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

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

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Foreword

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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.

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ISO 13167 was prepared by Technical Committee ISO/TC 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 may be required by some national authorities.

An international standard on a test method of isotopes of plutonium americium, curium activity concentrations in water samples is justified for test laboratory carrying out these measurements, required sometimes by national authorities, as laboratories may have to obtain a specific accreditation for radionuclide measurement in drinking water samples.

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

NOTE The guidance level is the activity concentration 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 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.

Water quality – plutonium, americium, curium and neptunium - Test method using alpha spectrometry

1 Scope

This document describes a test method for measuring actinides elements (^{238}Pu , $^{239+240}\text{Pu}$, ^{241}Am , ^{242}Cm , $^{243+244}\text{Cm}$ and ^{237}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 5×10^{-3} to 5×10^{-4} Bq/l for a volume of the test portion of 0,1 l to 5 l.

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 detection limit and decision threshold for ionizing radiation measurements*

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

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

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

3 Terms, definition and symbols,

For the purposes of this document, the terms, definitions and symbols given in ISO 18589-1, ISO 11074, ISO 31-9 and ISO 11929 apply and 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 becquerel per litre
c_A^*	Decision threshold, in becquerel per litre
$c_A^\#$	Detection limit, in becquerel per litre
$c_A^<, c_A^>$	Lower and upper limits of the confidence interval, in becquerel per litre
ε	Detection yield
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 second
t_g	Sample counting time, in second
$u(c_A)$	Standard uncertainty associated with the measurement result; in becquerel per litre
U	Expanded uncertainty, calculated by $U = k \cdot u(c_A)$ with $k = 1, 2, \dots$, in becquerel per litre
V	Volume of test sample, in litre

4 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 [1] [2] [3] [4].

Specific chemical separation and purification procedures are required in order to avoid interference from the presence of natural or artificial α emitters and stable nuclides in the sample, in quantities that are often larger than the actinide isotopes.

These procedures will 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 α emitting radionuclides, such as uranium and thorium isotopes, whose emissions may interfere with those of actinide isotopes.

The total yield for each analysis (product of chemical separation yield and detection efficiency) will be determined by adding a standard solution of tracer: ^{236}Pu can be used for plutonium isotopes and neptunium, ^{242}Pu can be used for plutonium isotopes only and ^{243}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}Am tracer behaviour. This may lead to a potential bias that shall be quantified.

It is possible to quantify neptunium on the basis of ^{236}Pu tracer behaviour. This may lead to a potential bias that shall be quantified.

5 Chemical reagents and equipment

5.1 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.

5.2 Equipment

Usual laboratory apparatus and in particular the following equipment:

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 ion-implanted silicon. This interaction instantly changes the conductivity of the silicon, proportional to the energy of the incoming alpha-particle. To achieve well-resolved spectra, the detection system needs to be maintained at a pressure <10 Pa. Resolution can be further enhanced through increasing distance between source and detector.

Pipette, suitable for the accurate transfer of (for example 100 µl) tracer solution with a total precision within ± 1 %.

Balance, for example, capable of achieving ± 0,1 mg precision.

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

6 Procedure

6.1 Sampling

Conditions of sampling shall follow ISO 5667-1.

The sample should be filtered to remove solids and then acidified (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.

6.2 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 [Fe(OH)₃] at 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 be measured to the same degree of oxidation, in order to achieve the identical chemical behaviour for all of them. As example, a primarily reduction step is carried out by adding NH₂OH HCl or NaHSO₃ or Na₂S₂O₃, then an oxidation step is done with NaNO₂ or H₂O₂.

6.3 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 [6] or by extraction chromatographic resin [7], [8].

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.

6.4 Preparation of the source to be measured

6.4.1 General

The source can be prepared by electrodeposition on a planchet, a stainless steel disk (6.4.2), or by co-precipitation (6.4.3).

6.4.2 Electrodeposition method

Electrodeposition is carried out after the chemical separation of the actinides from interfering elements. It allows the electrochemical deposition of the radionuclides 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 the metal cations, likely to form insoluble hydroxides can be deposited at the same time as the actinides.

6.4.3 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 on a filter. The procedure described in Annex D can be applied to the two chemical separation methods described in Annexes A and B.

6.5 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.

6.6 Measurement

The actinide activity concentration is calculated by counting the sample source for an appropriate time. The same equipment conditions 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.

The spectra should be inspected to confirm good peak separation and no interfering peaks.

7 Expression of results

7.1 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) or without tracer (for background quantification).