

FINAL DRAFT International Standard

ISO/FDIS 13165-4

ISO/TC 147/SC 3

Secretariat: AFNOR

Voting begins on: 2025-04-03

Voting terminates on: 2025-05-29

Water quality — Radium-226 —

Part 4: Test method using alpha spectrometry

Qualité de l'eau — Radium 226 — ttps://standards.iten.

Partie 4: Méthode d'essai par spectrométrie alpha

ISO/FDIS 13165-4

https://standards.iteh.ai/catalog/standards/iso/be0228ef-2e89-41ee-a096-1fd0fe0ee737/iso-fdis-13165-4

RECIPIENTS OF THIS DRAFT ARE INVITED TO SUBMIT, WITH THEIR COMMENTS, NOTIFICATION OF ANY RELEVANT PATENT RIGHTS OF WHICH THEY ARE AWARE AND TO PROVIDE SUPPORTING DOCUMENTATION.

IN ADDITION TO THEIR EVALUATION AS BEING ACCEPTABLE FOR INDUSTRIAL, TECHNO-LOGICAL, COMMERCIAL AND USER PURPOSES, DRAFT INTERNATIONAL STANDARDS MAY ON OCCASION HAVE TO BE CONSIDERED IN THE LIGHT OF THEIR POTENTIAL TO BECOME STANDARDS TO WHICH REFERENCE MAY BE MADE IN NATIONAL REGULATIONS.

iTeh Standards (https://standards.iteh.ai) Document Preview

ISO/FDIS 13165-4

https://standards.iteh.ai/catalog/standards/iso/be0228ef-2e89-41ee-a096-1fd0fe0ee737/iso-fdis-13165-4



COPYRIGHT PROTECTED DOCUMENT

© ISO 2025

All rights reserved. Unless otherwise specified, or required in the context of its implementation, no part of this publication may be reproduced or utilized otherwise in any form or by any means, electronic or mechanical, including photocopying, or posting on the internet or an intranet, without prior written permission. Permission can be requested from either ISO at the address below or ISO's member body in the country of the requester.

ISO copyright office CP 401 • Ch. de Blandonnet 8 CH-1214 Vernier, Geneva Phone: +41 22 749 01 11 Email: copyright@iso.org Website: www.iso.org Published in Switzerland

Contents

Forew	/ord	iv	
Introduction			
1	Scope	1	
2	Normative references	1	
3	Terms and definitions	2	
4	Symbols	2	
5	Principle	4	
6	Sampling handling and storage	5	
7	Procedure	6	
, Q	Auglity assurance and quality control program	6	
0	8.1 General	6	
	8.2 Instrument verification	6	
	8.3 Contamination	6	
	8.4 Interference control	6	
	8.6 Method verification	7	
	8.7 Demonstration of analyst capability	7	
9	Expression of results	7	
-	9.1 General Tob Stondardo	7	
	9.2 Tracer activity added	7	
	9.3 Count rate and net count rate	8	
	9.4 Total recovery	8	
	9.5 ACTIVITY CONCENTRATION OF 220 Ka	9 Q	
	9.7 Decision threshold	9	
	9.8 Detection limit		
	9.9 Probabilistically symmetric coverage interval		
	^{1/stand} 9.9.1 ¹¹ Limits of the probabilistically symmetric coverage interval	5-10	
	9.9.2 Shortest coverage interval	11	
10	Test report	11	
Annex	x A (informative) Radioactive interferences and an example of alpha spectrum	13	
Annex	K B (informative) Preparation of thin alpha source by electrodeposition	14	
Annex	x C (informative) Preparation of thin alpha source by barium sulfate micro-precipitation	17	
Annex	x D (informative) Method 1: Radium separation using a solid phase extraction disc	19	
Annex	k E (informative) Method 2: Radium pre-concentration, separation with a MnO ₂ resin and removal of potential radioactive interferences using an extraction chromatography resin	21	
Annex	x F (informative) Method 3: Preconcentration of radium using CaCO ₃ , separation of Ra from potential interferences using a cation exchange resin and extraction chromatography resin	24	
Annex	k G (informative) Method 4: Preconcentration of Ra using a lead sulfate coprecipitation and separation of Ra from potential interferences using a complexing agent	27	
Bibliography			

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 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).

ISO draws attention to the possibility that the implementation of this document may involve the use of (a) patent(s). ISO takes no position concerning the evidence, validity or applicability of any claimed patent rights in respect thereof. As of the date of publication of this document, ISO had not received notice of (a) patent(s) which may be required to implement this document. However, implementers are cautioned that this may not represent the latest information, which may be obtained from the patent database available at www.iso.org/patents. ISO shall not be held responsible for identifying any or all such patent rights.

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

For an explanation of 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 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 <u>www.iso.org/members.html</u>.

SO/FDIS 13165-4

https://standards.iteh.ai/catalog/standards/iso/be0228ef-2e89-41ee-a096-1fd0fe0ee737/iso-fdis-13165-4

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 ³H, ¹⁴C, ⁴⁰K and those originating from the thorium and uranium decay series, in particular ²¹⁰Pb, ²¹⁰Po, ²²²Rn, ²²⁶Ra, ²²⁸Ra, ²²⁷Ac, ²³²Th, ²³¹Pa, ²³⁴U and ²³⁸U, 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 ⁵⁵Fe, ⁵⁹Ni, ⁶³Ni, ⁹⁰Sr, ⁹⁹Tc, transuranic elements (e.g. Np, Pu, Am, Cm), and some gamma emitting radionuclides, such as ⁶⁰Co and ¹³⁷Cs, 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] and water bodies. 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]}. 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] 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]}, 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] and ISO 5667-20^[6].

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

NOTE 2 The guidance level calculated in Reference [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].

This document contains method(s) to support laboratories, which need to determine ²²⁶Ra in water samples. The method(s) described in this document can be used for various types of waters (see <u>Clause 1</u>). 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.

iTeh Standards (https://standards.iteh.ai) Document Preview

ISO/FDIS 13165-4

https://standards.iteh.ai/catalog/standards/iso/be0228ef-2e89-41ee-a096-1fd0fe0ee737/iso-fdis-13165-4

Water quality — Radium-226 —

Part 4: Test method using alpha spectrometry

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 ²²⁶Ra 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 $3 \text{ mBq} \cdot l^{-1}$ (or mBq·kg⁻¹), which is lower than the WHO criteria for safe consumption of drinking water (1 Bq·l⁻¹)^[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 ²²⁶Ra 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 <u>https://www.iso.org/obp</u>
- IEC Electropedia: available at <u>https://www.electropedia.org/</u>

4 Symbols

For the purposes of this document, the symbols and designations given in ISO/IEC Guide 98-3, 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} , $c_A^{ ho}$	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 $^{\rm 226}\rm Ra$, the measurand, respectively	Bq·l ⁻¹
$\widetilde{c_A}$	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
Е	Counting efficiency	
Φ	Distribution function of the standardized normal distribution; $\Phi(k_p) = p$ applies	
1-γ	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 (e.g. $*_{\rm 215_{Po}}$ is the decay constant of $^{\rm 215}{\rm Po}$)	s ⁻¹
т	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 $^{\rm 226}\rm Ra$, the measurand	
N _{0T}	Number of background counts measured on the alpha spectrum for a given time in the region of interest of $^{217}\rm{At}$, the progeny of $^{225}\rm{Ra}$ tracer	
Ng	Number of counts measured on the alpha spectrum for a given time in the region of interest of $^{\rm 226}\rm Ra$, the measurand	
N _T	Number of counts measured on the alpha spectrum for a given time in the region of interest of $^{217}\rm{At}$, the progeny of $^{225}\rm{Ra}$ tracer	
р	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 aros iten.ai	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
$T_{1/2ps://s}$	Radioactive half-life of the isotope (ex: $T_{1/2}^{215}$ Po is the radioactive half-life of 215 Po)	816 5 -4
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	
<i>u</i> _{rel}	Relative uncertainty	
$u(c_A)$	Standard uncertainty of the activity concentration of ²²⁶ Ra, the measurand	Bq·l−1
$\widetilde{u}\left(\widetilde{c_A}\right)$	Standard uncertainty of the estimator c_A as a function of an assumed true value $\widetilde{c_A}$ of 226 Ra, the measurand	Bq·l ^{−1}
$ ilde{u}ig(c^{\#}_{A}ig)$	Standard uncertainty of an estimate of $^{\rm 226}\rm Ra$, the measurand when the true value is equivalent to the detection limit	Bq·l−1
V	Sample volume	l
ω	Distribution function of the standardized normal distribution	

w Estimate of the calibration factor

If the results are expressed in mass activity, 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 <u>Figure 1</u>). It has a half-life of 1 600 a ± 7 a^[9]. Radium-226 decays through alpha emission to 222 Rn ^[9].



https://standards.iteh.ai/catalog/standards/iso/be0228ef-2e89-41ee-a096-1fd0fe0ee737/iso-fdis-13165-4 Figure 1 — ²³⁸U decay series



Figure 2 — ²³⁷Np decay series

To determine ²²⁶Ra in water, a water sample is collected, filtered and acidified (see <u>Clause 6</u> on sampling and storage).

Radium-225 tracer is added to the sample via a solution of ²²⁹Th in equilibrium with its progeny ²²⁵Ra (see 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 ²²⁶Ra 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 ²²⁸Th solution) and ²²³Ra (from a ²²⁷Ac solution) can also be used if no significant ²²⁴Ra or ²²³Ra activity is expected to be present in the sample. Also, ¹³³Ba can be used as a tracer if it is proven that it behaves like ²²⁶Ra. 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 <u>Annexes D</u> to <u>G</u>. The potential radioactive interferences for the measurement of ²²⁶Ra are listed in <u>Annex A</u>. 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 (BaSO₄) micro-precipitation according to Annexes B and C, respectively. Note that for the solid phase extraction method presented in 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]] 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 × 10⁻³) s, respectively^[9]. Astatine-217 activity is at a maximum 17 days after separation (see 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 <u>Clause 9</u> for more details).



X time in d

Y percentage activity in %

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

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. Guidance is given for the different types of water in References [10] to [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.