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Second edition
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Measurement of radioactivity in the environment — Soil —

Part 4:
Plutonium 238 and plutonium 239 + 240 — Test method using alpha spectrometry

Mesurage de la radioactivité dans l'environnement — Sol —

Partie 4: Plutonium 238 et plutonium 239 + 240 — 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).

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 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 the following URL: www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 85, *Nuclear energy, nuclear technologies and radiological protection*, Subcommittee SC 2, *Radiological protection*.

This second edition cancels and replaces the first edition (ISO 18589-4:2009), which has been technically revised.

The main change compared to the previous edition are as follows:

— The introduction has been reviewed accordingly to the generic introduction adopted for the standards published on the radioactivity measurement in the environment.

— Reference in the text to ISO 18589-2 has been made mandatory.

A list of all parts in the ISO 18589 series can be found on the ISO website.

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

Everyone is exposed to natural radiation. The natural sources of radiation are cosmic rays and naturally occurring radioactive substances which exist in the earth and flora and fauna, including the human body. Human activities involving the use of radiation and radioactive substances add to the radiation exposure from this natural exposure. Some of those activities, such as the mining and use of ores containing naturally-occurring radioactive materials (NORM) and the production of energy by burning coal that contains such substances, simply enhance the exposure from natural radiation sources. Nuclear power plants and other nuclear installations use radioactive materials and produce radioactive effluent and waste during operation and decommissioning. The use of radioactive materials in industry, agriculture and research is expanding around the globe.

All these human activities give rise to radiation exposures that are only a small fraction of the global average level of natural exposure. The medical use of radiation is the largest and a growing man-made source of radiation exposure in developed countries. It includes diagnostic radiology, radiotherapy, nuclear medicine and interventional radiology.

Radiation exposure also occurs as a result of occupational activities. It is incurred by workers in industry, medicine and research using radiation or radioactive substances, as well as by passengers and crew during air travel. The average level of occupational exposures is generally below the global average level of natural radiation exposure (see Reference [1]).

As uses of radiation increase, so do the potential health risk and the public's concerns. Thus, all these exposures are regularly assessed in order to:

— improve the understanding of global levels and temporal trends of public and worker exposure;

— evaluate the components of exposure so as to provide a measure of their relative importance;

— identify emerging issues that may warrant more attention and study. While doses to workers are mostly directly measured, doses to the public are usually assessed by indirect methods using the results of radioactivity measurements of waste, effluent and/or environmental samples.

To ensure that the data obtained from radioactivity monitoring programs support their intended use, it is essential that the stakeholders (for example nuclear site operators, regulatory and local authorities) agree on appropriate methods and procedures for obtaining representative samples and for handling, storing, preparing and measuring the test samples. An assessment of the overall measurement uncertainty also needs to be carried out systematically. As reliable, comparable and 'fit for purpose' data are an essential requirement for any public health decision based on radioactivity measurements, international standards of tested and validated radionuclide test methods are an important tool for the production of such measurement results. The application of standards serves also to guarantee comparability of the test results over time and between different testing laboratories. Laboratories apply them to demonstrate their technical competences and to complete proficiency tests successfully during interlaboratory comparisons, two prerequisites for obtaining national accreditation.

Today, over a hundred International Standards are available to testing laboratories for measuring radionuclides in different matrices.

Generic standards help testing laboratories to manage the measurement process by setting out the general requirements and methods to calibrate equipment and validate techniques. These standards underpin specific standards which describe the test methods to be performed by staff, for example, for different types of sample. The specific standards cover test methods for:

— naturally-occurring radionuclides (including ^{40}K, ^{3}H, ^{14}C and those originating from the thorium and uranium decay series, in particular ^{226}Ra, ^{228}Ra, ^{234}U, ^{238}U and ^{210}Pb) which can be found in materials from natural sources 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, and curium), ^{3}H, ^{14}C, ^{90}Sr and gamma-ray emitting radionuclides found in waste, liquid and gaseous effluent, in environmental matrices (water, air, soil and biota), in food and in animal feed as a result of authorized releases into the environment, fallout from the explosion in the atmosphere of nuclear devices and fallout from accidents, such as those that occurred in Chernobyl and Fukushima.

The fraction of the background dose rate to man from environmental radiation, mainly gamma radiation, is very variable and depends on factors such as the radioactivity of the local rock and soil, the nature of building materials and the construction of buildings in which people live and work.

A reliable determination of the activity concentration of gamma-ray emitting radionuclides in various matrices is necessary to assess the potential human exposure, to verify compliance with radiation protection and environmental protection regulations or to provide guidance on reducing health risks. Gamma-ray emitting radionuclides are also used as tracers in biology, medicine, physics, chemistry, and engineering. Accurate measurement of the activities of the radionuclides is also needed for homeland security and in connection with the Non-Proliferation Treaty (NPT).

This document describes the generic requirements to quantify the activity of ^{238}Pu and 239 + 240 isotopes of plutonium in soil samples after proper sampling, sample handling and test sample preparation in a testing laboratory or in situ.

This document is to be used in the context of a quality assurance management system (ISO/IEC 17025).

ISO 18589 is published in several parts for use jointly or separately according to needs. These parts are complementary and are addressed to those responsible for determining the radioactivity present in soil, bedrocks and ore (NORM or TENORM). The first two parts are general in nature describe the setting up of programmes and sampling techniques, methods of general processing of samples in the laboratory (ISO 18589-1), the sampling strategy and the soil sampling technique, soil sample handling and preparation (ISO 18589-2). ISO 18589-3 to ISO 18589-5 deal with nuclide-specific test methods to quantify the activity concentration of gamma emitters radionuclides (ISO 18589-3 and ISO 20042), plutonium isotopes (ISO 18589-4) and ^{90}Sr (ISO 18589-5) of soil samples. ISO 18589-6 deals with non-specific measurements to quantify rapidly gross alpha or gross beta activities and ISO 18589-7 describes in situ measurement of gamma-emitting radionuclides.

The test methods described in ISO 18589-3 to ISO 18589-6 can also be used to measure the radionuclides in sludge, sediment, construction material and products following proper sampling procedure.

This document is one of a set of International Standards on measurement of radioactivity in the environment.

Additional parts can be added to ISO 18589 in the future if the standardization of the measurement of other radionuclides becomes necessary.

Measurement of radioactivity in the environment — Soil —

Part 4:
Plutonium 238 and plutonium 239 + 240 — Test method using alpha spectrometry

1 Scope

This document describes a method for measuring ^{238}Pu and 239 + 240 isotopes in soil by alpha spectrometry samples using chemical separation techniques.

The method can be used for any type of environmental study or monitoring. These techniques can also be used for measurements of very low levels of activity, one or two orders of magnitude less than the level of natural alpha-emitting radionuclides.

The test methods described in this document can also be used to measure the radionuclides in sludge, sediment, construction material and products following proper sampling procedure[2][3][4][5][7][8].

The mass of the test portion required depends on the assumed activity of the sample and the desired detection limit. In practice, it can range from 0,1 g to 100 g of the test sample.

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 11074, *Soil quality — Vocabulary*

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

ISO 18589-1, *Measurement of radioactivity in the environment — Soil — Part 1: General guidelines and definitions*

ISO 18589-2, *Measurement of radioactivity in the environment — Soil — Part 2: Guidance for the selection of the sampling strategy, sampling and pre-treatment of samples*

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

ISO/IEC Guide 98-3, *Uncertainty of measurement — Part 3: Guide to the expression of uncertainty in measurement (GUM:1995)*

3 Terms, definitions and symbols

For the purposes of this document, the terms and definitions given in ISO 11074, ISO 18589-1 and ISO 80000-10 apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at http://www.electropedia.org/

4 Symbols

m	mass of the test portion, expressed in kilograms;
a	activity per unit of mass, expressed in becquerel per kilogram;
A	activity of the tracer added, expressed in becquerel, at the time of measurement;
t_g	sample counting time, expressed in seconds;
t_0	background counting time, expressed in seconds;
r_g, r_{gt}	gross count rate per second from measured plutonium and tracer, respectively
r_0, r_{0t}	background count rate per second from measured plutonium and tracer, respectively
R	total measurement yield;
$u(a)$	standard uncertainty associated with the measurement result, expressed in becquerel per kilogram;
U	expanded uncertainty, expressed in becquerel per kilogram, calculated by $U = k \cdot u(a)$ with $k = 1, 2, \ldots$;
a^*	decision threshold, expressed in becquerel per kilogram;
$a^\#$	detection limit, expressed in becquerel per kilogram;
$a^{\triangleleft}$, $a^{\triangleright}$	lower and upper limits of the confidence interval, expressed in becquerel per kilogram.

5 Principle

The plutonium is deposited as a thin source for measurement by alpha spectrometry using a grid chamber or semi-conductor detector-type apparatus. The sources are usually prepared by electro-deposition or co-precipitation after chemical separation and purification of the plutonium isotopes present in the test portion[9][10][11][12]. Direct deposition on the planchette, such as electro-spraying, can also be used.

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 greater than those of the plutonium isotopes during their measurement.

These procedures allow the removal of the main sources of interference, including

- the salt content of the leaching solutions, especially hydrolysable elements, in order to prepare the thinnest deposited source,
- other α-emitting radionuclides, such as ^{241}Am and the thorium isotopes, whose emissions can interfere with those of plutonium isotopes.

The total yield for each analysis (chemical separation yield, thin-layer deposit and measurement) is determined by adding a standard solution of ^{236}Pu or ^{242}Pu considered as tracer. As a result, the procedure shall include a valence cycle, adjusting the tracer and the plutonium isotopes being measured to the same oxidation state, in order to achieve identical chemical behaviour for all of them.

6 Chemical reagents and equipment

The chemical reagents and equipment are described in Annex A for plutonium desorption, in Annexes B, C and D for chemical treatment and in Annexes E and F for the preparation of the deposited source.

All the chemical reagents required to carry out this procedure shall be of analytical grade.

7 Procedure

7.1 Plutonium desorption

It is necessary to desorb the plutonium from the soil test portion and into solution. When the plutonium is adsorbed onto soil particles from an aqueous solution or onto global fallout particles directly deposited on the soil, it is readily desorbed by direct acid treatment. Plutonium metabolized by animals or plants forms an organic complex that can be found in soil samples. It is released by the destruction of organic matter present in the soil by calcination of the test sample at 550 °C to 600 °C. In some cases, when heated, plutonium can form refractory compounds that require hydrofluoric acid treatment or fusion to make them soluble[12].

Two methods of plutonium desorption are described in Annex A.

In order to quantify the recovery yield, a tracer is added at the start of this step of the procedure; time is allowed, usually up to one day, to obtain equilibrium before starting the plutonium desorption.

7.2 Chemical separation

There are three commonly used techniques for the chemical separation of plutonium: liquid-liquid extraction, extraction on an ion-exchange resin or specific-extraction chromatographic resin. One method from each technique is presented in Annexes B to D: organic solvent[14], separation by anionic resin[14] or by extraction chromatographic resin[16][17].

7.3 Preparation of the source to be measured

7.3.1 General

The source can be prepared by deposition, either by electro-deposition on a planchette (a stainless steel disk) (7.3.2), or by co-precipitation (7.3.3).

7.3.2 Electro-deposition method

Electro-deposition is carried out after the chemical separation of the plutonium from interfering elements. It allows the electrochemical deposition of the radionuclides in an ultra-thin layer onto the planchette[17][18]. The procedure described in Annex E applies to the three chemical separation methods described in Annexes B, C and D.

NOTE Electro-deposition is not a selective method because the metal cations likely to form insoluble hydroxides can be deposited at the same time as the plutonium.

7.3.3 Co-precipitation method

Co-precipitation, using fluoride compounds, can be carried out after the chemical separation of the plutonium 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 F can be applied to the three chemical separation methods described in Annexes B to D.

7.4 Background determination

Measure the background using a blank prepared for the method chosen, starting with a clean test portion (or directly distilled water).

7.5 Measurement

The plutonium activity per unit of mass is calculated by counting the sample source for an appropriate time. The same equipment conditions should be used for the measurements of the sample, the background and the reference measurements standards.

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.

8 Expression of results

8.1 Calculation of the activity per unit of mass

The plutonium activity is calculated by integrating the number of counts in the corresponding peaks of the radionuclide tracer, ^{238}Pu and/or $^{239+240}$Pu, of the alpha emission spectrum of the sample, obtained by alpha spectrometry. 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 plutonium isotopes, respectively.

r_{gt} and r_{g} are corrected for the background contribution and, if needed, for the contribution of the tailing of higher-energy peaks, which depends on the detector characteristics.

Background count rates are calculated from the alpha-emission spectrum of a blank sample by integrating the number of counts in the regions of interest (ROI) in which the peaks appear in the sample spectrum. The result of this integration, divided by the counting time, is the background count rate, $r_{0\mathrm{t}}$ and r_0, for the tracer and the plutonium isotopes, respectively.

The blank sample is obtained and measured by applying the procedure used in the analysis without soil and with or without tracer.

The activity per unit of mass, a, of the plutonium isotope is calculated as given in Formula (1):

$$a = \left(r_{\mathrm{g}} - r_0\right) / \left(m \cdot R\right) = \left(r_{\mathrm{g}} - r_0\right) \cdot w \qquad (1)$$

where $w = \dfrac{1}{m \cdot R}$.

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

$$R = \left(r_{\mathrm{gt}} - r_{0\mathrm{t}}\right) / A \qquad (2)$$

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

8.2 Standard uncertainty

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

$$\begin{aligned} u(a) &= \sqrt{w^2 \cdot \left[u^2\left(r_{\mathrm{g}}\right) + u^2\left(r_0\right)\right] + a^2 \cdot u_{\mathrm{rel}}^2(w)} \\ &= \sqrt{w^2 \cdot \left(r_{\mathrm{g}}/t_{\mathrm{g}} + r_0/t_0\right) + a^2 \cdot u_{\mathrm{rel}}^2(w)} \end{aligned} \qquad (3)$$

where the uncertainty of the counting time is neglected.

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

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

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

$$\begin{aligned} u_{\mathrm{rel}}^2(R) &= u_{\mathrm{rel}}^2\left(r_{\mathrm{gt}} - r_{0\mathrm{t}}\right) + u_{\mathrm{rel}}^2(A) \\ &= \left(r_{\mathrm{gt}}/t_{\mathrm{g}} + r_{0\mathrm{t}}/t_0\right) \Big/ \left(r_{\mathrm{gt}} - r_{0\mathrm{t}}\right)^2 + u_{\mathrm{rel}}^2(A) \end{aligned} \tag{5}$$

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

The calculation of the characteristic limits [in accordance with ISO 11929 (all parts)] requires a determination of $\tilde{u}(\tilde{a})$, i.e., the standard uncertainty of a as a function of its true value, as calculated by Formula (6):

$$\tilde{u}(\tilde{a}) = \sqrt{w^2 \cdot \left[\left(\tilde{a}/w + r_0\right)/t_{\mathrm{g}} + r_0/t_0\right] + \tilde{a}^2 \cdot u_{\mathrm{rel}}^2(w)} \tag{6}$$

8.3 Decision threshold

The decision threshold, a^*, is obtained from Formula (6) for $\tilde{a} = 0$ [in accordance with ISO 11929 (all parts)]. This yields Formula (7):

$$a^* = k_{1-\alpha} \cdot \tilde{u}(0) = k_{1-\alpha} \cdot w \cdot \sqrt{r_0/t_{\mathrm{g}} + r_0/t_0} \tag{7}$$

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

8.4 Detection limit

The detection limit, $a^\#$, is calculated by Formula (8) [in accordance with ISO 11929 (all parts)]:

$$\begin{aligned} a^\# &= a^* + k_{1-\beta} \cdot \tilde{u}\left(a^\#\right) \\ &= a^* + k_{1-\beta} \cdot \sqrt{w^2 \cdot \left[\left(a^\#/w + r_0\right)/t_{\mathrm{g}} + r_0/t_0\right] + a^{\#2} \cdot u_{\mathrm{rel}}^2(w)} \end{aligned} \tag{8}$$

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

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

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

$$a^\# = \frac{2 \cdot a^* + \left(k^2 \cdot w\right)/t_{\mathrm{g}}}{1 - k^2 \cdot u_{\mathrm{rel}}^2(w)} \tag{9}$$

8.5 Confidence limits

The lower limit, $a^\triangleleft$, and the upper limit, $a^\triangleright$, of the confidence interval are calculated using Formulae (10) and (11) [in accordance with ISO 11929 (all parts)]:

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

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

where

$\omega = \Phi[y/u(y)]$, where Φ is the distribution function of the standardized normal distribution.

ω may be set equal to 1 if $a \geq 4 \cdot u(a)$ and Formula (12) applies:

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

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

9 Test report

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

a) a reference to this document, i.e. ISO 18589-4:2019;

b) identification of the sample;

c) units in which the results are expressed;

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

Complementary information can be provided such as the following:

- 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 per unit of mass, a, is compared with the decision threshold [in accordance with ISO 11929 (all parts)], the result of the measurement should be expressed as $\leq a^*$ when the result is below the decision threshold,
  - when the activity per unit of mass, a, is compared with the detection limit, the result of the measurement can be expressed as $\leq a^\#$ when the result is below the detection limit. If the detection limit exceeds the guideline value, it shall be documented that the method is not suitable for the measurement purpose;
- any relevant information likely to affect the results.

Annex A
(informative)

Plutonium desorption

A.1 Principles

The radioactive tracers, ^{236}Pu or ^{242}Pu, are added during this initial treatment phase.

The test portion is ashed between 550 °C and 600 °C and in this situation the extraction of the plutonium might not be possible without a multiple-acid digestion (see A.4.1).

When the test portion of soil does not contain organic matter, plutonium from hot particles or high-fired plutonium, the sample should not be ashed but rather the plutonium extracted by nitric acid digestion (see A.4.2).

A.2 Chemical reagents

A.2.1 Certified solution of ^{236}Pu **or** ^{242}Pu **tracer.**

A.2.2 Hydrochloric acid, concentrated, $c(HCl) = 12{,}0$ mol/l, $\rho = 1{,}19$ g/ml, mass fraction $w(HCl) = 37$ %.

A.2.3 Nitric acid, concentrated, $c(HNO_3) = 14{,}4$ mol/l, $\rho = 1{,}40$ g/ml, mass fraction $w(HNO_3) = 65$ %.

A.2.4 Nitric acid, diluted, $c(HNO_3) = 8$ mol/l.

A.2.5 Hydrogen peroxide, $w(H_2O_2) = 30$ %.

A.2.6 Sodium nitrite ($NaNO_2$).

A.2.7 Hydrofluoric acid, concentrated, $c(HF) = 22{,}6$ mol/l, $\rho = 1{,}13$ g/ml, mass fraction $w(HF) = 48$ % to 51 %.

A.2.8 Oxalic acid.

A.2.9 Nitric acid, diluted, $c(HNO_3) = 4$ mol/l.

A.2.10 Calcium nitrate.

A.2.11 Ammonium hydroxide (NH_4OH).

A.2.12 Ferric chloride ($FeCl_3$) **solution.**

A.2.13 Sodium hydroxide (NaOH).

A.2.14 Hydrochloric acid, diluted, $c(HCl) = 9{,}0$ mol/l.

A.3 Equipment

A.3.1 Standard laboratory equipment.

A.3.2 Analytical balance, accurate to 0,1 mg.

A.3.3 Hot plate.

A.3.4 Centrifuge and **tubes.**

A.3.5 Furnace.

A.3.6 Crucible.

A.3.7 Beaker, Teflon[1].

A.4 Procedure

A.4.1 Multiple-acid digestion

This procedure, based on a cycle of acid leaching and dry evaporation, includes the following steps.

a) The test sample prepared in accordance with ISO 18589-2 shall be weighted between 0,1 g and 15 g. The mass of the test portion shall depend on the expected activity of the sample and the required detection limit.

b) Ash the test portion at between 550 °C and 600 °C for at least 5 h. Leave it to cool in the crucible (A.3.6).

c) Transfer the sample to a glass beaker and gradually add 10 ml of diluted HNO_3 (A.2.4) per gram of sample and stir.

d) Wait up to one day.

e) Add the ^{236}Pu or ^{242}Pu tracer solution (A.2.1) and homogenize by stirring.

f) Add slowly 150 ml of concentrated HNO_3 (A.2.3) and 50 ml of concentrated HCl (A.2.2).

g) Boil for 1 h while stirring.

h) Cool to room temperature.

i) Decant the liquid into another beaker and retain.

j) Repeat steps f) to h) combining the liquid with the reserved solution and evaporate to dryness.

k) Transfer the remaining soil to a Teflon beaker (A.3.7) with 30 ml of concentrated HNO_3 (A.2.3), add 15 ml of HF (A.2.7) and evaporate to dryness.

l) Add 30 ml of concentrated HNO_3 (A.2.3) and 30 ml of HF (A.2.7). Evaporate to dryness.

m) Add 5 ml of concentrated HNO_3 (A.2.3) and 1 ml H_2O_2 (A.2.5). Evaporate to dryness.

n) Add 20 ml of concentrated HNO_3 (A.2.3) in 5 ml amounts, drying between each aliquot.

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[1] Teflon™ is an example of a suitable product available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of this product.

o) Transfer the remaining solids to a centrifuge tube (A.3.4) using 8 mol/l HNO_3 (A.2.4). Centrifuge and mix this solution with the liquid retained from step i).

p) Repeat step n) twice with 50 ml of 8 mol/l HNO_3 (A.2.4).

q) Evaporate the mixed solution to near dryness and dissolve in 50 ml of 8 mol/l HNO_3 (A.2.4).

The test portion is ready to undergo radiochemical separation.

It is possible to use larger test portions, but a final step of plutonium precipitation is required to avoid possible interference with stable elements that it is necessary to eliminate before the radiochemical separation. This precipitation consists of the addition of $FeCl_3$ to the solution after digestion and the precipitation of iron when adding ammonia to pH 10. The supernatant is discarded and the analysis continues with the iron precipitate that contains the plutonium and the other actinides.

The dissolution may also be carried out using a microwave digestion apparatus. Operating conditions for each system should be adjusted to the type of apparatus and the nature of the soil to be digested.

A.4.2 Simple nitric acid digestion

This procedure is based on a cycle of acid leaching and dry evaporation.

a) The test sample prepared in accordance with ISO 18589-2 shall be weighted between 0,1 g and 15 g. The mass of the test portion depends on the expected activity of the sample and the required detection limit.

b) Gradually add 10 ml of 8 mol/l HNO_3 (A.2.4) per gram of sample.

c) Add the ^{236}Pu or ^{242}Pu tracer (A.2.1) and homogenize by stirring.

d) Digest on a hot plate (A.3.3) for at least 8 h with intermittent additions of H_2O_2 (A.2.5). Leave it to cool.

e) Transfer the test portion to a centrifuge tube (A.3.4) and separate the solid matter from the liquid phase. The supernatant is stored.

   Instead of centrifuging the test portion, it can be filtered using a fibreglass filter.

f) Rinse the beaker with 8 mol/l HNO_3 (A.2.4), add to the same tube (A.3.4), stir and centrifuge. Add the supernatant to the liquid retained in step e). Repeat the process until the supernatant is clear.

g) Evaporate the supernatant to dryness.

h) Add 50 ml of 8 mol/l HNO_3 (A.2.4).

i) Add 0,6 g of $NaNO_2$ (A.2.6), heat to remove the nitrous fumes and leave it to cool.

The test portion is ready to undergo a radiochemical separation.

It is possible to use larger test portions, but a final step of plutonium precipitation is required to avoid possible interference with stable elements that it is necessary to eliminate before the radiochemical separation. This precipitation consists of the addition of $FeCl_3$ to the solution after digestion and the precipitation of iron when adding ammonia to pH 10. The supernatant is discarded and the analysis continues with the iron precipitate that contains the plutonium and the other actinides.

The dissolution may also be carried out using a microwave digestion apparatus. Operating conditions for each system should be adjusted to the type of apparatus used and the nature of the soil to be digested.

A.4.3 Precipitation for plutonium and americium

When americium, in addition to plutonium, is measured on the same large-mass test portion, the specific precipitation procedure shall be adapted as follows.

a) Once the leaching is completed, add 50 g of oxalic acid (A.2.8) and 200 mg of Ca as nitrate (A.2.10).

b) Precipitate with NH_4OH (A.2.11) to a pH of 2,5. This allows the co-precipitation of Pu with calcium oxalate and the separation of Fe and other cations as the precipitation is done at a very low pH.

c) The system is maintained at 90 °C whilst stirring for 6 h and then the crystals are allowed to grow overnight.

d) The supernatants are transferred to a beaker and the precipitate is preserved.

e) Add 200 mg of Ca (A.2.10) to the supernatants and repeat the previous steps.

f) The final precipitate is dissolved with 8 mol/l HNO_3 (A.2.4) and then is transferred to a 250 ml beaker.

g) Evaporate on a hot plate (A.3.3) to dryness and eliminate the oxalate completely.

h) Once the oxalate is eliminated, dissolve in 4 mol/l HNO_3 (A.2.9) and add 50 mg of Fe in a solution of $FeCl_3$ (A.2.12). Then precipitate with NaOH (A.2.13) to a pH of 12.

i) Filtrate and eliminate the supernatants.

j) Dissolve the precipitate with 9 mol/l HCl (A.2.14).

k) Evaporate to dryness.

l) Add 50 ml of 8 mol/l HNO_3 (A.2.4).

m) Add 0,6 g of $NaNO_2$ (A.2.6), heat to remove the nitrous fumes and leave to cool.

The test portion is ready to undergo a radiochemical separation.

Annex B
(informative)

Chemical separation of plutonium by an organic solvent

B.1 Principle

The plutonium isotopes are extracted from the sample solution, in a nitric medium (1 mol/l to 10 mol/l), using an organic cation exchanger (HDEHP) after adjustment to valence IV. The purification of the organic phase is completed by washing the solution in 6 mol/l HCl. Finally, the plutonium is extracted again in an aqueous medium using a mixture of 6 mol/l HCl and KI.

B.2 Chemical reagents

B.2.1 HDEHP [di-(2-ethylhexyl) hydrogen phosphate] **solution**, 145 ml of HDEHP for 855 ml of heptane.

Ensure the reagent is pure by washing it in an equal volume of water whose pH after this operation shall be greater than 3.

B.2.2 Heptane (C_7H_{16}).

B.2.3 Hydrochloric acid, diluted, $c(\text{HCl}) = 6$ mol/l.

B.2.4 Potassium iodide (KI), crystallized.

B.2.5 Nitric acid, diluted, $c(\text{HNO}_3) = 4$ mol/l.

B.2.6 Sodium nitrite ($NaNO_2$), crystallized.

B.3 Equipment

B.3.1 Standard laboratory equipment.

B.3.2 Scales, to an accuracy of 0,1 mg.

B.3.3 Evaporator or hot plate.

B.3.4 Separatory funnels, adapted to the volumes being treated.

B.3.5 Stirrer, automatic, for the separatory funnel.

B.4 Procedure

This procedure is carried out after the digestion of the samples described in Annex A with three main steps: extraction, washing the organic phase and re-extraction of plutonium isotopes.

B.4.1 Extraction of plutonium

This procedure includes the following steps:

a) Take an aliquot or all of the solution being analysed, which shall be clear. If not, dilute the solution with HNO_3 (B.2.5).

b) Adjust the plutonium to an oxidation state of IV by adding several milligrams of $NaNO_2$ (B.2.6).

c) Leave to react for 10 min.

d) Transfer this solution into a separatory funnel and balance by stirring vigorously for 15 min in an equal volume of HDEHP diluted to 15 % in heptane (B.2.2).

B.4.2 Washing of the organic phase

This procedure includes the following steps:

a) Once settled, remove the aqueous phase.

b) Wash the organic phase in the same volume of HCl (B.2.3) for 5 min.

c) Leave to settle and throw away the aqueous phase. Repeat this operation until the solution is completely discoloured (to remove the iron).

B.4.3 Re-extraction of plutonium in an aqueous phase

This procedure includes the following steps:

a) Add 25 ml of 6 mol/l HCl (B.2.3) and 500 mg of KI (B.2.4) to the organic phase and re-extract the plutonium in an aqueous phase by stirring vigorously for 15 min.

b) Leave it to settle.

c) Transfer the aqueous phase into a second separatory funnel (B.3.4).

d) Wash for 5 min in an equal volume of heptane (B.2.2) to remove traces of HDEHP.

e) Collect the aqueous phase in a 100 ml beaker.

Annex C
(informative)

Chemical separation of plutonium on anionic resin

C.1 Principle

The plutonium isotopes are separated from the other radionuclides and from the soil matrix in an anionic complex form using an ion-exchange resin in a column with media of nitric and hydrochloric acid.

C.2 Chemical reagents

C.2.1 **Hydrochloric acid**, concentrated, $w(\text{HCl}) = 37\ \%$.

C.2.2 **Nitric acid**, concentrated, $w(\text{HNO}_3) = 65\ \%$.

C.2.3 **Ammonia**, concentrated, $w(\text{NH}_4\text{OH}) = 25\ \%$.

C.2.4 **Sodium nitrite** (NaNO_2).

C.2.5 **Anionic resin**, 1X8, 100/200 mesh.

C.2.6 **Nitric acid**, diluted, $c(\text{HNO}_3) = 8$ mol/l.

C.2.7 **Hydrochloric acid**, diluted, $c(\text{HCl}) = 8$ mol/l.

C.2.8 **Hydroxyl ammonium chloride** $c(\text{NH}_3\text{OH})\text{Cl} = 0{,}2$ mol/l in hydrochloric acid, $c(\text{HCl}) = 2$ mol/l.

C.3 Equipment

C.3.1 **Standard laboratory equipment.**

C.3.2 **Hot plate.**

C.3.3 **Column**, glass, 30 ml.

C.4 Procedure

C.4.1 General

This procedure is carried out, after the digestion of the sample as described in Annex A and includes two main steps: chemical separation and elution.

C.4.2 Separation of plutonium

a) Fill the column with the resin (C.2.5).

b) Prepare the 8 mol/l nitric solution (C.2.6).

c) Convert the resin to the nitrate form by passing 150 ml of the 8 mol/l HNO_3 (C.2.6) at a flow rate of approximately 1 ml/min.

d) Pour the Pu solution into the top of the column.

e) Wash the column and beaker with portions of 8 mol/l HNO_3 (C.2.6), up to 150 ml at a flow rate of approximately 1 ml/min. Discard the washings.

f) Wash the column with 80 ml of 8 mol/l HCl (C.2.7). Discard the washings.

C.4.3 Elution of plutonium

a) Place a clean beaker under the column.

b) Elute the Pu with 90 ml of 0,2 mol/l $(NH_3OH)Cl$ in 2 mol/l HCl (C.2.8) at a flow rate of approximately 0,5 ml/min.

c) Evaporate the eluate slowly until the volume is less than 25 ml and add carefully 2 ml of concentrated HNO_3 (C.2.2).

d) When the presence of relatively 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:

    1) Evaporate the eluate to dryness.

    2) Add 50 ml of 8 mol/l HNO_3 (C.2.6).

    3) Add 0,6 g of $NaNO_2$ (C.2.4) and heat to remove the nitrous fumes and leave to cool.

    4) Repeat the procedure from C.4.3 to separate and elute the Pu.

Annex D
(informative)

Chemical separation of plutonium by specific resins

D.1 Principle

This technique is based on the selective chromatographic extraction of Pu using a resin containing a specific extractant CMPO/TBP (for example TRU-Spec® 2)). The chemical separation is fast and well suited for monitoring plutonium activity in the environment.

D.2 Chemical reagents

D.2.1 Nitric acid (HNO_3), 3 mol/l containing aluminium nitrate, $c[Al(NO_3)_3]$ = 0,5 mol/l.

D.2.2 Nitric acid, $c(HNO_3)$ = 2 mol/l, containing 0,1 mol/l sodium nitrite, $c(NaNO_2)$ = 0,1 mol/l.

D.2.3 Nitric acid, concentrated, at least $w(HNO_3)$ = 69 %.

D.2.4 Nitric acid (HNO_3), diluted, different concentrations:

D.2.4.1 $c(HNO_3)$ = 3 mol/l.

D.2.4.2 $c(HNO_3)$ = 2 mol/l.

D.2.4.3 $c(HNO_3)$ = 1 mol/l.

D.2.4.4 $c(HNO_3)$ = 0,5 mol/l.

D.2.5 Ammonium thiocyanate, diluted, $c(NH_4SCN)$ = 0,1 mol/l.

D.2.6 Ascorbic acid.

D.2.7 Iron sulfamate, 0,6 = mol/l.

D.2.8 Hydrogen peroxide, $w(H_2O_2)$ = 30 %.

D.2.9 Hydrochloric acid, concentrated, $w(HCl)$ = 37 %.

D.2.10 Ammonium oxalate, diluted, $c(NH_4HC_2O_4)$ = 0,1 mol/l.

D.3 Equipment

D.3.1 Standard laboratory equipment.

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2) TRU-Spec® is an example of a suitable product available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of this product.

D.3.2 Balance, accurate to 0,1 mg.

D.3.3 Evaporator or **hot plate.**

D.3.4 Separatory funnels, adapted to the volumes to be treated.

D.3.5 Stirring apparatus, for the separatory funnel.

D.3.6 Resin columns, containing the extractant CMPO/TBP (TRU-Spec®).

D.4 Procedure

D.4.1 General

This procedure is carried out after the digestion of the samples as described in Annex A and includes two main steps: extraction and elution of plutonium.

D.4.2 Extraction of plutonium

The procedure includes the following steps:

a) Evaporate the solution being analysed to dryness.

b) Add 10 ml of 3 mol/l HNO_3 in 0,5 mol/l $Al(NO_3)_3$ (D.2.1). Dissolve the precipitate.

c) Add some drops of NH_4SCN (D.2.5). If the dissolution becomes red, add ascorbic acid (D.2.6) until the colour disappears. Then heat and leave to cool.

d) Repeat step c) if the dissolution is not complete.

e) Add 1 ml of 0,6 mol/l iron sulfamate (D.2.7). Stir until dissolution.

f) Add 0,1 g of ascorbic acid (D.2.6), heat until total dissolution and leave to cool.

g) Set up the CMPO/TBP (TRU-Spec®) column (D.3.6).

h) Prepare the resin by passing through it 25 ml of 3 mol/l HNO_3 containing 0,5 mol/l $Al(NO_3)_3$ (D.2.1) at a flow rate of approximately 1 ml/min.

i) Pour the Pu solution onto the top of the column (D.3.6).

j) Wash the beaker with 5 ml of 3 mol/l HNO_3 (D.2.4.1) and pour onto the top of the column.

k) Wash the column with 5 ml of 2 mol/l HNO_3 (D.2.4.2), 5 ml of 2 mol/l HNO_3 containing 0,1 mol/l $NaNO_2$ (D.2.2) and 5 ml of 0,5 mol/l HNO_3 (D.2.4.4). Discard the washings.

D.4.3 Elution of plutonium

The procedure includes the following steps:

a) Place a clean beaker under the column.

b) Elute the plutonium with 20 ml of 0,1 mol/l $NH_4HC_2O_4$ (D.2.10).

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

D.4.4 Oxalate decomposition

The procedure includes the following steps.

a) Add 1 ml of 69 % HNO_3 (D.2.3) and five drops of 30 % H_2O_2 (D.2.8), leave to dryness.

b) Add 1 ml of 69 % HNO_3 (D.2.3), and 1 ml of 37 % HCl (D.2.9), leave to dryness.

c) Add 1 ml of 69 % HNO_3 (D.2.3), leave to dryness.

d) Repeat step c) until the precipitate disappears.

e) Dissolve in 4 ml of 1 mol/l HNO_3 (D.2.4.3).

Annex E
(informative)

Preparation of the source by electro-deposition

E.1 Principle

Applying different voltages between two electrodes using a DC generator 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 actinide hydroxides.

E.2 Chemical reagents

E.2.1 Nitric acid, concentrated, $w(HNO_3)$ = 65 %.

E.2.2 Sodium sulfate, $c(Na_2SO_4)$ = 0,3 mol/l.

E.2.3 Sulfuric acid, concentrated, $w(H_2SO_4)$ = 95 % to 97 %.

E.2.4 Thymol blue, 0,04 %.

E.2.5 Ammonia, concentrated, $w(NH_4OH)$ = 25 %.

E.2.6 Sulfuric acid, diluted, $w(H_2SO_4)$ = 1 %.

E.2.7 Ammonium hydroxide, diluted, $w(NH_4OH)$ = 1 %.

E.3 Equipment

E.3.1 Electro-deposition apparatus, composed of

a) a glass or polyethylene electro-deposition cell;

b) a platinum wire (anode);

c) a planchette or stainless steel disc (cathode) with a diameter adapted to the electro-deposition cell;

d) a DC generator;

e) a hot plate;

f) a Petri dish.