FINAL
DRAFT

INTERNATIONAL STANDARD

ISO/FDIS 13167

ISO/TC **147**/SC **3**

Secretariat: **AFNOR**

Voting begins on:
2023-03-07

Voting terminates on:
2023-05-02

Water quality — Plutonium, americium, curium and neptunium — Test method using alpha spectrometry

Qualité de l'eau — Plutonium, americium, curium et neptunium — Méthode d'essai par spectrométrie alpha

Reference number
ISO/FDIS 13167:2023(E)

© ISO 2023

iTeh STANDARD PREVIEW
(standards.iteh.ai)

COPYRIGHT PROTECTED DOCUMENT

Contents

iTeh STANDARD PREVIEW
(standards.iteh.ai)

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 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 ISO/TC 147, *Water quality*, Subcommittee SC 3, *Radioactivity measurements*.

This second edition cancels and replaces the first edition (ISO 13167:2015), which has been technically revised.

The main changes are as follows:

— addition of a description for determination of bias in the chemical recoveries of americium and curium.

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, ^{231}Pa, ^{234}U, and ^{238}U, can be found in water bodies due to either natural processes (e.g. desorption from the soil, 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, and 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] and water bodies. Anthropogenic radionuclides used in 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] 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 risk.

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 ^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Am, ^{243}Cm, ^{244}Cm, ^{237}Np in drinking water is 1 Bq·l^{-1}[3]. For ^{242}Cm the GL is 10 Bq·l^{-1}.Bq·l^{-1}[3]. 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 [4], the value has been calculated using the formula provided in Reference [4] and the dose coefficient data from References [7] and [8].

NOTE 2   The guidance level calculated in Reference [4] is the activity concentration that, with an intake of 2 l·d^{-1} of drinking water for one year, results in an effective dose of 0,1 mSv·a^{-1} to members of the public. 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 methods to determine ^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Am, ^{242}Cm, ^{243}Cm, ^{244}Cm, ^{237}Np in water samples. It has been developed to support laboratories that need either a certification or accreditation to determine these nuclides in water samples. A certification or accreditation are sometimes required by local and national authorities as well as some customers. The certification and accreditation are provided by an independent body.

The methods described in this document can be used for various types of waters. Minor modifications such as sample volume and counting time can be made if needed to ensure that the characteristic limit, 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 — Plutonium, americium, curium and neptunium — 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 test method be carried out by suitably trained staff.

1 Scope

This document specifies a test method for measuring actinides (^{238}Pu, $^{239+240}$Pu, ^{241}Am, ^{242}Cm, $^{243+244}$Cm and ^{237}Np) in water samples by alpha spectrometry following a chemical separation.

This method can be used for any type of environmental study or monitoring after appropriate sampling and handling, and test sample preparation.

The detection limit of the test method is $5 \times 10{-}3$ to $5 \times 10{-}4$ Bq l^{-1} for a volume of test portion between 0,1 l to 5 l with a counting time of two to ten days. This is lower than the WHO criteria for safe consumption of drinking water (1 or 10) Bq·l^{-1} depending on radionuclide.[4]

The methods described in this document are applicable in the event of an emergency situation.

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

ISO 11929-1, *Determination of the characteristic limits (decision threshold, detection limit and limits of the coverage interval) for measurements of ionizing radiation — Fundamentals and application — Part 1: Elementary applications*

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

3   Terms, definitions and symbols

3.1   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/

3.2   Symbols

For the purposes of this document, the symbols given in ISO/IEC Guide 98-3, ISO/IEC Guide 99 ISO 80000-10, ISO 11929-1 and the following shall apply.

Symbol	Description	Unit
A	Activity of the tracer added	Bq
α	Probability of the false positive decision	
β	Probability of the false negative decision	
c_A	Activity concentration of the measurand measured in the sample	Bq·l^{-1}
c_A^*	Decision threshold of the measurand	Bq·l^{-1}
$c_A^\#$	Detection limit of the measurand	Bq·l^{-1}
$c_A^\triangleleft, c_A^\triangleright$	Lower and upper limits of the probabilistically symmetric coverage interval of the measurand, respectively	Bq·l^{-1}
$c_A^<, c_A^>$	Lower and upper limits of the shortest coverage interval of the measurand, respectively	Bq·l^{-1}
$\widetilde{c_A}$	Possible or assumed true quantity values of the measurand	Bq·l^{-1}
c_{AT}	Activity concentration of the tracer solution at the moment of separation	Bq·l^{-1}
ε	Counting efficiency	
f	Correction factor for possible bias for curium isotopes using ^{243}Am as a tracer or for ^{237}Np using ^{236}Pu as a tracer. For plutonium isotopes or for ^{241}Am, f is equal to 1	
Φ	Distribution function of the standardized normal distribution; $\Phi(k_p) = p$ applies	
$1-\gamma$	Probability for the coverage interval of the measurand	
k_p	Quantiles of the standardized normal distribution for the probabilities p (for instance $p = 1-\alpha$, $1-\beta$ or $1-\gamma/2$)	
λ	Decay constant of the isotope (ex: $\lambda_{215_{Po}}$ is the decay constant of ^{215}Po)	
m	Sample mass	kg
m_{ST}	Mass of tracer solution	g
N_0	Number of counts measured of the background on the alpha spectrum for a given time in the region of interest of the measurand.	Counts
N_{0T}	Number of counts measured of the background on the alpha spectrum for a given time in the region of interest of the tracer.	Counts
N_g	Number of counts measured on the alpha spectrum for a given time in the region of interest of the measurand.	Counts
N_T	Number of counts measured on the alpha spectrum for a given time in the region of interest of the tracer.	Counts
P_α	Probability of the isotope decaying by alpha particle emission (branching ratio)	
r_0	Background count rate in the region of interest of the measurand	Bq
r_{0T}	Background count rate in the tracer region of interest of the tracer	Bq

Symbol	Description	Unit
R	Total recovery	
R_c	Chemical recovery	
r_g	Gross count rate in the region of interest of the measurand	Bq
r_{net}	Net count rate of the measurand	Bq
r_{netT}	Net count rate of the tracer	Bq
r_T	Gross count rate in the region of interest of the tracer	Bq
$t_{1/2}$	Radiological half-life of the isotope of interest	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	
$u(c_A)$	Standard uncertainty of the activity concentration of the measurand	Bq·l⁻¹
$\tilde{u}(\widetilde{c_A})$	Standard uncertainty of the estimator c_A as a function of an assumed true value c_A of the measurand	Bq·l⁻¹
V	Sample volume	l

4   Principle

The actinide isotopes included in this document are deposited as a thin source for measurement by alpha spectrometry by means of a grid chamber detector or a semi-conductor detector type equipment. The sources are usually prepared by electrodeposition or co-precipitation after chemical separation and purification of the actinides isotopes present in the test portion.[9],[10],[11],[12]

Specific chemical separation and purification procedures are required to avoid interference from the presence of other α-emitters, and stable nuclides in the sample, in quantities that are often larger than the actinide isotopes of interest. Actinides can be pre-concentrated by iron hydroxide co-precipitation at pH 8. The resulting precipitate is dissolved with an acidic solution and passed through an ion exchange, or extraction chromatography resin (see Annexes A and B) to purify the analyte from potential interferences. The potential radiological interferences for the measurement of the various radionuclides relevant to this method are listed in Annex F.

After purification, a micro-precipitation with cerium fluoride (CeF_3) is performed or the analytes are electrodeposited. The actinides of interest are measured by alpha spectrometry for a suitable counting period. The activity concentrations of the actinides of interest are calculated and reported (see Clause 9 for more details).

These procedures allow the main sources of interference to be removed, namely:

— the salt content of the water sample, especially hydrolysable elements, in order to prepare the thinnest deposited source;

— other α-emitting radionuclides, such as uranium and thorium isotopes, whose emissions can interfere with those of actinide isotopes of interest.

The total yield for each analysis (product of chemical separation yield and detection efficiency) is determined by adding a standard solution of tracer: ²³⁶Pu can be used for plutonium isotopes and ²³⁷Np, ²⁴²Pu can be used for plutonium isotopes only and ²⁴³Am can be used for americium and curium isotopes. Enough tracer is added to obtain a good statistical precision and be easily distinguished from a blank sample (e.g. about 100 mBq is often suitable).

The procedure shall include a reduction/oxidation cycle to adjust the tracer and the analytes to the same oxidation state.

It is possible to quantify curium isotopes on the basis of ^{243}Am tracer recovery, or neptunium on the basis of ^{236}Pu tracer recovery. This can lead to a potential bias that shall be quantified using a standard solution, participation in inter-laboratory comparison tests, or establishment of the bias factor (see Annex E).

NOTE ^{235}Np, ^{236}Np, ^{238}Np and ^{239}Np can be used as yield tracers for ^{237}Np (if available), and ^{245}Cm as a yield tracer for other Cm isotopes but the test method of this document does not cover these measurements.

5   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 [13] to [20]. It is important that the laboratory receives a sample that is truly representative and has not been damaged or modified during transportation or storage.

The sample is filtered to remove suspended matter using a 0,45 µm filter. A smaller pore size filter can also be used, but the filtration can be more tedious and time consuming. The sample shall be acidified after filtration to pH < 2 with HNO_3.

6   Reagents and apparatus

6.1   Reagents

The chemical reagents and equipment are described in Annexes A and B for chemical separation and in Annexes C and D for the preparation of the deposited source.

Except for the certified standard solutions, all the chemical reagents needed to carry out this procedure shall be analytical grade.

6.2   Laboratory equipment

Usual laboratory equipment including the following:

6.2.1   Vacuum filtration system.

6.2.2   Filters, of pore size 0,45 µm or smaller.

6.2.3   Glass beakers.

6.2.4   Centrifuge.

6.2.5   Multi-hole vacuum box, for example, 12 positions. (optional)

6.2.6   Analytical balance, accuracy 0,1 mg.

6.2.7   Centrifuge tubes/bottles, for example, 50 ml and 500 ml in volume.

6.2.8   Pipettes.

6.2.9   Hot plate.

6.2.10   Magnetic Stirring plate.

6.2.11   Magnetic stirrer bars.

6.2.12 Metal discs with a sticky side.

6.2.13 Alpha spectrometer.

7 Procedure

Filter and acidify the sample and a blank sample prepared with ultrapure water as specified in Clause 5. A minimum of one blank sample is required for all the tests presented. However, the average of several blanks can be used and is preferred. Also, measuring blank samples at regular interval enables to rapidly detect a background issue when measuring the samples (see quality assurance and quality control program in Clause 8).

The radioactive tracers are added during this initial treatment phase.

If required, actinides can be concentrated by either evaporation or co-precipitation. If an evaporation step is performed, the resultant residue is dissolved with an acidic solution. If a co-precipitation is performed, it is often useful to add a carrier to the sample to aid collection of the precipitate. For example, iron nitrate or chloride can be added to precipitate the actinides along with $Fe(OH)_3$ at pH = 9. After centrifugation or filtration, the precipitate is dissolved with an acidic solution.

The procedure shall include an oxidation/reduction cycle to equilibrate the tracer(s) and the actinide isotopes. For example, a primarily reduction step can be carried out by adding $NH_2OH.HCl$, $NaHSO_3$ or $Na_2S_2O_3$, then an oxidation step can be done with $NaNO_2$ or H_2O_2.

7.1 Chemical separation

There are two commonly used techniques for the chemical separation of actinides: extraction on an ion exchange resin or specific extraction chromatographic resin. One method from each technique is presented in Annexes A and B: separation by anionic resin[21] or by extraction chromatographic resins.[22],[23]

It is also possible to use a combination of these techniques, for example, use an ion exchange resin followed by a specific extraction chromatographic resin for americium separation.

7.2 Preparation of the counting source

7.2.1 General

The counting source can be prepared by electrodeposition on a stainless-steel disc or by co-precipitation.

7.2.2 Electrodeposition method

Electrodeposition is carried out after the chemical separation of the actinides from interfering elements. It allows the electrochemical deposition of the actinides in an ultra-thin layer onto a stainless-steel disc. The procedure, described in Annex C, can follow either of the two chemical separation methods described in Annexes A and B.

NOTE   Electrodeposition is not a selective method because some stable metal cations are likely to form insoluble hydroxides, which can be deposited at the same time as the actinides.

7.2.3 Co-precipitation method

Co-precipitation, using fluoride compounds, can be carried out after the chemical separation of the actinides from other interfering elements. The procedure, described in Annex D, can follow either of the two chemical separation methods described in Annexes A and B.

7.3 Background determination

Measure the background activity using a blank sample (e.g. laboratory water) prepared following the selected method. This blank sample should be prepared without tracer to be used for obtaining the background count rates.

7.4 Counting efficiency determination

The counting efficiency is estimated by measuring a calibration source. It is required in order to determine the chemical recovery.

7.5 Measurement

The actinide activity concentration is calculated by counting the sample source for an appropriate counting time. The same instrumental parameters should be used for the sample, the background and the calibration source measurements.

The counting time required depends on the sample and background count rates and also the detection limit and decision threshold required.

It should be verified on the spectrum that no interference is present, and an adequate energy resolution is obtained.

8 Quality assurance and quality control program

8.1 General

Quality control operations shall meet the requirements of ISO/IEC 17025. Measurement methods shall be performed by suitably skilled staff under a quality assurance program.

8.2 Variables that can influence the measurement

Special care shall be taken in order to limit as much as possible the influence of parameters that can bias the measurement and lead to a non-representative result. Failure to take sufficient precautions during the different steps of the measurement process such as sampling, transportation and storage, reagents, transfer, instrument can require corrective factors to be applied to the measured results.

8.3 Instrument verification

Major instrumental parameters (e.g. detection efficiency, calibration, background signal) shall be periodically verified within a quality assurance program established by the laboratory and in accordance with the manufacturer's instructions.

Usually, a thin alpha source with a radionuclide of long radiological half-life of known activity such as a $^{239+240}$Pu source is employed to estimate the detector efficiency because there is no appreciable decay over the working life of the source. The efficiency source should have a similar geometry to the sample sources. The alpha peak energy is calibrated using a multi-isotope source, which can be obtained commercially. The background rate of each detector is determined with an empty source support (clean disc); this shall take at least as much time as the counting of a sample source.

8.4 Contamination

Verify the absence of reagent contamination through the periodic performance of reagent blank analysis. Laboratory procedures shall ensure that laboratory and equipment contamination as well as sample cross contamination is avoided.