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**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*

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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.

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](http://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](http://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 meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the WTO principles in the Technical Barriers to Trade (TBT) see the following URL: [Foreword - Supplementary information](#)

The committee responsible for this document is ISO/147, *Water quality*, Subcommittee SC 3, *Radioactivity measurements*.

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## 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 potassium 40, and those originating from 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 can be released from technological processes involving naturally occurring radioactive materials (e.g. the mining and processing of mineral sands or phosphate fertilizer production and use).
- Human-made radionuclides, such as transuranium elements (americium, plutonium, neptunium, curium), tritium, carbon 14, strontium 90 and some gamma emitting radionuclides, can also be found in natural waters as a result of authorized routine releases into the environment in small quantities in the effluent discharged from nuclear fuel cycle facilities. They are also released into the environment following their use in unsealed form for medical and industrial applications. They are also found in the water as a result of past fallout contamination resulting from the explosion in the atmosphere of nuclear devices and accidents such as those that occurred in Chernobyl and Fukushima.

Drinking water may thus contain radionuclides at activity concentrations which could 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] and as may be required by some national authorities.

An international standard on a test method for isotopes of plutonium, americium, curium and neptunium 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.

$^{238}\text{Pu}$ ,  $^{239}\text{Pu}$ ,  $^{240}\text{Pu}$ ,  $^{241}\text{Am}$ ,  $^{242}\text{Cm}$ ,  $^{243}\text{Cm}$ ,  $^{244}\text{Cm}$ ,  $^{237}\text{Np}$  activity concentrations can vary according to any local effluent authorized discharges from nuclear plant and environmental characteristics. The guidance level for  $^{238}\text{Pu}$ ,  $^{239}\text{Pu}$ ,  $^{240}\text{Pu}$ ,  $^{241}\text{Am}$ ,  $^{242}\text{Cm}$ ,  $^{243}\text{Cm}$ ,  $^{244}\text{Cm}$ ,  $^{237}\text{Np}$  in drinking water as recommended by WHO is 1 Bq/l for all of those isotopes, except for  $^{242}\text{Cm}$  (10 Bq/l) [WHO-Guidelines for drinking waters quality, 2011, Geneva].

**NOTE** The guidance level is the activity concentration (rounded to the nearest order of magnitude) with an intake of 2 l/day of drinking water for 1 year, that results in an effective dose of 0,1 mSv/year 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 set of International Standards on test methods dealing with the measurement of the activity concentration of radionuclides in water samples.

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

## 1 Scope

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

The method can be used for any type of environmental study or monitoring.

The volume of the test portion required depends on the assumed activity of the sample and the desired detection limit.

The detection limit of the test method is  $5 \times 10^{-3}$  to  $5 \times 10^{-4}$  Bq/l for a volume of the test portion of 0,1 l to 5 l with a counting time of two to ten days.

## 2 Normative references

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

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

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

## 3 Terms and definitions

For the purposes of this document, the terms, definitions and symbols given in ISO 80000-10 and ISO 11929 apply.

## 4 Symbols

The following symbols apply.

$A$	Activity of tracer added at the date of measurement, in becquerels
$c_A$	Activity concentration of the actinides isotopes in becquerels per litre
$c_A^*$	Decision threshold, in becquerels per litre
$c_A^\#$	Detection limit, in becquerels per litre
$c_A^\triangleleft, c_A^\triangleright$	Lower and upper limits of the confidence interval, in becquerels per litre
$\varepsilon$	Counting efficiency
$r_g, r_{gT}$	Gross count rate per second from measured actinides isotopes and tracer, respectively
$r_0, r_{0T}$	Background count rate per second from actinides isotopes and tracer, respectively
$R$	Total measurement yield
$R_c$	Chemical yield
$t_0$	Background counting time, in seconds
$t_g$	Sample counting time, in seconds
$u(c_A)$	Standard uncertainty associated with the measurement result, in becquerels per litre
$U$	Expanded uncertainty, calculated by $U = k \cdot u(c_A)$ with $k = 1, 2, \dots$ , in becquerels per litre
$V$	Volume of test sample, in litres
$f$	Correction factor for possible bias for curium isotopes using $^{243}\text{Am}$ as a tracer or for $^{237}\text{Np}$ using $^{236}\text{Pu}$ as a tracer. For plutonium isotopes or for $^{241}\text{Am}$ , $f$ is equal to 1.

## 5 Principle

Actinide isotopes are deposited as a thin source for measurement by alpha spectrometry using a grid chamber or semi-conductor detector type equipment. The sources are usually prepared by electrodeposition or co-precipitation after chemical separation and purification of the actinide isotopes present in the test portion.<sup>[1][2][3][4]</sup>

Specific chemical separation and purification procedures are required in order to avoid interference from the presence of other  $\alpha$  emitters, and stable nuclides in the sample, in quantities that are often larger than the actinide isotopes of interest.



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

- the salt content of the water sample, especially hydrolysable elements, in order to prepare the thinnest deposited source;
- other  $\alpha$  emitting radionuclides, such as uranium and thorium isotopes, whose emissions may 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:  $^{236}\text{Pu}$  can be used for plutonium isotopes and  $^{237}\text{Np}$ ,  $^{242}\text{Pu}$  can be used for plutonium isotopes only and  $^{243}\text{Am}$  can be used for americium and curium isotopes.

As a result, 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  $^{243}\text{Am}$  tracer behaviour. This may lead to a potential bias that shall be quantified using a standard solution and/or participation in inter-laboratory comparison tests.

It is possible to quantify neptunium on the basis of  $^{236}\text{Pu}$  tracer behaviour. This may lead to a potential bias that shall be quantified using a standard solution and/or participation in inter-laboratory comparison.

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

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### 6 Chemical reagents and equipment

#### 6.1 Chemical 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 Equipment

Usual laboratory apparatus and in particular the following equipment.

**6.2.1 Alpha-spectrometer**, of the grid chamber (with higher detection efficiency, but lower resolution) or semiconductor type (with lower detection efficiency, but higher resolution). Operation at constant temperature is recommended. Follow the manufacturer's instructions.

For semiconductor-type equipment, the measurements using alpha-spectrometry depend on the interaction of alpha-particles with an ion-implanted silicon detector. This interaction instantly changes the conductivity of the silicon, proportional to the energy of the incoming alpha-particle. If a well-resolved spectra is required, the detection system should be maintained at a pressure < 10 Pa. Resolution can be further enhanced through increasing distance between source and detector.

**6.2.2 Pipette**, suitable for the accurate transfer of (for example 100  $\mu\text{l}$ ) tracer solution with a total precision within  $\pm 1\%$ .

**6.2.3 Balance**, capable of achieving  $\pm 0,1$  mg precision.

In addition, the equipment for chemical separation is listed in [Annexes A and B](#) and the equipment for the preparation of the deposited source is listed in [Annexes C and D](#).

## 7 Procedure

### 7.1 Sampling

Conditions of sampling shall follow ISO 5667-1.

The sample should be filtered to remove solids and then acidified ( $\text{pH} < 2$  with nitric acid) as soon as possible after sampling prior to analysis, as specified in ISO 5667-3.

It is important that the laboratory receives a representative sample, unmodified during the transport or storage and in an undamaged container.

### 7.2 Concentration step and valence cycle

The radioactive tracers are added during this initial treatment phase.

If required, a concentration step can be done by evaporation or co-precipitation. After evaporation, the residue is dissolved with acid mixture. The co-precipitation with the iron hydroxide, for example,  $[\text{Fe}(\text{OH})_3]$  at  $\text{pH} = 8$  can be done by adding iron nitrate or chloride. After centrifugation or filtration, the precipitate is dissolved with acid mixture.

The procedure shall include a valence cycle, adjusting the tracer and the actinide isotopes to measure oxidation states, in order to achieve the identical chemical behaviour for all of them. For example, a primarily reduction step is carried out by adding  $\text{NH}_2\text{OH}\cdot\text{HCl}$ ,  $\text{NaHSO}_3$  or  $\text{Na}_2\text{S}_2\text{O}_3$ , then an oxidation step is done with  $\text{NaNO}_2$  or  $\text{H}_2\text{O}_2$ .

### 7.3 Chemical separation

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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<sup>[7]</sup> or by extraction chromatographic resins.<sup>[7],[8]</sup>

It is also possible to use a mix of [Annexes A and B](#): use of an ion exchange resin followed by the use of a specific extraction chromatographic resin for americium phase purification only.

### 7.4 Preparation of the source to be measured

#### 7.4.1 General

The source can be prepared by electrodeposition on a planchet, a stainless steel disk ([7.4.2](#)), or by co-precipitation ([7.4.3](#)).

#### 7.4.2 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 the planchet. The procedure described in [Annex C](#) applies to 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.

#### 7.4.3 Co-precipitation method

Co-precipitation, using fluoride compounds, can be carried out after the chemical separation of the actinides from other interfering elements. It allows the precipitation of the radionuclide(s) in the form

of a thin layer of cerium or lanthanum fluoride on a filter. The procedure described in [Annex D](#) can be applied to the two chemical separation methods described in [Annexes A and B](#).

## 7.5 Background determination

Measure the background using a blank sample prepared for the method chosen (for example: laboratory water). This blank sample should be prepared without tracer to be used for obtaining the background count rates.

## 7.6 Counting efficiency determination

The counting efficiency is estimated by measuring the calibration source. It is needed to determine the chemical recovery.

## 7.7 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 interferent is present and an adequate resolution is obtained.

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## 8 Expression of results (standards.iteh.ai)

### 8.1 Calculation of the activity concentration

The actinides activity concentration is calculated by integrating the number of counts in the corresponding peaks of the tracer and isotopes to be measured. The results of these integrations, divided by the counting time, are the gross count rates  $r_{gT}$  and  $r_g$  for the tracer and the actinide isotopes, respectively.

$r_{gT}$  and  $r_g$  are corrected for the background contribution and, if needed, of the tailing contribution of the highest derived energy peaks that depends on the detector characteristics.

Background count rates are calculated from the alpha emission spectrum of a blank sample, and integrating the number of counts in the regions of interest (ROI) in which the peaks appear in the sample spectrum. The results of these integrations, divided by the counting time, are the background count rates,  $r_{0T}$  and  $r_0$  for the tracer and the actinide isotopes, respectively.

The blank sample is obtained and measured, applying the procedure in use in the laboratory with tracer (for the test method qualification) or without tracer (for background quantification).

The activity concentration  $c_A$  of the actinides isotopes is calculated as given in Formula (1):

$$c_A = (r_{gT} - r_{0T}) / (V \cdot R) = (r_g - r_0) \cdot w \quad \text{with} \quad w = \frac{1}{V \cdot R} \quad (1)$$

The total measurement yield is determined from the activity  $A$  of the tracer added and from the net count rate in the corresponding peak as given in Formula (2):

$$R = (r_{gT} - r_{0T}) / A \cdot f \quad (2)$$

With  $f$  being the correction factor for possible bias when calculating results for curium isotopes using  $^{243}\text{Am}$  tracer or  $^{237}\text{Np}$  results using  $^{236}\text{Pu}$  tracer.  $f$  is the ratio between the Pu/Np and/or Am/Cm chemical yield