1.6) using a precision pipette (5.2.11) and 5 g of ammonium sulfate (5.1.10) accurately weighed using an analytical balance (5.2.2).

Stir the solution (5.2.3) to ensure that all solids are dissolved, allow the precipitate to form and then let the precipitate settle.

Decant the supernatant without disturbing the precipitate, leaving less than 30 ml of liquid in the glassware.

Quantitatively transfer the precipitate and the limited amount of liquid to a 50 ml HDPE or PP centrifuge tube (5.2.10) rinsing the beaker with laboratory water (5.1.1) to avoid loss of precipitate.

Centrifuge the solution for 5 min at 3 500 r/min (5.2.4).

Decant the excess supernatant carefully without disturbing the precipitate.

## 8.3 Purification of radium

Dissolve the precipitate in 10 ml of hot 0,25 mol/l EDTA solution (5.1.9) and 3 ml of ammonia solution (5.1.7) using precision pipettes (5.2.11). The volume of EDTA solution is changeable, depending on total contents of calcium and barium in the test sample, and is given in Table C.2. Carefully agitate the solution to dissolve the precipitate.

Add 5 ml of 100 g/kg ammonium sulfate solution (5.1.10) using a precision pipette (5.2.11) and adjust the pH to 4,2 to 4,5 (5.2.5) using the glacial acetic acid solution (5.1.8). As the pH is lowered, the precipitate should begin to re-form.

Warm up the solution in the HDPE or PP centrifuge tube (5.2.10) in a water bath at 80 °C for 2 min (5.2.6), cool it with cold tap water, then centrifuge for 5 min at 3 500 r/min (5.2.4). The resulting precipitate is purified barium (radium) sulfate precipitate. Discard the supernatant.

Dissolve the precipitate in 10 ml of hot 0,25 mol/l EDTA solution (5.1.9) and agitate the solution carefully to dissolve the precipitate into solution. This may require the use of a vortex mixer (5.2.7). The volume of EDTA solution is changeable, depending on total content of barium in the test sample, and is given in Table C.3.

Add 3 ml of 100 g/kg ammonium sulfate solution (5.1.10) to the solution using a precision pipette (5.2.11) and adjust the pH to 4,2 to 4,5 (5.2.5) using the glacial acetic acid solution (5.1.8). The precipitate should begin to re-form. Separate the precipitate by centrifugation for 5 min at 3 500 r/min (5.2.4). The precipitate shall not be left overnight and shall not be allowed to dry. The source shall be prepared as soon as the precipitate has been prepared.

## 8.4 Test sample preparation

Wash the precipitate twice with 20 ml of laboratory water (5.1.1), shake well, centrifuge and discard the supernatant to ensure removal of any residual solvents.

Add 3 ml of hot 0,25 mol/l EDTA solution (5.1.9) using a precision pipette (5.2.11) to suspend the precipitate. Make sure to break up the precipitate either through vortex (5.2.7) or suction through a transfer pipette (5.2.15).

Heat the suspension in a water bath at a moderate temperature (30 °C to 50 °C) for a minimum of 30 min (5.2.6).

Vortex the test sample (5.2.7) to ensure the precipitate gets well suspended and no cluster of precipitate is visible in the suspension. The steps of heating of the suspension and vortex of the sample may need to be repeated for obtaining a homogeneous suspension and the absence of cluster of precipitate.

Test sample stability is determined by the suspension of the precipitate. If the precipitate is not well reacted with the EDTA solution, it falls out more easily and quickly. It is suggested to break up the precipitate in the EDTA solution either through vortex, shaking or continued suction and expulsion through a transfer pipette (5.2.15) for stubborn precipitates. Heat is a major factor in the reaction between the precipitate and the EDTA solution. If a good suspension is difficult to achieve, heating in a water bath for a further 30 min followed by vortex/shaking helps force the reaction. This should be repeated until the sample can be held still without any settling occurring within a few minutes.

Quantitatively transfer the solution including partially dissolved $BaSO_4$ precipitate to a 20 ml plastic liquid scintillation vial (5.2.14) using a transfer pipette (5.2.15).

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

Add 14 ml of liquid scintillation cocktail (5.1.11) to the source solution and vortex or shake well until the 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.

Seal and shake the LSC source until the suspension appears homogenous.

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

## 8.5 Measurement

Count the test sample using the chosen optimum counting conditions.

The counting time depends on the test sample count rate and also on precision and detection limit required.

Count the test sample immediately after preparation to avoid extensive in-growth of progeny and the degradation of alpha spectrum due to nucleation of barium sulfate within the scintillation cocktail.

## 8.6 Chemical recovery

### 8.6.1 General

The overall counting efficiency takes into account both chemical recovery and counting efficiency.

### 8.6.2 Preparation of a QC sample with known $^{226}$Ra and $^{228}$Ra activities

Prepare a QC sample spiked with known activities of $^{226}$Ra and $^{228}$Ra.

Perform the test method.

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

### 8.6.3 Determination of overall counting efficiencies

Calculate the overall counting efficiencies of $^{226}$Ra and $^{228}$Ra (see Annex C) using Formulae (3) and (4):

$$\varepsilon^{c}_{226Ra} = \frac{n^{t}_{226Ra}}{A^{t}_{226Ra} \times m_{t-226Ra} \times e^{-\lambda_{226Ra} \times t_{t-226Ra}}} \tag{3}$$

$$\varepsilon^{c}_{228Ra} = \frac{n^{t}_{228Ra}}{A^{t}_{228Ra} \times m_{t-228Ra} \times e^{-\lambda_{228Ra} \times t_{t-228Ra}}} \tag{4}$$

Acceptance limits for overall counting efficiencies should be defined. The use of control charts according to ISO 7870-2[11] is advisable for this purpose.

Verify overall counting efficiencies at a periodicity established by the laboratory and whenever changes in materials (e.g. scintillation cocktail) or when maintenance operations are performed on the liquid scintillation counter (5.2.13). A verification or a recalibration is necessary when instrument quality control requirements (see ISO 17025:2017, 6.4.7) are not met.

### 8.6.4 Determination of chemical recovery

The chemical recovery can be calculated from the ratio of the overall counting efficiency and counting efficiency. It is recommended to calculate the chemical recovery indirectly using this method instead of the conventional gravimetric or tracer techniques due to the chemistry of the procedure and the technique of source preparation used. The addition of $^{133}$Ba as a tracer has previously shown inconsistent recovery, possibly due to the chemistry used during the procedure, and is therefore not suitable. Gravimetric determination requires drying of the precipitate, which causes inconsistent source preparation and is therefore not suitable. It is to be noted that, in this procedure, the chemical recovery is not used for the calculation of massic activities of $^{226}$Ra and $^{228}$Ra in the test sample, but can be used for quality control purpose only.

# 9 Quality control

Measurement methods shall be selected and associated procedures performed by suitably skilled staff under a quality assurance program with quality control.

Maintain confidence in the measurement results by regular use of certified reference materials and participation in interlaboratory comparisons and proficiency testing in accordance with ISO/IEC 17025:2017, Clause 6.

Laboratory procedures shall ensure that laboratory and equipment contamination as well as cross-sample contamination is avoided.

It is recommended that real samples should be analysed with minimum one quality control sample and one blank sample at the same time.

# 10 Expression of results

## 10.1 Calculation of massic activities of $^{226}$Ra and $^{228}$Ra at the sampling date

Calculate the massic activities of $^{226}$Ra and $^{228}$Ra of the test water sample using Formulae (5) and (6):

$$a_{226Ra} = \frac{n_{226Ra}}{\varepsilon^{c}_{226Ra} \times m_S} \times e^{\lambda_{226Ra} \times t_{226Ra}} \tag{5}$$

$$a_{228Ra} = \frac{n_{228Ra}}{\varepsilon^{c}_{228Ra} \times m_S} \times e^{\lambda_{228Ra} \times t_{228Ra}} \tag{6}$$

The massic activities of $^{226}$Ra and $^{228}$Ra are calculated using the overall counting efficiencies.

It is recommended that real samples are analysed with minimum one quality control sample and one blank sample. The analyst should pay attention to the quality control of overall efficiencies of $^{226}$Ra and $^{228}$Ra. It is advised that the analyst prepares control charts for counting efficiency and overall efficiency of $^{226}$Ra and $^{228}$Ra, as shown in Annex C. The validation data of the method are given in Annex D.

To express the result as an activity concentration, $c_a$, in becquerels per litre, multiply the initial result expressed in becquerels per kilogram by the density, $\rho$, in kilogram per litre, of the water sample, i.e. $c_a = \rho a$.

## 10.2 Standard uncertainty

According to ISO/IEC Guide 98-3, the standard uncertainty of the massic activity of $^{226}$Ra is calculated using Formula (7):

$$u(a_{226Ra})^2 = \left(\frac{a_{226Ra}}{n_{226Ra}}\right)^2 \times u(n_{226Ra})^2 + \left(-\frac{a_{226Ra}}{\varepsilon_{226Ra}}\right)^2 \times u(\varepsilon_{226Ra})^2 + \left(-\frac{a_{226Ra}}{m_s}\right)^2 \times u(m_s)^2$$
$$+ (a_{226Ra} \times t_{226Ra})^2 \times u(\lambda_{226Ra})^2 + (a_{226Ra} \times \lambda_{226Ra})^2 \times u(t_{226Ra})^2 \tag{7}$$

where the uncertainty of the counting time is neglected.

The relative uncertainty of the net count rate of $^{226}$Ra in the region of interest is calculated using Formula (8):

$$n^s_{226Ra} = r^s_{g-226Ra} - r_{0-226Ra} \text{ and } u\left(n^s_{226Ra}\right) = \sqrt{\left(\frac{r^s_{g-226Ra}}{T_{s-226Ra}}\right) + \left(\frac{r_{0-226Ra}}{t_{0-226Ra}}\right)} \tag{8}$$

The relative uncertainty of the counting efficiency $u(\varepsilon_{226Ra})$ is calculated using Formula (9):

$$u(\varepsilon_{226Ra})^2 = \left(\frac{\varepsilon_{226Ra}}{n^s_{226Ra}}\right)^2 \times u\left(n^s_{226Ra}\right)^2 + \left(\frac{\varepsilon_{226Ra}}{A_{226Ra}}\right)^2 \times u\left(A_{226Ra}\right)^2 + \left(\frac{\varepsilon_{226Ra}}{m_{s-226Ra}}\right)^2 \times u\left(m_{s-226Ra}\right)^2$$
$$+\left(\varepsilon_{226Ra} \times t_{s-226Ra}\right)^2 \times u\left(\lambda_{226Ra}\right)^2 + \left(\varepsilon_{226Ra} \times \lambda_{226Ra}\right)^2 \times u\left(t_{s-226Ra}\right)^2 \tag{9}$$

The relative uncertainty of the overall counting efficiency is calculated in the same way.

According to ISO/IEC Guide 98-3, the standard uncertainty of the massic activity of $^{228}$Ra is calculated using Formula (10):

$$u\left(a_{228Ra}\right)^2 = \left(\frac{a_{228Ra}}{n_{228Ra}}\right)^2 \times u\left(n_{228Ra}\right)^2 + \left(-\frac{a_{228Ra}}{\varepsilon_{228Ra}}\right)^2 \times u\left(\varepsilon_{228Ra}\right)^2 + \left(-\frac{a_{228Ra}}{m_s}\right)^2 \times u\left(m_s\right)^2$$
$$+\left(a_{228Ra} \times t_{228Ra}\right)^2 \times u\left(\lambda_{228Ra}\right)^2 + \left(a_{228Ra} \times \lambda_{228Ra}\right)^2 \times u\left(t_{228Ra}\right)^2 \tag{10}$$

where the uncertainty of the counting time is neglected.

The relative uncertainty of the net count rate of $^{228}$Ra in the region of interest is calculated using Formula (11):

$$n^s_{228Ra} = r^s_{g-228Ra} - r_{0-228Ra} \text{ and } u\left(n^s_{228Ra}\right) = \sqrt{\left(\frac{r^s_{g-228Ra}}{T_{s-228Ra}}\right) + \left(\frac{r_{0-228Ra}}{t_{0-228Ra}}\right)} \tag{11}$$

The relative uncertainty of the counting efficiency $u(\varepsilon_{228Ra})$ is calculated using Formula (12):

$$u\left(\varepsilon_{228Ra}\right)^2 = \left(\frac{\varepsilon_{228Ra}}{n^s_{228Ra}}\right)^2 \times u\left(n^s_{228Ra}\right)^2 + \left(-\frac{\varepsilon_{228Ra}}{A_{228Ra}}\right)^2 \times u\left(A_{228Ra}\right)^2 + \left(-\frac{\varepsilon_{228Ra}}{m_{s-228Ra}}\right)^2 \times u\left(m_{s-228Ra}\right)^2$$
$$+\left(\varepsilon_{228Ra} \times t_{s-228Ra}\right)^2 \times u\left(\lambda_{228Ra}\right)^2 + \left(\varepsilon_{228Ra} \times \lambda_{228Ra}\right)^2 \times u\left(t_{s-228Ra}\right)^2 \tag{12}$$

The relative uncertainty of the overall counting efficiency is calculated in the same way.

If replicate efficiency determinations are available, average efficiency and its uncertainty should be accordingly calculated.

Mass uncertainty should be estimated based on laboratory experience and can be greater than balance uncertainty since the occurrence of phenomena like sample evaporation should be taken into account.

NOTE The relative uncertainty of the overall counting efficiency is a dominant contributor to the standard uncertainty measurement result.

### 10.3 Decision threshold

The decision threshold, $a^*$, is obtained using Formula (13):

$$a^* = k_{1-\alpha}\,\tilde{u}(0) = k_{1-\alpha}\,w\sqrt{\frac{r_{0-x}}{T_{s-x}} + \frac{r_{0-x}}{t_{0-x}}} \tag{13}$$

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

### 10.4 Detection limit

The detection limit, $a^\#$, is calculated using Formula (14):

$$a^\# = a^* + k_{1-\beta}\tilde{u}\left(a^\#\right) = a^* + k_{1-\beta}\sqrt{w^2\left[\frac{a^\#/w + r_{0-x}}{T_{s-x}} + \frac{r_{0-x}}{t_{0-x}}\right] + a^{\#2}u_{\mathrm{rel}}^2(w)} \tag{14}$$

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

The detection limit can be calculated by solving Formula (14) for $a^\#$ or, more simply, by iteration with a starting approximation $a^\# = 2a^*$.

When taking $\alpha = \beta$, then $k_{1-\alpha} = k_{1-\beta} = k'$, the solution of Formula (14) is given by Formula (15):

$$a^\# = \frac{2a^* + \left(k'^2 w\right)/T_{s-x}}{1 - k'^2 u_{\mathrm{rel}}^2(w)} \tag{15}$$

### 10.5 Confidence limits

In accordance with ISO 11929, the lower, $a^\lhd$, and upper, $a^\rhd$, limits of the confidence interval are calculated using Formulae (16) and (17):

$$a^\lhd = a - k_p\,u(a); \quad p = \omega(1-\gamma/2) \tag{16}$$

$$a^\rhd = a + k_q\,u(a); \quad q = 1 - \omega\gamma/2 \tag{17}$$

where

$$\omega = \Phi\left[\frac{y}{u(y)}\right]$$

in which $\Phi$ is the distribution function of the standardized normal distribution.

$\omega$ = 1 may be set if $a \geq 4u(a)$ and Formula (18) applies:

$$a^{\lhd,\rhd} = a \pm k_{1-\gamma/2}\,u(a) \tag{18}$$

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

## 11 Interference control

High selectivity of the method is provided by chemical separation and the ability of pulse shape analysis afforded by liquid scintillation counting. However, possible interferences cannot be excluded.

If the solid precipitate is not completely suspended in EDTA, alpha peak broadening can occur due to the inability of alpha particles contained within unsuspended precipitate to fluoresce efficiently.

## 12 Test report

The test report shall conform to requirements and shall contain at least the following information:

a) the test method used, with reference to this document, i.e. ISO 22908:2020;

b) all information necessary for complete identification of the sample;

c) units in which the results are expressed;

d) test result, $a \pm u(a)$ or $a \pm U$, with the associated $k$ value.

Complementary information can be provided such as:

e) probabilities $\alpha$, $\beta$ and $(1 - \gamma)$;

f) decision threshold and the detection limit;

g) depending on the customer request there are different ways to present the result:

— when the massic activity, $a$, is compared with the decision threshold the result of the measurement should be expressed as $\leq a^*$ when the result is less than the decision threshold;

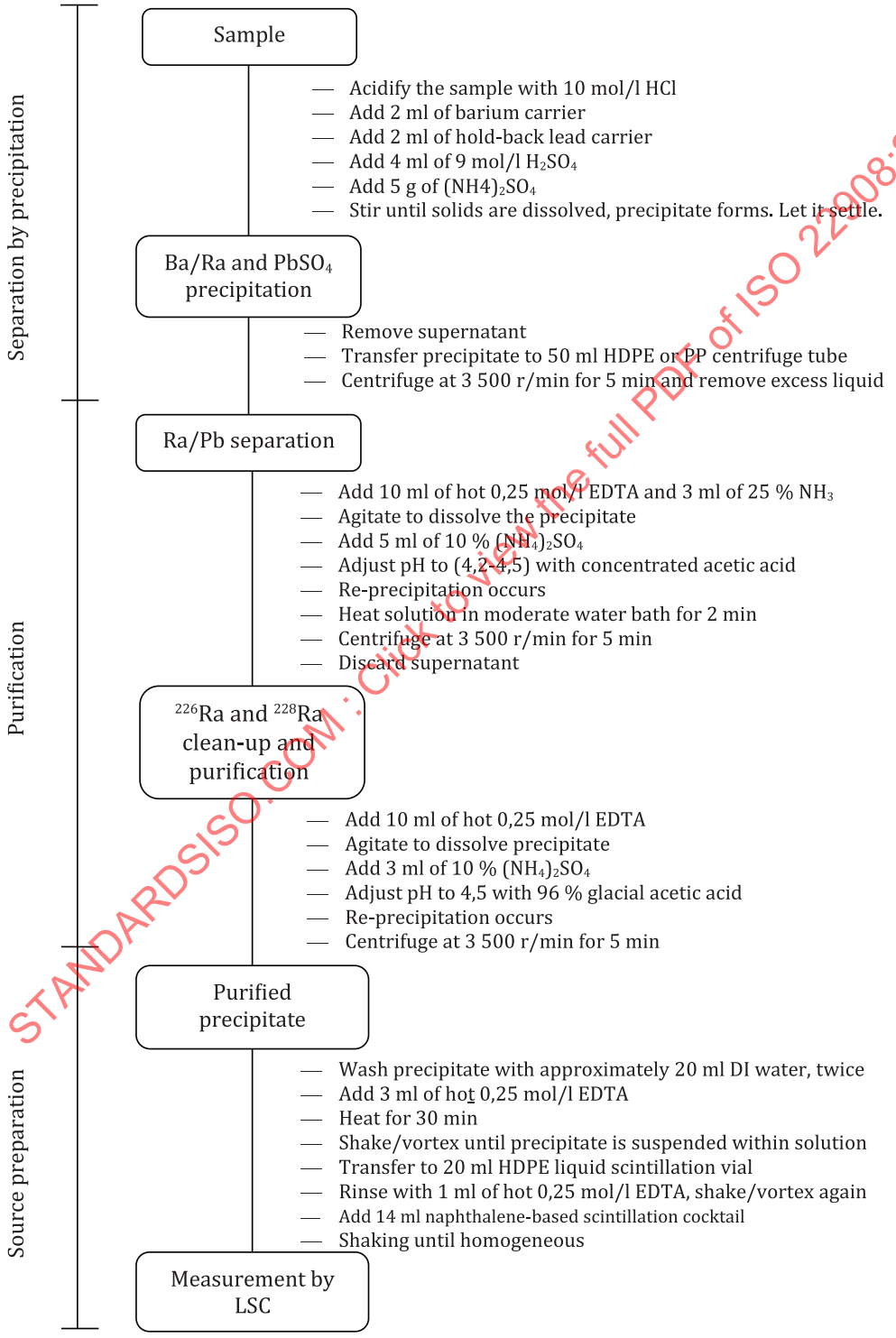
— when the massic activity, $a$, is compared with the detection limit, the result of the measurement can be expressed as $\leq a^{\#}$ when the result is below the detection limit;

— if the detection limit exceeds the guideline value, it shall be documented that the method is not suitable for the measurement purpose.

h) mention of any relevant information likely to affect the results.

# Annex A
(informative)

# Flow chart of the procedure



# Annex B
(informative)

# Decay series relevant to radium isotopes

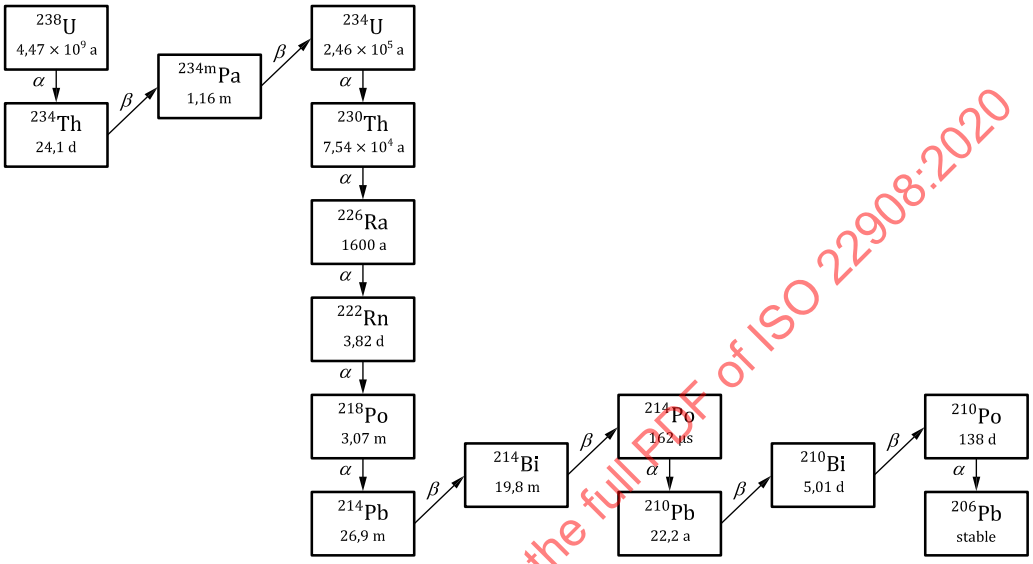



**Figure B.1 — $^{226}$Ra is a member of the $^{238}$U decay series**

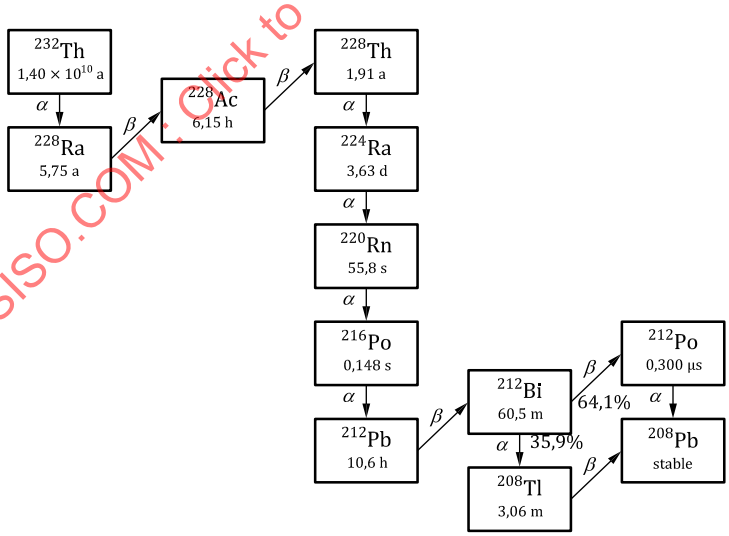



**Figure B.2 — $^{224}$Ra and $^{228}$Ra are members of the $^{232}$Th decay series**

# Annex C
(informative)

# Set-up parameters and procedure

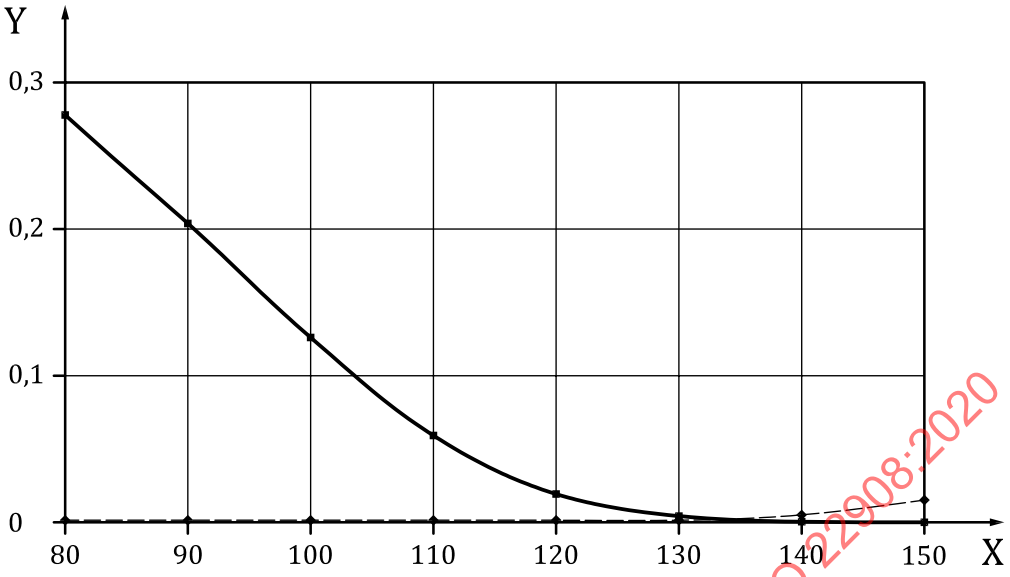
## C.1 Instrument set-up and calibration

Table C.1 shows results of alpha/beta discrimination setting using a range of discrimination factors from 80 to 150 and for a counting time of 60 min at each discrimination factor (see 7.1).

**Table C.1 — Results of optimum alpha/beta discrimination setting**

| Discrimination factor | Alpha counts | | Total counts | Alpha spillover | Beta counts | | Total counts | Beta spill-over |
|---|---|---|---|---|---|---|---|---|
| | Alpha MCA | Beta MCA | | | Alpha MCA | Beta MCA | | |
| 80 | 4 596 | 7,49 | 4 603 | 0,277 783 | 10 193 | 26 500 | 36 693 | 0,001 628 |
| 90 | 4 627 | 6,43 | 4 633 | 0,204 105 | 7 823 | 30 505 | 38 328 | 0,001 388 |
| 100 | 4 622 | 6,94 | 4 628 | 0,126 225 | 5 032 | 34 832 | 39 864 | 0,001 499 |
| 110 | 4 608 | 8,86 | 4 617 | 0,059 216 | 2 514 | 39 945 | 42 459 | 0,001 919 |
| 120 | 4 591 | 10,1 | 4 601 | 0,019 608 | 909 | 45 474 | 46 384 | 0,002 201 |
| 130 | 4 609 | 11,8 | 4 621 | 0,004 677 | 231 | 49 241 | 49 472 | 0,002 553 |
| 140 | 4 606 | 25,8 | 4 632 | 0,000 899 | 45,6 | 50 674 | 50 720 | 0,005 564 |
| 150 | 4 546 | 69,6 | 4 616 | 0,000 223 | 11,3 | 50 783 | 50 795 | 0,015 072 |

The obtained values are then graphed to determine the optimum discrimination factor. The correlation between spillover and discrimination factor is shown in Figure C.1.




**Key**

X discrimination factor

Y % spillover

_____ alpha spillover

_ _ _ _ _ _ beta spillover

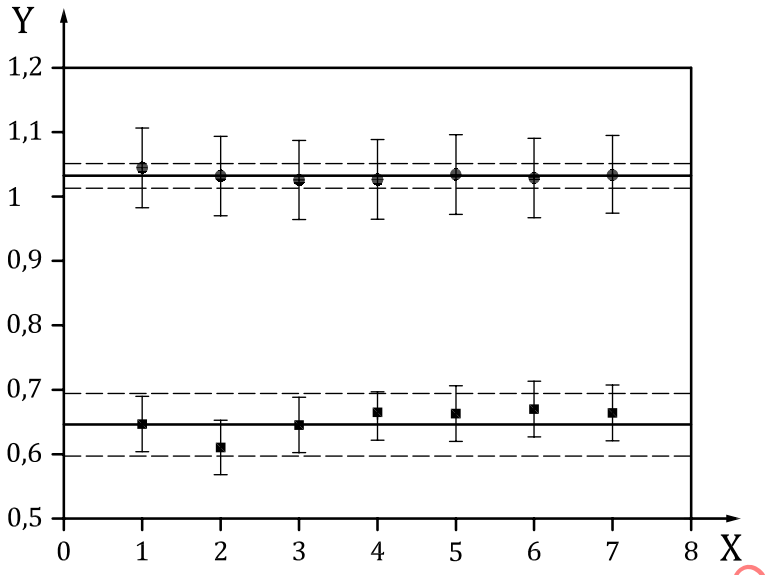
**Figure C.1 — Correlation between spillover and discrimination factor**

The optimum discrimination factor for this laboratory was calculated to be 130. The optimum discrimination factor has to be determined at each laboratory performing this procedure.

The lower and upper limits of the regions-of-interest are set using the known emission energies of $^{226}$Ra and $^{228}$Ra, approximately (4 500 to 5 000) keV and (0 to 50) keV, respectively. When using channels in the MCA, this converts to approximately (600 to 640) keV and (50 to 300) keV, respectively. Each liquid scintillation counter should be calibrated for radium analysis, including setting of regions, prior to any analysis.

## C.2 Counting efficiencies

Each spiked sample was counted seven times to provide a reasonable data set for the $^{226}$Ra and $^{228}$Ra counting efficiencies' calculations (see 7.2). Counting efficiencies' calculations results are represented on a control chart in Figure C.2.




**Key**

| | |
|---|---|
| X | number of run |
| Y | counting efficiency |
| ● | $^{226}$Ra counting efficiency |
| ■ | $^{228}$Ra counting efficiency |
| ——— | mean of counting efficiency |
| – – – | control line of counting efficiency (±3 $\sigma$) |

**Figure C.2 — Control chart for counting efficiencies of $^{226}$Ra and $^{228}$Ra**

The counting efficiencies were determined to be 1,03 and 0,646 with 6 % and 10 % of relative standard deviation for $^{226}$Ra and $^{228}$Ra respectively.

## C.3 Procedure

The volume of 0,25 mol/l EDTA solution (5.1.9) required at the first barium sulfate precipitate dissolution step (8.3 step 1) is given in Table C.2, as a function of the calcium and barium contents in the test sample.

**Table C.2 — Required volume of 0,25 mol/l EDTA solution (5.1.9) as a function of calcium and barium contents at the first dissolution step**

| Contents of calcium and barium in the test sample (mg) | | Volume of 0,25 mol/l EDTA solution (ml) |
|---|---|---|
| Calcium | Barium | |
| 0 | 50 | 15 |
| 0 | 75 | 26 |
| 0 | 100 | 35 |
| 300 | 30 | 52 |
| 400 | 30 | 65 |
| 500 | 30 | 75 |

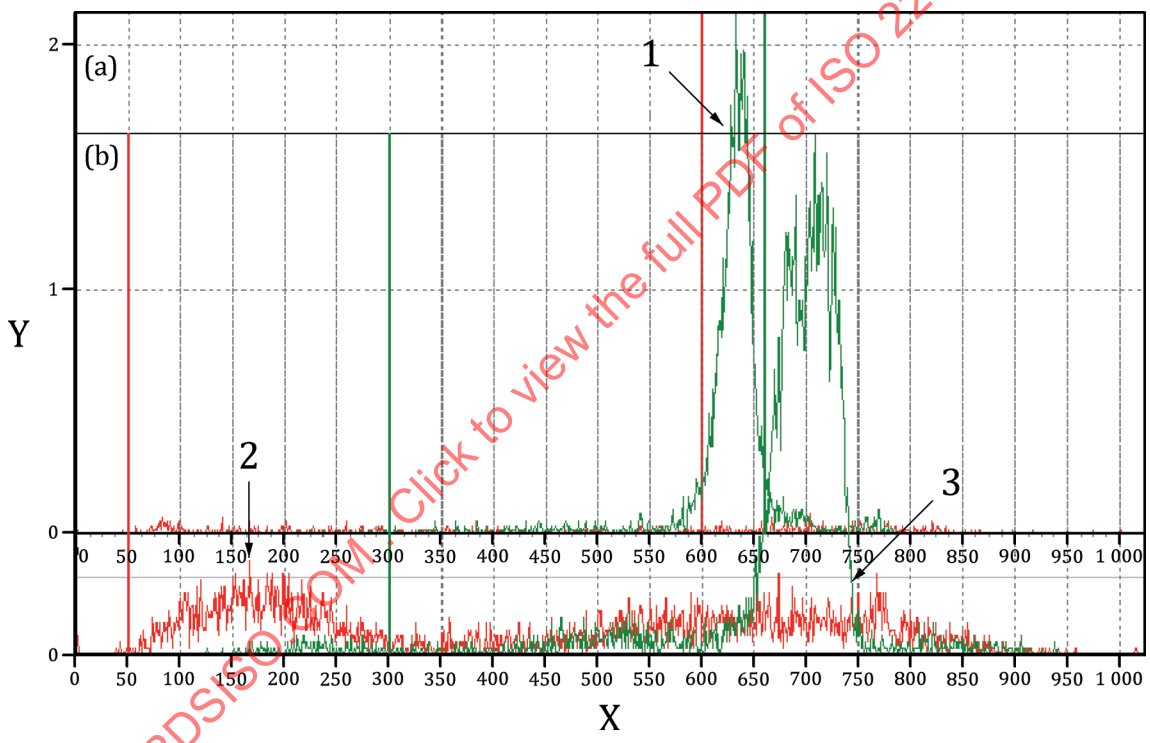
The volume of 0,25 mol/l EDTA solution (5.1.9) required at the second barium sulfate precipitate dissolution step (8.3 step 4) is given in Table C.3, as a function of the barium content in the test sample.

**Table C.3 — Required volume of 0,25 mol/l EDTA solution (5.1.9) as a function of barium content at the second dissolution step**

| Content of barium in the sample (mg) | Volume of 0,25 mol/l EDTA solution (ml) |
|---|---|
| 50 | 10 |
| 75 | 15 |
| 100 | 25 |

## C.4 Typical spectra

The negligible overlap of the $^{226}$Ra [Figure C.3 (a)] and $^{228}$Ra [Figure C.3 (b)] spectra is shown in Figure C.3 with their respective counting windows, as shown in spectral analysis software. The alpha peaks in the $^{228}$Ra spectrum are $^{228}$Ra decay progeny, i.e. alpha emitting progenies such as $^{228}$Th and $^{224}$Ra from in-growing $^{228}$Ac.

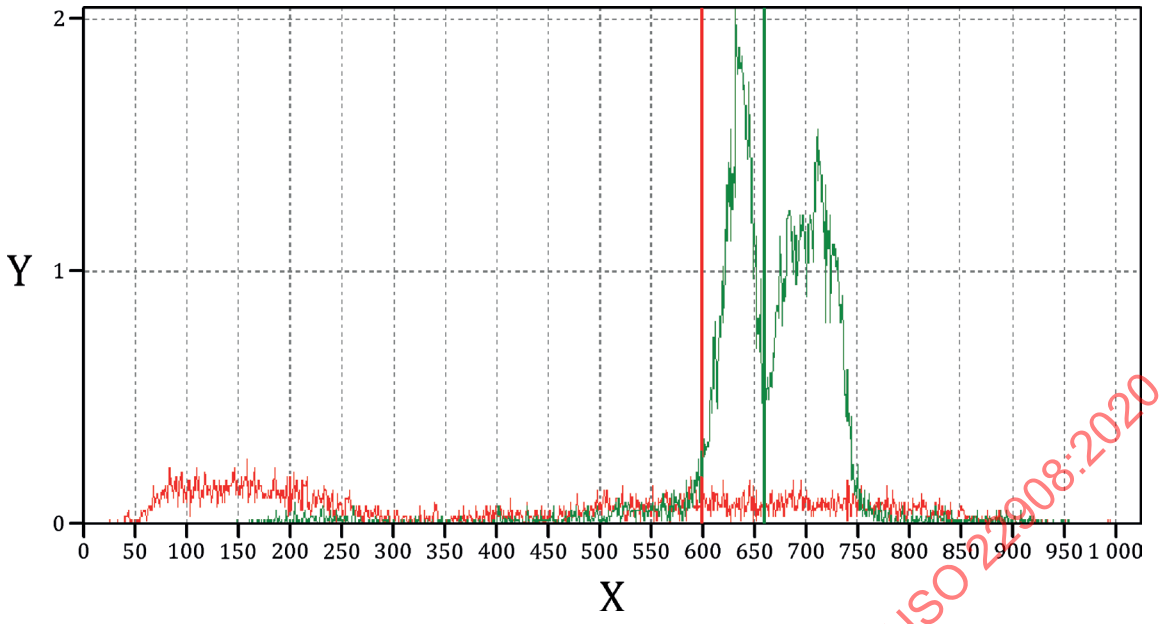



**Key**

X channel number
Y counts (1/s)
1 Alpha peak of $^{226}$Ra
2 low $\beta$-energy emitting $^{228}$Ra
3 Alpha peak of $^{228}$Ra decay progeny

**Figure C.3 — Negligible spectral overlap of (a) $^{226}$Ra spectrum and (b) $^{228}$Ra spectrum**

A typical LSC spectrum of a test water sample, containing both $^{226}$Ra and $^{228}$Ra, is given, as shown in the spectral analysis software, in Figure C.4.




**Key**

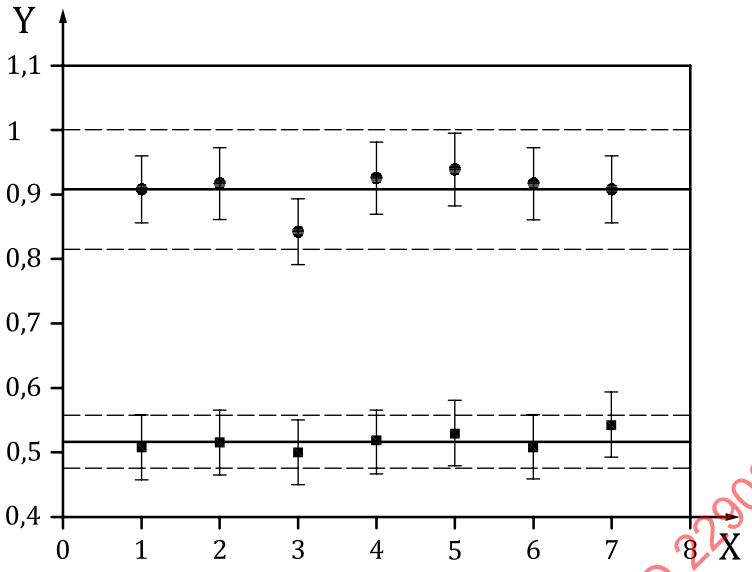
X channel number

Y counts (1/s)

**Figure C.4 — Typical spectrum of test water sample, containing both $^{226}$Ra and $^{228}$Ra**

## C.5 Overall counting efficiencies and chemical recoveries

The procedure was carried out seven times to provide a reasonable data set for the $^{226}$Ra and $^{228}$Ra overall counting efficiencies' calculations (see 8.6). Overall counting efficiencies' calculations results are represented on a control chart in Figure C.5.




**Key**

| | |
|---|---|
| X | number of run |
| Y | overall counting efficiency |
| ● | $^{226}$Ra counting efficiency |
| ■ | $^{228}$Ra counting efficiency |
| —— | mean of counting efficiency |
| _ _ _ | control line of counting efficiency (±3 σ) |

**Figure C.5 — Control chart for overall efficiencies of $^{226}$Ra and $^{228}$Ra**

The overall counting efficiencies were determined to be 0,908 and 0,516 with 6,6 % and 9,9 % of relative standard deviation for $^{226}$Ra and $^{228}$Ra respectively.

The chemical recoveries of $^{226}$Ra and $^{228}$Ra can be indirectly calculated from the counting efficiencies and overall counting efficiencies data. They are in the range (78 to 90) %.

# Annex D
(informative)

# Validation data

## D.1 General

For the validation of the procedure, four types of spiked water samples with different activity ratios of $^{228}Ra/^{226}Ra$, used as quality control samples, and a blank were prepared. One of the quality control samples was used for testing the reproducibility and the other three quality control samples were used for repeatability and trueness testing. The repeatability, reproducibility and trueness of the procedure were tested according to ISO 5725-1[12], ISO 5725-2[13], ISO 5725-4I[14] and ISO 21748[15]. Five laboratories from five different countries participated to the reproducibility testing. The Optiphase Hisafe 3®[1)] scintillation cocktail was used for the repeatability testing.

The following parameters were established via the validation process:

— Linearity, range of measurement;

— Repeatability;

— Reproducibility;

— Precision;

— Trueness;

— Detection limit;

— Uncertainty.

Quality control samples were run to ensure the accuracy of both the method and the instrumentation. Blank samples were run to monitor reagent radiological purity and ensure that there was no cross-contamination during the procedure. This also included the monitoring of the background to ensure that there was no excess background activity being counted by the instrumentation that could affect the results. All validation measurement results were subjected to a set of statistical tests for outlier detection (Dixon, Grubbs, Skewness, Kurtosis).

## D.2 Linearity, range of measurement

The linear range of measurement of the method was tested by measuring the $^{226}Ra$ and $^{228}Ra$ activities in laboratory water at activity concentrations in the range (0 to 100) Bq/l for both $^{226}Ra$ and $^{228}Ra$ [coverage factor ($k$ = 2)]. Results of measurements as a function of reference values are shown in Figure D.1.



1) Optiphase Hisafe 3 is an example of a suitable product available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of this product.