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Water quality — Actinium-227 — Test method using alpha-spectrometry

Qualité de l'eau — Actinium-227 — Méthode d'essai par spectrométrie alpha

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Foreword

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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 document 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).

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This document was prepared by Technical Committee ISO/TC 147, *Water quality*, Subcommittee SC 3, *Radioactivity measurements*.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

Radionuclides are present throughout the environment; thus, water bodies (e.g. surface waters, ground waters, sea waters) contain radionuclides which can be of either natural, or anthropogenic origin:

— naturally-occurring radionuclides, including, ^{3}H, ^{14}C, ^{40}K and those originating from the thorium and uranium decay series, in particular ^{210}Pb, ^{210}Po, ^{222}Rn, ^{226}Ra, ^{228}Ra, ^{227}Ac, ^{232}Th, ^{231}Pa, ^{234}U and ^{238}U, can be found in water bodies due to either natural processes (e.g. desorption from the soil and runoff by rain water) or released from technological processes involving naturally-occurring radioactive materials (e.g. mining, mineral processing, oil, gas, and coal production, water treatment and the production and use of phosphate fertilisers);

— anthropogenic radionuclides such as ^{55}Fe, ^{59}Ni, ^{63}Ni, ^{90}Sr, ^{99}Tc, transuranic elements (Np, Pu, Am, and Cm) and some gamma emitting radionuclides such as ^{60}Co and ^{137}Cs can also be found in natural waters. Small quantities of anthropogenic radionuclides can be discharged from nuclear facilities to the environment as a result of authorized routine releases. The radionuclides present in liquid effluents are usually controlled before being discharged to the environment[1] and water bodies. Anthropogenic radionuclides used for medical and industrial applications can be released to the environment after use. Anthropogenic radionuclides are also found in waters due to contamination from fallout resulting from above-ground nuclear detonations and accidents such as those that have occurred at the Chornobyl and Fukushima nuclear facilities.

Radionuclide activity concentrations in water bodies can vary according to local geological characteristics and climatic conditions and can be locally and temporally enhanced by releases from nuclear installations during planned, existing, and emergency exposure situations[2][3]. Some drinking-water sources can thus contain radionuclides at activity concentrations that could present a human health risk. The World Health Organization (WHO) recommends to routinely monitor radioactivity in drinking waters[4] and to take proper actions when needed to minimize the health risk.

National regulations usually specify the activity concentration limits that are authorized in drinking waters, water bodies, and liquid effluents to be discharged to the environment. These limits can vary for planned, existing, and emergency exposure situations. As an example, during either a planned or existing situation, the WHO guidance level for ^{227}Ac in drinking water is 0,1 $Bq \cdot l^{-1}$, see Notes 1 and 2. Compliance with these limits is assessed by measuring radioactivity in water samples and by comparing the results obtained with their associated uncertainties as specified by ISO/IEC Guide 98-3 and ISO 5667-20[5].

NOTE 1 If the value is not specified in Annex 6 of Reference [4], the value has been calculated using the formula provided in Reference [4] and the dose coefficient data from References [6] and [7].

NOTE 2 The guidance level calculated in Reference [4] is the activity concentration with an intake of 2 $l \cdot d^{-1}$ of drinking water for one year, results in an effective dose of 0,1 $mSv \cdot a^{-1}$ to members of the public. This is an effective dose that represents a very low level of risk to human health and which is not expected to give rise to any detectable adverse health effects[4].

This document contains method(s) to support laboratories, which need to determine ^{227}Ac in water samples. The method(s) described in this document can be used for various types of waters (see Scope). Minor modifications such as sample volume and counting time can be made if needed to ensure that the characteristic limit, decision threshold, detection limit and uncertainties are below the required limits. This can be done for several reasons such as emergency situations, lower national guidance limits, and operational requirements.

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WARNING — Persons using this document should be familiar with normal laboratory practices. This document does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to determine the applicability of any other restrictions.

IMPORTANT — It is essential that tests conducted according to this document be carried out by suitably trained staff.

1 Scope

This document specifies a test method to determine the activity concentration of ^{227}Ac in all types of waters by alpha spectrometry.

The test method is applicable to test samples of supply/drinking water, rainwater, surface and ground water, marine water, as well as cooling water, industrial water, domestic, and industrial wastewater after proper sampling and handling and test sample preparation (see ISO 5667-1, ISO 5667-3, ISO 5667-10). Filtration of the test sample is necessary.

The detection limit depends on the sample volume, the instrument used, the background count rate, the detection efficiency, the counting time, the chemical yield, and the progeny ingrowth. The method described in this document, using currently available alpha spectrometry apparatus, has a detection limit of approximately 0,03 Bq·l^{-1}, when directly measuring the alpha peak of ^{227}Ac. This detection limit is lower than the WHO criteria for safe consumption of drinking water for any actinide alpha emitter (0,1 Bq·l^{-1}).[4] This value can be achieved with a counting time of 48 h for a sample volume of 1 l.

Only a small fraction of ^{227}Ac decays through alpha emissions (~1,42 %). An option to lower the detection limit of the method is to wait, let the progenies of ^{227}Ac grow in, and measure an alpha progeny peak of ^{227}Ac (e.g. ^{215}Po). This is a longer technique, but a lower detection limit of approximately 0,000 2 Bq·l^{-1} can be obtained by re-counting the sample approximately 90 days after purification. The sample can be re-counted before 90 days, but with a higher detection limit.

The test method(s) described in this document can be used during planned, existing and emergency exposure situations as well as for wastewaters and liquid effluents with specific modifications that can increase the overall uncertainty, detection limit and threshold. For an emergency situation, it is preferable to reduce the counting time rather than the sample volume.

The analysis of ^{227}Ac adsorbed to suspended matter is not covered by this document.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

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

ISO/IEC Guide 99, *International vocabulary of metrology — Basic and general concepts and associated terms (VIM)*

ISO 5667-1, *Water quality — Sampling — Part 1: Guidance on the design of sampling programmes and sampling techniques*

ISO 5667-3, *Water quality — Sampling — Part 3: Preservation and handling of water samples*

ISO 5667-10, *Water quality — Sampling — Part 10: Guidance on sampling of waste water*

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

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

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

3 Terms, definitions and symbols

3.1 Terms and definitions

No terms and definitions are listed in this document.

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

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

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

3.2 Symbols

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

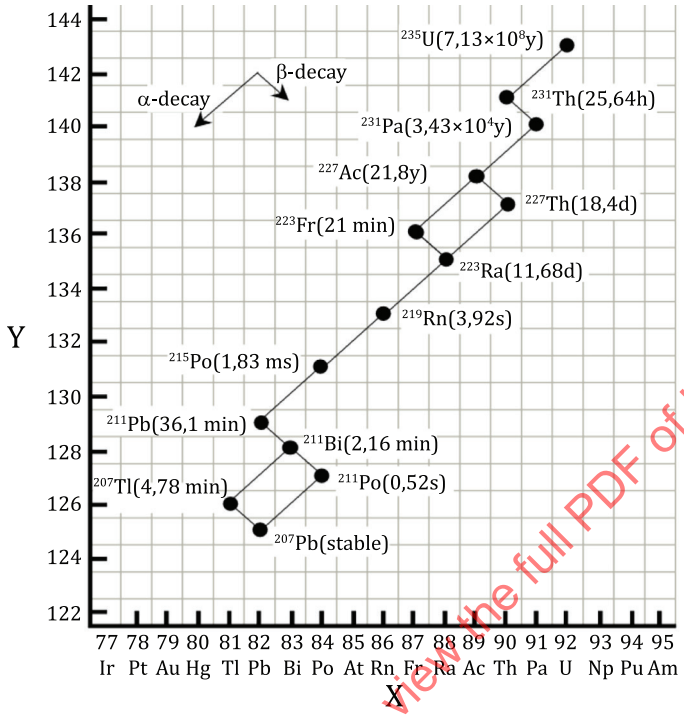
Symbol	Definition	Unit
A	Activity of ^{225}Ac tracer added	Bq
α	Probability of the false positive decision	
β	Probability of the false negative decision	
c_A	Activity concentration of ^{227}Ac measured in the sample	$Bq \cdot l^{-1}$
c_A^*	Decision threshold of the measurand	$Bq \cdot l^{-1}$
$c_A^\#$	Detection limit of the measurand	$Bq \cdot l^{-1}$
$c_A^\triangleleft, c_A^\triangleright$	Lower and upper limits of the probabilistically symmetric coverage interval of the measurand, respectively	$Bq \cdot l^{-1}$
$c_A^<, c_A^>$	Lower and upper limits of the shortest coverage interval of the measurand, respectively	$Bq \cdot l^{-1}$
$\widetilde{c_A}$	Possible or assumed true quantity values of the measurand	$Bq \cdot l^{-1}$
c_{AT}	Activity concentration of ^{225}Ac tracer solution at the moment of separation	$Bq \cdot l^{-1}$
ε	Counting efficiency	
ε_1	Counting efficiency for the first measurement of the indirect method	
ε_2	Counting efficiency for the second measurement of the indirect method	
F	Bias correction factor for the losses of ^{219}Rn	
Φ	Distribution function of the standardized normal distribution; $\Phi(k\,p) = p$ applies	
$1-\gamma$	Probability for the coverage interval of the measurand	
k_p	Quantiles of the standardized normal distribution for the probabilities p (for instance $p = 1-\alpha$, $1-\beta$ or $1-\gamma/2$)	
k_q	Quantiles of the standardized normal distribution for the probabilities q (for instance $q = 1-\alpha$, $1-\beta$ or $1-\gamma/2$)	
p, q	Probability for the coverage interval	

Symbol	Definition	Unit
λ	Decay constant of the isotope (ex: $\lambda_{215_{Po}}$ is the decay constant of ^{215}Po)	
m	Sample mass	kg
m_{ST}	Mass of tracer solution	g
N_0	Number of counts measured of the background on the alpha spectrum for a given time in the region of interest of ^{227}Ac, the measurand.	
N_{0T}	Number of counts measured of the background on the alpha spectrum for a given time in the region of interest of ^{225}Ac, the tracer.	
N_g	Number of counts measured on the alpha spectrum for a given time in the region of interest of ^{227}Ac, the measurand.	
N_T	Number of counts measured on the alpha spectrum for a given time in the region of interest of ^{225}Ac, the tracer.	
p, q	Probability for the coverage interval	
P_α	Probability of the isotope to decay through alpha particle emission (branching ratio)	
r_0	Background count rate in the region of interest of the measurand (^{227}Ac)	s^{-1}
r_{0T}	Background count rate in the tracer region of interest of the tracer (^{225}Ac)	s^{-1}
R	Total recovery	
R_c	Chemical recovery	
r_g	Gross count rate in the region of interest of the measurand (^{227}Ac)	s^{-1}
r_{net}	Net count rate of the isotope to measure (^{227}Ac)	s^{-1}
r_{netT}	Net count rate of the tracer (^{225}Ac)	s^{-1}
$r_{netT(1)}$	Net count rate of the tracer (^{225}Ac) for the first measurement of the indirect method	
$r_{netT(2)}$	Net count rate of the tracer (^{225}Ac) for the second measurement of the indirect method	
r_T	Gross count rate in the region of interest of the tracer (^{225}Ac)	s^{-1}
$t_{1/2}$	Radiological half-life of the isotope (ex: $t_{1/2}{}^{215}$Po is the radiological half-life of ^{215}Po)	s
t	Counting time	s
t_0	Counting time of the background by alpha spectrometry	s
t_1	Time elapsed between separation and counting	s
t_g	Sample counting time by alpha spectrometry	s
U	Expanded uncertainty	
u	Standard uncertainty	
u_{rel}^2	Relative uncertainty	
$u(c_A)$	Standard uncertainty of the activity concentration of ^{227}Ac	$Bq \cdot l^{-1}$
$\tilde{u}(\widetilde{c_A})$	Standard uncertainty of the estimator c_A as a function of an assumed true value $\widetilde{c_A}$ of the measurand	$Bq \cdot l^{-1}$
$\tilde{u}(c_A^{\#})$	Standard uncertainty of an estimate of the measurand when the true value is equivalent to the detection limit	
V	Sample volume	l
w	Ratio of activity concentration (c_A) on net count rate (r_{net}) (c_A/r_{net})	l^{-1}
ω	Distribution function of the standardized normal distribution	
$X_1, X_2, X_3, X_4, X_5, Z$	Terms for Formula 13	

If the results are expressed in mass activity, c_A is replaced by A and the volume, V, is replaced by the sample mass, m.

4 Principle

Actinium-227 is a naturally occurring radionuclide from the ^{235}U decay series (see Figure 1). It has a half-life of 21,772 ± 0,003 a[8], which is by far the longest half-life among Ac isotopes. Actinium-227 mainly decays through beta emission (98,58 %) to ^{227}Th and slightly through alpha emission (1,42 %) to ^{223}Fr (calculated based on the sum of alpha probabilities in Reference [8]).



Key

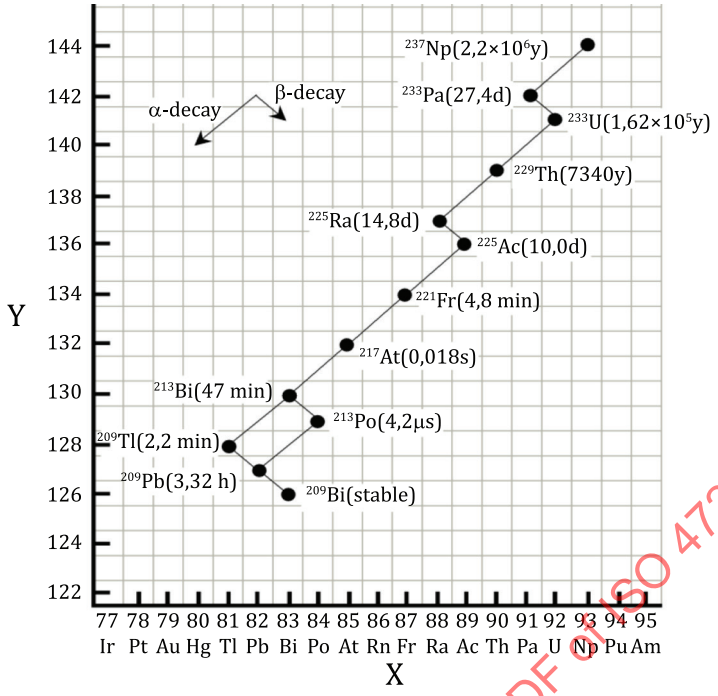
X atomic number (Z)

Y neutron number (N)

Figure 1 — Decay series of ^{235}U

To determine ^{227}Ac in water, a water sample of 1 l is collected, filtered, and acidified (see Clause 5).

The ^{225}Ac tracer is added to the sample from a ^{229}Th solution (see Figure 2). Given the relatively short radiological half-life of ^{225}Ac (10,0 ± 0,1d)[8], it is more practical to add ^{225}Ac tracer via a ^{229}Th solution of certified activity, which is in radiological equilibrium with its ^{225}Ac progeny. The parent ^{229}Th is separated from ^{225}Ac during the purification process. Enough tracer is added to obtain a good statistical precision and be easily distinguished from a blank sample (e.g. 15 mBq).



Key

X atomic number (Z)

Y neutron number (N)

Figure 2 — Decay series of ^{237}Np

Actinium is preconcentrated by coprecipitation at pH 3,5. The resulting precipitate is dissolved with an acidic solution. The solution is passed through an extraction chromatography resin (EXC) to purify Ac from potential interferences. The potential radioactivity interferences for the measurement of ^{227}Ac and the ^{225}Ac tracer are listed in Annex A. The main potential chemical interference is Ca^{2+}, which can precipitate with F^- and degrade the alpha resolution.

After purification, either a micro-precipitation with lanthanide fluoride or an electrodeposition is performed and ^{227}Ac is measured by alpha spectrometry for 48 h. The activity concentration of ^{227}Ac is calculated and reported (see Clause 9).

5 Sampling, handling and storage

Sampling, handling and storage of the water shall be done as specified in ISO 5667-1, ISO 5667-3 and ISO 5667-10. Guidance is given for the different types of water in References [9] to [16]. It is important that the laboratory receives a sample that is truly representative and has not been damaged nor modified during either transportation or storage.

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

6 Reagents and apparatus

6.1 Reagents

Use only reagents of recognized analytical grade. It is recommended to use acids and bases of trace metal grade or equivalent (a better purity grade can also be used).

6.1.1 **^{229}Th standard solution.**

6.1.2 **Titanium(III) trichloride in HCl solution (e.g. 12 mol·l^{-1} HCl),** $c(TiCl_3)$ = 0,78 mol·l^{-1}.

6.1.3 **Phosphoric acid solution,** $c(H_3PO_4)$ = 14,8 mol·l^{-1}.

6.1.4 **Sodium hydroxide solution,** $c(NaOH)$ = 10 mol·l^{-1}.

6.1.5 **Nitric acid solution,** $c(HNO_3)$ = 15,7 mol·l^{-1}.

6.1.6 **Sodium chloride solution,** $c(NaCl)$ = 0,5 mol·l^{-1}.

6.1.7 **Hydrogen peroxide solution,** $c(H_2O_2)$ = 8,82 mol·l^{-1}.

6.1.8 **Ultrapure water,** with a resistivity of more than 18,2 MΩ·cm at 25 °C and total organic carbon less than 1 µgl·l^{-1}.

6.1.9 **Nitric acid solution,** $c(HNO_3)$ = 2 mol·l^{-1}.

6.1.10 **Chromatographic extraction resin containing diglycolamine**, 2 ml cartridge.

6.1.11 **Hydrogen peroxide solution diluted in 2 mol·l^{-1} HNO_3,** $c(H_2O_2)$ = 0,44 mol·l^{-1} in $c(HNO_3)$ = 2 mol·l^{1}.

6.1.12 **Hydrochloric acid solution,** $c(HCl)$ = 0,1 mol·l^{-1}.

6.1.13 **Ethanol.**

6.1.14 **^{227}Ac standard solution.**

6.2 Apparatus

Usual laboratory equipment including the following:

6.2.1 **Vacuum filtration system.**

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

6.2.3 **Glass beakers.**

6.2.4 **Centrifuge.**

6.2.5 **Multi-hole vacuum box,** e.g. 12 positions.

6.2.6 **Analytical balance,** accuracy 0,1 mg.

6.2.7 **Centrifuge tubes (e.g. polypropylene),** e.g. 50 ml and 500 ml in volume.

6.2.8 **Pipettes.**

6.2.9 **Hot plate.**

6.2.10 Stirring plate.

6.2.11 Magnetic stirrer.

6.2.12 Metal discs with a sticky side.

6.2.13 Alpha spectrometer.

7 Procedure

7.1 Sample preparation

Filter and acidify the samples and a method blank sample prepared with ultrapure water as specified in Clause 5. A minimum of one method blank sample, which contains the tracer, is required, but several method blanks can be prepared. It is recommended to prepare spiked samples as well when performing the method for method validation.

In a large glass beaker (minimum 1 l), add $^{229}Th(^{225}Ac)$ (6.1.1) tracer solution by mass, m_{ST}.

Transfer approximately 1 l of the filtered and acidified sample, V, into the large glass beaker containing the tracer. Record the volume. Record the sample mass, m, to express the final activity concentration by sample mass.

Add 0,6 ml of 0,78 mol·l^{-1} $TiCl_3$ (6.1.2) and 0,6 ml of 14,8 mol·l^{-1} H_3PO_4 (6.1.3). Mix the sample to homogenize. A stirring plate with a magnetic stirrer is generally used to mix the sample, but the sample can be mixed by hand with a glass or plastic rod.

7.2 Coprecipitation

Add 14 ml of 10 mol·l^{-1} NaOH solution (6.1.4) to the sample for pre-pH adjustment and mix.

Adjust the pH to 3,5 using the 10 mol·l^{-1} NaOH solution (6.1.4) and a pH meter (or alternatively a pH paper with sufficient precision). A HNO_3 solution (e.g. 15,7 mol·l^{-1} HNO_3 (6.1.5)) can be used to reduce the pH if the pH goes above 3,5 during the pH adjustment step. Mix the sample well and wait 5 min. The pH shall be lower than 3,8 to avoid the precipitation of Ca^{2+} as $CaHPO_4$, but higher than 3,0 to not affect the chemical recovery. Calcium is partially retained by a diglycolamine based resin in 2 mol·l^{-1} HNO_3 and precipitates at the CeF_3 micro-precipitation step.

Centrifuge the sample in the same large centrifuge tube (e.g. 500 ml) to isolate the precipitate and dispose of the supernate.

Note that a large centrifuge tube is preferred to save time. Ideally, the sample is centrifuged in a single 1 l centrifuge tube, but this is currently not possible because it is commercially unavailable. The other option is to use the largest centrifuge tube available (e.g. 500 ml) and centrifuge by step the sample using the same centrifuge tube. The supernate is disposed after each centrifugation.

Rinse the precipitate twice, each time with 50 ml of 0,5 mol·l^{-1} NaCl (6.1.6), (add the solution, mix thoroughly, centrifuge and dispose of the supernate).

Dissolve the precipitate with 1,25 ml of the 15,7 mol·l^{-1} HNO_3 solution (6.1.5) and 0,25 ml of the 8,82 mol·l^{-1} H_2O_2 solution (6.1.7).

Transfer the dissolved sample from the large centrifuge tube to a new 50 ml centrifuge tube. Bring the sample volume to 10 ml with ultrapure water (6.1.8). Rinse the centrifuge tube twice with 5 ml to 10 ml of HNO_3 solution c(HNO_3) = 2 mol·l^{-1} (6.1.9) and transfer the rinse to the 50 ml centrifuge tube to reduce transfer losses.

Centrifuge the sample in the 50 ml centrifuge tube to remove some of the suspended particles. Then, filter the supernate through a 0,1 µm filter and keep the filtrate, which contains Ac.

7.3 Purification

Place a 2 ml diglycolamide based resin column or equivalent (6.1.10) on top of a multi-hole vacuum box using the appropriate connectors and reservoirs to pass the reagents through the resin. The separation can also be done by gravity.

Precondition the extraction resin with 5 ml of 2 mol·l^{-1} HNO_3 (6.1.9).

Load the sample through the resin at a flow rate of 1 ml·min^{-1} to 2 ml·min^{-1}.

Rinse the resin with 20 ml of the 0,44 mol·l^{-1} H_2O_2 solution diluted in 2 mol·l^{-1} HNO_3 (6.1.11).

Elute Ac from the resin into a glass beaker using 20 ml of 15,7 mol·l^{-1} HNO_3 solution (6.1.5). Record the elution time to calculate the time elapsed between separation and counting (t_1).

Carefully evaporate the sample to dryness making sure it does not splatter. Remove the beaker from the hot plate and let the beaker cool to room temperature.

Re-dissolve Ac with about 10 ml of 0,1 mol·l^{-1} HCl (6.1.12) and transfer the solution into a 50 ml centrifugation tube. The beaker can be rinsed with a few ml of 0,1 mol·l^{-1} HCl solution (6.1.12) to reduce transfer losses.

7.4 Thin layer source preparation

Prepare a thin layer source of Ac using either the micro-precipitation method described in Annex C or the electrodeposition method described in Annex B.

7.5 Measurement

Put the planchet in an alpha spectrometer and count the sample activity for 48 h. Refer to the user manual of the instrument to properly use the alpha spectrometer. The sample can be re-counted later to measure ^{215}Po, the progeny of ^{227}Ac, and obtain a lower detection limit.

8 Quality assurance and quality control program

8.1 General

Measurement methods shall be performed by suitably skilled staff under a quality assurance program, such as the one that is described in ISO/IEC 17025.

8.2 Variables that can influence the measurement

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

8.3 Instrument verification

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

Usually, a thin alpha source with a radionuclide of long radiological half-life of known activity such as a $^{239/240}$Pu source is employed to estimate the detector efficiency because there is no appreciable decay

over the working life of the source. The efficiency source should have a similar geometry to the sample. The alpha peak energy is calibrated using a multi-isotope source, which can be obtained commercially. The background count rate of each detector is determined with an empty source support (clean disc); this shall take at least as much time as the counting of a sample.

8.4 Contamination

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

8.5 Interference control

It is the user's responsibility to ensure that all potential interferences have been removed. The removal of potential interferences is limited by the decontamination factor of the method. The main interferences to the isotopes of interest for ^{227}Ac measurement by alpha spectrometry are listed in Annex A.

8.6 Method verification

A periodic verification of the method accuracy should be performed. This can be accomplished by:

— participating in intercomparison exercises;

— analysing reference materials;

— analysing spiked samples.

The repeatability of the method should be verified (e.g. by replicate measurements).

The chemical recovery (R_c) should be calculated for quality control. It is calculated using Formula (1):

$$R_c = \frac{R}{\varepsilon} = \frac{r_T - r_{0T}}{A \cdot \varepsilon} = \frac{r_{netT}}{A \cdot \varepsilon} \quad (1)$$

8.7 Demonstration of analyst capability

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

A similar evaluation should be performed by the analyst who routinely applies this procedure, with a periodicity defined by the laboratory. Acceptance limits should be within limits specified by the laboratory.

9 Expression of results

9.1 General

Measurement results are expressed as activity concentrations in Bq·l^{-1} or Bq·kg^{-1} with associated uncertainties, presented in a test report. The coverage factor for the expanded uncertainty is specified in the presentation of results.

9.2 Tracer activity added

The activity of ^{229}Th tracer added (A) is calculated using Formula (2):

$$A = m_{ST} \cdot c_{AT} \quad (2)$$

9.3 Count rate and net count rate

The count rates are calculated using Formulae (3) to (6):

$$r_g = N_g / t_g \tag{3}$$

$$r_T = N_T / t_g \tag{4}$$

$$r_0 = N_0 / t_0 \tag{5}$$

$$r_{0T} = N_{0T} / t_0 \tag{6}$$

It is recommended to count the background at least the same amount of time as for the sample.

The net count rate of the sample (r_{net}) and the tracer (r_{netT}) can be calculated using Formulae (7) and (8), respectively.

$$r_{net} = r_g - r_0 \tag{7}$$

$$r_{netT} = \frac{(r_T - r_{0T}) \cdot \lambda_{225_{Ac}} \cdot t_g \cdot e^{\lambda_{225_{Ac}}(t_1)}}{1 - e^{-\lambda_{225_{Ac}}(t_g)}} \tag{8}$$

The tracer, ^{225}Ac, decays significantly during a counting period of 48 h. This decay is corrected using Formula (8), which calculates the corrected count rate at the moment of separation.

The net count rate of the tracer, r_{netT}, is indirectly obtained from ^{217}At peak (7 200 keV), and not from ^{225}Ac peak due to the interference of ^{225}Ac with ^{227}Th, ^{223}Ra, and ^{224}Ra (see Annex A). The activity of ^{217}At is in equilibrium with the activity of ^{225}Ac when counting the sample: an almost complete equilibrium is obtained after 30 min (99 %).

9.4 Total recovery

The total recovery, R, is the product of the chemical recovery, R_c, and counting efficiency, ε. It is calculated using Formula (9):

$$R = R_c \cdot \varepsilon = r_{netT} / A \tag{9}$$

9.5 Activity concentration of ^{227}Ac in the sample

9.5.1 Direct measurement of ^{227}Ac

The net count rate of ^{227}Ac, r_{net}, can be directly obtained from ^{227}Ac alpha peak. This is a simple and direct measurement that gives a detection limit of about 30 mBq·l^{-1}.

The activity concentration of ^{227}Ac, c_A, is calculated using Formula (10):

$$c_A = \frac{r_{net}}{P_\alpha \cdot V \cdot R} = w \cdot r_{net} \tag{10}$$

The term P_α is 0,014 2 based on Reference [8].

The term w in Formula (10) is isolated [see Formula (11)] to later calculate the decision threshold, the detection limit, and the coverage intervals.

$$w = \frac{1}{P_\alpha \cdot V \cdot R} \tag{11}$$

The contribution in ^{227}Ac from the reagents is not considered in Formula (10). To determine the contribution of ^{227}Ac from the reagents, method blanks should be prepared in parallel. The average amount of ^{227}Ac measured from the method blanks is then subtracted from each sample measured before reporting the results.

^{227}Ac decay is considered negligible in this calculation and it is expected that the sample is counted shortly after separation because of the decay of the tracer. If for some reasons, the sample is counted months after the separation and it is desired to measure the ^{227}Ac peak directly and not ^{215}Po, then the count rate obtained, r_g, at the measurement date needs to be calculated for the separation date using radioactive decay formulae.

9.5.2 Indirect measurement of ^{227}Ac via ^{215}Po peak after an ingrowth period

For some applications, a lower detection limit can be needed. This can be achieved by measuring the progeny of ^{227}Ac, ^{215}Po, after a period of time, which is usually several weeks to a few months. The calculation of ^{227}Ac activity is more complicated using this method. The activity of ^{227}Ac based on ^{215}Po alpha peak and using ^{225}Ac as a recovery tracer, is calculated as follow:

— Since the tracer, ^{225}Ac, decays relatively quickly, it is recommended to measure the ^{217}At net count rate shortly after the chemical separation to obtain better statistical precision. The sample is then counted latter to measure ^{215}Po after it has had the opportunity to substantially reach equilibrium. The tracer net count rate, r_{netT}, is established from the first counting via ^{217}At peak using Formula (8). It is important to re-count the sample in the same conditions as the initial measurement. The initial counter efficiency, ε_1, is presumed to be similar for the second measurement, ε_2. However, if the counter efficiency is significantly different, the tracer count rate, r_{netT}, obtained from the initial measurement, $r_{netT(1)}$, needs to be the adjusted to be equivalent. The equivalent count rate for the second measurement ,$r_{netT(2)}$, is calculated using Formula (12):

$$r_{netT(2)} = (\varepsilon_2 / \varepsilon_1) \cdot r_{netT(1)} \tag{12}$$

— The $r_{netT(2)}$ value replaces the r_{netT} value in Formula (9). It is also possible to add a higher activity of tracer according to the anticipated measurement date, which allows the simultaneous measurement of ^{217}At and ^{215}Po. In this situation, r_{netT} is determined using Formula (8) based on ^{217}At count rate as for the direct method, while r_{net} is determined using Formula (13) based on ^{215}Po count rate as for the indirect method

— The equilibrium between ^{215}Po and ^{227}Ac takes about 4 months to reach 97 % equilibrium. The sample can be counted before the 4 months period (or after), which impacts the detection limit of the method. However, a mathematical correction is necessary to correct for the incomplete equilibrium before and when counting the sample. This can be done using Formula (13):

$$r_{net} = \left[\left(r_{215_{Po}} - r_{0\,215_{Po}}\right) \cdot t_{1/2\ ^{215}Po}\right] / \left(t_{1/2\ ^{227}Ac} \cdot Z \cdot F\right) \tag{13}$$

$$Z = \left[\lambda_{227_{Ac}} \cdot \lambda_{227_{Th}} \cdot \lambda_{223_{Ra}} \cdot \lambda_{219_{Rn}} \cdot (X_1 + X_2 + X_3 + X_4 + X_5)\right]$$

$$X_1 = \left[e^{-\lambda_{227_{Ac}} \cdot (t_g/2 + t_1)}\right] / \left[\left(\lambda_{227_{Th}} - \lambda_{227_{Ac}}\right)\left(\lambda_{223_{Ra}} - \lambda_{227_{Ac}}\right)\left(\lambda_{219_{Rn}} - \lambda_{227_{Ac}}\right)\left(\lambda_{215_{Po}} - \lambda_{227_{Ac}}\right)\right]$$

$$X_2 = \left[e^{-\lambda_{227_{Th}} \cdot (t_g/2 + t_1)}\right] / \left[\left(\lambda_{227_{Ac}} - \lambda_{227_{Th}}\right)\left(\lambda_{223_{Ra}} - \lambda_{227_{Th}}\right)\left(\lambda_{219_{Rn}} - \lambda_{227_{Th}}\right)\left(\lambda_{215_{Po}} - \lambda_{227_{Th}}\right)\right]$$

$$X_3 = \left[e^{-\lambda_{223_{Ra}} \cdot (t_g/2+t_1)} \right] / \left[\left(\lambda_{227_{Ac}} - \lambda_{223_{Ra}}\right)\left(\lambda_{227_{Th}} - \lambda_{223_{Ra}}\right)\left(\lambda_{219_{Rn}} - \lambda_{223_{Ra}}\right)\left(\lambda_{215_{Po}} - \lambda_{223_{Ra}}\right) \right]$$

$$X_4 = \left[e^{-\lambda_{219_{Rn}} \cdot (t_g/2+t_1)} \right] / \left[\left(\lambda_{227_{Ac}} - \lambda_{219_{Rn}}\right)\left(\lambda_{227_{Th}} - \lambda_{219_{Rn}}\right)\left(\lambda_{223_{Ra}} - \lambda_{219_{Rn}}\right)\left(\lambda_{215_{Po}} - \lambda_{219_{Rn}}\right) \right]$$

$$X_5 = \left[e^{-\lambda_{215_{Po}} \cdot (t_g/2+t_1)} \right] / \left[\left(\lambda_{227_{Ac}} - \lambda_{215_{Po}}\right)\left(\lambda_{227_{Th}} - \lambda_{215_{Po}}\right)\left(\lambda_{223_{Ra}} - \lambda_{215_{Po}}\right)\left(\lambda_{219_{Rn}} - \lambda_{215_{Po}}\right) \right]$$

Where, r_{215Po} is ^{215}Po count rate and F is the bias correction factor for the losses of ^{219}Rn when counting the sample by alpha spectrometry (see explanations below).

— When r_{net} value is calculated using Formula (13), the value can be used in Formula (10).

— Formula (13) calculates the total equivalent count rate of ^{227}Ac (alpha and beta) based on ^{215}Po at the moment of separation. Then, the ^{227}Ac equivalent count rate can be used in Formula (10). The P_α value in Formula (10) is 1 since ^{215}Po is a pure alpha emitter.

— ^{215}Po is obtained from the decay of ^{219}Rn. ^{219}Rn has a short radioactive half-life (3,98 ± 0,03 s[8]). Since the sample is under vacuum while it is counted, ^{219}Rn can be partially lost during the sample counting. A constant bias can be observed assuming the vacuum remains constant during the sample counting, which needs to be verified. A correction factor (F) for this bias can have to be determined. This can be done using known quantities of ^{227}Ac from spiked samples. The activity measured based on ^{215}Po alpha peak is divided by the activity measured from ^{227}Ac alpha peak (consider P_α value), which gives the F value.

9.6 Combined uncertainties

The uncertainties on $P_\alpha, \varepsilon, \lambda, t_{1/2}, t_g$ and t_0 are considered negligible for the calculation of $u(c_A)$. According to ISO/IEC Guide 98-3, the combined uncertainty of c_A is calculated using Formula (14):

$$u(c_A)=\sqrt{w^2\cdot\left(r_g/t_g+r_0/t_0\right)+c_A^2\cdot u_{rel}^2(w)} \tag{14}$$

For the indirect measurement method, $u(c_A)$ is calculated using Formula (15):

$$u(c_A)=\sqrt{w^2\cdot\left[r_g/t_g+r_0/t_0+u_{rel}^2(F)+u_{rel}^2(\varepsilon_1)+u_{rel}^2(\varepsilon_2)\right]+c_A^2\cdot u_{rel}^2(w)} \tag{15}$$

The relative standard uncertainty of w is calculated using Formula (16):

$$u_{rel}^2(w)=u_{rel}^2(R)+u_{rel}^2(V) \tag{16}$$

The relative standard uncertainty of R is calculated using Formula (17):

$$u_{rel}^2(R)=\left(r_T/t_g+r_{0T}/t_0\right)/(r_T-r_{0T})^2+u_{rel}^2(A) \tag{17}$$

The relative standard uncertainty of A is calculated using Formula (18):

$$u_{rel}^2(A)=u_{rel}^2(m_{ST})+u_{rel}^2(c_{AT}) \tag{18}$$

For quality assurance, the combined uncertainty of R_c, is calculated using Formula (19):

$$u(R_c)=R_c\sqrt{u_{rel}^2(R)+u_{rel}^2(\varepsilon)} \tag{19}$$

For the calculation of the characteristic limits according to ISO 11929-1, when $\tilde{u}(\tilde{c}_A)$ is needed, i.e. the standard uncertainty of c_A as a function of its true value, it is calculated by Formula (20):

$$\tilde{u}(\tilde{c}_A)=\sqrt{w^2\cdot\left[(\tilde{c}_A/w+r_0)/t_g+r_0/t_0\right]+\tilde{c}_A^2\cdot u_{rel}^2(w)} \tag{20}$$

9.7 Decision threshold

The decision threshold, c_A^*, expressed in Bq·l^{-1}, is obtained from Formula (21) (see ISO 11929-1). This yields:

$$c_A^*=k_{1-\alpha}\cdot w\cdot\sqrt{\left(r_0/t_g\right)+\left(r_0/t_0\right)} \tag{21}$$

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

When $t_g=t_0=t$, c_A^* is calculated using Formula (22):

$$c_A^*=k_{1-\alpha}\cdot w\cdot\sqrt{2N_0}/t \tag{22}$$

When the background is very low, or when $N_0=0$, c_A^* is calculated with Formula (23) according to ISO 11929-2:

$$c_A^*=k_{1-\alpha}\cdot w\cdot\sqrt{2(N_0+1)}/t \tag{23}$$

9.8 Detection limit

The detection limit, $c_A^{\#}$, is calculated using the implicit Formula (24) according to ISO 11929-1:

$$c_A^{\#} = c_A^{*} + k_{1-\beta} \cdot \tilde{u}\left(c_A^{\#}\right) = c_A^{*} + k_{1-\beta} \sqrt{w^2 \left[\left(c_A^{\#} / w + r_g / t_g\right) / t_g + u^2\left(r_g\right) / t_g^2\right] + c_A^{\#2} \cdot u_{rel}^2(w)} \tag{24}$$

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

The detection limit can be calculated by solving Formula (24) for $c_A^{\#}$ or, more simply, by iteration with a starting approximation $c_A^{\#} = 2 \cdot c_A^{*}$.

When taking $k_{1-\alpha} = k_{1-\beta} = k$, the solution of Formula (24) is given by Formula (25):

$$c_A^{\#} = \left[2c_A^{*} + \left(w \cdot k_{1-\alpha}^2\right) / t_g\right] / \left[1 - k_{1-\alpha}^2 \cdot u_{rel}^2(w)\right] \tag{25}$$

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

9.9 Probabilistically symmetric coverage interval

9.9.1 Limits of the probabilistically symmetric coverage interval

The lower, $c_A^{\triangleleft}$, and upper, $c_A^{\triangleright}$, coverage limits are calculated using Formulae (26) and (27) according to ISO 11929-1:

$$c_A^{\triangleleft} = c_A - k_p \cdot u(c_A); p = \omega \cdot (1 - \gamma / 2) \tag{26}$$

$$c_A^{\triangleright} = c_A + k_q \cdot u(c_A); q = 1 - \omega \cdot \gamma / 2 \tag{27}$$

where

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

$(1-\gamma)$ is the probability for the coverage interval of the measurand;

$\omega = 1$ may be set if $c_A \cdot \geq 4\, u(c_A)$.

In this case:

$$c_A^{\triangleleft}, c_A^{\triangleright} = c_A \pm k_{1-\gamma/2} \cdot u(c_A) \tag{28}$$

γ = 0,05 and then, $k_{1-\gamma/2}$ = 1,96 are values often chosen by default.

9.9.2 The shortest coverage interval

As described in detail in ISO 11929-1, the lower limit of the shortest coverage interval, $c_A^<$, and the upper limit of the shortest coverage interval, $c_A^>$, are calculated from a primary measurement result, c_A, of the measurand and the standard uncertainty, $u(c_A)$, associated with c_A, either by:

$$c_A^<, c_A^> = c_A \pm k_q \cdot u(c_A); p = [1 + \omega \cdot (1 - \gamma)/2] \tag{29}$$

In the case where $c_A^< < 0$:

$$c_A^< = 0, c_A^> = c_A \pm k_q \cdot u(c_A); q = 1 - \omega \cdot \gamma \tag{30}$$

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

The relations $0 \leq c_A^< < c_A^>$ apply and the approximation of Formula (28) is valid.

10 Test report

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

a) a reference to this document, i.e. ISO 4723:2023;

b) identification of the sample;

c) units in which the results are expressed;

d) the test result:

   1) when the activity concentration, c_A, is compared with the decision threshold (see ISO 11929 series);

      — if the result is less than the decision threshold, the result of the measurement is expressed as $\leq c_A^*$,

      — if the result is greater than the decision threshold, the result of the measurement is expressed as $c_A \pm u(c_A)$ or $c_A \pm U$ with the associated k value,

   2) when the activity concentration, C_A is compared with the detection limit;

      — if the result is less than the detection limit, the result of the measurement is expressed as $\leq c_A^\#$,

      — if the result is greater than the detection limit, the result of the measurement is expressed as $c_A \pm u(c_A)$ or $c_A \pm U$ with the associated k value.

Complementary information can be provided such as:

e) the uncertainty can also be expressed as the limits of the probabilistically symmetric coverage interval $c_A^\triangleleft$, $c_A^\triangleright$ and/or the limits of the shortest coverage interval $c_A^<$, $c_A^>$;

f) probabilities α, β and $(1 - \gamma)$;

g) decision threshold and the detection limit;

h) if the detection limit exceeds the guideline value, it shall be documented that the method is not suitable for the measurement purpose;

i) mention of any relevant information likely to affect the results.

NOTE It is occasionally requested by the customer or regulator to compare the primary measurement result, c_A, with the detection limit, $c_A^{\#}$, in order to decide whether the physical effect is recognized or not. Such stipulation is not in accordance with the ISO 11929 series. They have the consequence that it is decided too frequently that the physical effect is absent when in fact it is not absent.

Annex A
(informative)

Potential radioactive interferences and examples of alpha spectrum

A.1 Potential alpha interferences for ^{225}Ac, ^{227}Ac, and ^{215}Po[8]

Table A.1 — Potential alpha interferences for ^{225}Ac

Isotope	Energy keV
^{225}Ac	5 935
^{227}Th	6 038
^{223}Ra	5 820
^{224}Ra	5 789

Table A.2 — Potential alpha interferences for ^{227}Ac

Isotope	Energy keV
^{227}Ac	5 042
^{209}Po	4 977
^{226}Ra	4 871
^{229}Th	4 845
^{231}Pa	5 104
^{234}U	4 858
^{237}Np	4 872
^{242}Pu	4 985
^{247}Cm	4 870
^{248}Cm	5 078

Table A.3 — Potential alpha interferences for ^{215}Po

Isotope	Energy keV
^{215}Po	7 526
^{211}Po	7 594

Astatine-217 has no potential interferences. Its maximum alpha energy is 7 200 keV (99,9 % alpha probability).

A.2 Examples of alpha spectrum

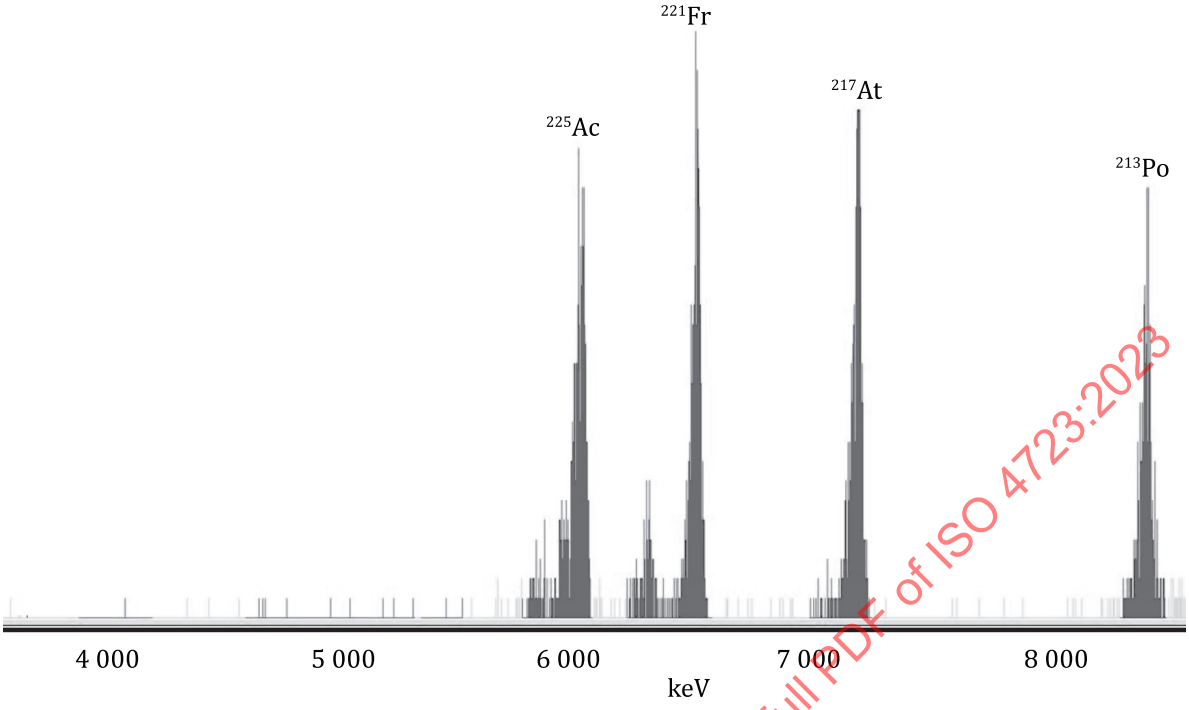


Figure A.1 — Method blank sample containing 15 mBq of ^{225}Ac and counted 48 h

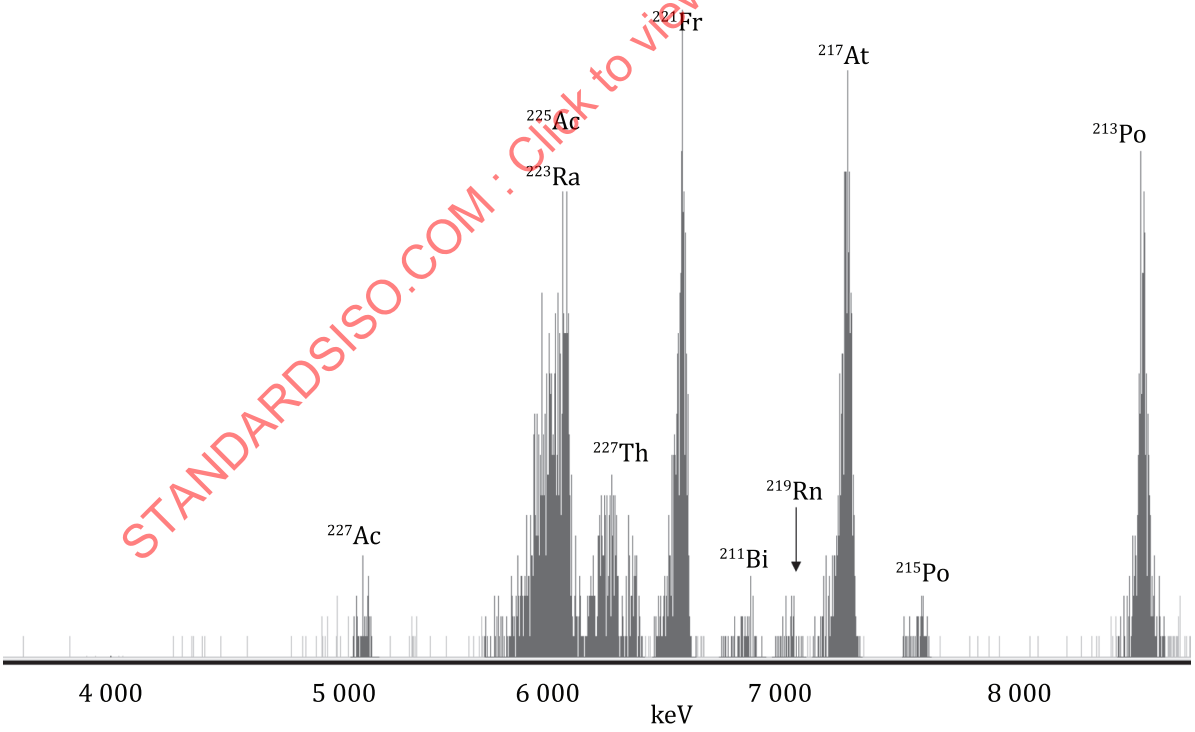


Figure A.2 — Spiked sample containing 15 mBq of ^{225}Ac tracer, 4 mBq of ^{227}Ac, counted 48 h shortly after separation

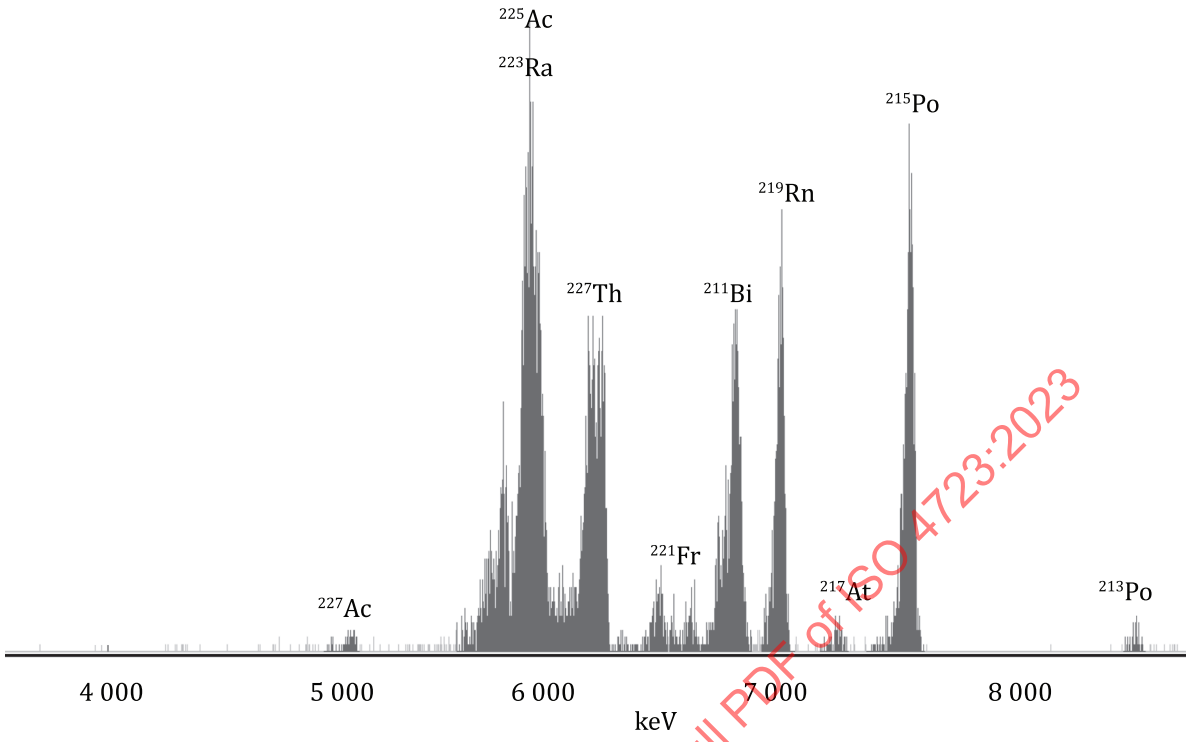


Figure A.3 — Spiked sample containing 15 mBq of ^{225}Ac tracer, 4 mBq of ^{227}Ac, counted 48 h, 40 days after separation