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A Procedure for the Rapid Determination of Pu Isotopes and Am-241 in Soil and Sediment Samples by Alpha Spectrometry

IAEA
International Atomic Energy Agency

A PROCEDURE FOR THE RAPID DETERMINATION OF Pu ISOTOPES AND Am-241 IN SOIL AND SEDIMENT SAMPLES BY ALPHA SPECTROMETRY

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FOREWORD

Reliable, comparable and ‘fit for purpose’ results are an essential requirement for any decision based on analytical measurements. For the analyst, the availability of tested and validated analytical procedures is a extremely important tool for production of such analytical measurements. For maximum utility, such procedures should be comprehensive, clearly formulated, and readily available to both the analyst and the customer for reference.

Since 2004 the Environment Programme of the IAEA has included activities aimed at the development of a set of procedures for the determination of radionuclides in terrestrial environmental samples. In this report, a rapid procedure for the determination of Pu and Am radionuclides in soil and sediment samples is described that can be used in emergency situations. The method provides accurate and reliable results for the activity concentrations of elevated levels of ^{239,240}Pu, ^{238}Pu and ^{241}Am in soil and sediment samples over the course of 24 hours. The procedure has been validated in accordance with ISO guidelines.

The IAEA wishes to thank all the participants for their valuable contributions to develop the procedure and review the publication, especially N. Vajda who prepared the draft of the manuscript. The IAEA officer responsible for this publication was. C.-K. Kim of the Agency’s Laboratories, Seibersdorf, Austria.

CONTENTS

1. INTRODUCTION

Americium (Am) and Plutonium (Pu) nuclides are artificial radionuclides, produced in the nuclear fuel cycle as well as in atomic bombs. They have been released to the environment from various sources, mainly due to accidents in nuclear facilities e.g. reactors, reprocessing plants and due to nuclear weapons tests. Detection of americium and plutonium nuclides in soil and sediment samples is of high interest during nuclear incidents for controlling and protecting the environment and furthermore to protect the population from the consequences of a possible contamination. In an emergency situation, only rapid analytical methods can provide adequate information for fast response.

Alpha spectrometric measurements have high sensitivity due to the typically low background and the high counting efficiency, and alpha spectrometric devices are available in many nuclear laboratories in contrast to other more sophisticated measuring equipment as mass spectrometers e.g. ICP-MS, AMS. Thus, alpha spectrometry is the best choice to detect alpha emitting nuclides in case of emergency. However, americium and plutonium nuclides have to be separated from the matrix components of the sample as well as from each other to obtain "infinitely thin" alpha sources where the self-absorption of alpha particles is neglected and spectral interferences are avoided.

To meet the double demands of speed and accuracy the radiochemical procedure is based on the following steps:

- destruction by fusion using lithium metaborate is fast (10 minutes) and complete,

- dissolution of the melt in dilute hydrochloric acid is fast (10 minutes) and complete,

- pre-concentration of actinides from acidic and reducing media using large amounts of hydrofluoric acid is highly selective, it precipitates alkaline earth and rare earth metals, co-precipitates the actinides quantitatively, while assuring high decontamination factors for many cationic and anionic components, the procedure takes 2 hours,

- separation by extraction chromatography using TRU® resin (Eichrom Industries Inc.) is selective for the actinides (americium, tetravalent plutonium as well as thorium, neptunium and uranium are retained, then americium, and plutonium are separately stripped), the use of small columns filled with 1 mL resin makes the procedure fast (2.5 hours including oxidation state adjustment)

- micro-co-precipitation of americium and plutonium with neodymium fluoride directly from the individual strip solutions is fast and reproducible, takes less than 1.5 hours.

The whole procedure can be performed within 6-7 hours followed by overnight counting of the alpha sources, thus providing results within 24 hours.

2. SCOPE

This report describes a method for the determination of ^{241}Am, ^{239,240}Pu and ^{238}Pu in soil and sediment samples by isotope dilution alpha spectrometry using chemical separation techniques. The method can be used for the relatively fast detection of radioactive emissions in emergency situation or for the measurement of elevated levels of activities in the environment.

The mass of the sample required for the analysis is typically 0.5 g.

3. NORMATIVE REFERENCES

- ISO 18589-4 (Draft), 2007. Measurement of radioactivity in the environment – Soil – Part 4: Measurement of plutonium isotopes (plutonium 238 and plutonium 239+240) by alpha spectrometry.
- ISO 11929-7, 2005. Determination of the detection limit and decision threshold for ionizing radiation measurement – Part 7: Fundamentals and general applications.
- ISO 17025, 2005. General requirements for the competence of testing and calibration laboratories.
- ISO/TS 21748, 2004. Guidance for the use of repeatability, reproducibility and trueness estimates in measurement uncertainty estimation.
- ISO/IEC Guide 98-3:2008. Guide to the expression of uncertainty in measurement.
- 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 methods for the determination of the trueness of a standard measurement method.
- ISO 7870, 1993. Control charts – General guide and introduction.
- ISO 7966, 1993. Acceptance control charts.

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 safety rules or chemical and radioactive safety is obligatory. Although the method has been carefully tested each laboratory should perform an individual validation procedure.

5. TERMS AND DEFINITIONS, SYMBOLS AND ABBREVIATIONS

In the following, *u(x)* indicates the uncertainty in quantity x:

a_0 : the specific activity of the analyte on the sampling date [Bq kg^{-1}]

a_1 : the specific activity of the analyte at the separation time [Bq kg^{-1}]

a^* : decision threshold [Bq kg^{-1}]

$a^\#$: detection limit [Bq kg^{-1}]

C : the certified specific activity of the analyte in the reference material [Bq kg^{-1}]

C_T : the certified specific activity of the tracer on the reference date [Bq g^{-1}]

f_T : the correction factor for the decay of the tracer during elapsed time [days] between the reference date of tracer and the beginning of the measurement

The correction factors (f_2) for the decay of the analytes during elapsed time [days] between the separation and the beginning of the measurement are taken to be equal to 1.

The correction factors (f_3) for the decay of the analytes during the counting time are taken to be equal to 1.

m_b : the uncertainty of balance [kg]

m_s : the mass of sample [kg]

m_T : the mass of the tracer taken [g]

R : the chemical recovery of the analyte

R_L : reproducibility limit [Bq kg^{-1}]

r_L : repeatability limit [Bq kg^{-1}]

n_n : net counts in ROI (region of interest) of analyte [counts]

n_{nt} : net counts in ROI (region of interest) of tracer [counts]

n_g : gross counts in ROI (region of interest) of analyte [counts]

n_{gt} : gross counts in ROI (region of interest) of tracer [counts]

n_0 : blank or background counts in ROI (region of interest) of analyte [counts]

n_{0t} : blank or background counts in ROI (region of interest) of tracer [counts]

r_n : net count rate in ROI (region of interest) of analyte [s^{-1}]

r_{nt} : net count rate in ROI (region of interest) of tracer [s^{-1}]

r_g : gross count rate in ROI (region of interest) of analyte [s^{-1}]

r_{gt} : gross count rate in ROI (region of interest) of tracer [s^{-1}]

r_0 : blank or background count rate in ROI (region of interest) of analyte [s^{-1}]

r_{0t} : blank or background count rate in ROI (region of interest) of tracer [s^{-1}]

S_r : standard deviation of repeatability [Bq kg^{-1}]

S_R : standard deviation of reproducibility [Bq kg^{-1}]

T_g : the sample counting time (s)

t_0 : the counting time of blank (s)

t_T : the time interval between the reference date of the tracer and the separation time [a]

t_1 : the time interval between the sampling date and the separation time [a]

ε : counting efficiency

w : auxiliary parameter in calculation of the detection limit, [kg^{-1}]

$\overline{X}$: the mean of all measured values of the control sample [Bq kg^{-1}]

Δ : relative bias of the method [%]

λ_A : the decay constant of the analyte [a^{-1}]

λ_T : the decay constant of the tracer [a^{-1}]

α : the probability of the error of the first kind; the probability of rejecting a hypothesis if it is true

β : the probability of the error of the second kind; the probability of accepting a hypothesis if it is false

6. PRINCIPLE

Small amounts of dry soil or sediment samples (≤0.5 g) are completely destructed by fusion with lithium metaborate and solubilized by 100 mL 1 mol L^{-1} HCl. Actinides are co-precipitated with calcium and lanthanide fluorides after reduction to tri- and tetravalent oxidation states. The precipitate is dissolved in 2 mol L^{-1} nitric acid with the addition of boric acid to complex insoluble fluorides. Actinides are selectively separated by extraction chromatography using TRU® resin that contains bis octyl-phenyl-N,N-di-i-butyl-carbamoyl-methyl-phosphine oxide and tri-butyl phosphate on an inert support (see in Annex I). This material has high capacity factors for tetra- and hexavalent actinides in a wide range of acidity and can also retain trivalent actinides from 1-3 mol L^{-1} HNO_3. Actinides can be selectively stripped by varying the concentration of HCl strip solution. All actinides including trivalent americium, tetravalent plutonium, thorium, neptunium as well as uranium probably as hexavalent species are retained by TRU resin from 2 mol L^{-1} HNO_3/0.1 mol L^{-1} $NaNO_2$ load solution. Am is selectively stripped from the column with 4 mol L^{-1} HCl, while Pu is eluted with 4 mol L^{-1} HCl/0.01 mol L^{-1} $TiCl_3$ as trivalent species while thorium, neptunium and uranium are still retained on the column. Alpha sources are prepared directly from the strip solutions without preliminary treatment [1, 2].

This procedure has no significant interferences by any alpha emitters unless alpha emitting lanthanides are present in the sample. Curium nuclides if present in the sample will behave in the same way as americium, but they do not cause spectral interferences. The americium source contains the lanthanide content of the sample (light lanthanides completely, heavy lanthanides partially), that might reduce the quality of the source by causing self-absorption in the deposited layer, but typically the lanthanide content of 0.5 g of soil or sediment does not cause significant spectrum degradation (the FWHM is ≤ 60 keV). The plutonium source might be contaminated with traces of thorium if samples have extremely high thorium content, but it is not the case if samples have less than 300 Bq kg^{-1} of ^{232}Th activity.

The specific activity of ^{239,240}Pu as well as that of ^{238}Pu will be determined from the activity of the tracer (most likely ^{242}Pu or ^{236}Pu) added and the ratio of net count rates of the analytes to those of the tracer in alpha spectrometry, the so called "isotope dilution alpha spectrometry". Analogously, the specific activity of ^{241}Am will be determined from the activity of the tracer (most likely ^{243}Am).

7. CHEMICAL REAGENTS AND EQUIPMENT

7.1. Equipment

- Standard laboratory equipment
- Teflon beakers
- Alpha spectrometer with Si semiconductor (PIPS) detector
- Vacuum pump
- Filtering set made of plastic with membranes of 0.10 µm and 0.45 µm pore sizes and 20 mm diameter
- Analytical balance with accuracy of 0.1 mg
- Hot plate with magnetic stirrer
- Fluxer (Corporation Scientific Claisse Inc.) with Pt crucible or gas burner with Pt crucible

7.2. Chemicals

- HCl (32%)
- HNO_3 (65%)
- HF (40%)
- H_3BO_3
- $LiBO_2$
- $NaNO_3$
- KI
- Na_2CO_3 (free of water)
- $Ca(NO_3)_2$
- Mohr salt: $Fe(NH_4)_2(SO_4)_2$
- NH_4SCN
- Hydrazine
- $NaNO_2$
- 15 % $TiCl_3$ provided in closed ampoules: After opening the ampoule the solution can be used no longer than one month. (Solutions stored in bottles that contain air in contact with the solution surface cannot be used.)
- $Nd(NO_3)_3$ or Nd_2O_3
- Ethanol
- ^{242}Pu or ^{236}Pu tracer
- ^{243}Am tracer
- Certified standard reference material
- TRU resin produced by Eichrom Industries Inc.: bis octyl-phenyl-N,N-di-i-butyl-carbamoyl-methyl-phosphine oxide and tri-butyl phosphate on an inert support

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

8. PROCEDURE

See the flowchart of the procedure in Annex III.

8.1. Sample destruction and dissolution

- Weigh Pu tracer into the Pt crucible and evaporate it gently to dryness on a hot plate.
- Weigh Am tracer into the Pt crucible and evaporate it gently to dryness on a hot plate.
- Weigh in about 0.5 g of the dry sample to be analyzed and distribute it evenly in the crucible.
- Add the following reagents one by one in the given order to the top of the sample:
  0.2 g $NaNO_3$ (oxidizing agent)
  0.2 g Na_2CO_3 (additive)
  2.0 g $LiBO_2$
  0.1 g KI (non wetting agent)
- Prepare 100 mL 1 mol L^{-1} HCl in a glass beaker of 300 mL volume, put a stirring bar in it.
- Make the fusion either using the Fluxer Claisse or a gas burner.

In the former case use the pre-prepared protocol P6 that heats and ignites the sample while it is twisted for 4 minutes and finally the melt is poured into the intensively stirred liquid. If the melt does not seem to be clear and homogeneous the protocol has to be stopped before the melt is emptied and it has to be repeated. Typically 2-3 repetitions are recommended.

In the latter case hold the Pt crucible with long handles in the flame and shake it by gently swirling the sample as long as a clear homogeneous melt is obtained (about 5-10 minutes). The Pt dish becomes red during the process. Finally, turn the hot crucible with a sudden movement upside down and let the hot melt pour in to the cold solution while the solution is stirred vigorously with a magnetic stirrer. Use a large stirring bar and a stirring speed, such that the liquid surface forms a conical shape.

- Stir and warm the solution without evaporation as long as it dissolves completely, typically for about 5-10 minutes. Solidified drops of the $LiBO_2$ melt that remained attached to the Pt wall can be removed and added to the solution.
- Cool the solution in a water bath (about 10 minutes).
- Filter the solution through a membrane of 0.45 µm pore size (diameter 2 cm) into a Teflon beaker of 200 mL volume to remove any undissolved particles. Filtration is typically fast (5 minutes).

8.2. Pre-concentration of actinides by co-precipitation with calcium fluoride

- Add 300 mg Ca containing solution to the filtrate and 100 mg Mohr salt if the sample is expected to have low Ca and Fe content, respectively. Low Ca content is indicated by the appearance of no or small amount of white precipitate by the addition of HF solution. The Fe content is low if the solution has no or slight yellow color.

- Add 3 mL of hydrazine to the solution and adjust the pH to 3-4 with drops of 32 % HCl if it is necessary. Some precipitate might form at this stage, which will be dissolved by the addition of the first portions of HF solution.
- Warm and stir the filtrate for about 1 hour to reduce the actinides to lower oxidation states. Check whether reduction has been completed by testing the presence of Fe^{3+} in the sample. (The reduction is complete when the small sample aliquot does not form red complex with the NH_4SCN test solution.)
- Add 25 mL 40 % HF to the sample and stir it for a further half an hour.
- Remove the sample from the hot plate and cool it in water bath. Let the precipitate settle.
- Filter the sample through a 0.45 μm pore size membrane (20 mm diameter) without disturbing the settled precipitate. Wash the beaker and the precipitate with 5 ml 4 % HF solution. (Use plastic tools!) Filtration is typically fast (5 minutes).
- Transfer the precipitate with the membrane to a small glass beaker.
- Add 400 mg boric acid and 10 mL 2 mol L^{-1} HNO_3 to the sample, carefully cleaning the filtration funnel. Samples are gently warmed to help dissolution without boiling the solution. Typically a clear solution is obtained.

8.3. Extraction chromatography (TRU resin)

- Adjust the desired oxidation states of the actinides by adding 50 mg of $NaNO_2$ to the cold solution and let it stand for 1 hour.
- Soak TRU resin (100 – 150 μm) in de-ionized water for at least 1 hour.
- Fill a plastic chromatographic column (inner diameter 7 mm) to 25 mm height with the soaked TRU resin and add quartz crystals to the top of the resin in a 3-4 mm thick layer. Wash the column with 20 mL distilled water, 10 mL 2 mol L^{-1} HNO_3 and 10 ml freshly prepared 2 mol L^{-1} HNO_3/0.01 mol L^{-1} $NaNO_2$ solution subsequently. The column picks up a slight green color due to the retained $NaNO_2$.
- Stir the sample solution intensively to remove bubbles formed by the decomposition of the $NaNO_2$ and pass it through the TRU resin column by gravity flow (about 1 mL/min). The column becomes green color.
- Rinse the beaker with 5 mL 2 mol L^{-1} HNO_3/0.01 mol L^{-1} $NaNO_2$ solution and pass it through the column.
- Wash the column with 10 mL 2 mol L^{-1} HNO_3/0.01 mol L^{-1} $NaNO_2$ solution.
- Elute Am from the column with 10 mL 4 mol L^{-1} HCl. Collect the eluate in a plastic beaker that is adequate for alpha source preparation (of 30-100 mL volume).
- Wash the column with 5 mL 4 mol L^{-1} HCl to remove traces of Am.
- Elute Pu from the column with 10 mL 4 mol L^{-1} HCl/0.01 mol L^{-1} $TiCl_3$. Collect the eluate in a plastic beaker that is adequate for alpha source preparation (30-100 mL volume). During elution the column becomes slightly grey. It is important to use fresh $TiCl_3$ solution that contains no oxidized titanium (Ti^{4+}).
- After removal of Am and Pu the column still retains Th, Np and U that can be stripped with 20 mL 0.1 mol L^{-1} HCl/0.1 mol L^{-1} HF and further purified by other extraction chromatographic procedures.

8.4. Alpha source preparation

- Am source: Add 10 mL distilled water, 100 µl of the stock solution containing 50 µg Nd/100 µl and 5 ml 40 % HF to the Am strip solution. Shake it and let it stand for half an hour. The solution becomes slightly opaque probably due to some organic material released from the column but it does not affect the source quality. The solution is filtered through 0.10 µm pore size membrane (e.g. polypropylene membrane Metricel) that has to be wetted with alcohol before passing the aqueous solution. Filtration should be slow (30 minutes). The beaker is rinsed with 2 mL 4 % HF, 2 mL ethanol and finally the funnel is rinsed with 2 mL ethanol, too. The removed membrane is dried at ≤ 50°C, then mounted on a metal sample holder and placed in the alpha chamber.
- Pu source: Add 100 µl 15 % $TiCl_3$ solution to the Pu strip solution and follow the same procedure as for preparation of Am sources.

8.5. Blank determination

Prepare at least one blank for a set of samples.

8.6. Measurement

The specific activity is calculated by counting the sample sources for an appropriate time. The counting time required depends on the sample and blank count rates and also the required detection limit and decision threshold. The alpha spectra should be inspected to confirm good peak resolution and no interfering peaks.

- Introduce the source into the vacuum chamber and pump until a vacuum of about 0.5 Pa (5×10^{-3} mbar) is obtained. Then switch on the bias voltage button of the detector.
- Record the file name, sample information (e.g. code number, sample name, sample mass, etc.)
- Integrate the counts in the peaks corresponding to ^{242}Pu, ^{239,240}Pu, ^{238}Pu and ^{243}Am, ^{241}Am peaks, respectively). The alpha spectra should be similar to the ones illustrated in Annex V. The FWHM of the peaks should be in the range of 60-80 keV for a 450 mm^2 area detector using a close detector-sample geometry.
- Integrate the channel counts in the same region of interest (ROI) in the sample spectrum from blank spectrum.

9. EXPRESSION OF RESULTS

9.1. Calculation of specific activity of analytes on sampling date

The ratio of the net counts of the tracer and analyte peak is used to calculate the specific activity of the analyte in the sample on the date of chemical separation, taking into account the specific activity of the tracer solution, the masses of the sample and the tracer solution used [3]. The specific activity of the analyte (a_1, Bq kg^{-1}, dry) at the separation time is calculated by the following formula (1):

$$a_1 = \frac{C_T \cdot r_n}{m_s \cdot r_{nt}} \cdot m_T \cdot f_T = \frac{C_T m_T f_T}{m_s} \frac{r_g - r_0}{r_{gt} - r_{0t}} \tag{1}$$

The decay of the tracer between its calibration date and counting is taken into correction by f_T as follows:

$$f_T = \exp(-\lambda_T \cdot t_T) \tag{2}$$

The decay of the analyte between separation and counting and during the measurement is disregarded.

Finally, the concentration of the analyte in the sample should be calculated back to the date of sample collection as shown in Eq.(3).

$$a_0 = a_1 \exp(\lambda_A t_1) \tag{3}$$

Among the analytes the decay correction according to (9.1-3) can be performed only for ^{238}Pu. In case of ^{239,240}Pu, decay correction within a period of 100 years can be disregarded. In case of ^{241}Am, a_0 can be calculated if the specific activity of the parent nuclide, ^{241}Pu is also known.

The calculation of the specific activities of the analytes on the sampling date is summarized in Annex IV-1. Basic nuclear data of the radionuclides are given in Annex V.

The detector efficiency is not needed in isotope dilution alpha spectrometry to calculate the specific activity, but allows one to calculate the chemical yield. The chemical recovery is determined from the activity of the tracer added and the net counts in the corresponding peak as follows:

$$R = \frac{r_{nt}}{C_T \cdot m_T \cdot \varepsilon} \cdot \exp(\lambda_T \cdot t_T) \tag{4}$$

The detector efficiency is determined from the activity of a calibration source that can be prepared in a similar process as those of the analytes. Efficiency determinations are typically performed independently from the analysis of the given sample set. The efficiency can be calculated according to equation (5) by replacing the actual values of the calibration procedure.

$$\varepsilon = \frac{r_{nt}}{C_T \cdot m_T \cdot R} \cdot \exp(\lambda_T \cdot t_T) \qquad (5)$$

Calculation of the activities of ^{239,240}Pu, ^{238}Pu, ^{241}Am are performed in the same way replacing the relevant data of the given analyte and the actual tracer in the equations.

9.2. Combined uncertainty

According to the Guide to the Expression of Uncertainty in Measurement [4, 5], the combined uncertainty is calculated and described in Annex IV.

9.3. Decision threshold

In accordance with ISO 11929-7, the decision threshold, a*, is obtained from the following equation (6):

$$a^* = \frac{k_{1-\alpha}}{m_s \cdot \varepsilon \cdot R} \cdot \sqrt{\frac{n_0}{T_g t_0} + \frac{n_0}{t_0 t_0}} \qquad (6)$$

If $\alpha=0.05$ is selected i.e. the probability of the error of the first kind is 5 % than $k_{1-\alpha} = 1.65$ according to the distribution function of the standardized normal distribution, what is often chosen as default.

The decision threshold of the measurement of ^{239,240}Pu in the standard reference material IAEA-135 has been calculated, result is shown in Table VI-4 in Annex VI.

9.4. Detection limit

In accordance with ISO 11929-7, the detection limit, a$^{\#}$, is calculated by the following equations (7) and (8):

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

$$a^{\#} = \frac{2 \cdot a^* + (k^2 \cdot w)/T_g}{1 - k^2 \cdot \frac{u(w)^2}{w^2}} \qquad (7)$$

$$w = \frac{1}{m_s \cdot \varepsilon \cdot R} \qquad (8)$$

The detection limit of the measurement of ^{239,240}Pu in standard reference material IAEA-135 has been calculated and the result is shown in Table VI-4 in Annex VI.

10. QUALITY CONTROL MEASUREMENT

The quality control of the procedure is carried out by analysis of standard reference material (SRM) *IAEA-135* of known activities of ^{239,240}Pu, ^{238}Pu and ^{241}Am. This material was selected for the QC purposes because of the elevated levels of the activities. The results of the control samples are evaluated in terms of relative bias, repeatability and reproducibility. The control charts showing the repeatability of the method and the method performance parameters (trueness, precision, repeatability) are shown in Figures VI-1, VI-2, VI-3 and Table VI-2, in Annex VI, respectively. Results of reproducibility tests are summarized in Table VII-1 and VII-2 in Annex VII.

10.1. Selectivity of the method, possible interferences

High selectivity of the method is basically provided by the selectivity of alpha spectrometry and that of the radiochemical separation. Nonetheless, possible interferences cannot be excluded. If the sample contains relatively big amount of lanthanides (more than 0.1 mg/sample) the resolution of the Am source becomes poor and peaks of ^{243}Am tracer will overlap with that of ^{241}Am. In this case an additional chemical procedure has to be performed to separate Am from lanthanides. If the sample contains relatively big amount of natural Th, some Th contamination can occur in the Pu source that can be removed by an additional chemical purification procedure.

10.2. Linearity, range of measurement

The method was tested by the determination of ^{241}Am and Pu isotopes in several standard reference materials *(IAEA-135, IAEA-367, NIST-4357, IAEA-384, IAEA-385, IAEA-368)*. Results of measurements as a function of reference values are shown in Fig. VI-4A and VI-4B. Linearity of the method was proved in the range of 4 and 310 Bq kg^{-1} in case of ^{241}Am and in the range of 6 and 220 Bq kg^{-1} in case of ^{239,240}Pu. It is very likely that the method can be used in a wider range starting from the detection limit to as high levels where dead time becomes significant (higher than 10 %).

Recommended range of the method for ^{241}Am and Pu isotopes is: 5-5000 Bq kg^{-1}. Sample sizes should be selected according to these criteria.

10.3. Trueness of the method (relative bias of the method)

A sample is analyzed with eleven replicates to evaluate the trueness. The relative bias of the method is calculated by the following formula (9):

$$\delta(\%) = \frac{C - \overline{X}}{C} \times 100 \qquad (9)$$

Statistical evaluation of the results of repeated analysis of SRM IAEA-135 is shown in Table VI-2 in Annex VI. Relative bias of the measurements varied between 7-10 %.

10.4. Precision of the method

Sum of Squared Score (z-score) and precision index (PI %) are calculated for the replicates according to the following formulas (10) and (11):

$$z - score = \frac{C - a_0}{\sqrt{u(C)^2 + u(a_0)^2}} \qquad (10)$$

$$PI\% = 100\sqrt{\frac{u(C)^2}{C^2} + \frac{u(a_0)^2}{a_0^2}} \qquad (11)$$

Statistical evaluation of the results of repeated analysis of SRM IAEA-135 is shown in Table VI-2 in Annex VI.

10.5. Repeatability limit (within –run precision)

The repeatability limit is estimated by analyzing eleven replicates of a standard reference soil sample IAEA-135 with known specific activities of ^{241}Am, ^{239,240}Pu and ^{238}Pu in repeatability conditions: (instrument, analyst, shortest time, etc.). The repeatability limit is calculated by the formula (12). Results of repeatability test are given in Table VI-1, while those of statistical evaluation are shown in Table VI-2 and VI-3.

$$r_L = S_r \times 2.8 \qquad (12)$$

10.6. Reproducibility limit

The reproducibility limit is usually estimated by analyzing several replicates of a standard reference material with known specific activity, but with at least one parameter being changed in the analytical system (analyst, analysis date, instrument, etc.). The reproducibility limit is calculated by the following formula (13):

$$R_L = S_R \times 2.8 \qquad (13)$$

Reproducibility tests for the new method have been performed at the Radiochemical laboratory of RadAnal Ltd (Hungary). The reproducibility limit is estimated by analyzing three replicates of the standard reference soil sample IAEA-135 with known specific activities of ^{241}Am, ^{239,240}Pu and ^{238}Pu. Results of reproducibility test are given in Table VII-1, while those of statistical evaluation are shown in Table VII-2 and VII-3.

10.7. Acceptance criteria

The method can be accepted if

$$|\text{z-score}| < 3,$$

$PI\ \% < 25\ \%$,

$|\delta| < 2.8 * S_R$

According to these criteria the method performs well. There was one outlier (sample 6) that might originate from inhomogeneity of the SRM IAEA-135 material.

For the statistical evaluation the absolute values of δ and z-score were used.

11. TEST REPORT

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

- Sample code
- Sampling date
- 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 [4] calculated using a coverage factor k. The following form is recommended:

  $a \pm u(a)$ with the associated k value. The coverage factor k=2 was used in the present report.

12. CONCLUSION

A novel rapid procedure has been developed and tested for the simultaneous determination of ^{239,240}Pu, ^{238}Pu and ^{241}Am in small environmental samples by alpha spectrometry. The method is recommended for application in the analysis of soil and sediment samples contaminated by elevated levels of the radionuclides, especially in emergency situations.

Results are obtained within one day.

According to the repeatability tests the measurement process is considered to perform adequately. Chemical recoveries are acceptably high.

Reproducibility tests under variable conditions have been performed.

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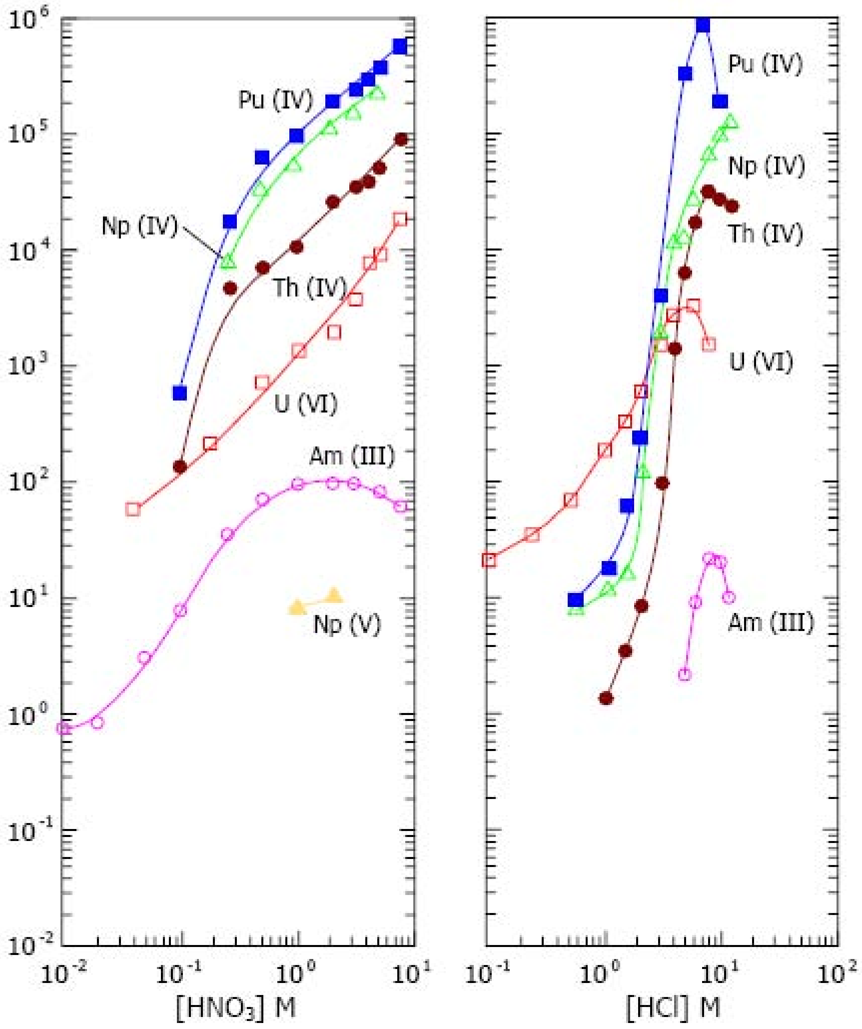
ANNEX I. CAPACITY FACTORS OF TRU RESIN IN NITRIC AND HYDROCHLORIC ACID

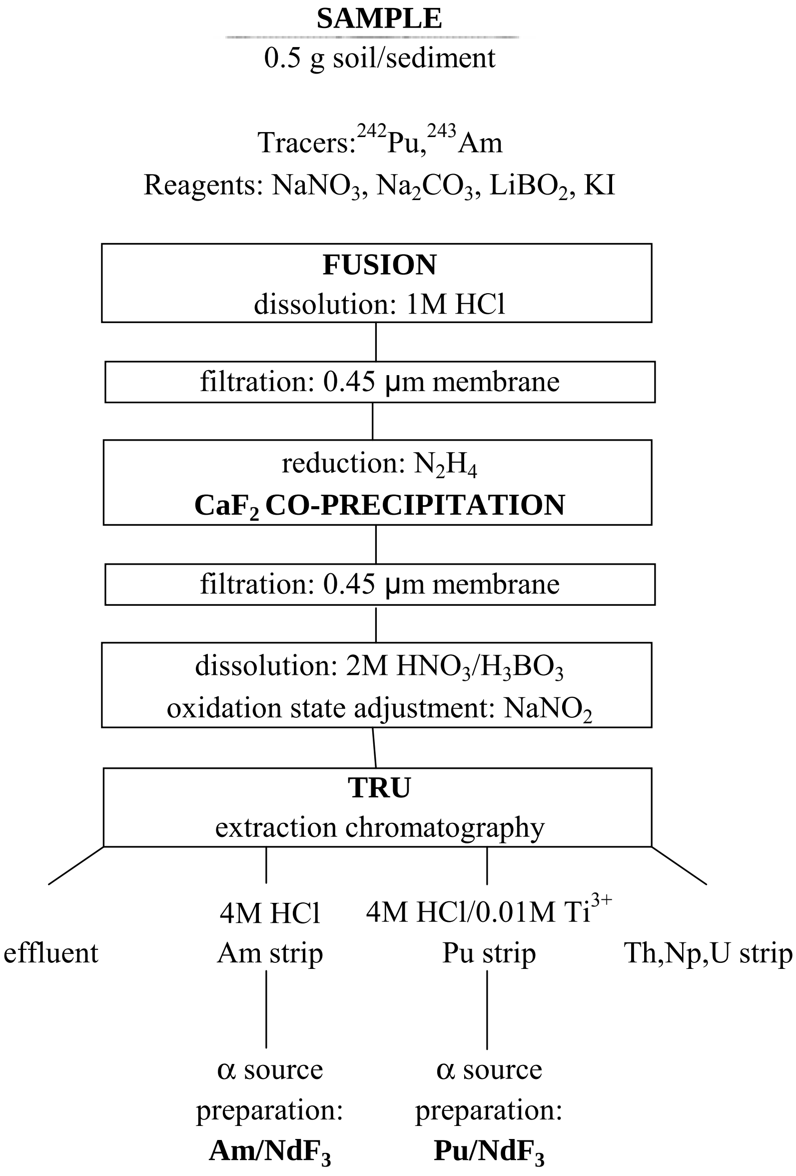


Source: www.eichrom.com [6]

ANNEX II. PREPARATION OF CHEMICAL REAGENTS

- 50 µg Nd/100 µl solution : Dissolve 115 mg of $Nd(NO_3)_3$ in 100 mL of de-ionized water.
- 2 mol L^{-1} HNO_3/0.01 mol L^{-1} $NaNO_2$ (eluent): For each sample dissolve about 25 mg $NaNO_2$ in 25 mL 2 mol L^{-1} HNO_3. Prepare always freshly.
- 4 mol L^{-1} HCl/0.01 mol L^{-1} Ti^{3+} solution (Pu strip solution): Mix 100 µL 15 % $TiCl_3$ (in HCl) solution with 10 mL 4 mol L^{-1} HCl solution. Always prepare freshly from fresh 15 % $TiCl_3$ (in HCl) solution that was stored in closed ampoule. After opening the ampoule the solution cannot be used for longer than one month.

ANNEX III. FLOW CHART FOR CHEMICAL SEPARATION OF AM AND PU BY TRU RESIN EXTRACTION CHROMATOGRAPHY



ANNEX IV. CALCULATION OF THE COMBINED UNCERTAINTY OF THE SPECIFIC ACTIVITIES OF THE ANALYTES ON SAMPLING DATE

Equations that are used to calculate the specific activity of the analyte at the separation time and the sampling date as well as the chemical recovery and the counting efficiency are described in chapter 9.1. The same formulas are used to calculate the combined uncertainties. Individual uncertainty components are discussed in detail in the present chapter.

IV.-1. Uncertainty in weighing the sample mass

The uncertainty associated with the mass of sample is estimated using the data from the calibration certificate of the analytical balance and the manufacturer's recommendations on the uncertainty estimation of the balance. If it is assumed that a balance with m_b mass uncertainty is used for weighing the sample and the linearity distribution is assumed to show a rectangular distribution, the standard uncertainty in the weighing of the sample mass can be calculated as $\frac{m_b}{\sqrt{3}}$.

The contribution for the linearity has to be accounted for twice, once for the tare and once for the gross mass (tare + sample), leading to an uncertainty $u(m_s)$ of (Eq.(IV-1):

$$u(m_s) = \sqrt{2 \times (\frac{m_b}{\sqrt{3}})^2} \qquad \text{(IV-1)}$$

IV.-2. Uncertainty of net counts of analyte and tracer

The uncertainty of the certified concentration of the tracer solution on a calibration, ($u(C_T)$) is provided by the producer. The uncertainty of net counts for tracer and analyte in alpha-spectra can be calculated as follows:

$$r_n = r_g - r_0 \quad \text{and} \quad u(r_g)^2 = \frac{n_g}{T_g^2} \quad , \quad u(r_0)^2 = \frac{n_0}{t_0^2} \qquad \text{(IV-2)}$$

$$r_{nt} = r_{gt} - r_{0t} \quad \text{and} \quad u(n_{gt})^2 = \frac{n_{gt}}{T_g^2} \quad , \quad u(n_{0t})^2 = \frac{n_{0t}}{t_0^2} \qquad \text{(IV-3)}$$

IV.-3. Uncertainty of decay correction factor

The uncertainty for decay correction factor, $u(f_T)$ can be calculated as follows:

$$u(f_T) = f_T \cdot t_T \cdot u(\lambda_T) \qquad \text{(IV-4)}$$

IV.-4. Combined uncertainty in the determination of the analyte at the sampling date

The combined uncertainty of the specific activity is calculated based on equation (1) and (2) using the general formula given elsewhere [3].

Differentiating equation (1), each partial derivative can be calculated as follows:

$$\frac{\partial a_1}{\partial C_T} = \frac{a_1}{C_T} \qquad \text{(IV-5)}$$

$$\frac{\partial a_1}{\partial r_n} = \frac{a_1}{r_n} \qquad \text{(IV-6)}$$

$$\frac{\partial a_1}{\partial r_{nt}} = -\frac{a_1}{r_{nt}} \qquad \text{(IV-7)}$$

$$\frac{\partial a_1}{\partial m_s} = -\frac{a_1}{m_s} \qquad \text{(IV-8)}$$

$$\frac{\partial a_1}{\partial m_T} = \frac{a_1}{m_T} \qquad \text{(IV-9)}$$

$$\frac{\partial a_1}{\partial f_T} = \frac{a_1}{f_T} \qquad \text{(IV-10)}$$

To determine the individual sensitivity parameters for the calculation of the uncertainty budget the following partial derivatives have to be also calculated:

$$\frac{\partial a_1}{\partial \lambda_T} = -a_1 t_T \qquad \text{(IV-11)}$$

$$\frac{\partial a_1}{\partial t_T} = a_1 \lambda_T \qquad \text{(IV-12)}$$

$$\frac{\partial a_1}{\partial r_g} = \frac{a_1}{r_g - r_0} \qquad \text{(IV-13)}$$

$$\frac{\partial a_1}{\partial r_0} = -\frac{a_1}{r_g - r_0} \qquad \text{(IV-14)}$$

$$\frac{\partial a_1}{\partial r_{gt}} = -\frac{a_1}{r_{gt} - r_{0t}} \qquad \text{(IV-15)}$$

$$\frac{\partial a_1}{\partial r_{0t}} = \frac{a_1}{r_{gt} - r_{0t}} \qquad \text{(IV-16)}$$

The uncertainty of measuring t_T is often regarded negligible.

The uncertainty of the analyte concentration at the separation time *u(a$_1$)* can be calculated from the law of error propagation. Substituting the partial derivatives into equation (1) the final expression for calculation of the combined uncertainty of the specific activity a_1 can be obtained (Eq.(IV-17)):

$$u(a_1)^2 = (\frac{a_1}{C_T})^2 u(C_T)^2 + (\frac{a_1}{r_g - r_0})^2 u(r_g)^2 + (\frac{a_1}{r_g - r_0})^2 u(r_0)^2 + (\frac{a_1}{r_{gt} - r_{0t}})^2 u(r_{gt})^2 +$$

$$+ (\frac{a_1}{r_{gt} - r_{0t}})^2 \cdot u(r_{0t})^2 + (\frac{a_1}{m_T})^2 \cdot u(m_T)^2 + (-\frac{a_1}{m_s})^2 \cdot u(m_s)^2 + (a_1 t_T)^2 u(\lambda_T)^2 + (a_1 \lambda_T)^2 \cdot u(t_T)^2 \qquad \text{(IV-17)}$$

For obtaining the correct numerical values expressions in equations (IV-2) and (IV-3) have to be substituted into equation (IV-17).

Combined uncertainty in the determination of the analyte on the sampling date, *u(a$_0$)* can be derived from the uncertainty on the separation time *u(a$_1$)* by differentiating equation (3). Each partial derivative can be calculated as follows:

$$\frac{\partial a_0}{\partial a_1} = \frac{a_0}{a_1} \qquad \text{(IV-18)}$$

$$\frac{\partial a_0}{\partial \lambda_A} = a_0 t_1 \qquad \text{(IV-19)}$$

$$\frac{\partial a_0}{\partial t_1} = a_0 \lambda_A \qquad \text{(IV-20)}$$

Therefore, the combined uncertainty of the specific activity of the analyte [Bq kg^{-1}, dry] on the sampling date (*u(a$_0$)*) can be calculated by the following formual (IV-21):

$$u\ (\mathrm{a}_0)^2 = (\frac{a_0}{a_1})^2 \cdot u(a_1)^2 + (\lambda_A a_0)^2 \cdot u(t_1)^2 + (t_1 a_0)^2 \cdot u(\lambda_A)^2 \qquad \text{(IV-21)}$$

To determine the uncertainty of the chemical recovery according to equation (4) the following formula (IV-22) is used:

$$\left(\frac{u(R)}{R}\right)^2 = \left(\frac{u(r_{nt})}{r_{nt}}\right)^2 + \left(\frac{u(C_T)}{C_T}\right)^2 + \left(\frac{u(\varepsilon)}{\varepsilon}\right)^2 + \left(\frac{u(m_T)}{m_T}\right)^2 \qquad \text{(IV-22)}$$

In equation IV-17 the uncertainty in the counting time is disregarded.

Expressing $u(r_{nt})$ as a function of the directly measured values and substituting it in equation (IV-22), the following formula (IV-23) is obtained for the calculation of the standard uncertainty of the chemical recovery:

$$\left(\frac{u(R)}{R}\right)^2 = \frac{r_{gt}/T_g + r_{0t}/t_0}{(r_{gt} - r_{0t})^2} + \left(\frac{u(C_T)}{C_T}\right)^2 + \left(\frac{u(\varepsilon)}{\varepsilon}\right)^2 + \left(\frac{u(m_T)}{m_T}\right)^2 \qquad \text{(IV-23)}$$

The relative standard uncertainty of the counting efficiency ε can be calculated according to equation (5) if the calibration procedure was similar to the sample preparation procedure as shown in Eq.(IV-24):

$$\left(\frac{u(\varepsilon)}{\varepsilon}\right)^2 = \frac{r_{gt}/T_g + r_{0t}/t_0}{(r_{gt} - r_{0t})^2} + \left(\frac{u(C_T)}{C_T}\right)^2 + \left(\frac{u(R)}{R}\right)^2 + \left(\frac{u(m_T)}{m_T}\right)^2 + \left(\frac{u(\lambda_T)}{\lambda_T}\right)^2 \qquad \text{(IV-24)}$$

where, $u(C_T)$ includes all the uncertainties related to the tracer activity, that is in the standard solution, preparation of the tracer solution.

IV.-5. Combined uncertainty in the determination of the detection limit

The detection limit is calculated according to equations (7). and (8).

The relative standard uncertainty of w is calculated using the following equation (IV-25):

$$\left(\frac{u(w)}{w}\right)^2 = \left(\frac{u(R)}{R}\right)^2 + \left(\frac{u(m_s)}{m_s}\right)^2 + \left(\frac{u(\varepsilon)}{\varepsilon}\right)^2 \qquad \text{(IV-25)}$$

where the relative standard uncertainty of R and ε can be substituted from equations (IV-23) and (IV-24), respectively.

ANNEX V. BASIC NUCLEAR DATA FOR PU AND AM ISOTOPES

TABLE V-1. RELEVANT DECAY DATA FOR Pu ISOTOPES AND ^{241}Am [7]

Radionuclide	Half-life (year)	Disintegration modes	E_α (MeV)	Intensity (%)
^{239}Pu	24110	α : 100%	5.105	11.94
		SF: 3E-10%	5.144	17.11
			5.157	70.77
^{240}Pu	6561	α : 100%	5.021	0.084
		SF: 5.7E-6%	5.124	27.10
			5.168	72.80
^{238}Pu	87.7	α : 100%	5.358	0.105
		SF: 1.9E-7%	5.456	28.98
			5.499	70.91
^{242}Pu	3.735E5	α : 100%	4.858	23.48
		SF: 5.5E-4%	4.902	76.49
^{241}Am	432.6	α : 100%	5.388	1.66
			5.442	13.1
			5.486	84.8
			5.545	0.37
^{243}Am	7370	α : 100%	5.181	1.36
		SF: 3.7E-9%	5.233	11.2
			5.275	87.1

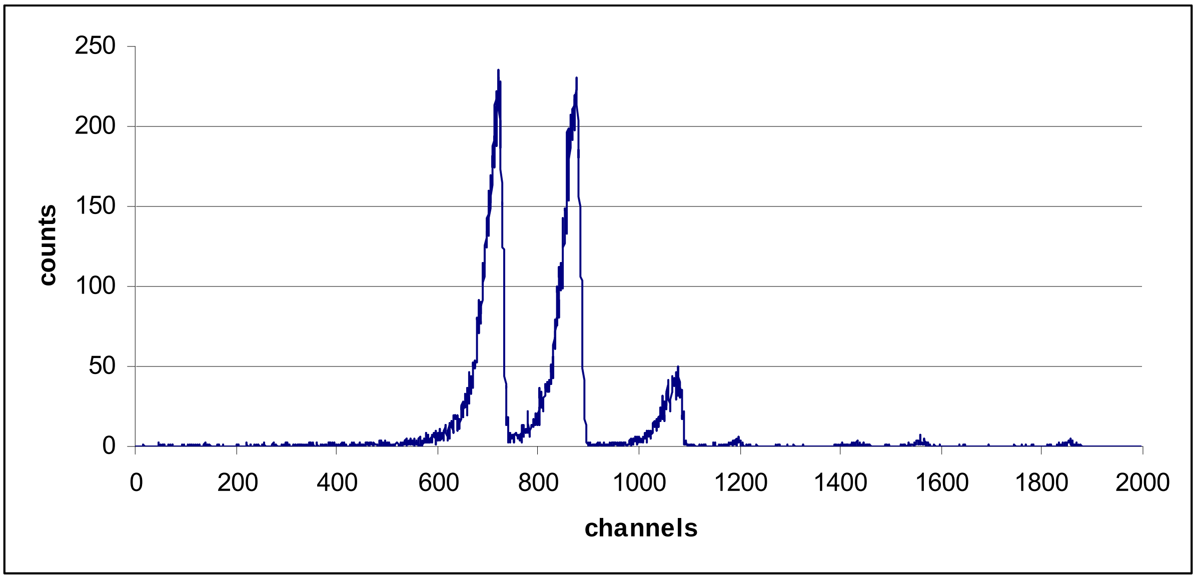


Fig. V-1. Typical plutonium alpha spectrum with ^{242}*Pu as yield tracer. Peaks in the spectrum from left to right are:* ^{242}*Pu,* ^{239,240}*Pu,* ^{238}*Pu*

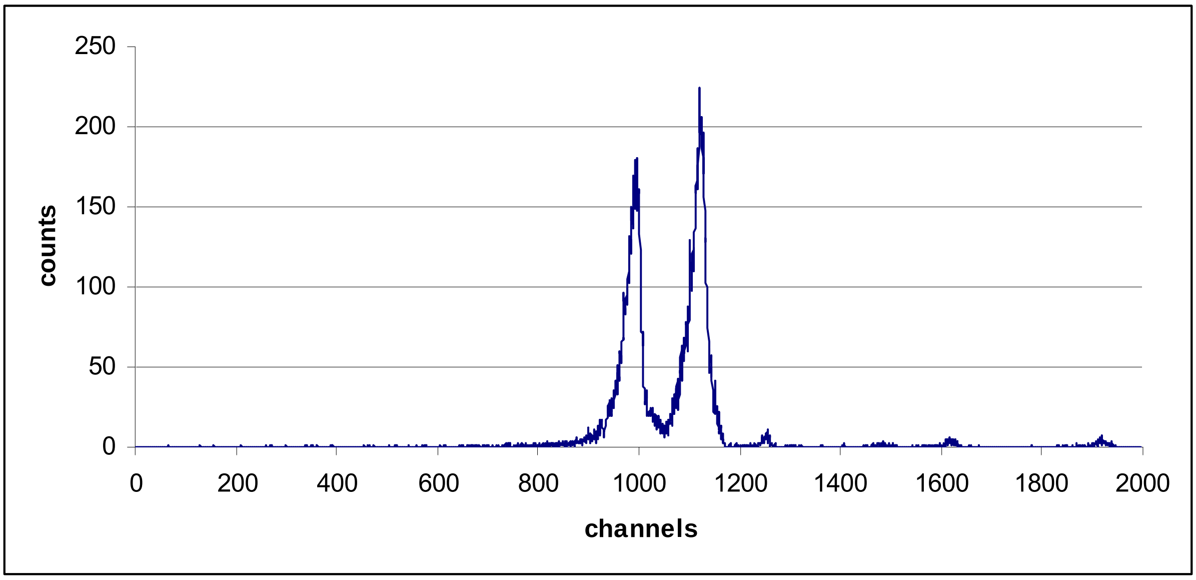


Fig. V-2. Typical americium alpha spectrum with ^{243}*Am as yield tracer. Peaks in the spectrum from left to right are:* ^{243}*Am,* ^{241}*Am*

ANNEX VI. THE RESULTS OF REPEATED MEASUREMENTS OF IAEA-135 STANDARD REFERENCE MATERIAL

TABLE VI-1. RESULTS OF REPEATED ANALYSIS OF SRM IAEA-135

Serial No.	**Sample code**	**^{241}Am**			**^{239,240}Pu**			**^{238}Pu**	
		yield -	act.conc. Bq/kg	unc. Bq/kg	**yield**	act.conc. Bq/kg	unc. Bq/kg	act.conc. Bq/kg	unc. Bq/kg
1	135B	0,84	320	11	0,64	225	9	40	3
2	135_4	0,81	339	17	0,60	242	15	43	5
3	135_5	0,93	292	14	0,59	225	15	41	5
4	135F	0,80	285	9	0,81	188	6	35	2
5	135_1	0,95	295	11	0,83	199	8	37	3
6	135_2	0,90	370	13	0,78	282	11	48	3
7	135_3	0,87	316	6	0,74	210	9	37	3
8	135_8	0,86	322	9	0,84	215	7	41	2
9	135_6	1,01	304	15	0,83	205	7	35	2
10	135_7	0,96	271	14	0,81	196	7	31	2
11	135_9	0,86	292	9	0,80	194	7	35	2
Average		0,89	**310**		0,75	**216**		**39**	
STDEV		0,06	28		0,09	27		5	
STDEV %		7,3	9		12,5	12		13	
Reference value at reference date			318	8		213	13	43	2
Reference value at measurement			**310**	8		**213**	13	**38**	2

Reference date:1992-01-01
uncertainties refer to k=2

TABLE VI-2. STATISTICAL EVALUATION OF THE RESULTS OF REPEATED ANALYSIS OF SRM IAEA-135

Serial No.	**Sample code**	**^{241}Am**			**^{239,240}Pu**			**^{238}Pu**		
		abs(bias) Bq kg^{-1}	abs(z-score)	precision index	abs(bias) Bq kg^{-1}	abs(z-score)	precision index	abs(bias) Bq kg^{-1}	abs(z-score)	precision index
1	135B	9,9	0,7	4,2	11,9	0,7	7,3	2,33	0,7	8,7
2	135_4	29,6	1,6	5,6	28,7	1,4	8,8	5,53	1,1	12,3
3	135_5	17,7	1,1	5,4	11,8	0,6	9,1	3,25	0,6	12,7
4	135F	25,2	2,1	4,0	24,9	1,7	7,0	2,76	1,0	7,7
5	135_1	15,1	1,1	4,4	14,3	0,9	7,4	1,06	0,3	9,1
6	135_2	60,0	4,0	4,3	68,9	4,0	7,3	10,57	2,9	8,2
7	135_3	5,6	0,6	3,2	3,0	0,2	7,5	1,12	0,3	9,4
8	135_8	11,9	1,0	3,9	2,4	0,2	6,9	3,26	1,1	7,5
9	135_6	5,5	0,3	5,6	7,7	0,5	7,0	2,38	0,8	7,8
10	135_7	38,9	2,4	5,9	16,9	1,2	7,0	6,81	2,5	8,1
11	135_9	18,2	1,5	3,9	19,1	1,3	7,0	3,25	1,2	7,8
Mean value		21,6	1,5	4,6	19,0	1,2	7,5	3,85	1,1	9,0
Relative mean value %		7,0			8,9			10,2		
Acceptance criteria		<78	<3	<25%	<76	<3	<25%	<14	<3	<25%

TABLE VI-3. THE RESULTS OF REPEATABILITY TESTS FOR THE DETERMINATION OF ^{239,240}Pu, ^{238}Pu AND ^{241}Am IN IAEA-135 STANDARD REFERENCE MATERIAL

Repeatability of ^{239,240}Pu measurement	
Mean ($\overline{X}$) in repeatability test, Bq kg^{-1}	216
Repeatability standard deviation (S_r), Bq kg^{-1}	27
Repeatability limit (r_L), Bq kg^{-1}	76
Relative mean bias, %	8.9
Mean bias, Bq kg^{-1}	19
z-score	1.2
Precision index, %	7.5
Repeatability of ^{238}Pu measurement	
Mean ($\overline{X}$) in repeatability test, Bq kg^{-1}	39
Repeatability standard deviation (S_r), Bq kg^{-1}	4.9
Repeatability limit (r_L), Bq kg^{-1}	14
Relative bias, %	10
Mean bias, Bq kg^{-1}	3.9
z-score	1.1
Precision index, %	9.0
Repeatability of ^{241}Am measurement	
Mean ($\overline{X}$) in repeatability test, Bq kg^{-1}	310
Repeatability standard deviation (S_r), Bq kg^{-1}	28
Repeatability limit (r_L), Bq kg^{-1}	78
Relative bias, %	7.0
Mean bias, Bq kg^{-1}	22
z-score	1.5
Precision index, %	4.6

* outlier: Sample 6

The measurement process is considered to be performing adequately if

$$|\delta| < 2.8*S_r$$

$$|\text{z-score}| < 3$$

$$\text{PI \%} < 25 \text{ \%}.$$

where S_r is the standard deviation, z-score is the Sum of Squared Scores, PI % is the precision index of the repeated measurements of the reference material. For δ % and z-score the absolute values were taken into account.

According to these criteria of ISO/TS 21748:2004 the tested method performs well.

TABLE VI-4. UNCERTAINTY BUDGET OF THE MEASUREMENT OF ^{239,240}Pu ACTIVITY IN ONE SAMPLE OF IAEA-135 STANDARD REFERENCE MATERIAL, COUNTING TIME OF SAMPLE AND BLANK WERE T_g=30000 AND t_0=80000 S, RESPECTIVELY. (COVERAGE FACTOR FOR UNCERTAINTY: k=1)

Symbol	**Value of variable**	**Uncertainty**	**Percent contribution to $(u_{a1})^2$**
n_{gt}, counts	894	30	48
$n_{0t,}$ counts	4	2	0.01
$n_{g,}$ counts	863	29	50
$n_{0,}$ counts	1	1	0.03
C_T, Bq g^{-1}	1.031	0.0076	2
m_T, g	0.10322	0.00008	0.03
m_s, kg	5.304E-4	8.2E-8	negligible
λ_T, a^{-1}	1.86E-6	1.9E-9	negligible
a_1, Bq kg^{-1}	194	9.4	
ε	0.335	0.0067	
R	0.80	0.03	
Decision threshold Bq kg^{-1}	0.27		
Detection limit Bq kg^{-1}	1.2		

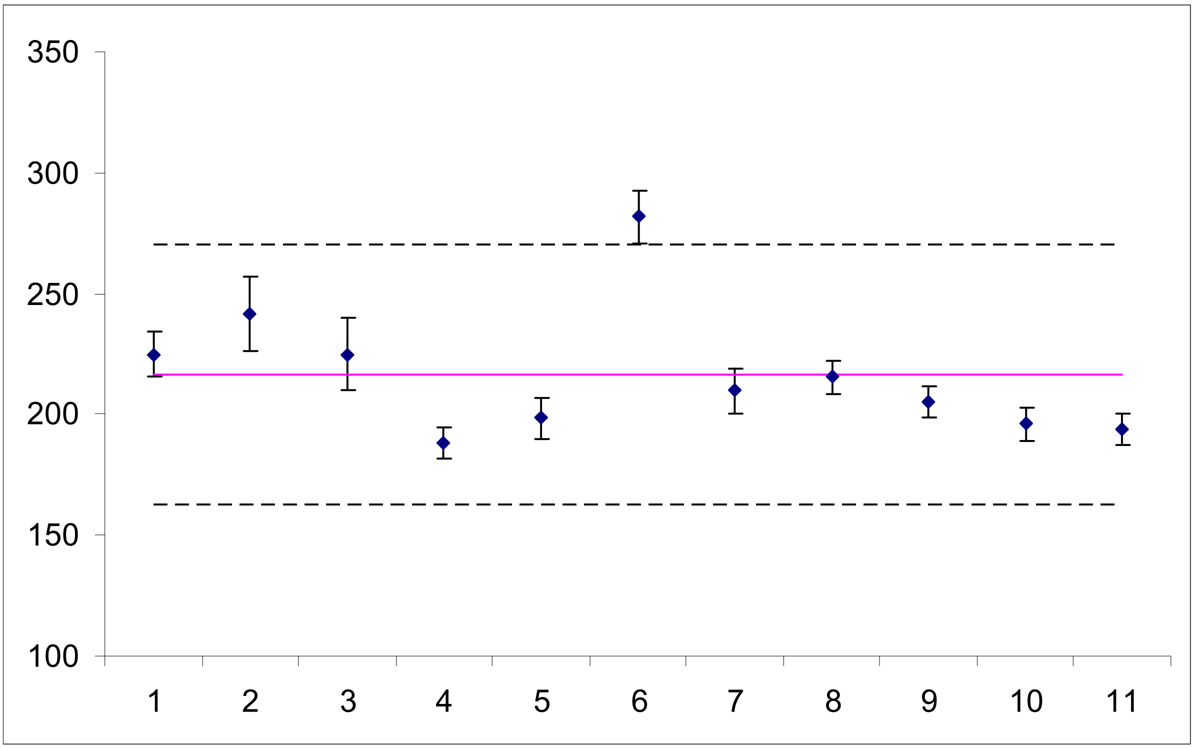


Fig. VI-1. Control chart for relative bias of ^{239,240}Pu determination in IAEA-135 standard reference soil: Measured specific activity of ^{239,240}Pu (Bq kg^{-1}) is plotted against the number of replicates. The straight line shows the average value, the dashed lines represent the standard deviation from the average, error bars belong to uncertainties of the individual measurements (k=2). The dashed lines indicate the 2σ uncertainty (STDEV) range.

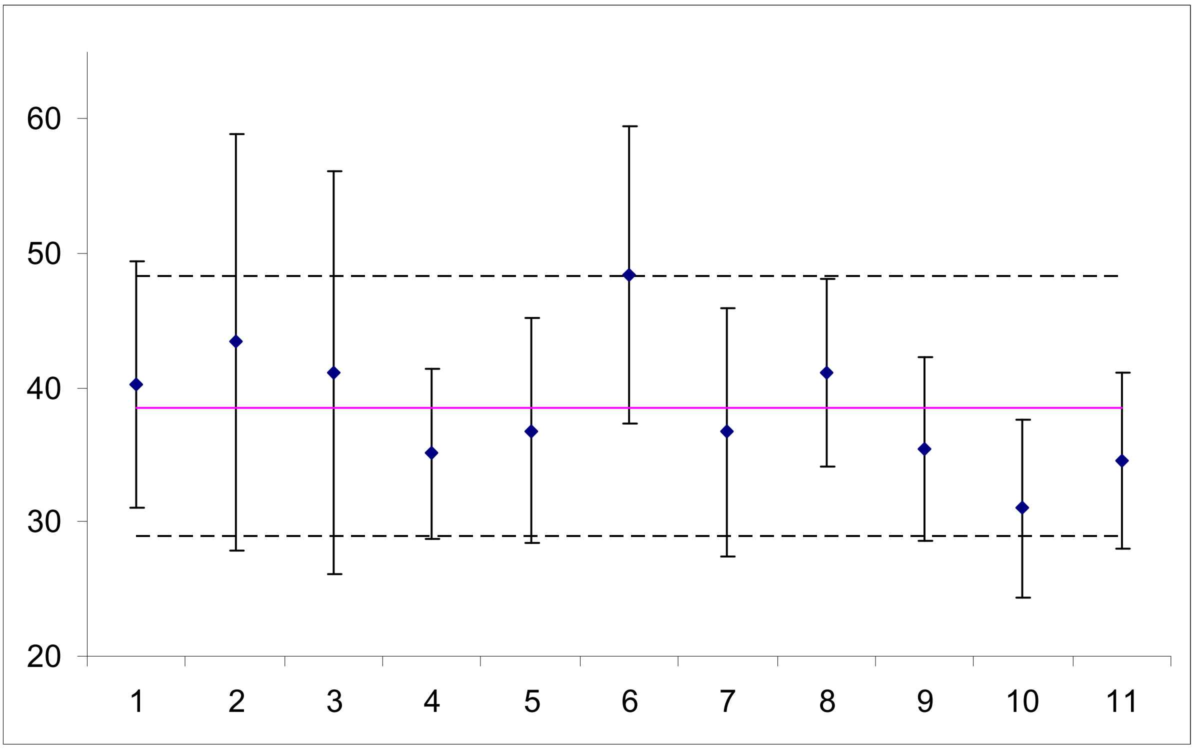


Fig. VI-2. Control chart for relative bias of ^{238}*Pu determination in IAEA-135 standard reference soil: Measured specific activity of* ^{238}*Pu (Bq kg*$^{-1}$*) is plotted against the number of replicates. The straight line shows the average value, the dashed lines represent the standard deviation from the average, error bars belong to uncertainties of the individual measurements (k=2). The dashed lines indicate the 2σ uncertainty (STDEV) range.*

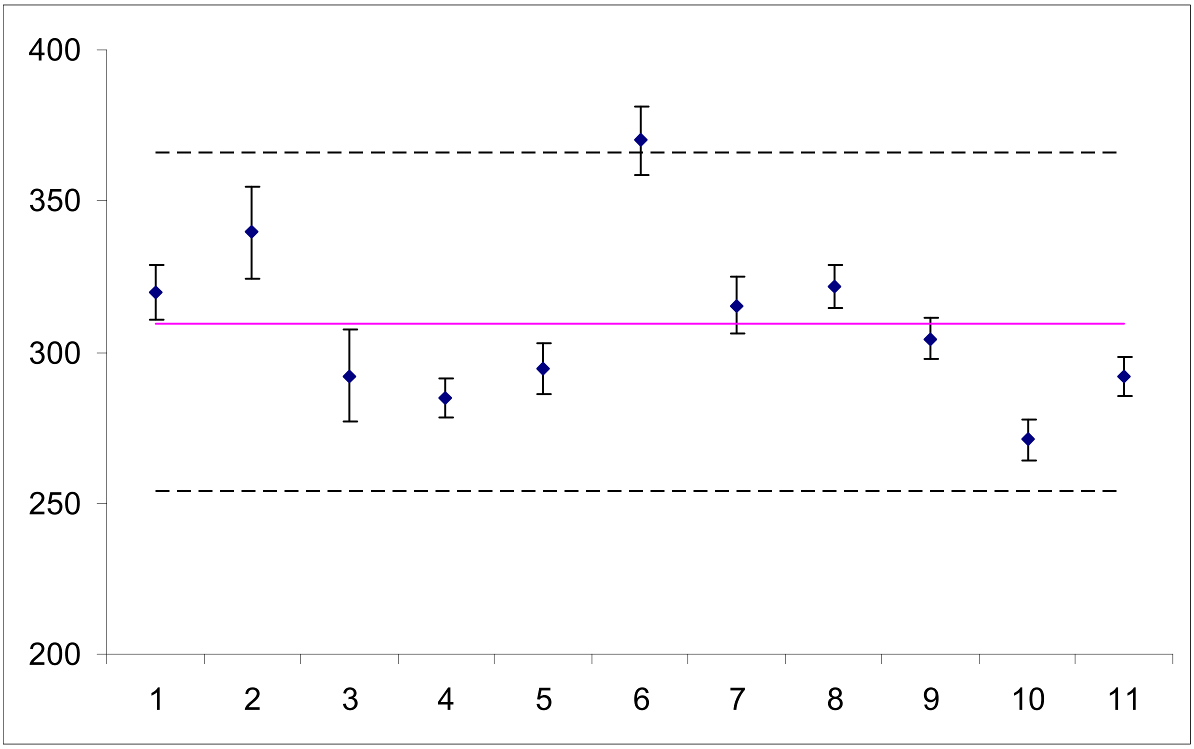


Fig. VI-3. Control chart for relative bias of ^{241}Am determination in IAEA-135 standard reference soil: Measured specific activity of ^{241}Am (Bq kg^{-1}) is plotted against the number of replicates. The straight line shows the average value, the dashed lines represent the standard deviation from the average, error bars belong to uncertainties of the individual measurements (k=2). The dashed lines indicate the 2σ uncertainty (STDEV) range.

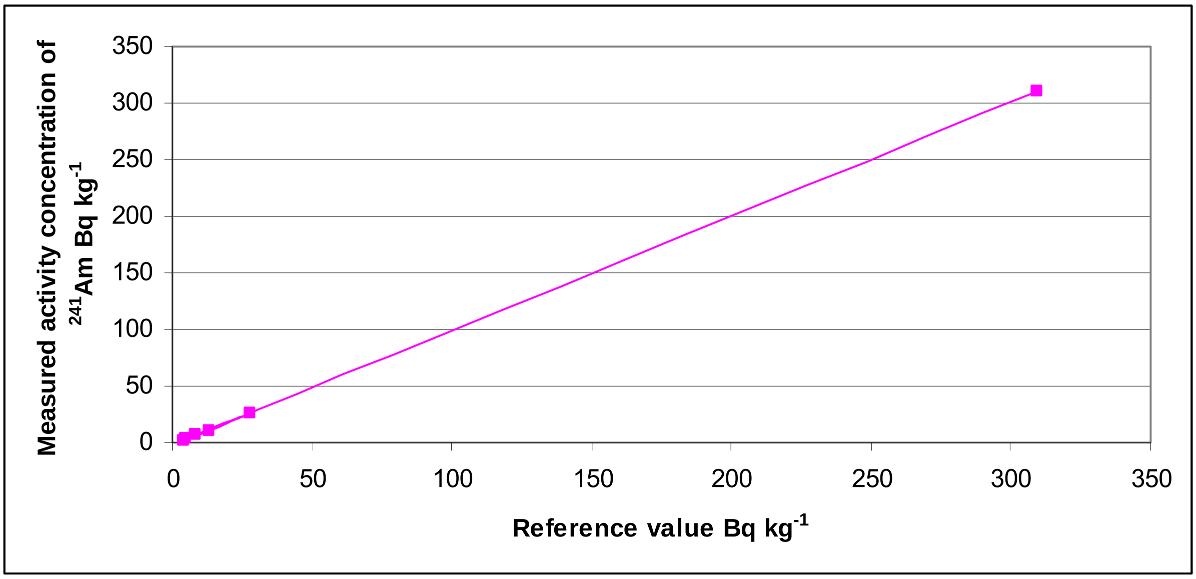


Fig. VI-4A. Method linearity shown as measured specific activities of standard reference materials (IAEA-135, IAEA-367, NIST-4357, IAEA-384, IAEA-385, IAEA-368) as a function of reference values in case of ^{241}*Am*

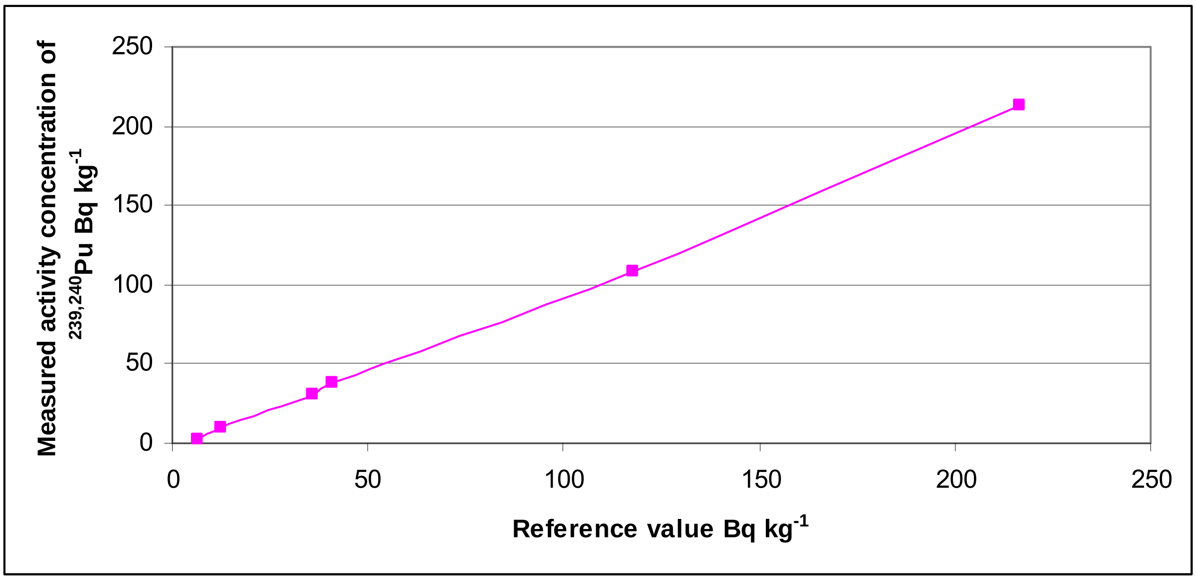


Fig. VI-4B. Method linearity shown as measured specific activities of standard reference materials (IAEA-135, IAEA-367, NIST-4357, IAEA-384, IAEA-385, IAEA-368) as a function of reference values in case of ^{239,240}*Pu*

ANNEX VII. THE RESULTS OF REPRODUCIBILITY MEASUREMENTS OF IAEA-135 STANDARD REFERENCE MATERIAL

TABLE VII-1. RESULTS OF MEASUREMENTS OF SRM IAEA-135 UNDER REPRODUCIBILITY CONDITIONS

Counting time: 25000-70000 sec
Chemical recoveries for Pu: 40-70 %
Chemical recoveries for Am: 80-95%

Serial No.	**Sample code**	**^{241}Am** act.conc. Bq/kg	unc. Bq/kg	**^{239,240}Pu** act.conc. Bq/kg	unc. Bq/kg	**^{238}Pu** act.conc. Bq/kg	unc. Bq/kg
1	StA	390	49	242	38	<LD	
2	StB	269	32	198	28	45,0	10,4
3	StC	316	38	201	24	35,5	6,6
Average		**325**		**213**		**40**	
STDEV		61		25		7	
STDEV %		19		12		17	
Reference value at reference date		**318**	8	**213**	13	**43**	2

Reference date:1992-01-01

Results were calculated at the reference time with the exception of ^{241}Am
Uncertainties refer to k=2

TABLE VII-2. STATISTICAL EVALUATION OF THE RESULTS OF REPRODUCIBILITY MEASUREMENTS

Serial No.	**Sample code**	**^{241}Am** abs(bias) Bq kg^{-1}	abs(z-score)	precision index	**^{239,240}Pu** abs(bias) Bq kg^{-1}	abs(z-score)	precision index	**^{238}Pu** abs(bias) Bq kg^{-1}	abs(z-score)	precision index
1	StA	72	1,5	12,8	29	0,7	16,9			
2	StB	49	1,5	12,2	15	0,5	15,4	2,0	0,2	23,6
3	StC	2,0	0,1	12,3	12	0,5	13,4	7,5	1,1	19,2
Mean value		41,1			18,8			4,7		
Relative mean value %		12,9			8,8			11,0		
Acceptance criteria		<171	<3	<25%	<70	<3	<25%	<20	<3	<25%

All results passed the statistical tests. In sample StA ^{238}Pu was not detected.

TABLE VIII-3. THE RESULTS OF REPRODUCIBILITY TESTS FOR THE DETERMINATION OF ^{239,240}Pu, ^{238}Pu AND ^{241}Am IN IAEA-135 STANDARD REFERENCE MATERIAL

Reproducibility of ^{239,240}Pu measurement	
Mean ($\overline{X}$) in reproducibility test, Bq kg^{-1}	213
Reproducibility standard deviation (S_R), Bq kg^{-1}	25
Reproducibility limit (R_L), Bq kg^{-1}	70
Relative mean bias, %	8.8
Mean bias, Bq kg^{-1}	19
z-score (abs)	0.6
Precision index, %	15
Reproducibility of ^{238}Pu measurement	
Mean ($\overline{X}$) in reproducibility test, Bq kg^{-1}	40
Reproducibility standard deviation (S_R), Bq kg^{-1}	7
Reproducibility limit (R_L), Bq kg^{-1}	17
Relative mean bias, %	4.7
Mean bias, Bq kg^{-1}	11
z-score (abs)	0.6
Precision index, %	21
Reproducibility of ^{241}Am measurement	
Mean ($\overline{X}$) in reproducibility test, Bq kg^{-1}	325
Reproducibility standard deviation (S_R), Bq kg^{-1}	61
Reproducibility limit (R_L), Bq kg^{-1}	171
Relative mean bias, %	41
Mean bias, Bq kg^{-1}	13
z-score (abs)	1
Precision index, %	12

* outlier: Sample 6

The measurement process is considered to be performing adequately if

$$|\delta| < 2.8 * S_R$$

$$|\text{z-score}| < 3$$

$$PI\ \% < 25\ \%.$$

where S_R is the standard deviation, z-score is the Sum of Squared Scores, PI % is the precision index of the repeated measurements of the reference material. For δ % and z-score the absolute values were taken into account.

According to these criteria of ISO/TS 21748:2004 the tested method performs well.

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