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**Water quality — Radium-226 —**

**Part 1:  
Test method using liquid scintillation  
counting**

*Qualité de l'eau — Radium 226 —*

*Partie 1: 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.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

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.

ISO 13165-1 was prepared by Technical Committee ISO/TC 147, *Water quality*, Subcommittee SC 3, *Radioactivity measurements*.

ISO 13165 consists of the following parts, under the general title *Water quality — Radium-226*:

— *Part 1: Test method using liquid scintillation counting*

— *Part 2: Test method using emanometry*

The following part is under preparation:

— *Part 3: Test method using coprecipitation and gamma-spectrometry*

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## Introduction

Radioactivity from several naturally occurring and human-made sources is present throughout the environment. Thus, water bodies (surface waters, groundwaters, sea waters) can contain radionuclides of natural and artificial origin (i.e. human-made).

- a) Natural radionuclides, including potassium-40, and those of the thorium and uranium decay series, in particular radium-226, radium-228, uranium-234, uranium-238, lead-210, can be found in water for natural reasons (e.g. desorption from the soil and wash-off by rain water) or release from technological processes involving naturally occurring radioactive materials (e.g. the mining and processing of mineral sands or phosphate fertilizer production and use).
- b) Human-made radionuclides such as transuranium elements (americium, plutonium, neptunium, curium), tritium, carbon-14, strontium-90 and gamma-emitting radionuclides can also be found in natural waters as they can be authorized to be routinely released into the environment in small quantities in the effluent discharged from nuclear fuel cycle facilities and following their use in unsealed form in medicine or industry. They are also found in water due to fallout from past explosions in the atmosphere of nuclear devices and the accidents at Chernobyl and Fukushima.

Drinking water can thus contain radionuclides at activity concentrations which present a risk to human health. In order to assess the quality of drinking-water (including mineral waters and spring waters) with respect to its radionuclide content and to provide guidance on reducing health risks by taking measures to decrease radionuclide activity concentrations, water resources (groundwater, river, lake, sea, etc.) and drinking water are monitored for their radioactivity content as recommended by the World Health Organization (WHO).

An International Standard on a test method of radium-226 activity concentrations in water samples is justified for test laboratories carrying out these measurements, which are sometimes required by national authorities, as laboratories may have to obtain a specific accreditation for radionuclide measurement in drinking water samples.

Radium-226 activity concentration can vary widely according to local geological and climatic characteristics and ranges from 0,001 Bq l<sup>-1</sup> in surface waters up to 50 Bq l<sup>-1</sup> in natural groundwaters; the guidance level for radium-226 in drinking water as recommended by WHO is 1 Bq l<sup>-1</sup> (Reference [Z]).

**NOTE** The guidance level is the activity concentration with an intake of 2 l day<sup>-1</sup> of drinking water for 1 year that results in an effective dose of 0,1 mSv year<sup>-1</sup> 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.

This International Standard is one of a series on determination of the activity concentration of radionuclides in water samples.

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# Water quality — Radium-226 —

## Part 1:

### Test method using liquid scintillation counting

**WARNING** — Persons using this part of ISO 13165 should be familiar with normal laboratory practice. This part of ISO 13165 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 part of ISO 13165 be carried out by suitably qualified staff.

## 1 Scope

This part of ISO 13165 specifies the determination of radium-226 ( $^{226}\text{Ra}$ ) activity concentration in non-saline water samples by extraction of its daughter radon-222 ( $^{222}\text{Rn}$ ) and its measurement using liquid scintillation counting.

Radium-226 activity concentrations which can be measured by this test method utilizing currently available liquid scintillation counters goes down to  $50 \text{ mBq l}^{-1}$ . This method is not applicable to the measurement of other radium isotopes.

## 2 Normative references

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The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. 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, *General requirements for the competence of testing and calibration laboratories*

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

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

## 3 Symbols, definitions 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.

- |       |  |
|-------|--|
| $a$   | massic activity of the sample at the measuring time, in becquerels per gram                              |
| $a_S$ | massic activity of the $^{226}\text{Ra}$ standard solution at the measuring time, in becquerels per gram |
| $a^*$ | decision threshold for the massic alpha-activity, in becquerels per gram                                 |

|   |  |
|---|--|
| $a^{\#}$                                | detection limit for the massic alpha-activity, in becquerels per gram                                    |
| $a^{\triangleleft}, a^{\triangleright}$ | lower and upper limits of the confidence interval, in becquerels per gram                                |
| $c_A$                                   | activity concentration, in becquerels per litre  |
| $m$                                     | mass of the test sample, in grams  |
| $m_1$                                   | mass of initial sample subject to heating or possibly concentration, in grams                            |
| $m_2$                                   | mass of heated or concentrated sample, in grams  |
| $m_3$                                   | mass of heated or concentrated sample transferred in the vial, in grams                                  |
| $m_S$                                   | mass of $^{226}\text{Ra}$ standard solution used for the preparation of the calibration sample, in grams |
| $r_0$                                   | blank sample count rate in the alpha-window, in reciprocal seconds                                       |
| $r_g$                                   | sample gross count rate in the alpha-window, in reciprocal seconds                                       |
| $r_S$                                   | count rate of the calibration sample in the alpha-window, in reciprocal seconds                          |
| $t_0$                                   | blank sample counting time, in seconds   |
| $t_g$                                   | sample counting time, in seconds   |
| $t_S$                                   | calibration sample counting time, in seconds   |
| $u(a)$                                  | standard uncertainty associated with the measurement result; in becquerels per gram                      |
| $U$                                     | expanded uncertainty, calculated using $U = ku(a)$ , with $k = 1, 2, \dots$ in becquerels per gram       |
| $w$                                     | factor equal to $1/\varepsilon m$  |
| $\varepsilon$                           | alpha-efficiency   |
| $\rho$                                  | density, in grams per litre  |

## 4 Principle

$^{226}\text{Ra}$  massic activity is determined by liquid scintillation counting of daughter  $^{222}\text{Rn}$  at isotopic equilibrium (99,56 %) reached 30 d after the preparation of the sample. The  $^{222}\text{Rn}$  is extracted from aqueous solution by means of a scintillation cocktail immiscible with water inside the scintillation vial (References [1]–[4]).

The aqueous sample is acidified, heated and, if possible, concentrated by slow evaporation in order to desorb  $^{222}\text{Rn}$  and to achieve a better detection limit. The concentrated aqueous sample is transferred into a radon-tight scintillation vial and a water-immiscible scintillation cocktail is added.

After 30 d, the sample is measured by liquid scintillation counting (LSC) applying alpha and beta discrimination: only alpha-emission of  $^{222}\text{Rn}$  and that of its short lived progeny ( $^{218}\text{Po}$ ,  $^{214}\text{Po}$ ) are considered, as this counting condition ensures a better detection limit.

## 5 Reagents and equipment

### 5.1 Reagents

All reagents shall be of recognized analytical grade and, except for 5.1.3 and 5.1.4, shall not contain any detectable alpha- and beta-activity.



**5.1.1 Laboratory water**, distilled or deionized, complying with ISO 3696, grade 3.

Deionized water can contain detectable amounts of  $^{222}\text{Rn}$  and short-lived daughters. It is therefore strongly recommended that water be boiled under vigorous stirring and allowed to stand for 1 day before use. Otherwise, flux it with nitrogen for about 1 h for 2 l.

**5.1.2 Nitric acid**,  $c(\text{HNO}_3) = 15,8 \text{ mol l}^{-1}$ ,  $\rho = 1,42 \text{ g ml}^{-1}$ , mass fraction  $w(\text{HNO}_3) = 70 \%$ .

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

**5.1.4  $^{226}\text{Ra}$  standard solution**

$^{226}\text{Ra}$  standard solutions shall be provided with calibration certificates containing at least the activity concentration, measurement uncertainty and/or statement of compliance with an identified metrological specification.

## 5.2 Equipment

**5.2.1 Balance.**

**5.2.2 Hotplate with magnetic stirrer and stirring bar.**

**5.2.3 pH-meter.**

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**5.2.4 Wide-mouth HDPE sample bottles**, volumes between 100 ml and 500 ml.

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**5.2.5 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.

**5.2.6 Polyethylene scintillation vials**, PTFE coated, 20 ml.

PTFE-coated polyethylene vials are the best choice, since they prevent both the diffusion of the cocktail into the wall of the vial and the absorption of radon from the environment. Glass vials exhibit a considerably higher background and generally degrade the achievable alpha and beta discrimination.

## 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 (from 0,1 l to 1 l) in a plastic bottle (5.2.4) according to ISO 5667-3. When preconcentration is desired, acidify the sample to pH 1 to pH 3 with  $\text{HNO}_3$  (5.1.2). 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).

## 7 Instrument set-up and calibration

### 7.1 Preparation of calibration sources

Transfer an accurately known mass,  $m_S$ , of the  $^{226}\text{Ra}$  standard solution (5.1.4) into a scintillation vial (5.2.6). Let the massic activity at the measuring time be  $a$ . Dilute with water (5.1.1) to the previously chosen volume, e.g. 10 ml. Add the scintillation cocktail (5.1.3), e.g. 10 ml.

Store the sample for at least 30 d to allow the achievement of secular equilibrium.

Ensure that the diluted standard solutions are between pH 0 and pH 2.

Store samples so as to ensure optimum preservation. Storage in the dark is recommended. Select a single generally applicable temperature in order not to affect distribution coefficients. This temperature shall be consistent with the characteristics of the scintillation cocktail (5.1.3, see manufacturer's instructions). Generally, if possible, storage in the scintillation chamber at around 15 °C is suitable.

### 7.2 Optimization of counting conditions

Set the alpha-counting window so that the energies of all the three alpha-emitters present in the cocktail phase:  $^{222}\text{Rn}$  (5,49 MeV);  $^{218}\text{Po}$  (6,00 MeV); and  $^{214}\text{Po}$  (7,69 MeV); are covered.

Count the  $^{226}\text{Ra}$  calibration sample in alpha and beta-discrimination mode (see manufacturer instructions) for an appropriate period, under different discriminator settings.

The best discriminator setting (working point) is chosen by visual inspection of the spectra in order to obtain an alpha-spectrum free of beta counts (see Annex A).

NOTE Since no water is present in the scintillation cocktail phase, the quenching is low and constant, while the alpha and beta discrimination is quite sharp.

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### 7.3 Detection efficiency

Let the counting rate be  $r_S$  for the counts of the  $^{226}\text{Ra}$  calibration sample in the alpha-window, as measured with the previously defined best discriminator setting.

Determine the alpha-efficiency:

$$\varepsilon = \frac{r_S - r_0}{a m_S} \quad (1)$$

Acceptance limits for efficiency should be defined.

NOTE The alpha-efficiency includes both counting and extraction efficiency. Usual values are in the range 200 % to 300 % ( $^{222}\text{Rn}$ ,  $^{218}\text{Po}$ ,  $^{214}\text{Po}$  alpha-emissions).

It is advisable to check the linearity of the method. Assess the efficiency using calibration samples whose activities cover the whole working range.

A more accurate estimate of efficiency can be obtained by preparing and measuring a sufficient number of calibration samples.

Verify 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 scintillation counter (5.2.5). A verification or a recalibration is necessary when instrument quality control requirements (see Clause 9) are not met.

## 7.4 Blank sample preparation and measurement

Acidify a laboratory water sample to between pH 0 and pH 2. Transfer the chosen quantity, e.g. 10 ml, into the scintillation vial (5.2.6). Add the scintillation cocktail (5.1.3), e.g. 10 ml, and mix thoroughly.

Store the blank sample for 30 d and then count it using the chosen optimum counting conditions. Let the measured counting rate in the alpha-window be  $r_0$ . If a preconcentration procedure is normally employed, prepare blank samples by the same method.

Acceptance limits for blank samples should also be defined on the basis of the sensitivity desired. The use of control charts (see ISO 8258[5]) is advisable for this purpose.

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

Perform blank measurements at a periodicity established by the laboratory (e.g. monthly) and whenever changes in materials (e.g. scintillation cocktail batch) or when maintenance operations are made on the scintillation counter (5.2.5). Verification or a recalibration is necessary when instrument quality control requirements (see Clause 9) are not met.

## 8 Procedure

### 8.1 Direct counting

Transfer a weighed (5.2.1) aliquot ( $m_1$ ) of the initial water sample (approximately 50 g) into a beaker. If the sample has not yet been acidified, adjust to pH 0 and pH 2 using nitric acid (5.1.2) and verify with a pH-meter (5.2.3).

Heat to approximately 80 °C under stirring for 30 min in a covered flask, to allow degassing of dissolved  $^{222}\text{Rn}$ . Allow the sample to cool and reweigh it to account for losses due to evaporation ( $m_2$ ).

### 8.2 Thermal preconcentration

Thermal preconcentration can be used when soft waters are examined (e.g. dry residue <500 mg l<sup>-1</sup>, as in most drinking waters) in order to decrease the detection limit of the method. Hard waters can give rise to salt precipitations which are difficult to dissolve completely.

Transfer a weighed (5.2.1) aliquot ( $m_1$ ) of the initial water sample (about 200 g) into a beaker. If the sample has not yet been acidified, adjust to between pH 1 and pH 3 with nitric acid (5.1.2) and verify with a pH-meter (5.2.3).

Slowly evaporate the sample on a hotplate (5.2.2) down to about 20 g. Allow the sample to cool to room temperature and weigh the concentrated sample ( $m_2$ ). Adjust the concentrated sample to between pH 0 and pH 2.

No precipitation should be observable, otherwise direct counting (8.1) or smaller preconcentration factors are to be applied.

If unknown, only a rough evaluation of the dry residue is needed. Any commonly used technique can be adopted.

**NOTE** The volume of acid required is small (normally about 0,1 ml of concentrated HNO<sub>3</sub> in 200 g sample when preconcentration is adopted) and its mass can be neglected.