# **90Sr, 241Am and Pu Radioisotopes** — multiple methods

## A procedure for the sequential determination of radionuclides in environmental samples

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It is the responsibility of the analyst to follow established safety and health practices. Although each laboratory identified as the source has tested the methods, each user should perform an individual validation procedure.

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# A Procedure for the Sequential Determination of Radionuclides in Environmental Samples

## Liquid Scintillation Counting and Alpha Spectrometry for $^{90}$Sr, $^{241}$Am and Pu Radioisotopes

IAEA

International Atomic Energy Agency

# A PROCEDURE FOR THE SEQUENTIAL DETERMINATION OF RADIONUCLIDES IN ENVIRONMENTAL SAMPLES

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## LIQUID SCINTILLATION COUNTING AND ALPHA SPECTROMETRY FOR $^{90}$Sr, $^{241}$Am AND Pu RADIOISOTOPES

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# FOREWORD

Since 2004, IAEA activities related to the terrestrial environment have aimed at the development of a set of procedures to determine radionuclides in environmental samples. Reliable, comparable and ‘fit for purpose’ results are an essential requirement for any decision based on analytical measurements. For the analyst, tested and validated analytical procedures are extremely important tools for the production of analytical data. For maximum utility, such procedures should be comprehensive, clearly formulated and readily available for reference to both the analyst and the customer.

This publication describes a combined procedure for the sequential determination of $^{90}$Sr, $^{241}$Am and Pu radioisotopes in environmental samples. The method is based on the chemical separation of strontium, americium and plutonium using ion exchange chromatography, extraction chromatography and precipitation followed by alpha spectrometric and liquid scintillation counting detection.

The method was tested and validated in terms of repeatability and trueness in accordance with International Organization for Standardization (ISO) guidelines using reference materials and proficiency test samples. Reproducibility tests were performed later at the IAEA Terrestrial Environment Laboratory. The calculations of the massic activity, uncertainty budget, decision threshold and detection limit are also described in this publication.

The procedure is introduced for the determination of $^{90}$Sr, $^{241}$Am and Pu radioisotopes in environmental samples such as soil, sediment, air filter and vegetation samples. It is expected to be of general use to a wide range of laboratories, including the Analytical Laboratories for the Measurement of Environmental Radioactivity (ALMERA) network for routine environmental monitoring purposes.

The IAEA wishes to thank all the participants for their valuable contributions to the development of the procedure and the review of this report, in particular N. Vajda (Hungary). Special thanks are due to C.-K. Kim. The IAEA officer responsible for this publication was A. Pitois of the IAEA Environment Laboratories.

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# CONTENTS

# 1. INTRODUCTION

$^{90}$Sr, $^{241}$Am and Pu radioisotopes are among the most hazardous radionuclides produced in nuclear fission and activation processes. They have been released into the environment due to incidents at nuclear power plants and reprocessing plants, nuclear weapon production facilities, the fallout from nuclear weapon tests and the burn up of satellites with a SNAP 9A power source. Monitoring their presence in the environment is of major importance that requires the availability of up-to-date validated analytical procedures. The present report discusses a combined radiochemical procedure that has been applied for the sequential determination of $^{90}$Sr, $^{241}$Am and Pu radioisotopes in environmental samples such as soil, sediment, air filter and vegetation samples.

A great variety of methods have been developed for the determination of plutonium radioisotopes as well as $^{241}$Am and $^{90}$Sr. Three review papers about the analytical methodologies for these radionuclides have been published [1–3]. Besides the individual determination of these radionuclides many attempts have been made to develop combined procedures in which Pu and other actinides are usually separated first followed by the separation of Sr. These procedures have the great advantage that the usually tedious sample pre-treatment is performed only once for the determination of the various analytes. Combined procedures are also of great importance in revealing correlations between radionuclides in the same sample, in this case between Sr, Am and Pu radionuclides.

Precipitation, co-precipitation, ion exchange, solvent extraction are frequently used in the conventional radiochemical methods (ISO 18589-4:2007 and ISO 18589-5:2009) [4, 5]. Pu can be retained selectively on anion exchange resin from concentrated nitric or hydrochloric acid, but for the separation of Am and Sr the conventional ion exchange techniques do not have high selectivity. From the early 1990's, new extraction chromatographic (EC) materials became available for the determination of various radionuclides. The development of the Sr specific crown ether based material, Sr resin, was a major breakthrough in the analysis of radiostrontium replacing conventional methods based on a series of precipitations. Almost parallel to this, various transuranium element-specific EC materials, i.e. the UTEVA, TRU, TEVA resins, were developed by Horwitz et al. [6–10]. For the selective separation of Am, TRU resin, a supported carbamoylmethyl phosphine oxide derivative dissolved in tri-butyl phosphate, has been used successfully. EC techniques can be advantageously combined into procedures for the simultaneous determination of actinides and radiostrontium isotopes.

Anion exchange chromatography often forms the basic part of a combined procedure. Pu and Th can be directly separated by anion exchange resins from concentrated $HNO_3$ solution while Sr and Am together with other sample components are collected in the effluent. After pre-concentration, e.g. with Ca oxalate, Am can be separated using a TRU column and further purified from lanthanide impurities either with an anion exchange resin or a supported liquid anion exchanger called TEVA resin. Finally, Sr is separated on a Sr resin column. Moreno et al. [11–13] used ion exchange chromatography, extraction chromatography and precipitation for the chemical separation of Pu, Am and Sr in environmental samples. Several other procedures were also based on this flow chart [11, 13–19].

Berlioz et al. [20] combined the cation exchange separation of Am with the separation of Pu and Sr using anion exchange chromatography and Sr resin, respectively. Agayev et al. [21] used a similar combined procedure for the determination of radiostrontium.

Recently, a great variety of combinations of EC procedures have been reported for the determination of various actinides and Sr. Sr resin is used in all of these procedures for the separation of Sr usually with acceptably high Sr chemical recoveries (>50%). Horwitz et al. [7] and Thakkar [22] recommended to use UTEVA and TRU tandem columns for the separation of actinides where U and Th are retained on the UTEVA column while Am and Pu are retained on the TRU column from 2 to 3M $HNO_3$ solution. Sr can be recovered from the effluent and can be separated on a Sr resin column. This procedure has been applied by LaRosa et al. [23] and Mellado et al. [24]. For the rapid determination of actinides and radiostrontium Maxwell et al. [25, 26] recommended the use of TEVA, TRU and Sr resin columns where Pu and Th are separated on TEVA, Am and U on TRU and Sr on Sr resin columns. All actinides can be separated on a single TRU column and Sr can be retained and separated from the effluent on Sr resin column. This procedure was applied by Spry et al. [27] and Olahova et al. [28].

The recommended procedure described in the present publication is based on the chemical separation of Pu, Am and Sr using ion exchange chromatography, extraction chromatography and precipitation followed by alpha spectrometric and liquid scintillation counting detection.

## 2. SCOPE

This publication describes a method for the sequential determination of $^{90}$Sr, $^{241}$Am and Pu radioisotopes in soil, sediment, air filter and vegetation samples using alpha spectrometry and liquid scintillation counting following the radiochemical separation of the analytes. The method can be used for the routine environmental monitoring purposes. The method can also be applied for water samples.

The list of radionuclides and their basic nuclear properties are summarized in Table 1 in Appendix I.

The mass of the sample required for the analysis is typically up to 10 g of ashed soil, sediment or vegetation sample.

## 3. NORMATIVE REFERENCES

- ISO 7870:1993. Control charts – General guide and introduction.
- ISO 7966:1993. Acceptance control charts.
- ISO 5725-1:1994. Accuracy (trueness and precision) of measurement methods and results – Part 1: General principles and definitions.

- ISO 5725-2:1994. Accuracy (trueness and precision) of measurement methods and results – Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method.

- ISO 5725-4:1994. Accuracy (trueness and precision) of measurement methods and results – Part 4: Basic method for the determination of the trueness of a standard measurement method.

- ISO Guide 1995. Guide to the expression of uncertainty in measurement.

- ISO/IEC Guide 43-1:1997. Proficiency testing by interlaboratory comparisons – Part 1: Development and operation of proficiency testing schemes.

- QUAM:2012.P1 EURACHEM/CITAC Guide, 2012. Quantifying Uncertainty in Analytical Measurement.

- ISO/TS 21748:2004. Guidance for the use of repeatability, reproducibility and trueness estimates in measurement uncertainty estimation.

- ISO 18589-4:2007 Measurement of radioactivity in the environment – Soil – Part 5: Measurement of Pu isotopes by α-spectrometry.

- ISO 18589-5:2009. Measurement of radioactivity in the environment – Soil – Part 5: Measurement of strontium 90.

- ISO 11929:2010. Determination of the characteristic limits (decision threshold, detection limit and limits of the confidence interval) for measurements of ionizing radiation – Fundamentals and application.

## 4. RESPONSIBILITIES

It is the responsibility of the analyst to follow this procedure and to establish appropriate safety and health practices. Compliance with national and/or internal chemical and radiological safety rules is obligatory. Special care has to be paid to handling dangerous and toxic chemicals, e.g. concentrated nitric, hydrochloric and hydrofluoric acids and radiotoxic elements. Work with methanol is to be performed in a fume hood.

## 5. TERMS AND DEFINITIONS, SYMBOLS AND ABBREVIATIONS

### Terms and definitions, symbols and abbreviations used in determination of alpha emitting radionuclides

$a_\alpha$: massic activity of alpha emitting analyte at the reference time or sampling date (Bq kg$^{-1}$, as dry mass).

$A_\alpha$: activity of the alpha emitting radionuclide used for efficiency calibration of the alpha spectrometer (Bq).

$C_T$: certified concentration of the tracer at the reference date used for alpha spectrometric analysis (Bq $g^{-1}$).

$f_1$: correction for decay of the analyte during the time interval between the reference time or sampling date ($t_E$) to starting time of the alpha spectrometric measurement ($t_S$).

$f_2$: correction for decay of the analyte during the alpha spectrometric counting interval $t_G$.

$f_3$: correction for decay of the tracer during the time interval between the reference date of the tracer ($t_C$) and starting time of the alpha spectrometric measurement ($t_S$).

$f_4$: correction for decay of the tracer during alpha spectrometric counting interval $t_G$.

$f_t$: tailing parameter in alpha spectrometry.

$f_{1cal1}$: correction for decay of the tracer used for efficiency calibration of the alpha spectrometer in the time interval from its calibration to the beginning of the 1st measurement.

$f_{1cal2}$: correction for decay of the tracer used for efficiency calibration of the alpha spectrometer in the time interval from its calibration to the beginning of the 2nd measurement.

$f_{2cal1}$: correction for decay of the tracer used for efficiency calibration of the alpha spectrometer in the counting interval of the 1st measurement.

$f_{2cal2}$: correction for decay of the tracer used for efficiency calibration of the alpha spectrometer in the counting interval of the 2nd measurement.

$I_{N1}$: net count rate of the 1st calibration source to determine the efficiency of the alpha spectrometer (counts $s^{-1}$).

$I_{N2}$: net count rate of the 2nd calibration source to determine the efficiency of the alpha spectrometer (counts $s^{-1}$).

$m_a$: net weight of ash used for analysis (kg).

$p_{\alpha A}$: sum of alpha emission probabilities of the individual lines in the ROI of the analyte.

$p_{\alpha T}$: sum of alpha emission probabilities of the individual lines in the ROI of the tracer.

$q=m_w/m_a$: wet weight per ash weight ratio.

$q_I$: isotopic impurity ratio of the analyte in the tracer solution.

$R_{GA}$: gross counting rate of the alpha emitting analyte in the sample (counts $s^{-1}$).

$R_{BA}$: blank counting rate in the ROI of the alpha emitting analyte (counts $s^{-1}$).

$R_{GT}$: gross counting rate of the alpha emitting tracer in the sample (counts $s^{-1}$).

$R_{BT}$: blank counting rate in the ROI of the alpha emitting tracer (counts $s^{-1}$).

$t_E$: reference time or sampling date for the determination of alpha emitting radionuclides.

$t_S$: starting time of the alpha spectrometric measurement.

$t_C$: reference date of the tracer in alpha spectrometric measurement.

$t_G$: acquisition time of the alpha spectrum of the analyte (s).

$t_B$: acquisition time of the alpha spectrum of the blank/background (s).

$V_T$: mass of the tracer solution used for alpha spectrometric analysis (g).

y: auxiliary parameter.

$\varepsilon$: detection efficiency of the alpha spectrometer.

$\eta$: chemical recovery of the alpha emitting radionuclide.

### Terms and definitions, symbols and abbreviations used in determination of $^{90}$Sr

$a_{Sr}$: massic activity of $^{90}$Sr at the reference time or sampling date (Bq kg$^{-1}$, as dry mass).

$a_{o,Sr}$: known activity (from a certified standard solution) of $^{90}$Sr standard solution at the reference date used for efficiency calibration of the liquid scintillation counting system (Bq).

$C_{Sr,sol}$: concentration of the standardized Sr carrier solution (mg Sr g$^{-1}$ solution).

$C_{Sr,nat}$: concentration of natural Sr in the sample (mg Sr g$^{-1}$, as dry mass).

$I_A$: gross count rate of the Sr source in the region A (channels 25–250) in liquid scintillation counting (counts min$^{-1}$).

$I_B$: gross count rate of the Sr source in the region B (channels 250–1000) in liquid scintillation counting (counts min$^{-1}$).

$I_{ABg}$: gross count rate of blank in the region A (channels 25–250) in liquid scintillation counting (counts min$^{-1}$).

$I_{BBg}$: gross count rate of blank in the region B (channels 250–1000) in liquid scintillation counting (counts min$^{-1}$).

$I_{A,CAL}$: gross count rate in region A in the efficiency calibration process of the liquid scintillation counting system (counts min$^{-1}$).

$I_{B,CAL}$: gross count rate in region B in the efficiency calibration process of the liquid scintillation counting system (counts min$^{-1}$).

$f_Y$: tailing parameter in liquid scintillation counting.

$f_{1Sr}$: decay correction factor for the decay of $^{90}$Sr in the time interval $t_{1,Sr}$ from the reference date till the beginning of the measurement.

$f_{2Sr}$: decay correction factor for the decay of $^{90}$Sr during measurement time $t_{2,Sr}$.

$f_g$: gravimetric factor of Sr in strontium oxalate monohydrate ($Sr/SrC_2O_4{\cdot}H_2O$).

$f_{1Sr,CAL}$: correction factor for decay of $^{90}$Sr during the time interval between the calibration time and starting time of the calibration measurement ($t_{1Sr,CAL}$).

$K$: auxiliary parameter (counts min$^{-1}$).

$K_{CAL}$: auxiliary parameter in the calibration process of the liquid scintillation counting system (counts min$^{-1}$).

$m_{ox+pap}$: mass of strontium oxalate and filter paper (mg).

$m_{pap}$: mass of filter paper used for filtering strontium oxalate (mg).

$m_{sol}$: mass of the Sr carrier solution added to the sample (g).

$r_{Sr}$: chemical recovery of Sr.

$r_{Sr,CAL}$: gravimetric recovery factor of Sr in the calibration process.

$t_S$: counting time of the sample in liquid scintillation counting (min).

$t_{1Sr}$: time interval between the reference date or sampling date and the beginning of the measurement of $^{90}$Sr (min).

$t_{2Sr}$: measurement time of $^{90}$Sr (min).

$t_{1Sr,CAL}$: time interval between the reference date of the $^{90}$Sr/$^{90}$Y certified standard solution and the beginning of the calibration measurement (min).

$\varepsilon_{Sr}$: counting efficiency of $^{90}$Sr in region A in liquid scintillation counting.

$\lambda_{Sr}$: decay constant of $^{90}$Sr (s$^{-1}$).

$\lambda_A$: decay constant of alpha emitting analyte (s$^{-1}$) if time interval is expressed in s.

$\lambda_T$: decay constant of alpha emitting tracer (s$^{-1}$) if time interval is expressed in s.

**Terms and definitions, symbols and abbreviations used for statistical evaluation of the results**

$a^*$: decision threshold (Bq kg$^{-1}$, as dry mass).

$a\#$: detection limit (Bq kg$^{-1}$, as dry mass).

$C$: the assigned/reference value of the analyte in the reference material (Bq kg$^{-1}$, as dry mass).

$r_L$: repeatability limit (Bq kg$^{-1}$, as dry mass).

$R_L$: reproducibility limit (Bq kg$^{-1}$, as dry mass).

$S_r$: standard deviation of repeatability (Bq kg$^{-1}$, as dry mass).

$S_R$: standard deviation of reproducibility (Bq kg$^{-1}$, as dry mass).

$\overline{X}$ : measured mean value (Bq kg$^{-1}$, as dry mass).

$\delta$: relative bias of the result (%).

$u(x)$: uncertainty of quantity $x$.

## 6. PRINCIPLE

A combined procedure for sequential determination of $^{90}Sr$, $^{241}Am$ and Pu radioisotopes is described. In the radiochemical procedure, tetravalent Pu is retained on an anion exchange resin from 8M $HNO_3$, Th is eluted with 9M HCl and Pu is stripped from the resin as trivalent species with 0.1M $NH_4I$–9M HCl solution. Am and Sr are pre-concentrated from the effluent with calcium oxalate, then Am is separated from the matrix components using a TRU resin, and from lanthanides using an anion exchange resin, finally Sr is selectively separated from the effluent using a Sr resin. The determination of $^{241}Am$ and Pu radioisotopes is performed by isotope dilution alpha spectrometry using $^{243}Am$ and $^{242}Pu$ or $^{236}Pu$ tracers. $^{90}Sr$ is determined by liquid scintillation counting.

The basic characteristics of the extraction chromatographic TRU and Sr resins are summarized in Figs. 1 and 2 in Appendix II. The flowchart of the procedure is shown in Fig. 3 in Appendix III.

According to the procedure, oxidation state of Pu is adjusted to the tetravalent state by reduction using ferrous ion (generated from ferric ion with hydrazinium hydroxide) as reducing agent followed by selective oxidation to Pu(IV) using sodium nitrite as follows:

(a) Reduction of Pu species to $Pu^{3+}$ with $Fe^{2+}$:

$$Pu^{4+}{}_{(aq)} + Fe^{2+}{}_{(aq)} \leftrightarrows Pu^{3+}{}_{(aq)} + Fe^{3+}{}_{(aq)}$$

$$PuO_2{}^{2+}{}_{(aq)} + 3Fe^{2+}{}_{(aq)} + 4H^+ \leftrightarrows Pu^{3+}{}_{(aq)} + 3Fe^{3+}{}_{(aq)} + 2H_2O$$

(b) Oxidation of Pu(III) to Pu(IV) and formation of the anionic nitrate complex:

$$Pu^{3+}{}_{(aq)} + HNO_{2\,(aq)} + H^+ \leftrightarrows Pu^{4+}{}_{(aq)} + NO_{(g)} + H_2O$$

The basic equations describing the extraction equilibria on the anion exchange resin and the EC materials, i.e. TRU and Sr resins, are the following:

(a) Extraction equilibrium for the separation of Pu using anion exchange resin:

$$Pu^{4+}{}_{(aq)} + 6NO^-{}_{3(aq)} + 2RESIN\text{–}NR_3{}^+(NO_3)^-{}_{(org)} \leftrightarrows (RESIN\text{–}NR_3{}^+)_2\,[\,Pu^{4+}(\,NO^-{}_3)_6]^{\,2-}{}_{(org)} + 2(NO_3)^-{}_{(aq)}$$

where $RESIN\text{–}NR_3{}^+(NO_3)^-{}_{(org)}$ represents the strong basic anion exchange resin in nitrate form.

(b) Extraction equilibrium for the separation of Am using the TRU resin:

$$Am^{3+}{}_{(aq)} + 3NO_3^-{}_{(aq)} + 3E_{(org)} \leftrightarrows Am(NO_3)_3.E_{3\,(org)}$$

where E is the extractant (octylphenyl-N,N-di-isobutylcarbamoylmethylphosphine oxide (CMPO**)** dissolved in tributylphosphate) on an inert support in the TRU resin.

(c) Extraction equilibrium for the separation of Sr using the Sr resin:

$$Sr^{2+}{}_{(aq)} + 2NO_3^-{}_{(aq)} + CE_{(org)} \leftrightarrows Sr(NO_3)_2\,CE_{(org)}$$

where CE is the extractant (bis-t-butyl-cis-dicyclohexano-18-crown-6) on an inert support in Sr resin.

# 7. EQUIPMENT AND CHEMICALS

## 7.1. EQUIPMENT

- Alpha spectrometry system;
- Liquid scintillation counting system;
- Gas proportional counter;
- Electrodeposition system;
- Polysulfone filter funnels of 50 mL capacity;
- Polytetrafluoroethylene (PTFE) beakers of about 250 mL capacity;
- High performance microwave digestion unit;
- Analytical balance with accuracy of 0.1 mg;
- Hot plate with magnetic stirrer;
- Drying oven;
- Electric muffle furnace;
- pH meter;
- Micropipettes;
- Liquid scintillation glass vials;
- Standard laboratory equipment;
- Acid resistant, ventilated fume hood.

## 7.2. CHEMICALS

- Tracer solution of $^{243}$Am, useful range 0.05 to 1.0 Bq $g^{-1}$;
- Tracer solution of $^{242}$Pu or $^{236}$Pu, useful range 0.05 to 1.0 Bq $g^{-1}$;
- Sr carrier solution, useful range 10 to 50 mg Sr $g^{-1}$;
- Anion exchange resin (AG 1–X8 or Dowex 1–X8 (100–200 mesh));
- Anion exchange resin (AG 1–X4 (100–200 mesh) or corresponding resin);
- TRU resin (50–100 µm);
- Sr resin (50–100 µm);
- Calcium carrier as $Ca(NO_3)_2$ in 0.1M $HNO_3$ solution (100 mg $Ca^{2+}$ $mL^{-1}$);
- Hydrazinium hydroxide $N_2H_5OH$;
- Sodium nitrite $NaNO_2$;
- $HNO_3$ solutions at the following concentrations: 1M, 2M, 3M, 8M and 14.4M (65%);
- HCl solutions at the following concentrations: 4M, 9M and 10M (32%);
- 0.1M $NH_4I$–9M HCl freshly prepared;
- 5% $NaHSO_4$;
- Liquid scintillation cocktail, which is a gel type or is suitable for alpha/beta separation;
- Oxalic acid $H_2C_2O_4.H_2O$;
- Boric acid $H_3BO_3$;
- Mohr's salt $(NH_4)_2Fe(II)(SO_4)_2{\cdot}6H_2O$;
- Ethanol (80%);
- $Nd_2O_3$;
- 5% and 40% HF;
- Nd carrier as $Nd(NO_3)_3$ in 1M $HNO_3$ solution (0.5 mg $Nd^{3+}$ $mL^{-1}$);
- $NaNO_2$ (25%);

- $NH_3$ (25%);
- Ascorbic acid;
- Ammonium sulfate $(NH_4)_2SO_4$;
- Concentrated sulfuric acid;
- Electroplating solution;
- Membrane filter (25 mm diameter, 0.1 µm and 0.2 µm pore size);
- 1M $NH_4SCN$;
- 2,2'-bipyridine in ethanol (0.1 mg $mL^{-1}$);
- 1M $HNO_3$–93% $CH_3OH$;
- 0.1M HCl–0.5M $NH_4SCN$–80% $CH_3OH$;
- 1.5M HCl–86% $CH_3OH$;
- Bromocresol green 0.1% wt/vol in ethanol.

The preparation of chemical reagents is described in Appendix IV. All the chemical reagents needed to carry out this procedure must be of analytical grade.

# 8. PROCEDURE

## 8.1. SAMPLE DECOMPOSITION

(1) Ash the sample at 600°C in a programmable electric muffle furnace.
(2) Determine water content of the sample with small sample aliquots that are dried at the desired temperature and duration.
(3) Add up to 10 g of ashed soil, sediment or vegetation samples to PTFE (Polytetrafluoroethylene) beaker of about 250 mL capacity containing a PTFE coated magnetic stirring bar.
(4) Add 10 mg Sr carrier, $^{243}$Am and either $^{236}$Pu or $^{242}$Pu tracers. Typically, tracers of 0.01–0.05 Bq activity are added to low level environmental samples. The selection of the type and amount of Pu tracer depend on the expected massic activity of the alpha emitting Pu radioisotope.
(5) Cautiously add 40 mL of 40% HF in the sample, and then boil covered for about 2 hours followed by evaporation with PTFE cover raised on PTFE clips to a thick slurry.
(6) Repeat the step (5) and digest three times the sample with 50 mL of 65% $HNO_3$.
(7) Add 50 mL of 32% HCl and 2–3 g of boric acid to the wet residue and then boil for 2 hours.
(8) Transfer the solution into a glass beaker with a few mL of 65% $HNO_3$ and evaporate to near dryness.
(9) Add 50 mL of 65% $HNO_3$ then evaporate to a moist residue without baking the sample.
(10) If the destruction is not complete (which is indicated by the evolution of brownish vapor at the end of the evaporation), evaporate again the residue with 10 mL of 65% $HNO_3$.
(11) Add 70 mL of 1M $HNO_3$ to the solution then heat it for 1 hour to dissolve as much of the sample as possible.
(12) Filter the solution through a 0.2 µm pore size polypropylene membrane to remove small amounts of insoluble material.

(13) Wash the filter with 3 mL of 1M $HNO_3$ used for rinsing the beaker and 1 mL of 80% ethanol, then dry it for 5 minutes at 80°C in an oven followed by 1 hour in a vacuum desiccator.

(14) Measure gross alpha and beta activity of the filter using a gas proportional counter. If significant alpha and beta activities remain on the filter, the residue is further processed as described above in steps 5–13. Activity may be due to U and Th progeny that are "locked" in resistant minerals like zircon that are extremely difficult to dissolve with mineral acids.

## 8.2. CHEMICAL SEPARATION

### 8.2.1. Oxidation state adjustment

(1) Add 2 mL of 25% $NH_3$ and 2 mL of hydrazinium hydroxide $N_2H_5OH$ drop-wise and slowly, with vigorous stirring to the solution obtained from 8.1. step (12) to allow transient precipitation (e.g. iron hydroxide) to re-dissolve. Thus, the oxidation state of Pu is adjusted to Pu(III).

(2) Take a drop of the sample in a small weighing boat and add a drop of 1M $NH_4SCN$ solution, then check the color of the solution. The reduction of Fe(III) to Fe(II) is usually controlled by a thiocyanate test: the purple color indicates the presence of Fe(III). Because the Fe(III)-SCN test is so sensitive, it is difficult to assess the degree of Fe(III) reduction, since even a very small concentration of Fe(III) will give a positive signal. A test to examine the production of Fe(II) in the presence of Fe(III) is based on 2,2'-bipyridine. A drop of the sample solution added to several drops of 0.1 mg $mL^{-1}$ of 2,2'-bipyridine in ethanol will give a red-pink color if Fe(II) is present in significant concentration; there is no color (or perhaps very light yellow) for this reagent in the presence of Fe(III). (If the sample does not contain Fe, 0.1 mg of Mohr's salt is added).

(3) If the reduction of Fe is not complete, additionally add hydrazinium hydroxide $N_2H_5OH$ as long as the thiocyanate or bipyridine tests indicate the presence of significant amount of Fe(II). Most often a complete reduction of Fe(III) to Fe(II) is not accomplished. This may be due to the presence of phosphate, which strongly complexes Fe(III) and hinders its reduction. However, the reduction of Pu to Pu(III) will be controlled by the Fe(II)-Fe(III) couple and Pu reduction will be obtained if a significant fraction of the Fe(III) has been reduced.

(4) Cool the solution in an ice bath, then add slowly and carefully 30 mL of 65% $HNO_3$ to bring it to about 4 M $HNO_3$.

(5) Boil the solution for about 20 min to destroy the excess of hydrazinium hydroxide and oxidize Fe (II) to Fe (III). The gas evolution should stop and a yellow colour should appear.

(6) Cool the solution to room temperature and then add 5 g of sodium nitrite $NaNO_2$ to stabilize the tetravalent oxidation state of Pu. A light blue colour should appear.

(7) Boil again the solution to decompose excess $HNO_2$, then cool it when the gas evolution has stopped.

(8) Add 70 mL of cold 65% $HNO_3$ to the solution to produce a final 200 mL solution of 8M $HNO_3$.

### 8.2.2. Anion exchange separation of Pu

(1) Fill a slurry of strong basic anion exchange resin in the chloride form (Bio-Rad AG 1–X8 or Dowex 1–X8, 100–200 mesh) into a glass column (1 cm inner diameter and 14 cm resin length) and cover the top of resin with a 1 cm layer of coarse-grain quartz granules.
(2) Wash the column with 100 mL of 2M $HNO_3$ to convert the resin from chloride to nitrate form, and then condition the resin with 50 mL of 8M $HNO_3$.
(3) Load the feed solution on the column.
(4) Wash the column with 50 mL of 8M $HNO_3$.
(5) Combine the effluent and wash solutions for the analysis of Am and Sr radionuclides.
(6) Remove Th from the column with 100 mL of 9M HCl.
(7) Strip Pu from the column with 100 mL of freshly prepared 0.1M $NH_4I$–9M HCl solution. The iodide reduces Pu(IV) to Pu (III) which does not form an anionic chloride complex.

### 8.2.3. Preparation of Pu source by micro co-precipitation technique

(1) Add 1 mL of 5% $NaHSO_4$ to the Pu strip solution and evaporate 3 to 4 times to dryness with 2.5 mL of 65% $HNO_3$ to volatilize iodine, convert the chloride to the nitrate and oxidize Pu (III) to Pu (IV).
(2) Dissolve the residue in a few mL of hot 1M $HNO_3$, transfer it into a plastic tube with up to 20 mL of 1M $HNO_3$ and then add 100 μL of the Nd carrier solution at 0.5 mg $mL^{-1}$ (50 μg of Nd).
(3) Add 100 mg of Mohr‘s salt $(NH_4)_2Fe(II)(SO_4)_2 \cdot 6H_2O$ to reduce Pu to the trivalent state. Under these conditions some of the U is possibly reduced to the tetravalent state by Fe(II).
(4) Add 1 mL of 25% $NaNO_2$ solution to oxidize Pu(III) and any U(IV) to Pu(IV) and U(VI).
(5) Add 5 mL of 40% HF to the solution to form a $NdF_3$ suspension that adsorbs the tri- and tetravalent actinides.
(6) After 30–45 min, filter the solution through a membrane filter of diameter 25 mm and pore size 0.1 μm.
(7) Wash twice the filter with 2 to 3 mL of 5% HF and once with 2 to 3 mL of 80% ethanol, then dry it in an oven at 60°C for 20 to 30 min and store in a vacuum desiccator for 20 min.
(8) Mount the filter on a stainless steel disc and place it in an alpha spectrometer.

### 8.2.4. Preconcentration of Am and Sr by co-precipitation

(1) Evaporate the combined effluent from 8.2.2 step (5) from the anion exchange column to a moist residue.
(2) Dissolve the residue in 150 mL of de-ionized water, then add 10 g of oxalic acid to the solution.
(3) Adjust the pH of the solution while stirring and heating to 5.0 to 5.5 with small portions of 25% ammonia in the presence of 1 mL of 0.1% bromocresol green indicator to precipitate calcium-magnesium-strontium oxalates. Under these conditions, in many cases, most of the Fe remains in solution in the form of soluble oxalate complexes. If the amount of Ca in the sample solution is less than approximately 500 mg, add about 3 to 5 mL of Ca carrier solution at 100 mg Ca $mL^{-1}$.
(4) Centrifuge the oxalate precipitate and wash three times with 25 mL of de-ionized water.

(5) Dissolve the precipitate in 25 to 30 mL of 65% $HNO_3$, heat the solution for 30 minutes and then evaporate it to a moist residue.
(6) Repeat the evaporation to a moist residue with additional 25 to 30 mL of 65% $HNO_3$ until the fuming of brown gases ceases. The amount of nitric acid needed to destroy and dissolve the Ca oxalate depends on the Ca content in the sample solution.

### 8.2.5. Separation of Am by extraction chromatography

(1) Dissolve the moist residue from 8.2.4 step (6) in 20 to 30 mL of 2M $HNO_3$. If the residue is not dissolved in the solution, the centrifuging or the filtration with 0.45μm membrane filter is recommended.
(2) After filtering, Fe(III) content in the sample solution is checked by the thiocyanate test. If the test is positive (red color), 300 mg ascorbic acid is initially added to the solution to reduce Fe(III). If this amount is not sufficient, up to 500 mg in total ascorbic acid may be added.
(3) TRU resin column of bed volume 1.3 mL and column length 26 mm is prepared and conditioned with 25 mL of 2M $HNO_3$.
(4) The sample solution is loaded onto the column and the resin is washed with 10 mL of 2M $HNO_3$ under gravity flow.
(5) The combined effluent is used for the analysis of $^{90}$Sr.
(6) Column is washed with 4 mL of 9M HCl and Am is stripped together with the lanthanides with 15 mL of 4M HCl solution. Any traces of Th and U that might be present remain on the column providing a further purification of the Am fraction.

### 8.2.6. Separation of Am from lanthanides by ion exchange

(1) Evaporate three times the stripped solution to dryness with 1–2 mL of 65% $HNO_3$ to convert it to a nitrate.
(2) Dissolve the residue in 10 mL 1M $HNO_3$–93% $CH_3OH$.
(3) Fill an anion exchange resin, e.g. AG 1–X4 (mesh 100–200) or corresponding resin, in a glass column of inner diameter 10 mm and column length 120 mm.
(4) Precondition the column with 100 mL 1M $HNO_3$–93% $CH_3OH$.
(5) Load the sample solution on the column under gravity flow then wash it with 20 mL 1M $HNO_3$–93% $CH_3OH$ to rinse out the feed solution.
(6) Elute lanthanides with 80 mL 0.1M HCl–0.5M $NH_4SCN$–80% $CH_3OH$ followed by 20 mL of 1M $HNO_3$–93% $CH_3OH$.
(7) Strip Am from the column with 70 mL 1.5M HCl–86% $CH_3OH$ solution.

### 8.2.7. Preparation of Am source by electrodeposition

(1) Evaporate three times the Am fraction from 8.2.6. step (7) to dryness with 2–3 mL of 65% $HNO_3$.
(2) Dissolve the residue in 10 mL of electroplating solution and transfer it to an electrodeposition cell.
(3) Deposit Am by electrolysis on a polished stainless steel disk (disk diameter: 14-16 mm, deposition time: 1.5 hour, constant current: 0.9–1.0 A, keeping a current density of 0.45–0.65 A $cm^{-2}$).

(4) At the end of the deposition time, add 1 mL of 25% $NH_3$ solution into the deposition cell, wait for 20 s and switch off the current.
(5) Disassemble the cell, wash the disc with de-ionized water, then with acetone, and let it dry.

Alternatively, the Am source can be also prepared by the micro co-precipitation technique. The resolution in the alpha spectrum is however usually better using electrodeposition.
The preparation of Am source by the micro co-precipitation technique is as follows:

(1) Evaporate three times the Am fraction with 2 mL of 65% $HNO_3$ to dryness after adding 1 mL of 5% $NaHSO_4$ to destroy the thiocyanate ions.
(2) Dissolve the residue in 20 mL 1M $HNO_3$.
(3) Prepare the Am source in a similar way as Pu sources but Mohr's salt and $NaNO_2$ are not added (see in 8.2.3.).

### 8.2.8. Separation of Sr using Sr resin

(1) Add 3 mL of 65% $HNO_3$ to the combined effluent from 8.2.5. step (5) of the TRU resin column to adjust the acidity to about 3M $HNO_3$.
(2) Precondition a Sr resin column of inner diameter 10 mm and column length about 100 mm with 100 mL of 3M $HNO_3$.
(3) Load the sample solution on the column under gravity flow (approximately 1 drop $s^{-1}$).
(4) Wash the column with 100 mL of 3M $HNO_3$ to remove most of the alkaline earth metal interferences.
(5) Elute Sr from the column with 30 mL de-ionized water.

### 8.2.9. Preparation of Sr source by precipitation

(1) Add 300 mg of oxalic acid to the Sr strip solution.
(2) After adding about 3 mL of 25% $NH_3$ (pH=9 to 10), heat the solution to form strontium oxalate precipitate.
(3) Cool the solution to room temperature.
(4) Filter the precipitate through a pre-weighed filter paper then determine the chemical recovery of Sr by gravimetric method.
(5) Place the filter with the oxalate precipitate into a liquid scintillation vial and then add exactly 1 mL of 1M $HNO_3$ to the vial to dissolve the precipitate.
(6) Add 15 mL of scintillation cocktail to the vial and mix it.

### 8.2.10. Counting conditions

(1) Count the alpha sources in the alpha spectrometer typically for 1 to 5 days.
(2) Count Sr source in the liquid scintillation counter for 20 to 1000 min depending on the activity of the sample.

# 9. EXPRESSION OF RESULTS

## 9.1. CALCULATION OF THE RESULTS OF ALPHA SPECTROMETRY

### 9.1.1. Calculation of the Pu and Am massic activities

The method used for the calculation of the massic activity of alpha emitting radionuclides is described in detail in the IAEA-TECDOC-1401 [29].

The calculation is based on isotope dilution in which the activity of the analyte is calculated on the basis of the known tracer activity $(C_T.V_T)$ added to the sample. Gross peak areas in selected regions in the alpha spectra are determined by the appropriate alpha software. The ratio of the net peak areas (or count rates) of the analyte $(R_{GA} - R_{BA})$ and the tracer $(R_{GT} - R_{BT})$ are taken to be equal to the ratio of the disintegration rates. In case of overlapping peaks, tailing correction has to be performed to calculate the net count rates. Typical alpha spectra of Pu and Am sources with the appropriate region settings are shown in Figs. 4 and 5 in Appendix V.

The massic activity of the analyte $(a_\alpha)$, i.e. $^{238}$Pu, $^{239,240}$Pu or $^{241}$Am at the reference time, is calculated according to the formula below:

$$a_\alpha = \frac{C_T \cdot V_T}{m_a \cdot q} \cdot f_1 \cdot f_2 \cdot f_3 \cdot f_4 \cdot \frac{p_{\alpha T}}{p_{\alpha A}} \cdot \left(\frac{R_{GA} - R_{BA}}{R_{GT} - R_{BT}} - q_I\right) \tag{1}$$

where the decay correction factors are defined as follows:

$$f_1 = e^{\lambda_A \cdot (t_S - t_E)} \tag{2}$$

$$f_2 = \frac{\lambda_A \cdot t_G}{1 - e^{-\lambda_A \cdot t_G}} \tag{3}$$

$$f_3 = e^{-\lambda_T \cdot (t_S - t_C)} \tag{4}$$

$$f_4 = \frac{\lambda_T \cdot t_G}{1 - e^{-\lambda_T \cdot t_G}} \tag{5}$$

In equation (1) $m_a$ is the mass of ash sample, $q$ is the dry sample mass to ash ratio while $p_{\alpha A}$, $p_{\alpha T}$ and $q_I$ are corrections according to alpha emission probabilities in the appropriate ROIs and the impurity of the tracer, respectively.

### 9.1.2. Calculation of the Pu and Am chemical recoveries

The chemical recovery can be calculated from the tracer net count rate $(R_{GT} - R_{BT})$ in the same spectrum, if the counting efficiency (ε) is known, according to the following equation:

$$\eta = \frac{R_{GT} - R_{BT}}{\varepsilon \cdot C_T \cdot V_T \cdot f_3} \tag{6}$$

### 9.1.3. Determination of the counting efficiency of the alpha spectrometer

In order to determine the counting efficiency of the alpha spectrometer, calibration sources of known activities were prepared from certified standard reference solutions (e.g. $^{242}$Pu, $^{243}$Am) by micro co-precipitation using $NdF_3$, or by electrodeposition, as described in 8.2.3. and 8.2.7.

The filtrate of the 1st $NdF_3$ source was collected and a 2nd $NdF_3$ source was prepared from the solution by adding a 2nd portion of the Nd solution (50 µg $Nd^{3+}$) and repeating the filtration. Both sources were measured in the alpha spectrometer and the sum of the net count rates was related to the total activity of the standard solution to avoid possible filtration losses. The efficiency of the alpha spectrometer was calculated as follows:

$$\varepsilon = \frac{I_{N1} \cdot f_{1cal1} \cdot f_{2cal1} + I_{N2} \cdot f_{1cal2} \cdot f_{2cal2}}{A_\alpha} \tag{7}$$

## 9.2. CALCULATION OF THE RESULTS OF LIQUID SCINTILLATION COUNTING

### 9.2.1. Calculation of the massic activity of $^{90}$Sr

The determination of the massic activity of $^{90}$Sr is performed using the double energetic windows method. The method is described in detail by Moreno et al. [12, 13]. This method enables the determination of $^{90}$Sr without waiting until the radiochemical equilibrium between $^{90}$Sr and $^{90}$Y is reached.

The first energetic window, ROI A, includes the total $^{90}$Sr spectrum and the low energy region of $^{90}$Y spectrum. The second window, ROI B, includes the high energy region of the $^{90}$Y spectrum. A typical LSC spectrum of $^{90}$Sr source with the region setting is shown in Fig. 6 in Appendix VI.

The $^{90}$Sr activity in the source is determined by subtracting the contribution of $^{90}$Y ($f_Y \cdot (I_B - I_{BBg})$) to the net count rate in ROI A, ($I_A - I_{ABg}$). The $^{90}$Y contribution is calculated from the net count rate of $^{90}$Y recorded in ROI B, ($I_B - I_{BBg}$), and the measured ratio of net count rates of $^{90}$Y in ROI A to ROI B ($f_Y$ tailing parameter). The massic activity of $^{90}$Sr ($a_{Sr}$) can be calculated according to equation (8) or to the modified equation (9):

$$a_{Sr} = \frac{(I_A - I_{ABg}) - f_Y \cdot (I_B - I_{BBg})}{m_a \cdot r_{Sr} \cdot \varepsilon_{Sr} \cdot q \cdot 60} \cdot f_{1Sr} \cdot f_{2Sr} \tag{8}$$

$$a_{Sr} = \frac{K \cdot f_{1Sr} \cdot f_{2Sr}}{m_a \cdot r_{Sr} \cdot \varepsilon_{Sr} \cdot q \cdot 60} \tag{9}$$

Where:

$$f_Y = \frac{I_{A,CAL} - I_{ABg}}{I_{B,CAL} - I_{BBg}} \tag{10}$$

$$K = (I_A - I_{ABg}) - f_Y \cdot (I_B - I_{BBg}) \tag{11}$$

$$f_{1Sr} = e^{\lambda_{Sr} \cdot t_{1Sr}} \tag{12}$$

$$f_{2Sr} = \frac{\lambda_{Sr} \cdot t_{2,Sr}}{1 - e^{-\lambda_{Sr} \cdot t_{2,Sr}}} \tag{13}$$

In equation (8) the chemical recovery of Sr ($r_{Sr}$) and the counting efficiency of $^{90}$Sr in ROI A have to be determined from independent measurements as explained in 9.2.2. and 9.2.3.

The tailing parameter ($f_Y$) is determined by the measurement of a pure $^{90}$Y source as explained in 9.2.3., $f_{1Sr}$ and $f_{2Sr}$ are decay correction factors, for the decay of $^{90}$Sr in the time interval $t_{1,Sr}$ from the reference date till the beginning of the measurement, and for the decay of $^{90}$Sr during measurement time $t_{2,Sr}$, respectively.

### 9.2.2. Calculation of the chemical recovery of Sr

The chemical recovery factors of Sr in the sample experiment and also in the calibration experiment are determined by gravimetry using the formula below:

$$r_{Sr} = \frac{f_g \cdot (m_{ox+pap} - m_{pap})}{C_{Sr,sol} \cdot m_{sol} + C_{Sr,nat} \cdot m_a} \tag{14}$$

### 9.2.3. Calibration of the liquid scintillation counting

Both the efficiency *($\varepsilon_{Sr}$)* and the shape/tailing parameter *($f_y$)* are obtained from an independent calibration experiment where Sr and Y are separated from a certified standard solution of known activity. The tracer solution in 3M $HNO_3$ is passed through a Sr resin column and washed with 3M $HNO_3$. Sr source is prepared from the Sr strip solution as Sr oxalate and counted in the liquid scintillation counter to determine counting efficiency. Y source is prepared from the combined effluent and wash solution of the Sr resin column that is evaporated to dryness and taken up in 1 mL of 1M $HNO_3$. The solution is mixed with 15 mL of scintillation cocktail and counted immediately to determine $f_y$. The chemical procedure is described in 8.2.8. and 8.2.9.

The following equations are used for the calculation of the efficiency:

$$\varepsilon_{Sr} = \frac{(I_{A,CAL} - I_{ABg}) - f_Y \cdot (I_{B,CAL} - I_{BBg})}{a_{0,Sr} \cdot r_{Sr,CAL} \cdot 60} \cdot f_{1Sr,CAL} \tag{15}$$

$$\varepsilon_{Sr} = \frac{K_{CAL}}{a_{0,Sr} \cdot r_{Sr,CAL} \cdot 60} \cdot f_{1Sr,CAL} \tag{16}$$

Where:

$$K_{CAL} = (I_{A,CAL} - I_{ABg}) - f_Y \cdot (I_{B,CAL} - I_{BBg}) \tag{17}$$

$$f_{1Sr,CAL} = e^{\lambda_{Sr} \cdot t_{1Sr,CAL}} \tag{18}$$

The tailing factor $f_Y$ is calculated according to equation (10) by measuring the separated $^{90}$Y source.

## 9.3. COMBINED UNCERTAINTY

The combined uncertainties of the massic activities of the alpha emitting radionuclides *($a_\alpha$)* and $^{90}$Sr *($a_{Sr}$)* at the time of sampling can be calculated according to the law of uncertainty propagation using the mathematical approach. The algorithms to calculate the combined uncertainty and the sensitivity factors are given in Appendix VII and in Appendix VIII, respectively. Standard uncertainties can be calculated by the spreadsheet method, as well [12].

### 9.3.1. Calculation of the combined uncertainty of the Pu and Am massic activities

The method used to calculate the combined uncertainties of the massic activities of the alpha emitting radionuclides *($a_\alpha$)* is described in detail in IAEA-TECDOC-1401 [29].

The combined uncertainty of the concentration of the alpha emitting analyte (e.g. $^{238}$Pu, $^{239,240}$Pu and $^{241}$Am) on the sampling/reference date *$u(a_\alpha)$ is* calculated as follows:

$$
\begin{aligned}
u\,(a_\alpha)^2 = {} & (\frac{a_\alpha}{C_T})^2 \cdot u(C_T)^2 + (\frac{a_\alpha}{V_T})^2 \cdot u(V_T)^2 + (-\frac{a_\alpha}{q})^2 \cdot u(q)^2 + (-\frac{a_\alpha}{m_a})^2 \cdot u(m_a)^2 \\
& + (\frac{a_\alpha}{p_{\alpha T}})^2 \cdot u(p_{\alpha T})^2 + (\frac{a_\alpha}{p_{\alpha A}})^2 \cdot u(p_{\alpha A})^2 + (\frac{a_{\alpha 1}}{f_1})^2 \cdot u(f_1)^2 + (\frac{a_\alpha}{f_2})^2 \cdot u(f_2)^2 + (\frac{a_\alpha}{f_3})^2 \cdot u(f_3)^2 + (\frac{a_\alpha}{f_4})^2 \cdot u(f_4)^2 \\
& + (\frac{a_\alpha}{y_T} \cdot \frac{1}{R_{GT} - R_{BT}})^2 \cdot u(R_{GA})^2 + (-\frac{a_\alpha}{y_T} \cdot \frac{1}{R_{GT} - R_{BT}})^2 \cdot u(R_{BA})^2 + (-\frac{a_\alpha}{y_T} \cdot \frac{R_{GA} - R_{BA}}{(R_{GT} - R_{BT})^2})^2 \cdot u(R_{GT})^2
\end{aligned}
\tag{19}
$$

Calculation of partial derivatives is shown in Appendix VII.

The individual uncertainty components can be obtained from various sources, e.g. the producer specifies the uncertainty of the tracer *$u(C_T)$*, uncertainties of nuclear parameters can be obtained from relevant tables, e.g., *$u(\lambda)$, $u(p_\alpha)$,* uncertainties of masses are determined from the properties of the balance, uncertainties of nuclear measurements are calculated based on the decay statistics (Poisson), e.g. *$u(R_{GA})$* and *$u(R_{GT})$* are calculated similarly:

$$u(R_{GA}) = \sqrt{\frac{R_{GA}}{t_G}}\,,\; u(R_{GT}) = \sqrt{\frac{R_{GT}}{t_G}} \tag{20}$$

The uncertainties of the background counts should be determined as the standard deviation of repeated background counting.

Uncertainties of the correction factors are deduced from derivation of the appropriate equations:

$$u(f_1) = f_1 \cdot (t_S - t_E) \cdot u(\lambda_A) \tag{21}$$

$$u(f_2) = f_2 \cdot (1 - f_2 \cdot e^{-\lambda_A \cdot t_G}) \cdot \frac{u(\lambda_A)}{\lambda_A} \tag{22}$$

$$u(f_3) = f_3 \cdot (t_S - t_C) \cdot u(\lambda_T) \tag{23}$$

$$u(f_4) = f_4 \cdot (1 - f_4 \cdot e^{-\lambda_T \cdot t_G}) \cdot \frac{u(\lambda_T)}{\lambda_T} \tag{24}$$

Examples for the calculation of the combined uncertainty of the massic activity of $^{238}$Pu in the IAEA-135 reference material are given in Table 2 in Appendix IX. Uncertainty of the massic activity of $^{239,240}$Pu and $^{241}$Am can be calculated in a similar way. The spreadsheet method was used to calculate the uncertainty as described in the papers of Kragten [30] and Holmes [31].

### 9.3.2. Calculation of the combined uncertainty of the massic activity of $^{90}$Sr

The method used to calculate the combined uncertainty of the massic activity of $^{90}$Sr $(a_{Sr})$ is described in detail by Moreno et al. [12].

The combined uncertainty of the massic activity on the sampling/reference date $u(a_{\alpha})$ *is* calculated as follows:

$$u(a_{Sr})^2 = \frac{a_{Sr}^2}{K^2}\cdot u(I_A)^2 + \frac{a_{Sr}^2}{K^2}\cdot u(I_{A,Bg})^2 + \frac{(f_Y \cdot a_{Sr})^2}{K^2}\cdot u(I_B)^2 + \frac{(f_Y \cdot a_{Sr})^2}{K^2}\cdot u(I_{B,Bg})^2 +$$

$$\frac{(I_B - I_{B,Bg})^2 \cdot {a_{Sr}}^2}{K^2}\cdot u(f_Y)^2 + \frac{a_{Sr}^2}{\varepsilon_{Sr}^2}\cdot u(\varepsilon_{Sr})^2 + \frac{a_{Sr}^2}{r_{Sr}^2}\cdot u(r_{Sr})^2 + \frac{a_{Sr}^2}{m_a^2}\cdot u(m_a)^2 +$$

$$\frac{a_{Sr}^2}{q^2}\cdot u(q)^2 + a_{Sr}^2 \cdot t_1^2 \cdot u(\lambda_{Sr})^2 \qquad (25)$$

Calculation of the partial derivatives is shown in Appendix VIII.

The individual uncertainty components can be obtained from various sources, e.g. the producer specifies the uncertainty of the tracer used for calibration, uncertainties of nuclear parameters can be obtained from relevant tables $(u(\lambda))$, uncertainties of masses $(m_a, q)$ are determined from the properties of the balance, uncertainties of nuclear measurements are calculated based on the decay statistics (Poisson), e.g. $u(I_A)$ and $u(I_B)$ are calculated similarly:

$$u(I_A) = \sqrt{\frac{I_A}{t_{2Sr}}}\ ,\ u(I_B) = \sqrt{\frac{I_B}{t_{2Sr}}} \qquad (26)$$

The uncertainties of the background counts should be determined as the standard deviation of repeated background counting. Uncertainties of the tailing factor $(f_Y)$ and the counting efficiency $(\varepsilon_{Sr})$ are determined from the calibration experiments using the law of uncertainty propagation in each case. The uncertainty of the chemical recovery $(r_{Sr})$ has to be determined from the gravimetric and elemental analytical techniques.

An example for the calculation of the combined uncertainty of the massic activity of $^{90}$Sr in the IAEA-135 reference material is given in Table 3 in Appendix IX. The spreadsheet method was used to calculate the uncertainty as described in the papers of Kragten [30] and Moreno [12].

## 9.4. DECISION THRESHOLD AND DETECTION LIMIT

In accordance with ISO 11929:2010, the decision threshold, $a^*$ is obtained from the following equation:

$$a^* = k_{1-\alpha} \cdot u(0) \tag{27}$$

where $k_{1-\alpha} = 1.645$ is chosen referring to a probability not greater than 5% that the error of the first kind (i.e. wrongly rejecting the hypothesis that the analyte is present) occurs.
For the true value of the massic activity of the alpha emitting radionuclide $a_a$=0 Bq kg$^{-1}$, one usually expects $R_{GA}=R_{GB}$ and therefore:

$$u(R_{GA}) = \sqrt{\frac{R_{GB}}{t_G}} \tag{28}$$

In the equation (27), *u(0)* is calculated according to the given method of uncertainty calculation by replacing $R_{GA}$ with $R_{GB}$ and $u(R_{GA})$ with equation (28) into the basic equation of uncertainty calculation that can be either the mathematical or the numerical/spreadsheet approach. As a result of the calculation one gets for the value of $a_a$=0 Bq kg$^{-1}$ and the calculated uncertainty equals *u(0)*. The decision threshold of $^{239,240}$Pu, $^{241}$Am and $^{90}$Sr can be calculated by this method.

If $a_a \neq 0$ Bq kg$^{-1}$ at the end of the calculations then $R_{GA}$ should not be replaced simply by the blank value, $R_{GB}$, but a modified value has to be used that expresses the “real background” of the analyte. This is the situation when peaks are partially or completely overlapping. In this case the tailing of one peak represents the background for the analyte, and this value has to replace the original $R_{GA}$ value in calculating *u(0)*. This is for example the situation when the massic activity of $^{238}$Pu is to be determined in the presence of $^{236}$Pu tracer.
The tailing of the latter isotope represents an increased background for the analyte. In this case the sum of the calculated tailing and the background has to replace the value of $R_{GA}$ in the calculation of *u(0)*.

u(0) is calculated for each analyte using the general expression of the standard uncertainty. The same spreadsheet can also be used to determine the decision threshold that is used to calculate the massic activity.

In accordance with ISO 11929:2010, the detection limit, $a^\#$, is calculated by the following equation:

Assuming $\alpha = \beta$ then $k_{1-\alpha} = k_{1-\beta} = k$,

$$a^\# = 2k_{1-\alpha} \cdot u(0) + \frac{k_{1-\beta}^2}{a} \cdot (u^2(a) - u^2(0)) \tag{29}$$

where $a$ refers to $a_a$ or $a_{Sr}$ in case of alpha emitting radionuclides and $^{90}$Sr, respectively, and u(a) is the measurement uncertainty of the massic activity of the relevant radionuclide.

Results of calculations of uncertainties and determination of decision threshold and detection limit are shown in Tables 4-7 in Appendix X for the analysis of $^{238}$Pu, $^{239,240}$Pu, $^{241}$Am and $^{90}$Sr in the IAEA-135 reference material.

The IAEA-135 reference material is a sediment sample from the Irish sea that has elevated activities of anthropogenic radionuclides due to contamination of various sources. About 1 g of the material is enough to perform the measurements.

Measurement uncertainties of the high massic activities of $^{239,240}$Pu and $^{241}$Am are 1 to 3%, and those of lower activities of $^{238}$Pu and $^{90}$Sr are around 10%. The decision threshold for the alpha emitting radionuclides is small, around 0.3 to 3 Bq kg$^{-1}$ due to the low background of the alpha spectrometer. The decision threshold of $^{90}$Sr determination is about an order of magnitude higher because the background of the liquid scintillation counter is higher. Detection limits are about the double of the relevant decision threshold values.

## 10. METHOD VALIDATION

The procedure was validated in terms of trueness, repeatability, reproducibility, linearity and chemical recovery. Trueness, repeatability, linearity and chemical recovery were evaluated using seven IAEA reference materials, representing a great variety of soil and sediment matrices at different activity levels. Reproducibility tests were performed at the IAEA Terrestrial Environment Laboratory in Seibersdorf, Austria, by a new staff.

The list of IAEA standard reference materials used for the method repeatability study and the results of repeated measurements of the IAEA standard reference materials are shown in Tables 8–10 in Appendix XI. A summary of the repeatability measurements results is given in Table 11 in Appendix XI.

The materials used for the method reproducibility study and the results of repeated measurements of these materials are shown in Tables 12–16 in Appendix XII. These materials were provided in the frame of the Mixed Analyte Performance Evaluation Program (MAPEP) organized by the Department of Energy (DOE), US, in which the IAEA Terrestrial Environment Laboratory in Seibersdorf, Austria, regularly participates. A summary of the reproducibility measurements results is given in Table 17 in Appendix XII.

### 10.1. SELECTIVITY OF THE SEQUENTIAL METHOD, POSSIBLE INTERFERENCES

High selectivity of the method is provided by the specificity of the chemical separations based on ion exchange, extraction chromatography and precipitations as well as the nuclear measurement techniques. Especially alpha spectrometry is known for isotope selectivity. In case of liquid scintillation counting, the repeated counting of the samples can confirm the presence of $^{90}$Sr based on the shape of the beta spectra and the half-life measurement.

Possible interferences in the determination of the alpha emitter Pu and Am radionuclides are the following:

- Pu and Am can contaminate each other if the separation fails.
- Pu sources may contain traces of Th or U which can deteriorate the source quality.
- The resolution of Am sources can be poor if samples have high lanthanide content and the anion exchange separation is not working properly. An additional purification procedure can eliminate these problems.

Possible interferences in the determination of $^{90}$Sr are the following:

- The presence of other strontium radioisotopes (e.g. that of $^{89}$Sr) in the source cannot be eliminated, since the radiochemical separation is generally not able to separate radioisotopes from the same element, but the shape of the beta spectra can however give information on $^{89}$Sr contamination.
- Traces of Pb and Ba isotopes may contaminate the measurement source if the chemical separation fails.

## 10.2. LINEARITY, RANGE OF MEASUREMENT

The method was tested for a wide range of massic activities in different matrices. The massic activities of $^{241}$Am, $^{238}$Pu, $^{239,240}$Pu and $^{90}$Sr varied in the ranges of 1 to 300 Bq kg$^{-1}$, 0.1 to 50 Bq kg$^{-1}$, 0.5 to 200 Bq kg$^{-1}$ and 10 to 100 Bq kg$^{-1}$, respectively. Linearity of the measurements under the experimental conditions was shown by the good agreement between the measured data and the reference values. It is likely that the linearity of the method is valid in a much broader range than the one under study starting from the detection limit up to high activities where dead time becomes high and dead time corrections are necessary (below 1% dead time level).

## 10.3. TRUENESS OF THE METHOD

Several replicates were analyzed in order to evaluate the trueness. The relative bias of the method is calculated using the following formula:

$$\delta(\%) = \frac{\overline{X} - C}{C} \times 100 \tag{30}$$

Relative biases are calculated either from the average values of repeated measurements or from individual measurement.

Relative biases of repeatability and reproducibility measurements are summarized in Table 11 in Appendix XI and in Table 17 in Appendix XII, respectively.

## 10.4. REPEATABILITY (WITHIN-RUN PRECISION)

The repeatability limit was estimated by analyzing the replicates of the samples of “known” massic activities in repeatability conditions (same instrument, analyst, etc.). The repeatability limit was calculated using the following formula:

$$r_L = S_r \times 2.8 \tag{31}$$

Acceptance criteria: the method can be accepted if $|\delta| < 2.8\ S_r$.

Results of repeatability measurements are summarized in Table 11 in Appendix XI.

## 10.5. REPRODUCIBILITY (BETWEEN-RUN PRECISION)

The reproducibility limit was estimated by analyzing several replicates of a material with known massic activity, but with at least one parameter being changed in the analytical system (analyst, analysis date, instrument, etc.). The reproducibility limit was calculated using the following formula:

$$R_L = S_R \times 2.8 \tag{32}$$

Acceptance criteria: the method can be accepted if $|\delta| < 2.8\ S_R$.

Results of reproducibility measurements are summarized in Table 17 in Appendix XII.

## 10.6. CHEMICAL RECOVERIES

Chemical recoveries for all analytes in the combined procedure are acceptably high, Pu recoveries are around 90%, Sr and Am recoveries are around 50%. For the latter elements the many separation steps justify the somewhat higher chemical losses. Results are shown in Table 18 in Appendix XIII.

## 10.7. RESULTS OF METHOD VALIDATION

The combined procedure performed well both in repeatability and reproducibility tests. The test results met the requirements of repeatability, reproducibility and trueness, i.e.:

- The absolute mean bias $|\delta|$ in the repeatability test is smaller than the repeatability limit ($r_L$): $|\delta| < r_L$;
- The absolute mean bias $|\delta|$ in the reproducibility test is smaller than the reproducibility limit ($R_L$): $|\delta| < R_L$

According to the criteria of ISO/TS 21748:2004 the combined method for the simultaneous determination of $^{238}$Pu, $^{239,240}$Pu, $^{241}$Am and $^{90}$Sr in environmental samples performs well in repeatability and reproducibility tests for each radionuclide.

## 11. TEST REPORT

The test report has to conform to ISO 17025 requirements and should contain the following information:

- Sample code;
- Sampling date (if available);
- Date of separation of the analyte;
- Reference date of the tracer solution;
- Analysis request code;
- Responsible person;
- Reference to the measurement and evaluation procedure used;
- Identification of the sample;
- Units in which the results are expressed;
- Unless otherwise required, the test result should be stated together with the expanded uncertainty u calculated using a coverage factor k [32]. The following form is recommended:

$a \pm u(a)$ with the associated k value.

## 12. CONCLUSION

A combined procedure was developed and tested for the sequential determination of $^{238}$Pu, $^{239,240}$Pu, $^{241}$Am and $^{90}$Sr in environmental samples using alpha spectrometry and liquid scintillation counting. After digestion of the samples by acids, the radionuclides Pu, Am and Sr are radiochemically separated using sequential ion exchange, extraction chromatography and precipitation operations. Chemical recoveries are acceptably high, typically for Pu about 90% and for Am and Sr about 50%.

According to the repeatability and reproducibility tests, the measurement process is considered to perform adequately.

The method is recommended for the analysis of various environmental samples, e.g. soil, sediment, air filter, vegetation and water samples contaminated by low or elevated levels of $^{238}$Pu, $^{239,240}$Pu, $^{241}$Am and $^{90}$Sr.

# APPENDIX I

## NUCLEAR DATA OF RELEVANT RADIONUCLIDES

TABLE 1. NUCLEAR DATA OF RELEVANT RADIONUCLIDES [33]

| RADIONUCLIDE | Half-life (year) | Disintegration modes | $E_{\alpha}$ or $E_{\beta Max}$ (MeV) | Intensity (%) |
|---|---|---|---|---|
| $^{238}$Pu | 87.7 | α : 100% | 5.358 | 0.104 |
| | | SF: 1.9E-7% | 5.456 | 28.85 |
| | | | 5.499 | 71.04 |
| $^{239}$Pu | 24100 | α : 100% | 5.1058 | 11.87 |
| | | SF: 3E-10% | 5.144 | 17.14 |
| | | | 5.157 | 70.79 |
| $^{240}$Pu | 6561 | α : 100% | 5.021 | 0.0863 |
| | | SF: 5.7E-6% | 5.124 | 27.16 |
| | | | 5.168 | 72.74 |
| $^{242}$Pu | 3.735E5 | α : 100% | 4.858 | 23.44 |
| | | SF: 5.5E-4% | 4.902 | 76.53 |
| $^{241}$Am | 432.6 | α : 100% | 5.388 | 1.66 |
| | | SF: 3.6E-10% | 5.443 | 13.23 |
| | | | 5.486 | 84.45 |
| | | | 5.544 | 0.38 |
| $^{243}$Am | 7367 | α : 100% | 5.181 | 1.383 |
| | | SF: 3.8E-9% | 5.233 | 11.46 |
| | | | 5.275 | 86.74 |
| $^{90}$Sr | 28.80 | $\beta^-$ : 100% | 0.546 | 100 |
| $^{90}$Y | 0.00731 | $\beta^-$ : 100% | 2.2798 | 99.98 |

# APPENDIX II

## CAPACITY FACTORS OF THE TRU AND SR EXTRACTION CHROMATOGRAPHIC RESINS

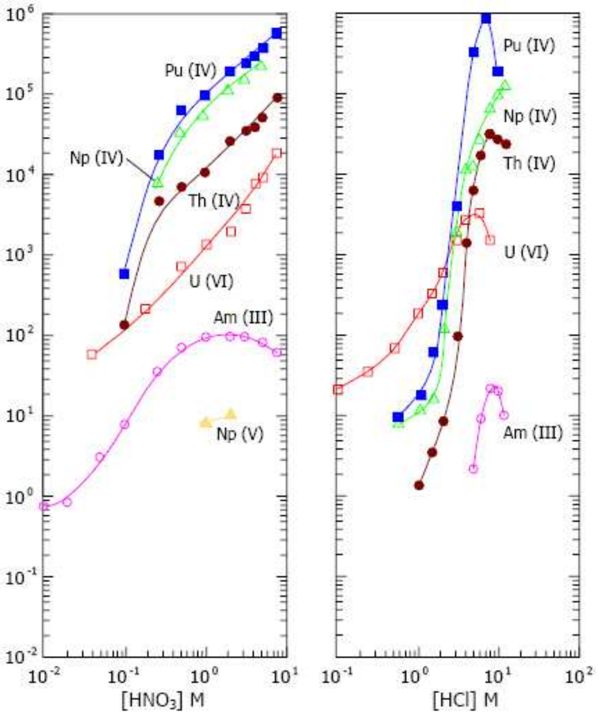

*FIG. 1. Capacity factors of TRU resin in nitric and hydrochloric acid media (www.eichrom.com).*

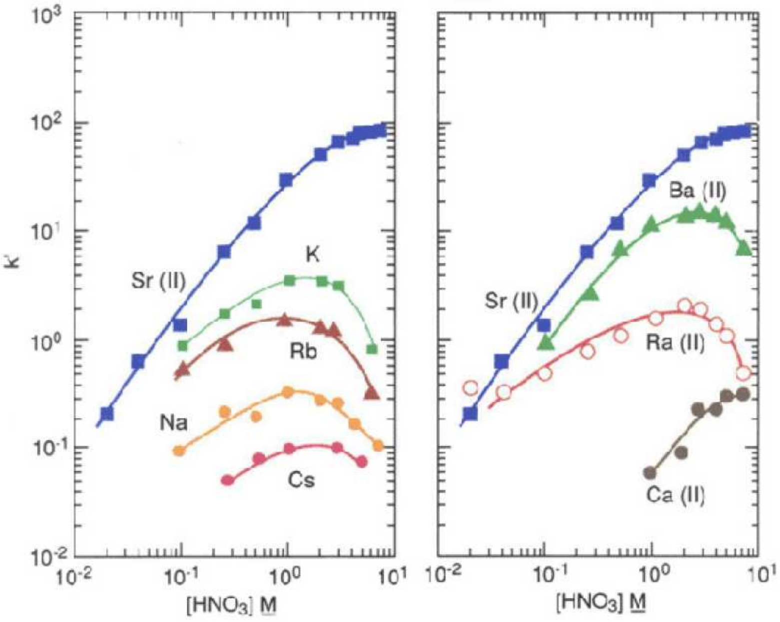

*FIG. 2. Capacity factors of Sr resin in nitric acid media (www.eichrom.com).*

# APPENDIX III

## FLOW CHART OF THE RADIOCHEMICAL PROCEDURE

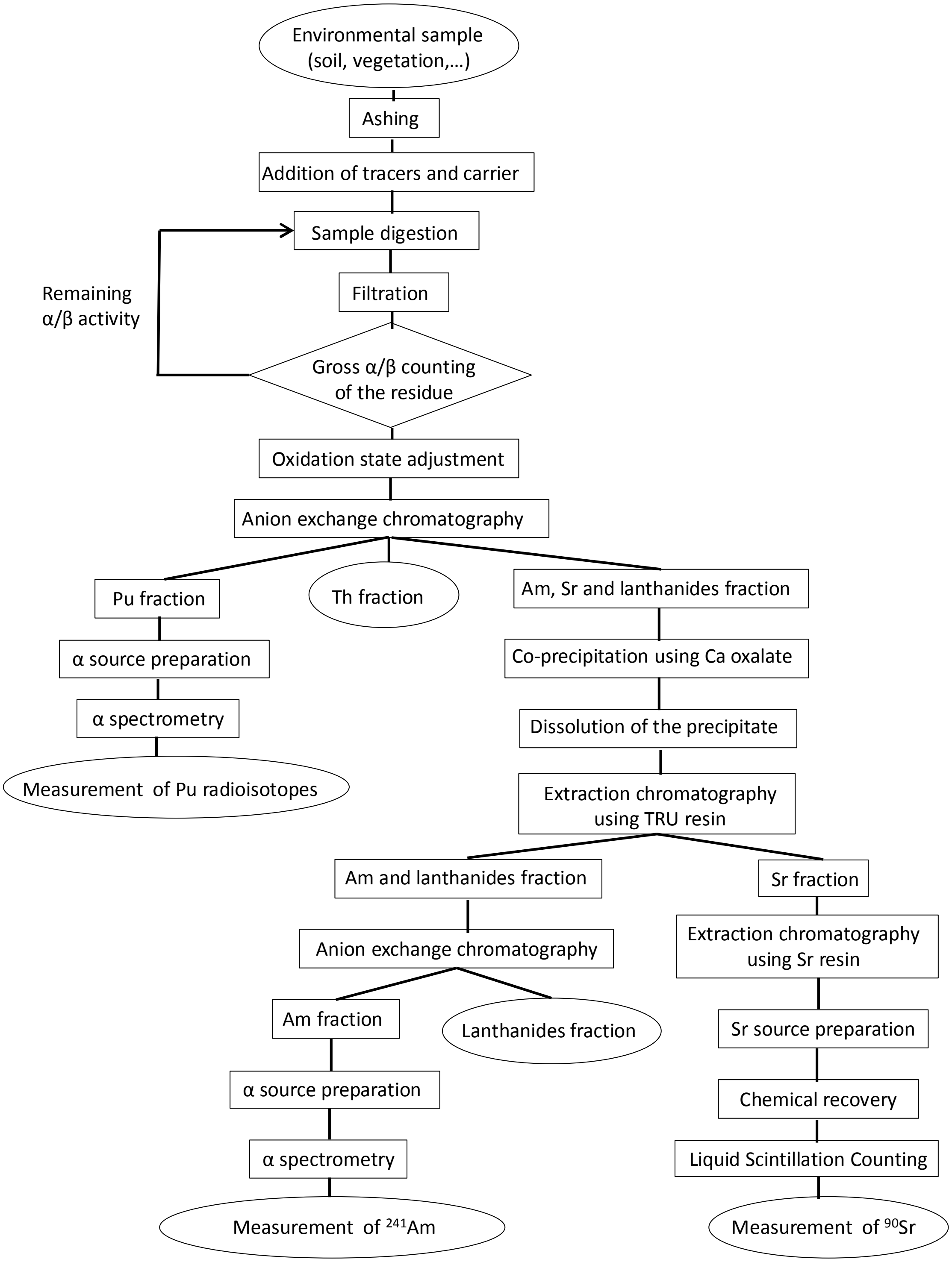

*FIG. 3. Flow chart of the procedure.*

# APPENDIX IV

## PREPARATION OF CHEMICALS

- Calcium carrier solution at 100 mg $mL^{-1}$ in 0.1M $HNO_3$: dissolve 58.93 g of $Ca(NO_3)_2.4H_2O$ g in de-ionized water, add 725 µL of 65% $HNO_3$ and dilute to 100 mL with de-ionized water.

- 0.1M $NH_4I$–9M HCl: dissolve 14.49 g of $NH_4I$ in 90 mL of de-ionized water, then make the solution up to 1 L with 10M HCl. This solution should be prepared just before its use.

- 25% $NaHSO_4$ solution**:** dissolve 25 g of $NaHSO_4$ in de-ionized water. Dilute up to 100 mL with de-ionized water.

- Nd carrier solution at 0.5 mg $mL^{-1}$ in 1M $HNO_3$: dissolve 0.583 g of 99.9% $Nd_2O_3$ in 2 mL concentrated HCl by boiling gently for a few minutes. Cool and dilute to 100 mL with de-ionized water (5 mg $mL^{-1}$ of Nd). Take 10 mL of the stock solution and dilute to 100 mL with 1M $HNO_3$ (0.5 mg $mL^{-1}$ of Nd).

- 25% $NaNO_2$: dissolve 2.5 g of $NaNO_2$ in 10 mL of de-ionized water. This solution should be prepared just before its use.

- 1M $HNO_3$–93% $CH_3OH$: mix 72.5 mL of 65% $HNO_3$ with $CH_3OH$ in a 1 L flask.

- 0.1M HCl–0.5M $NH_4SCN$–80% $CH_3OH$: mix 100 mL of 1M HCl and 100 mL of 5M $NH_4SCN$ with 800 mL of $CH_3OH$.

- 1.5M HCl–86% $CH_3OH$ solution: mix 125 mL of concentrated HCl with 860 mL of $CH_3OH$ and dilute to 1 L with de-ionized water.

- Electroplating solution: dissolve 100 g of $(NH_4)_2SO_4$ in 900 mL of de-ionized water. Adjust the pH with concentrated $H_2SO_4$ to pH 2.00 ± 0.05 using a pH-meter.

# APPENDIX V

## TYPICAL ALPHA SPECTRA OF PU AND AM SOURCES

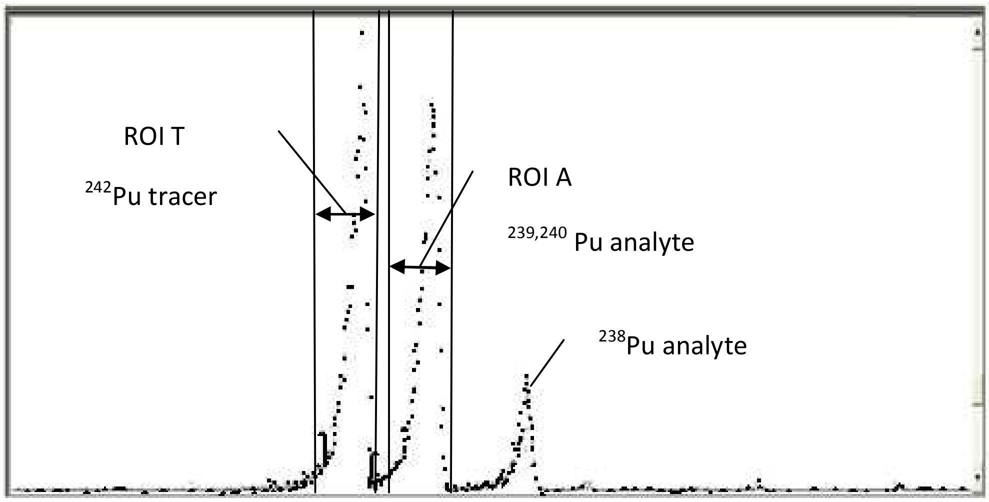

*FIG. 4. Typical alpha spectrum of a Pu source (counts as a function of channels)*

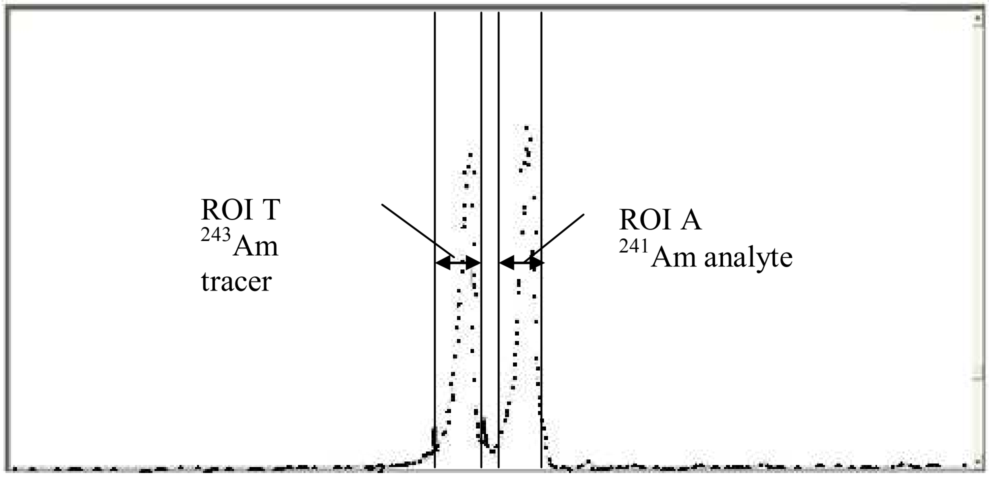

*FIG. 5. Typical alpha spectrum of an Am source (counts as a function of channels)*

# APPENDIX VI

## TYPICAL LIQUID SCINTILLATION SPECTRUM OF 90SR

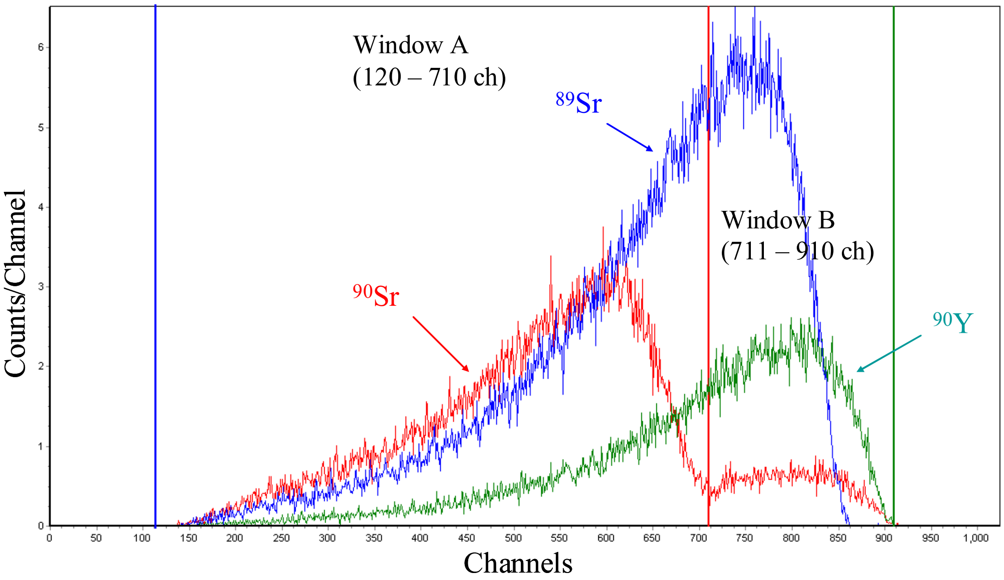

*FIG. 6. Typical LSC spectrum of a $^{90}$Sr source showing the spectra of separated $^{90}$Y and the possible interference due to $^{89}$Sr*

# APPENDIX VII

## UNCERTAINTY CALCULATION OF ALPHA SPECTROMETRIC RESULTS

This supplement describes how to calculate the sensitivity factors and how to derive an equation for calculation of the combined uncertainty of the massic activity. The massic activity of the alpha emitting analyte is calculated according to equation (33) as follows:

$$a_\alpha = \frac{C_T \cdot V_T}{m_a \cdot q} \cdot f_1 \cdot f_2 \cdot f_3 \cdot f_4 \cdot \frac{p_{\alpha T}}{p_{\alpha A}} \cdot (\frac{R_{GA} - R_{BA}}{R_{GT} - R_{BT}} - q_I) \tag{33}$$

Assuming that there is no correlation among the individual parameters of the equation, the combined uncertainty is calculated according to the general formula of uncertainty propagation:

$$u(a_\alpha)^2 = \sum\left(\left(\frac{\partial a_\alpha}{\partial x_i}\right)^2 \cdot u(x_i)^2\right) \tag{34}$$

if covariances are not taken into account and $x_i$ symbolizes the parameters of the equation.

Sensitivity factors are partial derivatives of the massic activity against the individual parameters $x_i$. Differentiating equation (33), each partial derivative can be calculated as follows:

$$\frac{\partial a_\alpha}{\partial C_T} = \frac{a_\alpha}{C_T} \tag{35}$$

$$\frac{\partial a_\alpha}{\partial V_T} = \frac{a_\alpha}{V_T} \tag{36}$$

$$\frac{\partial a_\alpha}{\partial q} = -\frac{a_\alpha}{q} \tag{37}$$

$$\frac{\partial a_\alpha}{\partial m_a} = -\frac{a_\alpha}{m_a} \tag{38}$$

$$\frac{\partial a_\alpha}{\partial p_{\alpha T}} = \frac{a_\alpha}{p_{\alpha T}} \tag{39}$$

$$\frac{\partial a_\alpha}{\partial p_{\alpha A}} = -\frac{a_\alpha}{p_{\alpha A}} \tag{40}$$

$$\frac{\partial a_\alpha}{\partial f_1} = \frac{a_\alpha}{f_1} \tag{41}$$

$$\frac{\partial a_\alpha}{\partial f_2} = \frac{a_\alpha}{f_2} \tag{42}$$

$$\frac{\partial a_\alpha}{\partial f_3} = \frac{a_\alpha}{f_3} \tag{43}$$

$$\frac{\partial a_\alpha}{\partial f_4} = \frac{a_\alpha}{f_4} \tag{44}$$

$$\frac{\partial a_\alpha}{\partial R_{GA}} = \frac{a_\alpha}{y} \cdot \frac{1}{R_{GT} - R_{BT}} \tag{45}$$

$$\frac{\partial a_\alpha}{\partial R_{BA}} = -\frac{a_\alpha}{y} \cdot \frac{1}{R_{GT} - R_{BT}} \tag{46}$$

$$\frac{\partial a_\alpha}{\partial R_{GT}} = -\frac{a_\alpha}{y} \cdot \frac{R_{GA} - R_{BA}}{(R_{GT} - R_{BT})^2} \tag{47}$$

$$\frac{\partial a_\alpha}{\partial R_{BT}} = -\frac{a_\alpha}{y} \cdot \frac{R_{GA} - R_{BA}}{(R_{GT} - R_{BT})^2} \tag{48}$$

$$\frac{\partial a_\alpha}{\partial q_1} = -\frac{a_\alpha}{q_1} \tag{49}$$

Where

$$y = \frac{R_{GA} - R_{BA}}{R_{GT} - R_{BT}} - q_1 \tag{50}$$

Replacing equations from (35) to (50) in equation (34) one gets the final expression for the uncertainty of $a_\alpha$ that is shown in equation (19) in 9.3.1.

# APPENDIX VIII

## UNCERTAINTY CALCULATION OF 90SR RESULTS

This supplement describes how to calculate the sensitivity factors and how to derive an equation for calculation of the combined uncertainty of the massic activity. The massic activity of $^{90}$Sr is calculated according to equation (51) as follows:

$$a_{Sr} = \frac{(I_A - I_{ABg}) - f_Y \cdot (I_B - I_{BBg})}{m_a \cdot r_{Sr} \cdot \varepsilon_{Sr} \cdot q \cdot 60} \cdot f_{1Sr} \cdot f_{2Sr} \tag{51}$$

The general formula for calculating the uncertainty of the massic activity of $^{90}$Sr is the same as for alpha emitting radionuclides shown in equation (34):

$$u(a_{Sr})^2 = \sum\left(\left(\frac{\partial a_{Sr}}{\partial x_i}\right)^2 \cdot u(x_i)^2\right) \tag{52}$$

Differentiating equation (51) the partial derivatives can be calculated as follows:

$$\frac{\partial a_{Sr}}{\partial I_A} = \frac{a_{Sr}}{K} \tag{53}$$

$$\frac{\partial a_{Sr}}{\partial I_B} = -\frac{f_Y \cdot a_{Sr}}{K} \tag{54}$$

$$\frac{\partial a_{Sr}}{\partial I_{A,Bg}} = -\frac{a_{Sr}}{K} \tag{55}$$

$$\frac{\partial a_{Sr}}{\partial I_{B,Bg}} = \frac{f_Y \cdot a_{Sr}}{K} \tag{56}$$

$$\frac{\partial a_{Sr}}{\partial f_Y} = -\frac{(I_B - I_{B,Bg}) \cdot a_{Sr}}{K} \tag{57}$$

$$\frac{\partial a_{Sr}}{\partial \varepsilon_{Sr}} = -\frac{a_{Sr}}{\varepsilon_{Sr}} \tag{58}$$

$$\frac{\partial a_{Sr}}{\partial r_{Sr}} = -\frac{a_{Sr}}{r_{Sr}} \tag{59}$$

$$\frac{\partial a_{Sr}}{\partial m_a} = -\frac{a_{Sr}}{m_a} \tag{60}$$

$$\frac{\partial a_{Sr}}{\partial q} = -\frac{a_{Sr}}{q} \tag{61}$$

$$\frac{\partial \mathrm{a}_{\mathrm{Sr}}}{\partial \lambda_{\mathrm{Sr}}} = \mathrm{a}_{\mathrm{Sr}} \cdot \mathrm{t}_{1\mathrm{Sr}} \tag{62}$$

Where

$$K = (I_A - I_{ABg}) - f_Y \cdot (I_B - I_{BBg})$$

and $f_{2Sr}$ is taken to be equal to 1.

Replacing equations from (53) to (62) in equation (52) one gets the final expression for the uncertainty of $a_{Sr}$ that is shown in equation (25) in 9.3.2.

# APPENDIX IX

## EXAMPLES FOR THE CALCULATION OF COMBINED UNCERTAINTIES BY THE SPREADSHEET METHOD

TABLE 2. SPREADSHEET TO CALCULATE COMBINED UNCERTAINTY OF THE MASSIC ACTIVITY OF $^{238}$Pu IN THE IAEA-135 REFERENCE MATERIAL

| **SPREADSHEET METHOD FOR UNCERTAINTY CALCULATION IN THE ACTIVITY CONCENTRATION OF Pu-238 in SRM IAEA-135** | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $t_B$, s | 406964 | | | | | | | | | | | | |
| **Ref. Date** | $t_G$ , s | 5866 | **$R_{GA}$, cps** | **$R_{BA}$, cps** | **$R_{GT}$, cps** | **$R_{BT}$, cps** | **$f_t$** | **$C_TV_T$, Bq** | **$m_a$, kg** | **1/q** | **$l_T$ years** | **$t_S$-$t_C$, years** | **$l_A$ years** | **$t_S$-$t_E$, years** |
| **1-1-92** | **Parameters** | | 0,08319 | 2,21E-05 | 2,78E-01 | 2,21E-05 | 0,03 | 1,740 | 0,00491 | 0,909 | 2,42E-01 | 3,170 | 7,90E-03 | 7,28 |
| | **Uncertainty** | | 0,00377 | 7,37E-06 | 1,31E-02 | 7,37E-06 | 1,58E-03 | 0,016 | 0,00001 | 0,009 | 6,79E-04 | 0,003 | 2,70E-05 | 0,003 |
| | | | | | | | | | | | | | | |
| **$R_{GA}$, cps** | 0,083 | | **0,087** | 0,083 | 0,083 | 0,083 | 0,083 | 0,083 | 0,083 | 0,083 | 0,083 | 0,083 | 0,083 | 0,083 |
| **$R_{BA}$, cps** | 2,21E-05 | | 2,21E-05 | **2,95E-05** | 2,21E-05 | 2,21E-05 | 2,21E-05 | 2,21E-05 | 2,21E-05 | 2,21E-05 | 2,21E-05 | 2,21E-05 | 2,21E-05 | 2,21E-05 |
| **$R_{GT}$, cps** | 0,278 | | 0,278 | 0,278 | **0,291** | 0,278 | 0,278 | 0,278 | 0,278 | 0,278 | 0,278 | 0,278 | 0,278 | 0,278 |
| **$R_{BT}$, cps** | 4,91E-06 | | 4,91E-06 | 4,91E-06 | 4,91E-06 | **2,95E-05** | 4,91E-06 | 4,91E-06 | 4,91E-06 | 4,91E-06 | 4,91E-06 | 4,91E-06 | 4,91E-06 | 4,91E-06 |
| **$f_t$** | 0,030 | | 0,030 | 0,030 | 0,030 | 0,030 | **0,032** | 0,030 | 0,030 | 0,030 | 0,030 | 0,030 | 0,030 | 0,030 |
| **$C_TV_T$, Bq** | 1,740 | | 1,740 | 1,740 | 1,740 | 1,740 | 1,740 | **1,756** | 1,740 | 1,740 | 1,740 | 1,740 | 1,740 | 1,740 |
| **$m_a$, kg** | 4,91E-03 | | 4,91E-03 | 4,91E-03 | 4,91E-03 | 4,91E-03 | 4,91E-03 | 4,91E-03 | **4,92E-03** | 4,91E-03 | 4,91E-03 | 4,91E-03 | 4,91E-03 | 4,91E-03 |
| **1/q** | 0,909 | | 0,909 | 0,909 | 0,909 | 0,909 | 0,909 | 0,909 | 0,909 | **0,918** | 0,909 | 0,909 | 0,909 | 0,909 |
| **$l_T$ years** | 0,242 | | 0,242 | 0,242 | 0,242 | 0,242 | 0,242 | 0,242 | 0,242 | 0,242 | **0,243** | 0,242 | 0,242 | 0,242 |
| **$t_S$-$t_C$, years** | 3,170 | | 3,170 | 3,170 | 3,170 | 3,170 | 3,170 | 3,170 | 3,170 | 3,170 | 3,170 | **3,173** | 3,170 | 3,170 |
| **$l_A$ years** | 0,008 | | 0,008 | 0,008 | 0,008 | 0,008 | 0,008 | 0,008 | 0,008 | 0,008 | 0,008 | 0,008 | **0,008** | 0,008 |
| **$t_S$-$t_E$, years** | 7,279 | | 7,279 | 7,279 | 7,279 | 7,279 | 7,279 | 7,279 | 7,279 | 7,279 | 7,279 | 7,279 | 7,279 | **7,282** |
| | | | | | | | | | | | | | | |
| **net intensity of $^{238}$Pu, cps** | 0,075 | | 0,079 | 0,075 | 0,074 | 0,075 | 0,074 | 0,075 | 0,075 | 0,075 | 0,075 | 0,075 | 0,075 | 0,075 |
| **net intensity of $^{236}$Pu, cps** | 0,278 | | 0,278 | 0,278 | 0,291 | 0,278 | 0,278 | 0,278 | 0,278 | 0,278 | 0,278 | 0,278 | 0,278 | 0,278 |
| **$a_{Pu238}$, Bq kg$^{-1}$** | **42,55** | | **44,69** | **42,54** | **40,43** | **42,55** | **42,30** | **42,95** | **42,46** | **42,97** | **42,46** | **42,52** | **42,56** | **42,55** |
| **$a_i$ - a** | | | 2,14E+00 | -4,19E-03 | -2,12E+00 | 4,18E-03 | -2,50E-01 | 4,00E-01 | -8,65E-02 | 4,21E-01 | -9,14E-02 | -2,82E-02 | 8,37E-03 | 9,20E-04 |
| **S($a_i$ - a)$^2$** | 9,497 | | 4,59E+00 | 1,76E-05 | 4,49E+00 | 1,75E-05 | 6,26E-02 | 1,60E-01 | 7,48E-03 | 1,77E-01 | 8,36E-03 | 7,97E-04 | 7,01E-05 | 8,47E-07 |
| **u($a_{Pu238}$), Bq kg$^{-1}$** | **3,08** | | | | | | | | | | | | | |
| SF by Spreadsheet | $da/dx_i$ | | 5,69E+02 | -5,69E+02 | -1,62E+02 | 5,7E+02 | -1,58E+02 | 2,45E+01 | -8,65E+03 | 4,68E+01 | -1,35E+02 | -1,03E+01 | 3,10E+02 | 3,36E-01 |
| SF by Differentiation | $da/dx_i$ | | 5,69E+02 | -5,69E+02 | -1,70E+02 | 1,7E+02 | -1,58E+02 | 2,45E+01 | -8,67E+03 | 4,68E+01 | -1,35E+02 | -1,03E+01 | 3,10E+02 | 3,36E-01 |
| **Contribution, %** | $[(da/dx_i)^2.u_{xi}^2]*100/u_e^2$ | | 48,3 | 0,0 | 47,3 | 0,0 | 0,7 | 1,7 | 0,1 | 1,9 | 0,1 | 0,0 | 0,0 | 0,0 |
| Remark: tailing correction was performed where $f_t$: correction factor for tailing of $^{236}$Pu peak into $^{238}$Pu peak | | | | | | | | | | | | | | |
| SF: sensitivity factor | | | | | | | | | | | | | | |

# TABLE 3. SPREADSHEET TO CALCULATE COMBINED UNCERTAINTY OF THE MASSIC ACTIVITY OF $^{90}$Sr IN THE IAEA-135 REFERENCE MATERIAL

| **SPREADSHEET METHOD FOR UNCERTAINTY CALCULATION OF THE ACTIVITY CONCENTRATION OF Sr-90 IN IAEA-135** | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | **Parameter $x_i$** | **$m_a$** | **1/q** | **$r_{Sr}$** | **$e_{Sr}$** | **$f_y$** | **$I_B$** | **$I_{B,Bkg}$** | **$I_A$** | **$I_{A,Bkg}$** | **$l_{Sr}$** | **$t_{1,Sr}$** |
| | **Unit** | kg | | | | | cpm | cpm | cpm | cpm | $s^{-1}$ | s |
| | **Value $x_i$** | 1,09E-03 | 0,9075 | 0,838 | 0,675 | 0,49 | 5,65 | 5,05 | 9,58 | 7,09 | 7,63E-10 | 2,03E+08 |
| | **$u(x_i)$** | 9,00E-08 | 0,001 | 0,007 | 0,012 | 0,01 | 0,12 | 0,27 | 0,15 | 0,13 | 8,00E-12 | 3,60E+03 |
| **$t_s$, min** | 400 | | | | | | | | | | | |
| **$m_a$** | 0,00109 | **0,0011** | 0,0011 | 0,0011 | 0,0011 | 0,0011 | 0,0011 | 0,0011 | 0,0011 | 0,0011 | 0,0011 | 0,0011 |
| **1/q** | 0,9075 | 0,9075 | **0,909** | 0,908 | 0,908 | 0,908 | 0,908 | 0,908 | 0,908 | 0,908 | 0,908 | 0,908 |
| **$r_{Sr}$** | 0,838 | 0,838 | 0,838 | **0,845** | 0,838 | 0,838 | 0,838 | 0,838 | 0,838 | 0,838 | 0,838 | 0,838 |
| **$e_{Sr}$** | 0,675 | 0,675 | 0,675 | 0,675 | **0,687** | 0,675 | 0,675 | 0,675 | 0,675 | 0,675 | 0,675 | 0,675 |
| **$f_y$** | 0,49 | 0,49 | 0,49 | 0,49 | 0,49 | **0,498** | 0,49 | 0,49 | 0,49 | 0,49 | 0,49 | 0,49 |
| **$I_B$** | 5,65 | 5,65 | 5,65 | 5,65 | 5,65 | 5,65 | **5,77** | 5,65 | 5,65 | 5,65 | 5,65 | 5,65 |
| **$I_{B,Bg}$** | 5,05 | 5,05 | 5,05 | 5,05 | 5,05 | 5,05 | 5,05 | **5,32** | 5,05 | 5,05 | 5,05 | 5,05 |
| **$I_A$** | 9,58 | 9,58 | 9,58 | 9,58 | 9,58 | 9,58 | 9,58 | 9,58 | **9,73** | 9,58 | 9,58 | 9,58 |
| **$I_{A,Bg}$** | 7,09 | 7,09 | 7,09 | 7,09 | 7,09 | 7,09 | 7,09 | 7,09 | 7,09 | **7,22** | 7,09 | 7,09 |
| **$l_{Sr}$** | 7,63E-10 | 7,63E-10 | 7,63E-10 | 7,63E-10 | 7,63E-10 | 7,63E-10 | 7,63E-10 | 7,63E-10 | 7,63E-10 | 7,63E-10 | **7,71E-10** | 7,63E-10 |
| **$t_{1,Sr}$** | 2,03E+08 | 2,03E+08 | 2,03E+08 | 2,03E+08 | 2,03E+08 | 2,03E+08 | 2,03E+08 | 2,03E+08 | 2,03E+08 | 2,03E+08 | 2,03E+08 | **2,03E+08** |
| **$a_{Sr}$ Bq kg$^{-1}$** | **62,7** | **62,69** | **62,77** | **62,18** | **61,62** | **62,57** | **61,03** | **66,47** | **67,12** | **58,90** | **62,80** | **62,70** |
| $a_i$ - a | | -5,16E-03 | 6,91E-02 | -5,19E-01 | -1,08E+00 | -1,31E-01 | -1,66E+00 | 3,78E+00 | 4,42E+00 | -3,80E+00 | 1,02E-01 | 1,72E-04 |
| K,cpm | 2,196 | 2,67E-05 | 4,77E-03 | 2,70E-01 | 1,16E+00 | 1,71E-02 | 2,76E+00 | 1,43E+01 | 1,95E+01 | 1,44E+01 | 1,04E-02 | 2,97E-08 |
| $\sum(a_i - a)^2$ | 52,462 | **$(a_i - a)^2$** | | | | | | | | | | |
| **$u(a_{Sr})$ Bq kg$^{-1}$** | **7,2** | | | | | | | | | | | |
| ua/a, % | 11,6 | | | | | | | | | | | |
| SF by Kragten | da/d$x_i$ | -5,74E+04 | 69,09 | -74,20 | -89,65 | -17,13 | -13,99 | 13,99 | 28,55 | -28,55 | 1,27E+10 | 0,00 |
| SF by Differentiation | da/d$x_i$ | -5,74E+04 | 69,09 | -74,82 | -92,86 | -17,13 | -13,99 | 13,99 | 28,55 | -28,55 | 1,27E+10 | 0,00 |
| **Contribution, %** | $[(da/dx_i)^2.u_{xi}^2].100/u_a^2$ | **0,00** | **0,01** | **0,52** | **2,36** | **0,03** | **5,26** | **27,15** | **37,15** | **27,49** | **0,02** | **0,00** |
| **SF: sensitivity factor** | | | | | | | | | | | | |

# APPENDIX X

## UNCERTAINTY BUDGET, DECISION THRESHOLD AND DETECTION LIMIT FOR $^{238}$Pu, $^{239+240}$Pu, $^{241}$Am AND $^{90}$Sr IN IAEA-135 REFERENCE MATERIAL

TABLE 4. RESULTS OF CALCULATION OF THE MASSIC ACTIVITY OF $^{238}$Pu IN IAEA-135 REFERENCE MATERIAL

| **$^{238}$Pu in SRM IAEA-135** | | **Parameter value** | **Standard unc.** | **Relative standard unc. %** | **% contribution to combined standard unc.** |
|---|---|---|---|---|---|
| **Parameters** | **Unit** | | | | |
| **Sample mass** | | | | | |
| $m_a$ | kg | 4.91E-03 | 0.00001 | 0.20 | 0.1 |
| 1/q | - | 0.909 | 0.009 | 0.99 | 1.9 |
| **Sample counting** | | | | | |
| $R_{GA}$ | cps | 0.083 | 0.00377 | 4.53 | 48.3 |
| $R_{BA}$ | cps | 2.21E-05 | 7.37E-06 | 33.33 | negligible |
| $R_{GT}$ | cps | 0.278 | 1.31E-02 | 4.69 | 47.3 |
| $R_{BT}$ | cps | 4.91E-06 | 7.37E-06 | 150 | negligible |
| $f_t$ | - | 0.030 | 1.58E-03 | 5.27 | 0.7 |
| $t_B$ | s | 406964 | | | |
| $t_G$ | s | 5866 | | | |
| **Decay corrections** | | | | | |
| $l_T$ | $y^{-1}$ | 0.242 | 6.79E-04 | 0.28 | 0.1 |
| $t_S$-$t_C$ | y | 3.170 | 0.0027 | 0.09 | negligible |
| $l_A$ | $y^{-1}$ | 0.008 | 2.70E-05 | 0.34 | negligible |
| $t_S$-$t_E$ | y | 7.279 | 0.003 | 0.04 | negligible |
| **Tracer activity** | | | | | |
| $C_TV_T$ | Bq | 1.740 | 0.016 | 0.94 | 1.7 |
| **Results** | | | | | |
| **$a_A$** | Bq kg$^{-1}$, as dry mass | **42.55** | **3.08** | 7.24 | |
| **Decision threshold** | Bq kg$^{-1}$, as dry mass | 1.2 | | | |
| **Detection limit** | Bq kg$^{-1}$, as dry mass | **3.1** | | | |

Tailing correction due to $^{236}$Pu tracer has been performed.

TABLE 5. RESULTS OF CALCULATION OF THE MASSIC ACTIVITY OF $^{239,240}$Pu IN IAEA-135 REFERENCE MATERIAL

| **$^{239,240}$Pu in SRM IAEA-135** | | **Parameter value** | **Standard unc.** | **Relative standard unc. %** | **% contribution to combined standard unc.** |
|---|---|---|---|---|---|
| **Parameters** | **Unit** | | | | |
| **Sample mass** | | | | | |
| $m_a$, kg | kg | 4.91E-03 | 1.00E-05 | 0.20 | 0.2 |
| 1/q | - | 9.09E-01 | 9.00E-03 | 0.99 | 3.8 |
| **Sample counting** | | | | | |
| $R_{GA}$ | cps | 4.18E-01 | 8.44E-03 | 2.02 | 15.60 |
| $R_{BA}$ | cps | 2.21E-05 | 7.37E-06 | 33.33 | negligible |
| $R_{GT}$ | cps | 2.78E-01 | 1.31E-02 | 4.69 | 76.90 |
| $R_{BT}$ | cps | 4.91E-06 | 7.37E-06 | 150 | negligible |
| $t_B$ | s | 4.07E+05 | | | |
| $t_G$ | s | 5.87E+03 | | | |
| **Decay corrections** | | | | | |
| $l_T$ | $y^{-1}$ | 2.42E-01 | 6.79E-04 | 0.28 | 0.20 |
| $t_S$-$t_C$ | y | 3.17E+00 | 2.74E-03 | 0.09 | negligible |
| $l_A$ | $y^{-1}$ | 2.88E-05 | 3.58E-08 | 0.12 | negligible |
| $t_S$-$t_E$ | y | 7.28E+00 | 2.74E-03 | 0.04 | negligible |
| **Tracer activity** | | | | | |
| $C_TV_T$ | Bq | 1.74E+00 | 0.016 | 0.94 | 3.40 |
| **Results** | Bq kg$^{-1}$, as dry mass | **224.5** | **3.39** | 1.51 | |
| **Decision threshold** | Bq kg$^{-1}$, as dry mass | **0.30** | | | |
| **Detection limit** | Bq kg$^{-1}$, as dry mass | **0.74** | | | |

## TABLE 6. RESULTS OF CALCULATION OF THE MASSIC ACTIVITY OF $^{241}$Am IN IAEA-135 REFERENCE MATERIAL

| **$^{241}$Am in SRM IAEA-135** | | **Parameter value** | **Standard unc.** | **Relative standard unc. %** | **% contribution to combined standard unc.** |
|---|---|---|---|---|---|
| **Parameters** | **Unit** | | | | |
| **Sample mass** | | | | | |
| $m_a$, kg | kg | 0.00491 | 0.00001 | 0.2 | 0.8 |
| 1/q | - | 0.909 | 0.009 | 1.0 | 18.1 |
| **Sample counting** | | | | | |
| $R_{GA}$ | cps | 0.520 | 6.61E-03 | 1.3 | 32.4 |
| $R_{BA}$ | cps | 2.46E-06 | 2.46E-06 | 100 | negligible |
| $R_{GT}$ | cps | 0.515 | 6.57E-03 | 1.3 | 31.9 |
| $R_{BT}$ | cps | 2.457E-06 | 2.46E-06 | 100 | negligible |
| $f_t$ | - | 0.04 | 0.0014 | 3.5 | 0.4 |
| $t_B$ | s | 406964 | | | |
| $t_G$ | s | 11923 | | | |
| **Decay corrections** | | | | | |
| $l_T$ | $y^{-1}$ | 9.40E-05 | 1.91E-07 | 0.2 | negligible |
| $t_S$-$t_C$ | y | 3.217 | 0.003 | 0.1 | negligible |
| $l_A$ | $y^{-1}$ | 1.60E-03 | 1.85E-06 | 0.1 | negligible |
| $t_S$-$t_E$ | y | 7.30 | 0.003 | 0.0 | negligible |
| **Tracer activity** | | | | | |
| $C_T V_T$ | Bq | 1.75E+00 | 0.016 | 0.9 | 16.4 |
| **Results** | | | | | |
| **$a_A$** | Bq kg$^{-1}$, as dry mass | **341.0** | **8.00** | 2.3 | |
| **Decision threshold** | Bq kg$^{-1}$, as dry mass | 2.9 | | | |
| **Detection limit** | Bq kg$^{-1}$, as dry mass | **6.4** | | | |

Tailing correction due to $^{243}$Am tracer has been performed.

# TABLE 7. RESULTS OF CALCULATION OF THE MASSIC ACTIVITY OF $^{90}$Sr IN IAEA-135 REFERENCE MATERIAL

| **$^{90}$Sr in SRM IAEA-135** | | **Parameter value** | **Standard unc.** | **Relative standard unc. %** | **% contribution to combined standard unc.** |
|---|---|---|---|---|---|
| **Parameters** | **Unit** | | | | |
| **Sample mass** | | | | | |
| $m_a$, kg | kg | 0.0011 | 9.00E-08 | 0.0 | negligible |
| 1/q | - | 0.908 | 0.001 | 0.1 | 0.01 |
| **Sample counting** | | | | | |
| $I_B$ | cpm | 5.65 | 0.12 | 2.1 | 5.3 |
| $I_{B,Bg}$ | cpm | 5.05 | 0.27 | 5.3 | 27.1 |
| $I_A$ | cpm | 9.58 | 0.15 | 1.6 | 37.1 |
| $I_{A,Bg}$ | cpm | 7.09 | 0.13 | 1.9 | 27.5 |
| $f_Y$ | - | 0.49 | 0.01 | 1.6 | 0.03 |
| $t_S$ | min | 400 | | | |
| **Decay corrections** | | | | | |
| $l_{Sr}$ | $s^{-1}$ | 7.63E-10 | 8.00E-12 | 1.0 | 0.02 |
| $t_{1,Sr}$ | s | 2.03E+08 | 3.60E+03 | 0.0 | negligible |
| **Chemical recovery** | | | | | |
| $r_{Sr}$ | - | 0.838 | 0.007 | 0.8 | 0.52 |
| **Calibration** | | | | | |
| $e_{Sr}$ | - | 0.675 | 0.012 | 1.8 | 2.4 |
| **Results** | | | | | |
| **$a_{Sr}$** | Bq kg$^{-1}$, as dry mass | **62.7** | **7.20** | 11.5 | |
| **Decision threshold** | Bq kg$^{-1}$ , as dry mass | 11.1 | | | |
| **Detection limit** | Bq kg$^{-1}$ , as dry mass | **19.1** | | | |

## APPENDIX XI

## REPEATABILITY STUDY

TABLE 8. LIST OF SAMPLES ANALYZED FOR METHOD REPEATABILITY

| Nr. | RM Code |
|---|---|
| 1 | IAEA-367, Bikini coral |
| 2 | IAEA-368, Mururoa coral |
| 3 | IAEA-135, Irish sea sediment |
| 4 | IAEA-326, soil |
| 5 | IAEA-327, soil |
| 6 | Soil-6, soil |
| 7 | IAEA-375, soil |

## TABLE 9. RESULTS OF REPEATED MEASUREMENTS OF IAEA REFERENCE MATERIALS

| RM sample | $^{90}$Sr | | $^{241}$Am | | $^{238}$Pu | | $^{239+240}$Pu | |
|---|---|---|---|---|---|---|---|---|
| (mass of sample in grams) | Bq kg$^{-1}$ | bias % | Bq kg$^{-1}$ | bias % | Bq kg$^{-1}$ | bias % | Bq kg$^{-1}$ | bias % |
| 367-1 (2) | | | 27.0±2.8 | 4.4 | < 0.5 | | 41.6±1.1 | 12.1 |
| 367-2 (2) | | | 26.0±3.2 | 0.6 | < 0.5 | | 39.0±0.5 | 5.1 |
| 367-3 (2) | | | 33.7±5.2 | 30.4 | < 0.5 | | 58.4*±0.7 | 57.4 |
| 367-4 (5) | 117±6 | 22.5 | 22.8±1.7 | -11.8 | < 0.3 | | 37.8±1.5 | 1.9 |
| 367-5 (5) | 100±5 | 4.7 | 27.0±2.0 | 4.4 | < 0.3 | | 37.9±1.5 | 2.2 |
| 367-6 (5) | | | | | < 0.3 | | 38.4±1.7 | 3.5 |
| 367-7 (5) | | | | | < 0.3 | | 38.0±1.6 | 2.4 |
| **Average ± STDEV** | 108.5±12 | | 27.3±4.0 | | | | 38.8±1.4 | |
| **Reference Value** | 95.5±33.5 | | 25.9±1.9 | | 0.23±0.03 | | 37.1±2.7 | |
| | 95.5±35% | | 25.9±7% | | 0.23±13% | | 37.1±7% | |
| 368-1 (2) | | | 1.2±0.1 | -9.8 | 9.0±0.3 | 9.1 | 32.0±0.9 | 1.6 |
| 368-2 (2) | | | 1.0±0.1 | -22.7 | 8.9±0.4 | 7.9 | 36.2±1.1 | 14.9 |
| 368-3 (2) | | | 1.3±0.1 | -3.8 | 8.8±0.6 | 6.7 | 34.1±0.7 | 8.3 |
| 368-4 (10) | < 2.4 | | 1.2±0.1 | -11.9 | 8.0±0.5 | -3.0 | 30.2±1.2 | -4.1 |
| 368-5 (10) | < 2.4 | | 1.3±0.1 | -0.1 | 7.6±0.6 | -7.9 | 31.0±1.2 | -1.6 |
| **Average ± STDEV** | | | 1.2±0.1 | | 8.5±0.6 | | 32.7±2.4 | |
| **Reference value** | 0.57±0.12 | | 1.35±0.2 | | 8.25±0.65 | | 31.5±2.5 | |
| | 0.57±21% | | 1.35±11% | | 8.25±8% | | 31.5±8% | |
| 135-1 (2) | | | 324.4±10 | 2.2 | 43.1±1.1 | -0.5 | 240±12 | 11.4 |
| 135-2 (1) | 57±7 | -10.9 | 283.0±20 | -10.9 | 42.2±3.7 | -2.5 | 216±8 | 0.3 |
| 135-3 (1) | | | | | 43.2±3.8 | 0.0 | 215±8 | -0.2 |
| 135-4 (1) | | | | | 48.0±4.7 | 10.9 | 227±10 | 5.4 |
| **Average ± STDEV** | | | 303.7±29 | | 44.2±2.6 | | 224.5±12 | |
| **Reference value** | 64±8 | | 317.5±7.5 | | 43.3±1.7 | | 215.4±10 | |
| | 64±13% | | 317.5±2% | | 43.3±4% | | 215.4±5% | |

Results are decay corrected to the corresponding reference dates.
Results for $^{241}$Am have been corrected for the ingrowth of $^{241}$Am from $^{241}$Pu
Combined absolute uncertainties were calculated (k=1) by taking into consideration uncertainties associated with counting statistics, standards, efficiency ($^{241}$Pu and $^{90}$Sr), recovery factor ($^{241}$Pu and $^{90}$Sr), decay correction, etc .
*outlier

## TABLE 10. RESULTS OF REPEATED MEASUREMENTS OF IAEA REFERENCE MATERIALS

| RM sample | n | $^{90}$Sr Bq kg$^{-1}$ | bias % | n | $^{241}$Am Bq kg$^{-1}$ | bias % | n | $^{238}$Pu Bq kg$^{-1}$ | $^{239+240}$Pu Bq kg$^{-1}$ | bias % |
|---|---|---|---|---|---|---|---|---|---|---|
| IAEA-326 | 2 | 10.5±1.1 | 4.0 | | 0.21±0.03 | 5.5 | 2 | < 0.036 | 0.49±0.04 | 0.0 |
| | 4 | 11.2±1.1 | 10.9 | | 0.20±0.03 | 0.5 | 4 | < 0.036 | 0.47±0.03 | -4.1 |
| | | | | | 0.21±0.06 | 5.5 | | | | |
| | | | | | 0.20±0.03 | 0.5 | | | | |
| | | | | | 0.18±0.06 | -9.5 | | | | |
| **Reference or** | | Info | | | Info | | | | | |
| **information Value** | | 10.1±0.6 | | | 0.199±0.039 | | | 0.019±0.003 | 0.49±0.02 | |
| IAEA-327 | 3 | < 2.9 | | | 0.20±0.03 | -9.1 | 3 | < 0.036 | 0.57±0.04 | -1.7 |
| | 4 | < 2.9 | | | 0.27±0.02 | 22.7 | 4 | < 0.036 | 0.58±0.03 | 0.0 |
| | | | | | 0.23±0.02 | 4.5 | | | | |
| | | | | | 0.24±0.03 | 9.1 | | | | |
| **Reference or** | | Info | | | Info | | | | Info | |
| **Information Value** | | 2.39±0.14 | | | 0.22±0.030 | | | 0.020±0.003 | 0.58±0.02 | |
| Soil-6 | 1 | 28.2±2.1 | -6.0 | | 0.39±0.11 | | 1 | < 0.036 | 0.99±0.03 | -4.4 |
| | 3 | 28.6±2.1 | -4.7 | | 0.45±0.07 | | 3 | < 0.036 | 1.03±0.04 | -0.6 |
| | | | | | 0.42±0.04 | | | | | |
| **Reference or** | | | | | No Ref. | | | No Ref. | | |
| **Information Value** | | 30±2 | | | Info | | | Info | 1.036±0.04 | |
| IAEA-375 | 1 | 90±6 | -16.7 | 1 | 0.25±0.03 | 92.3 | 1 | 0.09±0.01 | 0.34±0.02 | 13 |
| | 7 | 99±6 | -8.3 | 7 | 0.16±0.03 | 23.1 | 7 | 0.063±0.007 | 0.29±0.03 | -3.3 |
| | 1 | 103±6 | -4.6 | 1 | 0.48±0.03 | 269 | 1 | | 0.54±0.02 | 80 |
| **Reference or** | | | | | Info | | | Info | Info | |
| **Information Value** | | 108±6 | | | 0.13±0.02 | | | 0.071±0.014 | 0.30±0.04 | |

TABLE 11. SUMMARY OF REPEATABILITY MEASUREMENTS RESULTS FOR THE DETERMINATION OF $^{241}$Am, $^{238}$Pu, $^{239,240}$Pu AND $^{90}$Sr IN VARIOUS SAMPLES

| **Repeatability of $^{241}$Am measurement in IAEA-367 RM** | |
|---|---|
| Mean ($\overline{X}$) in repeatability test, Bq kg$^{-1}$ | **27.3** |
| Repeatability standard deviation ($S_r$), Bq kg$^{-1}$ | **4.0** |
| Repeatability limit ($r_L$), Bq kg$^{-1}$ | **11** |
| Relative mean bias (%) | **5.6** |
| Mean bias, Bq kg$^{-1}$ | **1.5** |
| **Repeatability of $^{241}$Am measurement in IAEA-368 RM** | |
| Mean ($\overline{X}$) in repeatability test, Bq kg$^{-1}$ | **1.2** |
| Repeatability standard deviation ($S_r$), Bq kg$^{-1}$ | **0.1** |
| Repeatability limit ($r_L$), Bq kg$^{-1}$ | **0.3** |
| Relative mean bias (%) | **-9.7** |
| Mean bias, Bq kg$^{-1}$ | **-0.13** |
| **Repeatability of $^{241}$Am measurement in IAEA-135 RM** | |
| Mean ($\overline{X}$) in repeatability test, Bq kg$^{-1}$ | **303.7** |
| Repeatability standard deviation ($S_r$), Bq kg$^{-1}$ | **29.3** |
| Repeatability limit ($r_L$), Bq kg$^{-1}$ | **82.0** |
| Relative mean bias (%) | **-4.3** |
| Mean bias, Bq kg$^{-1}$ | **-13.8** |

| **Repeatability of $^{238}$Pu measurement in IAEA-368 RM** | |
|---|---|
| Mean ($\overline{X}$) in repeatability test, Bq kg$^{-1}$ | **8.5** |
| Repeatability standard deviation ($S_r$), Bq kg$^{-1}$ | **0.6** |
| Repeatability limit ($r_L$), Bq kg$^{-1}$ | **1.7** |
| Relative mean bias (%) | **2.5** |
| Mean bias, Bq kg$^{-1}$ | **0.21** |
| **Repeatability of $^{238}$Pu measurement in IAEA-135 RM** | |
| Mean ($\overline{X}$) in repeatability test, Bq kg$^{-1}$ | **44.2** |
| Repeatability standard deviation ($S_r$), Bq kg$^{-1}$ | **2.6** |
| Repeatability limit ($r_L$), Bq kg$^{-1}$ | **7.3** |
| Relative mean bias (%) | **2.0** |
| Mean bias, Bq kg$^{-1}$ | **0.85** |

| **Repeatability of $^{239,240}$Pu measurement in IAEA-367 RM** | |
|---|---|
| Mean ($\overline{X}$) in repeatability test, Bq kg$^{-1}$ | **38.8** |
| Repeatability standard deviation ($S_r$), Bq kg$^{-1}$ | **1.4** |
| Repeatability limit ($r_L$), Bq kg$^{-1}$ | **4.1** |
| Relative mean bias (%) | **4.54** |
| Mean bias, Bq kg$^{-1}$ | **1.68** |
| **Repeatability of $^{239,240}$Pu measurement in IAEA-368 RM** | |
| Mean ($\overline{X}$) in repeatability test, Bq kg$^{-1}$ | **32.7** |
| Repeatability standard deviation ($S_r$), Bq kg$^{-1}$ | **2.4** |
| Repeatability limit ($r_L$), Bq kg$^{-1}$ | **6.8** |
| Relative mean bias (%) | **3.8** |
| Mean bias, Bq kg$^{-1}$ | **1.2** |
| **Repeatability of $^{239,240}$Pu measurement in IAEA-135 RM** | |
| Mean ($\overline{X}$) in repeatability test, Bq kg$^{-1}$ | **224.5** |
| Repeatability standard deviation ($S_r$), Bq kg$^{-1}$ | **11.7** |
| Repeatability limit ($r_L$), Bq kg$^{-1}$ | **32.7** |
| Relative mean bias (%) | **4.23** |
| Mean bias, Bq kg$^{-1}$ | **9.10** |

| **Repeatability of $^{90}$Sr measurement in IAEA-375 RM** | |
|---|---|
| Mean ($\overline{X}$) in repeatability test, Bq kg$^{-1}$ | **98.4** |
| Repeatability standard deviation ($S_r$), Bq kg$^{-1}$ | **6.0** |
| Repeatability limit ($r_L$), Bq kg$^{-1}$ | **16.8** |
| Relative mean bias (%) | **-8.8** |
| Mean bias, Bq kg$^{-1}$ | **-9.6** |
| **Repeatability of $^{90}$Sr measurement in Soil-6 RM** | |
| Mean ($\overline{X}$) in repeatability test, Bq kg$^{-1}$ | **28.5** |
| Repeatability standard deviation ($S_r$), Bq kg$^{-1}$ | **2.1** |
| Repeatability limit ($r_L$), Bq kg$^{-1}$ | **5.9** |
| Relative mean bias (%) | **-5.0** |
| Mean bias, Bq kg$^{-1}$ | **-1.5** |

# APPENDIX XII

## REPRODUCIBILITY STUDY

TABLE 12: LIST OF SAMPLES ANALYZED FOR METHOD REPRODUCIBILITY

| Nr. | Original Code | Matrix |
|---|---|---|
| 1 | MAPEP-05-RdF13 | Air filter |
| 2 | MAPEP-05-RdV13 | Vegetation |
| 3 | MAPEP-05-MaW13 | Water |
| 4 | MAPEP-05-MaS13 | Soil |
| 5 | MAPEP-06-RdF15 | Air filter |
| 6 | MAPEP-06-RdV15 | Vegetation |
| 7 | MAPEP-06-MaW15 | Water |
| 8 | MAPEP-06-MaS15 | Soil |
| 9 | MAPEP-07-RdF17 | Air filter |
| 10 | MAPEP-07-RdV17 | Vegetation |
| 11 | MAPEP-07-MaW17 | Water |
| 12 | MAPEP-07-MaS17 | Soil |
| 13 | MAPEP-08-RdF18 | Air filter |
| 14 | MAPEP-08-RdV18 | Vegetation |
| 15 | MAPEP-08-MaW18 | Water |
| 16 | MAPEP-08-MaS18 | Soil |
| 17 | MAPEP-09-RdF21 | Air filter |
| 18 | MAPEP-09-RdV21 | Vegetation |
| 19 | MAPEP-09-MaW21 | Water |
| 20 | MAPEP-09-MaS21 | Soil |

TABLE 13. REPRODUCIBILITY TEST FOR THE DETERMINATION OF $^{239,240}$Pu IN THE MAPEP PROFICIENCY TEST

Matrices: Air Filter (RdF), Vegetation (RdV), Water Standard (MaW), Soil Standard (MaS)

| Study | Result | Unc value | Ref. value | Flag | Bias (%) | Units | Confidence interval |
|---|---|---|---|---|---|---|---|
| MAPEP-05-RdF13 | 0.116 | 0.003 | 0.165 | **A** | 0.6 | (Bq/sample) | 0.12 – 0.21 |
| MAPEP-05-RdV13 | 0.008 | 0.001 | 0.0006 | **N** | | (Bq/sample) | |
| MAPEP-05-MaW13 | 2.6 | 0.03 | 2.4 | **A** | 8.3 | (Bq L$^{-1}$) | 1.68 – 3.12 |
| MAPEP-05-MaS13 | 88.3 | 1.4 | 89.5 | **A** | -1.3 | (Bq kg$^{-1}$) | 62.65 – 116.35 |
| MAPEP-06-RdF15 | 0.0011 | 0.0003 | 0.00041 | **A** | | (Bq/sample) | |
| MAPEP-06-RdV15 | 0.165 | 0.004 | 0.164 | **A** | 0.6 | (Bq/sample) | 0.11 – 0.21 |
| MAPEP-06-MaW15 | 0.015 | 0.001 | 0.0071 | **W** | | (Bq L$^{-1}$) | |
| MAPEP-06-MaS15 | 45.6 | 1.6 | 45.85 | **A** | -0.5 | (Bq kg$^{-1}$) | 32.09 – 59.61 |
| MAPEP-07-RdF17 | 0.08 | 0.002 | 0.0839 | **A** | -4.6 | (Bq/sample) | 0.0587 – 0.1091 |
| MAPEP-07-RdV17 | 0.208 | 0.004 | 0.2135 | **A** | -2.6 | (Bq/sample) | 0.1495 – 0.2776 |
| MAPEP-07-MaW17 | 2.05 | 0.03 | 2.22 | **A** | -7.7 | (Bq L$^{-1}$) | 1.55 – 2.89 |
| MAPEP-07-MaS17 | 40.6 | 0.9 | 44.5 | **A** | -8.8 | (Bq kg$^{-1}$) | 31.2 – 57.9 |
| MAPEP-08-RdF18 | 0.116 | 0.002 | 0.1141 | **A** | 1.7 | (Bq/sample) | 0.0799 – 0.1483 |
| MAPEP-08-RdV18 | 0.268 | 0.003 | 0.284 | **A** | -5.6 | (Bq/sample) | 0.199 – 0.369 |
| MAPEP-08-MaW18 | 0.011 | 0.001 | 0.0141 | **A** | | (Bq L$^{-1}$) | |
| MAPEP-08-MaS18 | 87.2 | 1.6 | 90.1 | **A** | -3.2 | (Bq kg$^{-1}$) | 63.1 – 117.1 |
| MAPEP-09-RdF21 | 0.134 | 0.003 | 0.138 | **A** | -2.9 | (Bq/sample) | 0.097 – 0.179 |
| MAPEP-09-RdV21 | 0.245 | 0.003 | 0.258 | **A** | -5 | (Bq/sample) | 0.181 – 0.335 |
| MAPEP-09-MaW21 | 1.51 | 0.02 | 1.64 | **A** | -7.9 | (Bq L$^{-1}$) | 1.15 – 2.13 |
| MAPEP-09-MaS21 | 118.6 | 1.8 | 116.3 | **A** | 2 | (Bq kg$^{-1}$) | 81.4 – 151.2 |

A=accepted within 20%, N=not accepted, W=warning (accepted within 30%)

## TABLE 14. REPRODUCIBILITY TEST FOR THE DETERMINATION OF $^{238}$Pu IN THE MAPEP PROFICIENCY TEST

Matrices: Air Filter (RdF), Vegetation (RdV), Water Standard (MaW), Soil Standard (MaS)

| Study | Result | Unc value | Ref value | Flag | Bias (%) | Units | Confidence interval |
|---|---|---|---|---|---|---|---|
| MAPEP-05-RdF13 | 0.202 | 0.003 | 0.195 | **A** | 3.6 | (Bq/sample) | 0.14 – 0.25 |
| MAPEP-05-RdV13 | 0.223 | 0.003 | 0.224 | **A** | -0.4 | (Bq/sample) | 0.16 – 0.29 |
| MAPEP-05-MaW13 | 0.03 | 0.03 | 0.018 | **A** |  | (Bq $L^{-1}$) |  |
| MAPEP-05-MaS13 | 0.003 | 0.002 | 0.48 | **W** |  | (Bq $kg^{-1}$) |  |
|  |  |  |  |  |  |  |  |
| MAPEP-06-RdF15 | 0.068 | 0.0012 | 0.067 | **A** | 1.5 | (Bq/sample) | 0.05 – 0.09 |
| MAPEP-06-RdV15 | 0.141 | 0.003 | 0.137 | **A** | 2.9 | (Bq/sample) | 0.1 – 0.18 |
| MAPEP-06-MaW15 | 0.925 | 0.029 | 0.91 | **A** | 1.6 | (Bq $L^{-1}$) | 0.7 – 1.3 |
| MAPEP-06-MaS15 | 61.6 | 2.7 | 61.15 | **A** | 0.7 | (Bq $kg^{-1}$) | 42.81 – 79.5 |
|  |  |  |  |  |  |  |  |
| MAPEP-07-RdF17 | 0.0693 | 0.002 | 0.0669 | **A** | 3.6 | (Bq/sample) | 0.0468 – 0.087 |
| MAPEP-07-RdV17 | 0.152 | 0.003 | 0.1484 | **A** | 2.4 | (Bq/sample) | 0.1039 – 0.1929 |
| MAPEP-07-MaW17 | 1.37 | 0.03 | 2.25 | **N** | -39.1 | (Bq $L^{-1}$) | 1.58 – 2.93 |
| MAPEP-07-MaS17 | 29.3 | 0.6 | 31.3 | **A** | -6.4 | (Bq $kg^{-1}$) | 21.9 – 40.7 |
|  |  |  |  |  |  |  |  |
| MAPEP-08-RdF18 | 0.107 | 0.004 | 0.1053 | **A** | 1.6 | (Bq/sample) | 0.0737 – 0.1369 |
| MAPEP-08-RdV18 | 0.145 | 0.004 | 0.147 | **A** | -1.4 | (Bq/sample) | 0.103 – 0.191 |
| MAPEP-08-MaW18 | 0.6 | 0.01 | 0.73 | **A** | -17.8 | (Bq $L^{-1}$) | 0.51 – 0.95 |
| MAPEP-08-MaS18 | 76.9 | 1.7 | 72.8 | **A** | 5.6 | (Bq $kg^{-1}$) | 51 – 94.6 |
|  |  |  |  |  |  |  |  |
| MAPEP-09-RdF21 | 0.094 | 0.003 | 0.091 | **A** | 3.3 | (Bq/sample) | 0.064 – 0.118 |
| MAPEP-09-RdV21 | 0.0016 | 0.003 | 0.0016 | **A** |  | (Bq/sample) |  |
| MAPEP-09-MaW21 | 0.0186 | 0.0012 | 0.018 | **A** |  | (Bq $L^{-1}$) |  |
| MAPEP-09-MaS21 | 67.9 | 1.3 | 63.2 | **A** | 7.4 | (Bq $kg^{-1}$) | 44.2 – 82.2 |

A=accepted within 20%, N=not accepted, W=warning (accepted within 30%)

## TABLE 15. REPRODUCIBILITY TEST FOR THE DETERMINATION OF $^{241}$Am IN THE MAPEP PROFICIENCY TEST

Matrices: Air Filter (RdF), Vegetation (RdV), Water Standard (MaW), Soil Standard (MaS)

| Study | Result | Unc value | Ref value | Flag | Bias (%) | Units | Confidence interval |
|---|---|---|---|---|---|---|---|
| MAPEP-05-RdF13 | 0.159 | 0.002 | 0.145 | **A** | 9.7 | (Bq/sample) | 0.1 – 0.19 |
| MAPEP-05-RdV13 | 0.111 | 0.003 | 0.102 | **A** | 8.8 | (Bq/sample) | 0.07 – 0.13 |
| MAPEP-05-MaW13 | 1.86 | 0.03 | 1.72 | **A** | 8.1 | (Bq $L^{-1}$) | 1.2 – 2.24 |
| MAPEP-05-MaS13 | 106 | 1.1 | 109 | **A** | -2.8 | (Bq $kg^{-1}$) | 76.3 – 141.7 |
| | | | | | | | |
| MAPEP-06-RdF15 | 0.092 | 0.003 | 0.093 | **A** | -1.1 | (Bq/sample) | 0.07 – 0.12 |
| MAPEP-06-RdV15 | 0.162 | 0.012 | 0.156 | **A** | 3.8 | (Bq/sample) | 0.11 – 0.2 |
| MAPEP-06-MaW15 | 1.305 | 0.081 | 1.3 | **A** | 0.4 | (Bq $L^{-1}$) | 0.91 – 1.69 |
| MAPEP-06-MaS15 | 57.1 | 1 | 57.08 | **A** | 0 | (Bq $kg^{-1}$) | 39.96 – 74.2 |
| | | | | | | | |
| MAPEP-07-RdF17 | 0.093 | 0.003 | 0.0977 | **A** | -4.8 | (Bq/sample) | 0.0684 – 0.127 |
| MAPEP-07-RdV17 | 0.17 | 0.02 | 0.1806 | **A** | -5.9 | (Bq/sample) | 0.1264 – 0.2348 |
| MAPEP-07-MaW17 | 1.61 | 0.04 | 1.71 | **A** | -5.8 | (Bq $L^{-1}$) | 1.2 – 2.22 |
| MAPEP-07-MaS17 | 30.6 | 0.5 | 34.8 | **A** | -12.1 | (Bq $kg^{-1}$) | 24.4 – 45.2 |
| | | | | | | | |
| MAPEP-08-RdF18 | 0.159 | 0.005 | 0.158 | **A** | 0.6 | (Bq/sample) | 0.111 – 0.205 |
| MAPEP-08-RdV18 | 0.247 | 0.007 | 0.24 | **A** | 2.9 | (Bq/sample) | 0.168 – 0.312 |
| MAPEP-08-MaW18 | 1.12 | 0.04 | 1.23 | **A** | -8.9 | (Bq $L^{-1}$) | 0.86 – 1.6 |
| MAPEP-08-MaS18 | 126.4 | 2.4 | 127.2 | **A** | -0.6 | (Bq $kg^{-1}$) | 89 – 165.4 |

A=accepted within 20%, N=not accepted, W=warning (accepted within 30%)

## TABLE 16. REPRODUCIBILITY TEST FOR THE DETERMINATION OF $^{90}$Sr IN THE MAPEP PROFICIENCY TEST

Matrices: Air Filter (RdF), Vegetation (RdV), Water Standard (MaW), Soil Standard (MaS)

| Study | Result | Unc value | Ref value | Flag | Bias (%) | Units | Confidence interval |
|---|---|---|---|---|---|---|---|
| MAPEP-05-RdF13 | 1.34 | 0.04 | 1.35 | **A** | -0.7 | (Bq/sample) | 0.94 – 1.75 |
| MAPEP-05-RdV13 | 1.84 | 0.05 | 1.65 | **A** | 11.5 | (Bq/sample) | 1.15 – 2.14 |
| MAPEP-05-MaW13 | -0.025 | 0.08 | | **A** | | (Bq L$^{-1}$) | |
| MAPEP-05-MaS13 | 668 | 10 | 640 | **A** | 4.4 | (Bq kg$^{-1}$) | 448 – 832 |
| | | | | | | | |
| MAPEP-06-RdF15 | 0.8 | 0.07 | 0.792 | **A** | 1 | (Bq/sample) | 0.55 – 1.03 |
| MAPEP-06-RdV15 | 1.72 | 0.05 | 1.561 | **A** | 10.2 | (Bq/sample) | 1.09 – 2.03 |
| MAPEP-06-MaW15 | 13.19 | 0.42 | 13.16 | **A** | 0.2 | (Bq L$^{-1}$) | 9.21 – 17.11 |
| MAPEP-06-MaS15 | 344 | 14 | 314.35 | **A** | 9.4 | (Bq kg$^{-1}$) | 220.05 – 408.66 |
| | | | | | | | |
| MAPEP-07-RdF17 | 0.56 | 0.01 | 0.6074 | **A** | 7.8 | (Bq/sample) | 0.4252 – 0.7896 |
| MAPEP-07-RdV17 | 1.28 | 0.03 | 1.5351 | **A** | -16.6 | (Bq/sample) | 1.0746 – 1.9956 |
| MAPEP-07-MaW17 | 7.89 | 1.4 | 8.87 | **A** | -11 | (Bq L$^{-1}$) | 6.21 – 11.53 |
| MAPEP-07-MaS17 | 258 | 7.19 | 319 | **A** | -19.1 | (Bq kg$^{-1}$) | 223.3 – 414.7 |
| | | | | | | | |
| MAPEP-08-RdF18 | 1.55 | 0.03 | 1.548 | **A** | 0.11 | (Bq/sample) | 1.084 – 2.012 |
| MAPEP-08-RdV18 | 1.19 | 0.03 | 1.273 | **A** | -6.5 | (Bq/sample) | 0.891 – 1.655 |
| MAPEP-08-MaW18 | 10.5 | 0.6 | 11.4 | **A** | -7.9 | (Bq L$^{-1}$) | 7.98 – 14.82 |
| MAPEP-08-MaS18 | 507 | 10 | 493 | **A** | 2.8 | (Bq kg$^{-1}$) | 345 – 641 |

A=accepted within 20%, N=not accepted, W=warning (accepted within 30%)

TABLE 17. SUMMARY OF REPRODUCIBILITY MEASUREMENTS RESULTS FOR THE DETERMINATION OF $^{241}$Am, $^{238}$Pu, $^{239,240}$Pu AND $^{90}$Sr IN MAPEP-07-MAS18 SOIL SAMPLES

| **Reproducibility of $^{241}$Am measurement** | |
|---|---|
| Mean ($\overline{X}$) in reproducibility test, Bq kg$^{-1}$ | **126.4** |
| Reproducibility standard deviation ($S_r$), Bq kg$^{-1}$ | **2.4** |
| Reproducibility limit ($r_L$), Bq kg$^{-1}$ | **6.72** |
| Relative mean bias (%) | **-0.6** |
| Mean bias, Bq kg$^{-1}$ | **0.76** |
| **Reproducibility of $^{238}$Pu measurement** | |
| Mean ($\overline{X}$) in reproducibility test, Bq kg$^{-1}$ | **76.9** |
| Reproducibility standard deviation ($S_r$), Bq kg$^{-1}$ | **1.7** |
| Reproducibility limit ($r_L$), Bq kg$^{-1}$ | **4.76** |
| Relative mean bias (%) | **5.6** |
| Mean bias, Bq kg$^{-1}$ | **-4.1** |
| **Reproducibility of $^{239,240}$Pu measurement** | |
| Mean ($\overline{X}$) in reproducibility test, Bq kg$^{-1}$ | **87.2** |
| Reproducibility standard deviation ($S_r$), Bq kg$^{-1}$ | **1.6** |
| Reproducibility limit ($r_L$), Bq kg$^{-1}$ | **4.48** |
| Relative mean bias (%) | **-3.2** |
| Mean bias, Bq kg$^{-1}$ | **2.88** |

| **Reproducibility of $^{90}$Sr measurement** | |
|---|---|
| Mean ($\overline{X}$) in reproducibility test, Bq kg$^{-1}$ | **507** |
| Reproducibility standard deviation ($S_r$), Bq kg$^{-1}$ | **10** |
| Reproducibility limit ($r_L$), Bq kg$^{-1}$ | **28** |
| Relative mean bias (%) | **2.8** |
| Mean bias, Bq kg$^{-1}$ | **-13.8** |

Results were calculated on the basis of 20% uncertainty of the reference value that is the acceptance criteria in the proficiency test.

# APPENDIX XIII

## CHEMICAL RECOVERIES

TABLE 18. CHEMICAL RECOVERIES OBTAINED BY THE ANALYSIS OF STANDARD REFERENCE MATERIALS

| Sample | n | Chemical recovery (%) |
|---|---|---|
| $^{90}$Sr | | |
| IAEA-326 | 6 | 53 |
| IAEA-327 | 7 | 44 |
| Soil-6 | 4 | 63 |
| IAEA-375 | 8 | 78 |
| $^{238}$Pu and $^{239,240}$Pu | | |
| IAEA-326 | 6 | 91 |
| IAEA-327 | 7 | 87 |
| Soil-6 | 4 | 87 |
| IAEA-375 | 8 | 91 |
| $^{241}$Am | | |
| IAEA-326 | 5 | 37 |
| IAEA-327 | 4 | 44 |
| Soil-6 | 3 | 49 |
| IAEA-375 | 9 | 84 |

n is the number of independent measurements

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