INTERNATIONAL STANDARD

ISO 13167

First edition
2015-12-15

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 13167:2015(E)

ISO copyright office
Ch. de Blandonnet 8 • CP 401
CH-1214 Vernier, Geneva, Switzerland
Tel. +41 22 749 01 11
Fax +41 22 749 09 47
copyright@iso.org
www.iso.org

Contents

Page

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 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*.

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 used 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}Pu, ^{239}Pu, ^{240}Pu, ^{241}Am, ^{242}Cm, ^{243}Cm, ^{244}Cm, ^{237}Np activity concentrations 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 (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.

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}Pu, $^{239+240}$Pu, ^{241}Am, ^{242}Cm, $^{243+244}$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 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
$c_{\mathrm{A}}^{\#}$	Detection limit, in becquerels per litre
$c_{\mathrm{A}}^{\triangleleft}, c_{\mathrm{A}}^{\triangleright}$	Lower and upper limits of the confidence interval, in becquerels per litre
ε	Counting efficiency
r_{g} , r_{gT}	Gross count rate per second from measured actinides isotopes and tracer, respectively
r_0, $r_{0\mathrm{T}}$	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
$u(c_{\mathrm{A}})$	Standard uncertainty associated with the measurement result, in becquerels per litre
U	Expanded uncertainty, calculated by $U = k \cdot u\left(c_{\mathrm{A}}\right)$ with k = 1, 2,..., in becquerels per litre
V	Volume of test sample, in litres
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.

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

Specific chemical separation and purification procedures are required in order 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.

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 α 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}Pu can be used for plutonium isotopes and ^{237}Np, ^{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 using a standard solution and/or participation in inter-laboratory comparison tests.

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 using a standard solution and/or participation in inter-laboratory comparison.

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

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 µl) tracer solution with a total precision within ± 1 %.

6.2.3 Balance, capable of achieving ± 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 ($pH < 2$ 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, $[Fe(OH)_3]$ 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 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 $NH_2OH.HCl$, $NaHSO_3$ or $Na_2S_2O_3$, then an oxidation step is done with $NaNO_2$ or H_2O_2.

7.3 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 resins.[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.

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.

8 Expression of results

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):

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

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):

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

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

For plutonium isotopes and ^{241}Am, the factor f is equal to 1.

The counting efficiency ε allows one to calculate the chemical yield R_c. This value is important for quality control.

8.2 Standard uncertainty

According to the GUM (ISO/IEC Guide 98-3), the standard uncertainty of c_A is calculated by Formula (3):

$$u(c_A)=\sqrt{w^2\cdot(u^2(r_g)+u^2(r_0))+c_A^2 . u_{rel}^2(w)}=\sqrt{w^2 .\left(r_g/t_g+r_0/t_0\right)+c_A^2 . u_{rel}^2(w)} \tag{3}$$

where the uncertainty of the counting time is neglected.

The relative standard uncertainty of w is calculated by Formula (4):

$$u_{rel}^2(w)=u_{rel}^2(R)+u_{rel}^2(V) \tag{4}$$

The relative standard uncertainty of R is calculated by Formula (5):

$$u_{rel}^2(R)=u_{rel}^2(r_{gT}-r_{0T})+u_{rel}^2(f)+u_{rel}^2(A)=(r_{gT}/t_g+r_{0T}/t_0)/(r_{gT}-r_{0T})^2+u_{rel}^2(f)+u_{rel}^2(A) \tag{5}$$

$u_{rel}(A)$ includes all the uncertainties related to the tracer activity: that is in the standard solution, preparation of the tracer solution and the addition of the tracer solution to sample.

For the calculation of the characteristic limits according to ISO 11929, $\tilde{u}(\tilde{c}_A)$ is needed, i.e. the standard uncertainty of c_A as a function of its true value, calculated by Formula (6):

$$\tilde{u}(\tilde{c}_A)=\sqrt{w^2\cdot((\tilde{c}_A/w+r_0)/t_g+r_0/t_0)+\tilde{c}_A^2\cdot u_{rel}^2(w)} \tag{6}$$

8.3 Decision threshold

In accordance with ISO 11929, the decision threshold, c_A^*, is obtained from the above Formula (6) for $\tilde{c}_A=0$. This yields Formula (7):

$$c_A^{\ *}=k_{1-\alpha} .\ \tilde{u}(0)=k_{1-\alpha} . w . \sqrt{r_0/t_g+r_0/t_0} \tag{7}$$

α = 0,05 with $k_{1-\alpha}=1{,}65$ is often chosen by default.

8.4 Detection limit

In accordance with ISO 11929, the detection limit, $c_A^{\ \#}$, is calculated by Formula (8):

$$\begin{aligned}&c_A^{\ \#}=c_A^{\ *}+k_{1-\beta}\cdot\tilde{u}(c_A^{\ \#})=\\&c_A^{\ *}+k_{1-\beta}\cdot\sqrt{w^2\cdot((c_A^{\ \#}/w+r_0)/t_g+r_0/t_0)+c_A^{\ \#2}\cdot u_{rel}^2(w)}\end{aligned} \tag{8}$$

$\beta=0{,}05$ with $k_{1-\beta}=1{,}65$ is often chosen by default.

The detection limit can be calculated by solving Formula (8) for $c_A^{\ \#}$ or, more simply, by iteration with a starting approximation $c_A^{\ \#}=2\cdot c_A^{\ *}$.

When taking $\alpha = \beta$, then $k_{1-\alpha} = k_{1-\beta} = k$ and the solution of Formula (8) is given by Formula (9):

$$c_A{}^{\#} = \frac{2 \cdot c_A{}^{*} + \left(k^2 \cdot w\right)/t_g}{1 - k^2 \cdot u_{\mathrm{rel}}^2\left(w\right)} \quad (9)$$

8.5 Confidence limits

In accordance with ISO 11929, the lower, $c_A{}^{\triangleleft}$, and upper, $c_A{}^{\triangleright}$, limits of the confidence interval are calculated using Formulae (10) and (11):

$$c_A{}^{\triangleleft} = c_A - k_p \cdot u(c_A);\, p = \omega \cdot (1 - \gamma/2) \quad (10)$$

$$c_A{}^{\triangleright} = c_A + k_q \cdot u(c_A);\, q = 1 - \omega \cdot \gamma/2 \quad (11)$$

where

$\omega = \Phi(y/u(y))$ with Φ being the distribution function of the standardized normal distribution;

$\omega = 1$ may be set if $c_A \geq 4 \cdot u(c_A)$ and Formula (12) applies:

$$c_A{}^{\triangleleft,\triangleright} = c_A \pm k_{1-\gamma/2} \cdot u(c_A) \quad (12)$$

$\gamma = 0{,}05$ with $k_{1-\gamma/2} = 1{,}96$ is often chosen by default.

9 Quality assurance and quality control programme

9.1 General

Quality control operations shall meet the requirements of ISO/IEC 17025.

9.2 Influence quantities

Special precautions shall be taken to minimize the influence of quantities that can affect the measurement results:

- spike of tracer with an inappropriate activity (too small or too large) compared to the actinide activity to be quantified;
- poor chemical separation with interferences on the alpha spectrum;
- a small chemical yield (a value of at least 30 % is expected) which can be a consequence of important losses during the chemical separation steps or in the preparation of the source;

The chemical yield R_c can be calculated using Formula (13):

$$R_c = R/\varepsilon \quad (13)$$

- presence in the test sample of a small amount of the actinide isotope that is used as the tracer, e.g. ^{242}Pu. In this case, ^{236}Pu can be used as tracer instead.

9.3 Instrument verification and calibration

Major instrument parameters (energy calibration, efficiency calibration, energy resolution, and background spectrum) shall be periodically checked within a quality assurance programme established by the laboratory and following the manufacturer's instructions.

Make sure the whole of the data acquisition chain is performing satisfactorily, using an alpha-emitting radioactive standard source (e.g. ^{239}Pu).

9.4 Method verification

The test method repeatability shall also be checked, e.g. by replicate measurements.

The acceptance limits of the test parameters contained in 9.2 and 9.3 shall be defined.

Periodical verifications of the accuracy of the method shall be run. These may be accomplished by:

- participating in inter-laboratory comparison tests;
- analysing reference materials.

9.5 Demonstration of analyst capability

If an analyst has not used this procedure before, a precision and bias test shall be performed by running a duplicate measurement of a reference or spiked material. Acceptance limits shall be defined by the laboratory.

A similar test shall be performed by analysts routinely using this procedure with a periodicity defined by the laboratory. Acceptance limits shall be defined.

10 Test report

The test report shall conform to ISO/IEC 17025 requirements and shall contain the following information:

a) reference to this standard;

b) identification of the sample;

c) units in which the result is expressed;

d) the test result, $c_A \pm u(c_A)$ or $c_A \pm U$, with the associated k value.

Complementary information can be provided such as:

- probabilities α, β and $(1 - \gamma)$;
- decision threshold and the detection limit;
- depending on the customer request there are different ways to present the result:
  - when the activity concentration c_A is compared with the decision threshold, in accordance with ISO 11929, the result of the measurement should be expressed as $\leq c_A^*$ when the result is below the decision threshold;
  - when the activity concentration c_A is compared with the detection limit, the result of the measurement can be expressed as $\leq c_A^\#$ when the result is below the detection limit;
- chemical yield value;
- any relevant information likely to affect the results.

If the detection limit exceeds the guideline value, it shall be documented that the method is not suitable for the measurement purpose.

Annex A
(informative)

Chemical separation of actinides on anionic resin

A.1 Principle

The actinide isotopes are separated from the other radionuclides and from the matrix in an anionic complex form using an ion exchange resin in a column in a nitric acid medium and hydrochloric one.

A.2 Apparatus

Usual laboratory apparatus and the following.

A.2.1 Hot plate.

A.2.2 Glass column.

A.3 Reagents

A.3.1 Tracer solutions.

A.3.2 Hydrochloric acid, concentrated, (HCl) : 37 %.

A.3.3 Nitric acid, concentrated, (HNO_3) : 65 %.

A.3.4 Ammonia, concentrated, (NH_4OH) : 25 %.

A.3.5 Sodium nitrite ($NaNO_2$).

A.3.6 Anionic resin 1 × 4 50/100 mesh or 1 × 8 100/200 mesh.

A.3.7 Nitric acid, solution $c(HNO_3)$: 8 mol/l.

A.3.8 Hydrochloric acid, solution $c(HCl)$: 2, 8 and 10 mol/l.

A.3.9 Hydroxylamine hydrochloride $NH_2OH.HCl$, 0,2 mol/l in hydrochloric acid (HCl), 2 mol/l.

A.3.10 Methanol.

A.3.11 Solution A: 10 % (vol) 10 mol/l HNO_3 and 90 % (vol) of methanol, freshly made.

A.3.12 Solution B: 30 % (vol) 0,5 mol/l HNO_3 and 70 % (vol) of methanol, freshly made.

A.4 Procedure

A.4.1 General

Add a known activity of tracers to the water sample.

This procedure is carried out with two main steps: chemical separation and elution.

In all steps, if not specified, the flow rate should be of approximately 1 ml/min.

NOTE In some cases, the flow through resin columns is very poor because of sample composition. Working with vacuum is therefore very helpful to support the flow.

A.4.2 Separation of plutonium and neptunium

Carry out the following steps.

a) Fill the column with the resin (for example, a 150 ml volume column can be filled with about 100 ml of prepared resin).

b) Prepare a 8 mol/l nitric acid solution.

c) Convert the resin to the nitrate form by passing 150 ml of the 8 mol/l HNO_3.

d) Place a clean beaker under the column and load the actinide solution on the column.

e) Wash the beaker and column with portions of 8 mol/l HNO_3 up to 150 ml with a flow of approximately 1 ml/min. This eluate E1 contains Am, Cm, Fe and U.

f) Place a clean beaker under the column and wash the column with 80 ml of 8 mol/l HCl. This eluate E2 contains Th.

A.4.3 Elution of plutonium and neptunium

A.4.3.1 Carry out the following steps.

a) Place a clean beaker under the column.

b) Elute the plutonium and neptunium, E3, with 90 ml of 0,2 mol/ $NH_2OH.HCl$ in 2 mol/l HCl with a flow of approximately 0,5 ml/min.

c) Evaporate the eluate E3 slowly until the volume is less than 25 ml and add carefully 2 ml of concentrated HNO_3.

A.4.3.2 When the presence of relative important amounts of other actinides is suspected, it is necessary to carry out a purification process that basically consists of the repetition of the following steps.

a) Evaporate the eluate E3 to dryness.

b) Add 50 ml of 8 mol/l HNO_3.

c) Add 0,6 g of $NaNO_2$ and heat to remove the nitrous fumes and leave to cool.

d) Repeat the procedure from A.4.3.1 to separate and elute the plutonium and neptunium.

e) Prepare the source by electrodeposition or co-precipitation, as described in Annex C and Annex D, respectively.

A.4.4 Separation of americium and curium

Carry out the following steps.

a) Evaporate the eluate E1 to dryness.

b) Dissolve the residue with 50 ml of 10 mol/l HCl.

c) Fill the column with 15 ml of anionic resin.

d) Prepare 50 ml of a 10 mol/l HCl solution and wash the column to convert the resin to the chloride form. Discard the washings.

e) Place a clean beaker under the column and pour the solution obtained in b) into the top of the column.

f) Wash the beaker and column with portions of 10 mol/l HCl up to 50 ml. The eluate E4 is obtained from e) and f).

g) Evaporate the eluate E4 to dryness.

A.4.5 Purification of americium and curium

Carry out the following steps.

a) Dissolve the residue of eluate E4 with 10 ml of 10 mol/l HNO_3.

b) Stir and add 90 ml of methanol.

c) Fill the column with 15 ml of anionic resin.

d) Prepare 50 ml of a fresh solution A and add to the resin.

e) Pour the solution into the top of the column.

f) Wash the beaker and column with 50 ml of solution A.

g) Place a clean beaker under the column and elute americium and curium with 100 ml of a fresh solution B as E5.

h) Evaporate to dryness the eluate E5.

i) Dissolve the residue with:

    1) 1 ml of concentrated HNO_3 in case of electrodeposition;

    2) 50 ml of 0,2 mol/l HCl in case of co-precipitation.

j) Prepare the source by electrodeposition or co-precipitation, as described in Annex C and Annex D, respectively.

Annex B
(informative)

Chemical separation of actinides by specific resins

B.1 Principle

This technique is based on the selective chromatographic extraction of plutonium isotopes, ^{241}Am, curium isotopes and ^{237}Np using a resin coated with a specific extractant CMPO/TBP. The chemical separation is fast and well suited for monitoring plutonium and americium activity in the environment.

B.2 Apparatus

Usual laboratory apparatus and the following.

B.2.1 Scales, to an accuracy of 0,1 mg.

B.2.2 Evaporator or hot plate.

B.2.3 CMPO/TBP extractant-coated resin columns (2 ml volume in general).

B.3 Reagents

B.3.1 Tracer solutions.

B.3.2 Nitric acid (HNO_3): 3 mol/l in aluminium nitrate ($Al(NO_3)_3$): 0,5 mol/l.

B.3.3 Nitric acid (HNO_3): 2 mol/l in sodium nitrite $NaNO_2$: 0,1 mol/l.

B.3.4 Nitric acid, concentrated, (HNO_3) : 69 % minimum.

B.3.5 Different nitric acid (HNO_3) solutions: 3 mol/l, 2 mol/l, 0,5 mol/l, 1 mol/l.

B.3.6 Ascorbic acid.

B.3.7 Hydrogen peroxide (H_2O_2): 30 %.

B.3.8 Hydrochloric acid, concentrated, (HCl),: 37 %.

B.3.9 Hydrochloric acid solution (HCl): 0,2 mo/l.

B.3.10 Ammonium hydrogen oxalate ($NH_4HC_2O_4$): 0,1 mol/l.

B.4 Procedure

B.4.1 General

Add a known activity of tracers to the water sample acidified with nitric acid.

This procedure is carried out with two main steps: chromatographic extraction and elution of americium, curium, plutonium and neptunium. In all steps, if not specified, the flow rate should be of approximately 1 ml/min.

In some cases, a ferric hydroxide co-precipitation can be added before the separation steps to concentrate actinides.

NOTE In some case, the flow through resin columns is very poor because of sample composition. Working with vacuum is therefore very helpful to support the flow.

B.4.2 Extraction of americium and curium

Carry out the following operations.

a) Evaporate the solution to be analysed to dryness.

b) Add 10 ml of 3 mol/l HNO_3 in 0,5 mol/l $Al(NO_3)_3$ to dissolve the precipitate.

c) Add 0,1 g of ascorbic acid to keep all Fe as Fe(II) (to ensure reduction of Pu and Np but also to be sure no Fe(III) could interfere with Pu(III) and Am(III) uptake), heat until total dissolution and leave to cool.

d) Set up the CMPO/TBP column.

e) Prepare the resin by passing 25 ml of 3 mol/l HNO_3 in 0,5 mol/l $Al(NO_3)_3$.

f) Pour the solution into the top of the column.

g) Wash the beaker with 5 ml of 3 mol/l HNO_3, pour into the top of the column.

h) Wash the column with 5 ml of 2 mol/l HNO_3, 5 ml of 2 mol/l HNO_3 in 0,1 mol/l $NaNO_2$. Discard the washings.

i) Place a clean beaker under the column and elute americium and curium with 5 ml 0,5 mol/l HNO_3, 3 ml 9 mol/l HCl and 20 ml of 4 mol/l HCl (E6).

j) Evaporate the eluate E6 to dryness.

k) Dissolve the residue with:

    1) 1 ml of concentrated HNO_3 in case of electrodeposition;

    2) 50 ml of 0,2 mol/l HCl in case of co-precipitation.

l) Prepare the source by electrodeposition or co-precipitation, as described in Annex C and Annex D, respectively.

B.4.3 Elution of plutonium and neptunium

Carry out the following operations.

a) Place a clean beaker under the column.

b) Elute plutonium and neptunium as E7 with 20 ml of 0,1 mol/l $NH_4HC_2O_4$ in 1 mol/l HCl (U is not eluted).

c) Evaporate the eluate E7 to dryness. The white precipitate is in the oxalate form.

Thorium is known to be very insoluble in water. If the presence of thorium is suspected in the sample, it is necessary, prior to Pu/Np elution, to add a step to wash the column with 20 ml of 4 mol/l HCl in 0,1 mol/l HF to elute thorium as it interferes with plutonium in α-spectrometry.

B.4.4 Oxalate decomposition

Carry out the following operations.

a) Add 1 ml of 69 % HNO_3, and five drops of 30 % H_2O_2, evaporate to dryness.

b) Add 1 ml of 69 % HNO_3, and 1 ml of 37 % HCl, evaporate to dryness.

c) Add 1 ml of 69 % HNO_3, evaporate to dryness.

d) Repeat the step c) until the precipitate disappears.

e) Dissolve the residue in 4 ml of 1 mol/l HNO_3 (Solution E8).

f) Evaporate the solution E8 to dryness.

g) Dissolve the residue with:

   1) 1 ml of concentrated HNO_3 in case of electrodeposition;

   2) 50 ml of 0,2 mol/l HCl in case of co-precipitation.

h) Prepare the source by electrodeposition or co-precipitation, as described in Annex C and Annex D, respectively.

Annex C
(informative)

Preparation of the source by electrodeposition

C.1 Principle

Using a DC generator to apply different voltages between two electrodes leads to the reduction of the metal cations dissolved in the electrolyte. The reduction that takes place at the cathode leads to the formation of a deposit of actinides in hydroxide form.

C.2 Apparatus

C.2.1 Electrodeposition apparatus, generally composed of the following.

C.2.1.1 Glass or polyethylene electrodeposition cell.

C.2.1.2 Platinum wire (anode).

C.2.1.3 Stainless steel disk (cathode) with a diameter adapted to the electrodeposition cell.

C.2.1.4 DC power supply.

C.2.2 Hot plate.

C.2.3 Petri dish.

C.3 Reagents

C.3.1 Nitric acid, concentrated (HNO_3): 65 %.

C.3.2 Sodium sulfate (Na_2SO_4): 0,3 mol/l.

C.3.3 Sulfuric acid, concentrated (H_2SO_4): 95 % to 97 %.

C.3.4 Thymol blue ($C_{27}H_{30}O_5S$): 0,04 %.

C.3.5 Ammonia, concentrated (NH_4OH): 25 %.

C.3.6 Sulfuric acid (H_2SO_4): 1 %.

C.3.7 Ammonia (NH_4OH): 1 %.