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Water quality — Radium-226~~ —~~ —

Part 4:
Test method using alpha spectrometry

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Qualité de l'eau — Radium 226 —

Partie 4: Méthode d'essai par spectrométrie alpha

FDIS stage

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO ~~documents~~document 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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This document was prepared by Technical Committee ~~*[or Project 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

Radionuclides are present throughout the environment; thus, water bodies (e.g. surface waters, ground waters, sea waters) contain radionuclides, which can be of either natural or anthropogenic origin.

- ~~—~~Naturally-occurring radionuclides, including ^{3}H, ^{14}C, ^{40}K and those originating from the thorium and uranium decay series, in particular ^{210}Pb, ^{210}Po, ^{222}Rn, ^{226}Ra, ^{228}Ra, ^{227}Ac, ^{232}Th, ^{231}Pa, ^{234}U and ^{238}U, can be found in water bodies due to either natural processes (e.g. desorption from the soil and runoff by rain water) or released from technological processes involving naturally occurring radioactive materials (e.g. mining, mineral processing, oil, gas and coal production, water treatment, and the production and use of phosphate fertilisers).

- ~~—~~Anthropogenic radionuclides such as ^{55}Fe, ^{59}Ni, ^{63}Ni, ^{90}Sr, ^{99}Tc, transuranic elements (e.g. Np, Pu, Am, Cm), and some gamma emitting radionuclides, such as ^{60}Co and ^{137}Cs, can also be found in natural waters. Small quantities of anthropogenic radionuclides can be discharged from nuclear facilities to the environment as a result of authorized routine releases. The radionuclides present in liquid effluents are usually controlled before being discharged to the environment[1~~[1]~~] and water bodies. Anthropogenic radionuclides used for medical and industrial applications can be released to the environment after use. Anthropogenic radionuclides are also found in waters due to contamination from fallout resulting from above-ground nuclear detonations and accidents such as those that have occurred at the Chornobyl and Fukushima nuclear facilities.

Radionuclide activity concentrations in water bodies can vary according to local geological characteristics and climatic conditions and can be locally and temporally enhanced by releases from nuclear facilities during planned, existing, and emergency exposure situations[2][3~~,[2][3]~~]. Some drinking water sources can thus contain radionuclides at activity concentrations that can present a human health risk. The World Health Organization (WHO) recommends to routinely monitor radioactivity in drinking waters[4~~[4]~~] and to take proper actions when needed to minimize the health risks.

National regulations usually specify the activity concentration limits that are authorized in drinking waters, water bodies, and liquid effluents to be discharged to the environment. These limits can vary for planned, existing~~,~~ and emergency exposure situations. As an example, during either a planned or existing situation, the WHO guidance level for ^{226}Ra in drinking water is 1 Bq·l^{-1}[4~~[4],~~], see NOTES 1 and 2. Compliance with these limits is assessed by measuring radioactivity in water samples and by comparing the results obtained, with their associated uncertainties, as specified by ISO/IEC Guide 98-3[5~~[5]~~] and ISO 5667-20[6~~[6].~~].

NOTE 1 If the value is not specified in Annex 6 of Reference [4~~[4],~~], the value has been calculated using the formula provided in Reference [4~~[4]~~] and the dose coefficient data from References [7~~[7]~~] and [8~~[8].~~].

NOTE 2 The guidance level calculated in Reference [4~~[4]~~] is the activity concentration that results in an effective dose of 0,1 mSv·a^{-1} to members of the public for an intake of 2 l·d^{-1} of drinking water for one year. This is an effective dose that represents a very low level of risk to human health and which is not expected to give rise to any detectable adverse health effects[4~~[4].~~].

This document contains method(s) to support laboratories, which need to determine ^{226}Ra in water samples. The method(s) described in this document can be used for various types of waters (see Clause 1~~Clause 1).~~). Minor modifications such as sample volume and counting time can be made if needed to ensure that the decision threshold, detection limit~~,~~ and uncertainties are below the required limits. This can be done for several reasons such as emergency situations, lower national guidance limits~~,~~ and operational requirements.

Water quality — Radium-226~~—~~ —

Part 4:
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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 essential that tests conducted according to this document be carried out by suitably trained staff.

1 Scope

This document specifies methods to determine ^{226}Ra by alpha spectrometry in supply water, drinking water, rainwater, surface and ground water, marine water, as well as cooling water, industrial water, domestic, and industrial wastewater after proper sampling, handling~~,~~ and test sample preparation.

The detection limit depends on the sample volume, the instrument used, the background count rate, the detection efficiency, the counting time~~,~~ and the chemical yield. The detection limit of the methods described in this document, using currently available alpha spectrometry apparatus, is equal to or lesser than 3 mBq·l^{-1} (or mBq·kg^{-1}), which is lower than the WHO criteria for safe consumption of drinking water (1 Bq·l^{-1})[4]~~).[4]~~. This value can typically be achieved with a counting time of 48 h for a test sample volume of 40 ml.

The method described in this document is applicable in the event of an emergency situation.

Filtration of the test sample is necessary for the methods described in this document if suspended solids are present. The analysis of ^{226}Ra adsorbed to suspended matter is not covered by this method, because it requires a mineralization step. In this case, the measurement is made on the different phases obtained. The final activity is the sum of all the measured activity concentrations.

It is the user's responsibility to ensure the validity of this test method for the water samples tested.

2 Normative references

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

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

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

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

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

ISO 5667~~-~~-10, *Water quality — Sampling — Part 10: Guidance on sampling of waste water*

ISO 11929 (all parts), *Determination of the characteristic limits (decision threshold, detection limit and limits of the confidence interval) for measurements of ionizing radiation — Fundamentals and application*

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

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

3 Terms and definitions

No terms and definitions are listed in this document.

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

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

4 Symbols

For the purposes of this document, the symbols and designations given in ISO~~ 80000-10, ISO 11929 series,~~ ~~ISO~~/IEC Guide 98-3, ~~and~~ ISO/IEC Guide 99, ISO 80000-10, the ISO 11929 series and the following shall apply.

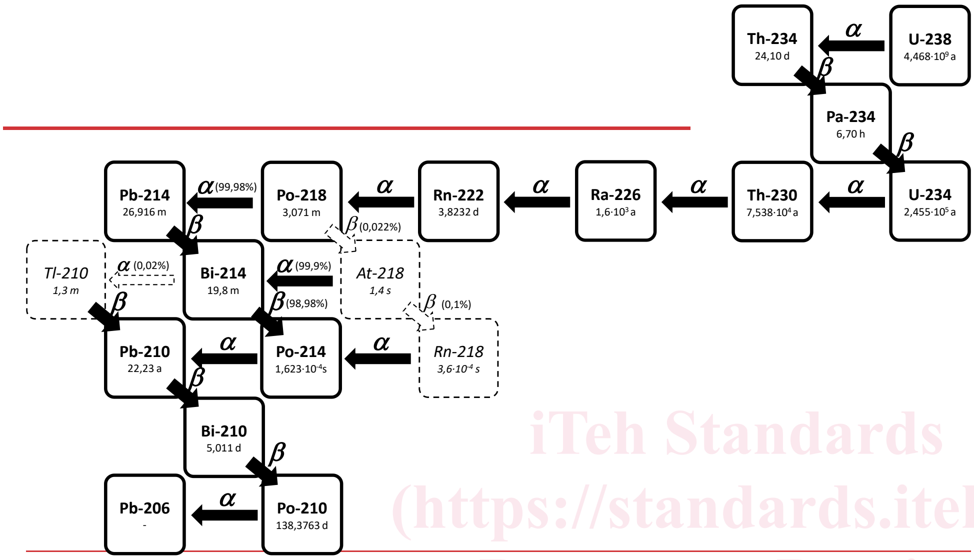
A_{T}	Activity of ^{225}Ra, the tracer added	Bq
α	Probability of the false positive decision	
β	Probability of the false negative decision	
c_A	Activity concentration of ^{226}Ra, the measurand	Bq·l^{-1}
c_A^*	Decision threshold of ^{226}Ra, the measurand	Bq·l^{-1}
$c_A^\#$	Detection limit of ^{226}Ra, the measurand	Bq·l^{-1}
$c_A^\triangleleft$, $c_A^\triangleright$	Lower and upper limits of the probabilistically symmetric coverage interval of ^{226}Ra, the measurand, respectively	Bq·l^{-1}
$c_A^<$, $c_A^>$	Lower and upper limits of the shortest coverage interval of ^{226}Ra, the measurand, respectively	Bq·l^{-1}
~~$\tilde{c}_A$~~$\tilde{c}_A$	Possible or assumed true quantity values of ^{226}Ra, the measurand	Bq·l^{-1}
$c_{A_{\mathrm{T}}}$	Activity concentration of ^{225}Ra tracer solution at the moment of separation	Bq·g^{-1}
ε	Counting efficiency	
Φ	Distribution function of the standardized normal distribution; $\Phi(k_p) = p$ applies	
$1-\gamma$	Probability for the coverage interval of ^{226}Ra, the measurand	
k_p	Quantiles of the standardized normal distribution for the probabilities p (for instance, $p = 1-\alpha$, $1-\beta$ or $1-\gamma/2$)	
k_q	Quantiles of the standardized normal distribution for the probabilities q (for instance, $q = 1-\alpha$, $1-\beta$ or $1-\gamma/2$)	
λ	Decay constant of the isotope (~~ex: $\lambda_{215_{\mathrm{Po}}}$~~ e.g. $\lambda_{215_{\mathrm{Po}}}$ is the decay constant of ^{215}Po)	s^{-1}
m	Sample mass	kg
m_{ST}	Mass of tracer solution	g

N_0	Number of background counts measured on the alpha spectrum for a given time in the region of interest of ^{226}Ra, the measurand	
$N_{0\mathrm{T}}$	Number of background counts measured on the alpha spectrum for a given time in the region of interest of ^{217}At, the progeny of ^{225}Ra tracer	
N_g	Number of counts measured on the alpha spectrum for a given time in the region of interest of ^{226}Ra, the measurand	
N_T	Number of counts measured on the alpha spectrum for a given time in the region of interest of ^{217}At, the progeny of ^{225}Ra tracer	
p	Probability for the coverage interval of ^{226}Ra, the measurand	
q	Probability for the coverage interval of ^{226}Ra, the measurand	
r_o	Background count rate in the region of interest of ^{226}Ra, the measurand	s^{-1}
r_{oT}	Background count rate in the region of interest of ^{217}At, the progeny of ^{225}Ra tracer	s^{-1}
R	Total recovery	
R_c	Chemical recovery	
r_g	Gross count rate in the region of interest of ^{226}Ra, the measurand	s^{-1}
r_{net}	Net count rate of ^{226}Ra, the measurand	s^{-1}
r_{netT}	Net count rate of ^{217}At, the progeny of ^{225}Ra tracer	s^{-1}
r_{AnetT}	Apparent net count rate of ^{225}Ra, the tracer	s^{-1}
r_T	Gross count rate in the region of interest of ^{217}At, the progeny of ^{225}Ra tracer	s^{-1}
t	Time	s
$T_{1/2}$	Radioactive half-life of the isotope (ex: $T_{1/2}$ ^{215}Po is the radioactive half-life of ^{215}Po)	s
t_0	Counting time of the background by alpha spectrometry	s
t_1	Time elapsed between separation and counting	s
t_g	Sample counting time by alpha spectrometry	s
U	Expanded uncertainty	
u	Standard uncertainty	
u_{rel}	Relative uncertainty	
$u(c_A)$	Standard uncertainty of the activity concentration of ^{226}Ra, the measurand	$\mathrm{Bq{\cdot}l}^{-1}$
~~$\tilde{u}$ $(\tilde{c}_A)$~~$\tilde{u}$ $(\tilde{c}$	Standard uncertainty of the estimator c_A as a function of an assumed true value ~~$\tilde{c}_A$~~$\tilde{c}_A$ of ^{226}Ra, the measurand	$\mathrm{Bq{\cdot}l}^{-1}$
$\tilde{u}(c_A^\#)$	Standard uncertainty of an estimate of ^{226}Ra, the measurand when the true value is equivalent to the detection limit	$\mathrm{Bq{\cdot}l}^{-1}$
V	Sample volume	l
ω	Distribution function of the standardized normal distribution	
w	Estimate of the calibration factor	l^{-1}

If the results are expressed in mass activity, ~~the symbol~~ c_A is replaced by a and the volume~~ (V)~~, is replaced by the sample mass~~ (m)~~.

5 Principle

Radium-226 is a naturally occurring isotope in the ^{238}U decay series (see Figure 1~~Figure 1).~~). It has a half-life of 1 600 a ± 7 a[9~~.[9]~~]. Radium-226 decays through alpha emission to ^{222}Rn [9~~[9].~~].



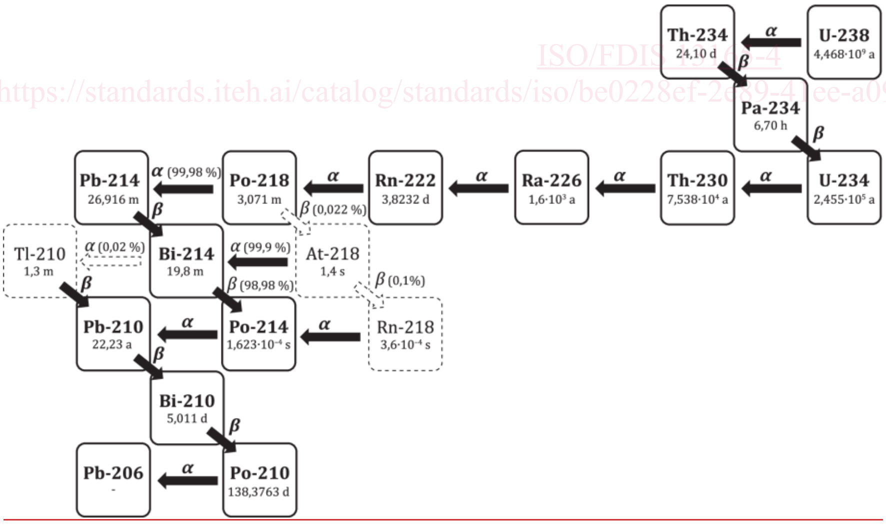
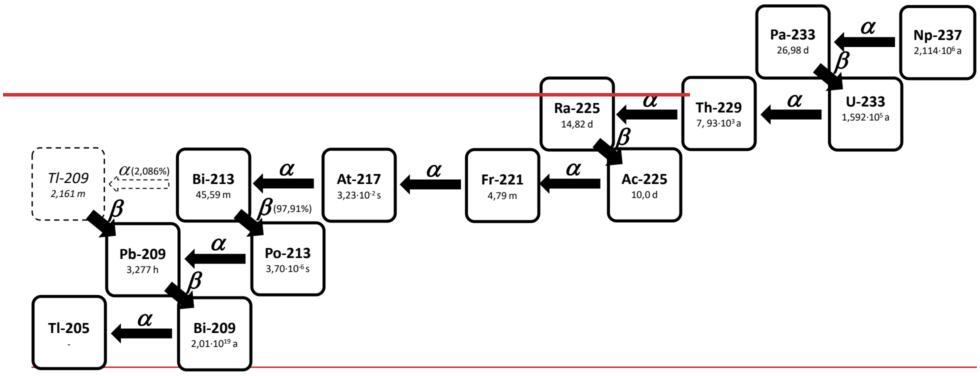


Figure 1 — ^{238}U decay series



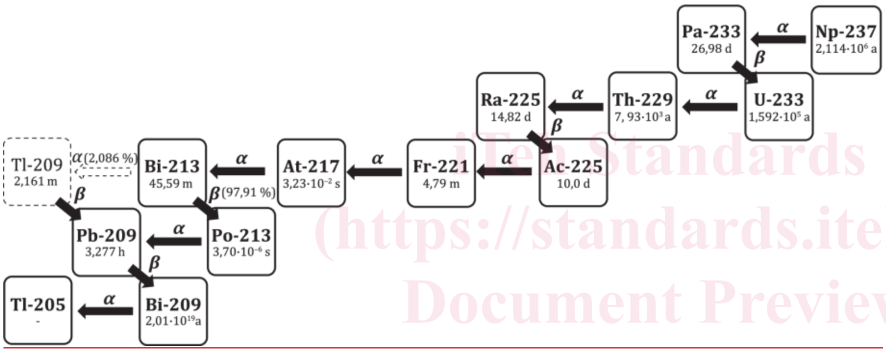


Figure 2 — ^{237}Np decay series

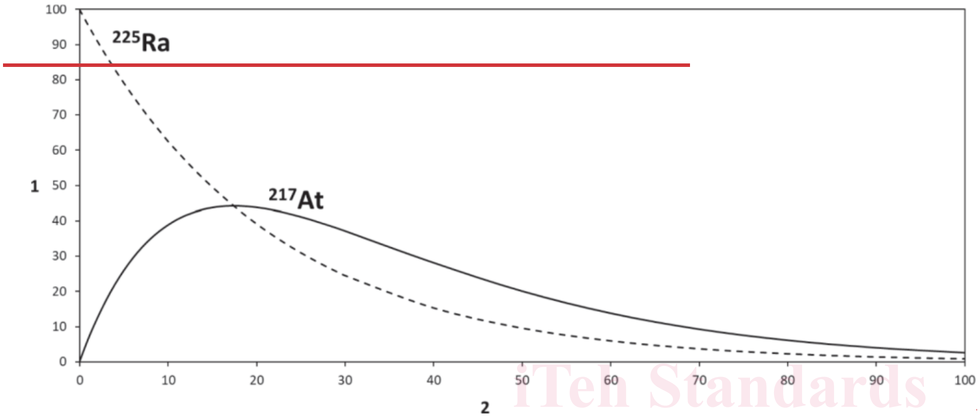
To determine ^{226}Ra in water, a water sample is collected, filtered~~,~~ and acidified (see Clause 6~~Clause 6~~ on sampling and storage).

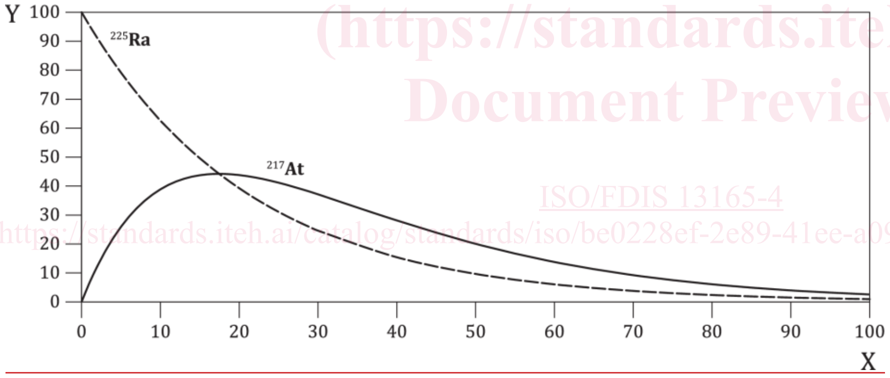
Radium-225 tracer is added to the sample via a solution of ^{229}Th in equilibrium with its progeny ^{225}Ra (see Figure 2~~Figure 2).~~). Enough tracer is added to obtain a good statistical precision and be easily distinguished from the blank sample (e.g. 15~~-~~ mBq to 30 mBq). Radium-225 is the preferred tracer for ^{226}Ra determination by alpha spectrometry, because it is usually not present in environmental samples. Note that other tracers can also be used. Radium-224 (from a ^{228}Th solution) and ^{223}Ra (from a ^{227}Ac solution) can also be used if no significant ^{224}Ra or ^{223}Ra activity is expected to be present in the sample. Also, ^{133}Ba can be used as a tracer if it is proven that it behaves like ^{226}Ra. Barium-133 is measured by gamma spectrometry.

Radium is pre-concentrated. Then, it is separated from potential interferences using one of the methods presented in Annexes D~~Annex D~~ to G~~G.~~. The potential radioactive interferences for the measurement of ^{226}Ra are listed in Annex A~~Annex A.~~. Potential matrix interferences such as Ca and Sr also need to be removed.

After purification, a thin source layer of ^{226}Ra is prepared by either electrodeposition or barium sulfate ($BaSO_4$) micro-precipitation according to Annexes B~~Annex B~~ and C~~C,~~, respectively. Note that for the solid phase extraction method presented in Annex D~~Annex D,~~, ^{226}Ra is extracted at the surface of the disc as a thin source layer and, in that case, no thin source layer needs to be prepared. The containerized thin source layer can be stored to let the beta emitting ^{225}Ra ~~(~~[half-life of (14,82 ± 0,19) d[9~~[9])~~]] tracer decay products ^{225}Ac, ^{221}Fr~~,~~ and ^{217}At in-grow, which are mainly alpha emitters with radioactive half-lives of (10,0 ± 0,1) d, (4,79 ± 0,02) min, and (32,3 ± 0,4~~ x ~~ × 10~~-~~$^{-3}$) s, respectively[9~~.~~[9]]. Astatine-217 activity is at a maximum 17 days after separation (see Figure 3~~Figure 3).~~). It is a function of time and can be calculated at the time of measurement. The activity of ^{225}Ra tracer added can be increased to reduce the time needed between separation and measurement.

Radium-226 is measured by alpha spectrometry, usually for 48 h. The activity concentration of ^{226}Ra is calculated and reported (see Clause 9~~Clause 9~~ for more details).





Key

~~1~~X ~~percentage activity~~time in ~~%~~d
~~2~~Y ~~time~~percentage activity in ~~day~~%

Figure 3 — Percentage activity of ^{225}Ra (dash line) and ^{217}At (solid line) as a function of time after separation of ^{225}Ra from ^{229}Th

6 Sampling, handling and storage

Sampling, handling~~,~~ and storage of the water shall be done as specified in ISO 5667-1, ISO 5667-3 and ISO 5667-10~~ and~~. Guidance is given for the different types of water in References [10~~[10]~~] to [17~~[17]~~]. It is important that the laboratory receives a sample that is truly representative and has neither been damaged nor modified during either transportation or storage.