Procedure for determining the specific activities of americium-241 and curium isotopes in fish by alpha spectrometry

G-α-SPEKT-FISCH-02

Authors:

M.-O. Aust

G. Kanisch

U. Rieth

Federal coordinating office for fish and fishery products, crustacean, shell fish and aquatic plants

(Leitstelle für Fisch und Fischereierzeugnisse, Krustentiere, Schalentiere, Meereswasserpflanzen)

ISSN 1865-8725 Version February 2022

Procedures Manual for monitoring of radioactive substances in the environment and of external radiation
(Messanleitungen für die „Überwachung radioaktiver Stoffe in der Umwelt und externer Strahlung")

Procedure for determining the specific activities of americium-241 and curium isotopes in fish by alpha spectrometry

1 Scope

The procedure described in the following is suitable for determining the specific activities of the americium isotope Am-241 and the curium isotopes Cm-242 und Cm-(243+244) in fish samples (fish flesh and whole fish). It is possible to determine specific activities at levels less than 1 $mBq \cdot kg^{-1}$ fresh mass.

The procedure is used in the IMIS-routine programme [1] and for radioecological research. It is very time consuming and requires experienced laboratory staff.

2 Sampling

For sampling, it is referred to Procedure G-γ-SPEKT-FISCH-01.

3 Analysis

3.1 Principle of the procedure

The sample material is ashed according to Procedure G-γ-SPEKT-FISCH-01.

Usually, the specific activities of Am-241 and curium isotopes are determined along with other alpha emitting radionuclides. In this case, the radiochemical extraction is carried out from the hydrochloric acid extract received after the separation of plutonium according to the Procedure G-α-SPEKT-FISCH-01. Details on tracer addition are listed in that specific procedure. If the specific activities of Am-241 and the curium isotopes are to be determined exclusively, a defined amount of Am-243 tracer is added to fish ash as internal standard.

After an extensive radiochemical separation including several procedural steps like extraction, chemical reduction, back-extraction, chemical oxidation and anion exchange, Am-241 and the curium istotopes are electrochemically deposited on stainless steel plates and their activities are determined using a low-level alpha spectrometer.

ISSN 1865-8725 Version February 2022

3.2 Sample preparation

No special pretreatment of the hydrochloric acid extract received from step 3.3.13 of Procedure G-α-SPEKT-FISCH-01 is required. The extract is directly usable for the radiochemical separation beginning at step 3.3.2.

Fish ash from sample preparation according to Procedure G-γ-SPEKT-FISCH-01 is used for exclusively determining the specific activities of Am-241 and the curium isotopes.

Before the separation procedure described in Section 3.4 typically 50 g of fish ashed at 500°C temperature; the procedure is designed for processing a maximum of 100 g of ash. In addition, a blank sample is added to every sample set. Before the analysis, all glassware is prepared according to Section 8.3.1 and the two ion extraction columns according to Section 8.3.2.

3.2.1 The ash is processed in a muffle furnace at a maximum of 500 °C for up to 48 hours. Directly after cooling down, the ash is determined and the ash is stored in a desiccator.

3.2.2 If not directly processed, the ash is dried at 110°C for one hour before start of analysis and cooled down to room temperature in a desiccator.

3.2.3 50 g up to 100 g fish ash are weighed into a 600 ml beaker and the weight noted in the analysis protocol.

3.2.4 A known activity of Am-243 is added as internal standard; typically, around 0,05 Bq are used.

3.2.5 300 ml of nitric acid (8 $mol \cdot l^{-1}$) are added to the ash; the beaker is covered with a watch glass.

3.2.6 The solution in the beaker is stirred on a heating plate and boiled for 30 minutes.

Further steps of the analysis are described in 3.3.1 of this procedure.

3.3 Radiochemical separation

3.3.1 Separation of plutonium isotopes from extracts of fish ash

3.3.1.1 While stirring, 5 ml sodium nitrite solution 1 (7,25 $mol \cdot l^{-1}$) are carefully added to the hot solution.

Note:
The addition of sodium nitrite leads to a strong reaction with formation of nitrous fumes! Sodium nitrite is used for the chemical reduction plutonium from oxidation state VI to oxidation state IV.

3.3.1.2 The solution is left to cool down to room temperature before it is transferred to a centrifuge beaker. Afterwards it is centrifuged at about the 3160-fold the acceleration of gravity (3160 *g*) for 30 minutes.

Note:
If the centrifuge allows only the adaption of rotor speed in rotations per minute, the user manual oft he centriuge/rotor has to be checked for the correct conversion.

3.3.1.3 The supernatant is transferred into a 1000 ml beaker and is covered until further processing.

3.3.1.4 The remaining precipitate is transferred to a 600 ml beaker using a few nitric acid (8 mol·l^{-1}). The volume of the solution is increased to 300 ml by addition of nitric acid (8 mol·l^{-1}).

Note:
Caution! Formation of nitrous fumes!

3.3.1.5 The solution is stirred on a heating plate for 30 minutes and boiled until no nitrous fumes are released any more.

3.3.1.6 Another 5 ml sodium nitrite solution 1 (7,25 mol·l^{-1}) are added under stirring and the solution is left to cool down to room temperature. Afterwards, the solution is centrifuged according to step 3.3.1.2.

3.3.1.7 The resulting centrifugate is unified with the centrifugate of step 3.3.3 and transferred to a 1000 ml separating funnel. The precipitate is discarded.

Note:
If the solution remains unprocessed for a longer time, e. g. overnight, the oxidation state VI of plutonium must be re-adjusted with 5 ml sodium nitrite solution 1 (7,25 mol·l-1).

3.3.1.8 Plutonium is extacted from the nitric acid solution using 25 ml TOPO solution dissolved in cyclohexane (0,2 mol·l^{-1}), which is added to the solution inside the separating funnel. Afterwards, the 1000 ml separating funnel is shaken for 15 minutes.

3.3.1.9 The nitric acid phase (lower phase) is drained into a 1000 ml beaker, while the organic phase (upper phase) is discarded as no determination of the specific activity of plutonium isotopes according to the Procedure G-α-SPEKT-FISCH-01 is scheduled.

3.3.1.10 Another 25 ml TOPO-solution dissolved in cyclo¬hexane (0,2 mol·l^{-1}) is added to the nitric acid phase, transferred into the 1000 ml separating funnel from step 3.3.1.8 and shaken for 15 minu¬tes.

3.3.1.11 The nitric acid phase (lower phase) is drained into a 1000 ml beaker and used for radiochemical separation according to Section 3.3.2.

3.3.1.12 The organic phase is discarded as in step 3.3.1.9.

3.3.2 Processing of the exctracts after removal of plutonium isotopes

3.3.2.1 The volume of the nitric acid solution from step 3.3.1.11 containing americium and curium is reduced on a heating plate to 100 ml bis 200 ml; emerging precipitates are ignored.

3.3.2.2 The solution is left to cool down to room temperature.

3.3.2.3 Afterwards, the solution is filled up to 300 ml and sodium hydroxide solution (10 mol·l^{-1}) is added dropwise until a nitric acid concentration of 0,1 mol·l^{-1} (pH 1, to be controlled using a freshly calibrated pH-meter) is reached.

3.3.2.4 If a precipitate is emerging during pH-adjustion, the solution is transferred to a centrifuge beaker and 3160-fold the acceleration of gravity (3160 *g*) for 30 minutes. The solutions are transferred to a 1000 ml beaker and stored.

3.3.2.5 The precipitate is suspended in the fewest possible amount of nitric acid (8 mol·l^{-1}), dissolved by addition of destilled water to approx. 100 ml and adjused to pH 1 using sodium hydroxide solution (10 mol·l^{-1}). If the solution is clear, it is combined with the solution of step 3.3.2.4. The combined solutions are further processed according to step 3.3.2.7.

3.3.2.6 If a precipitate is still present, steps 3.3.2.4 and 3.3.2.5 are repeated. If the precipitate is still present the steps are repeated for a third time. The solutions are combined with those of steps 3.3.2.4 and 3.3.2.5. The precipitate is discarded after the second repetition of steps 3.3.2.4 and 3.3.2.5.

3.3.2.7 The combined solutions are transferred to a 1000 ml separating funnel.

3.3.2.8 For the extraction of americium and curium, 25 ml of a mixture of TOPO in cyclohexane (0,2 mol·l^{-1}) are added to the separating funnel, which is shaken for 15 minutes, afterwards.

3.3.2.9 The nitric acid phase (lower phase) is drained into a 1000 ml beaker, while the organic phase (upper phase) is transferred inside a 250 ml separation funnel.

3.3.2.10 Another 25 ml TOPO-solution dissolved in cyclohexane (0,2 mol·l^{-1}) is added to the nitric acid phase, transferred into the 1000 ml separating funnel and shaken for 15 minutes.

3.3.2.11 The nitric acid phase (lower phase) is drained into a 1000 ml beaker and discarded, while the organic phase (upper phase) is unified with that from step 3.3.2.9 inside the 250 ml separating funnel.

3.3.2.12 The organic phase inside the 250 ml separating funnel is shaken twice for 5 minutes, each, after addition of 50 ml nitric acid. The aqueous solution is discarded, afterwards.

3.3.2.13 For the back-extraction of americium and curium from the organic phase, 50 ml of nitric acid (8 mol·l^{-1}) are added to the 250 ml separating funnel and shaken for 15 minutes.

3.3.2.14 The nitric acid solution (lower phase) is collected inside a 250-m-beaker.

3.3.2.15 The step 3.3.2.13 is repeated twice. Resulting nitric acid solutions are unified with from step 3.3.2.14. Afterwards, the organic phase is discarded.

3.3.2.16 The nitric acid solutions are slowly reduced to dryness at a temperature of 60 °C bis 80 °C using a sand bath.

Note:
Caution! In this step the danger of superheating associated with significant loss in chemical yield exists.

3.3.2.17 Afterwards, 20 ml hydrochloric acid (9 mol·l^{-1}) are added to the dry residue. If the residue does not completely dissolve, it is solubilised by gently heating to 50 °C to 70 °C on a heating plate.

3.3.2.18 The cooled down solution is loaded on a prepared 2-layer ion exchange column (see Section 8.3.2) and is percolated through it at a velocity of 1 ml per minute. The eluate is collected inside a 250 ml beaker; it contains the americium-curium-fraction.

Note:
Polonium, thorium, uranium and partially iron and plutonium are retarted on the column material.

3.3.2.19 For almost complete elution of americium and curium from the 2-layer ion exchange column, it is washed three times using 20 ml hydrochlic acid (9 mol·l^{-1}) and the eluate is also collected in the beaker of step 3.3.2.18.

3.3.2.20 The eluate containing americium and curium is slowly reduced to dryness at a temperature of 60 °C bis 80 °C using a sand bath.

Note:
Caution! In this step the danger of superheating associated with significant loss in chemical yield exists.

3.3.2.21 The residue is dissolved in 20 ml nitric acid (12 mol·l^{-1}). A white precipitate may occur, that remains also after heating. The supernatant is decanted into a 250 ml separating funnel. The residue is washed twice using 20 ml nitric acid (12 mol·l^{-1}), each. The solutions are combined with that in the 250 ml separating funnel.

3.3.2.22 The beaker is washed twice using 5 ml DDCP solution in n-heptane (0,5 mol·l^{-1}), each. The washing solution is also added to the solution in the 250 ml separating-funnel. The mixture is shaken for 2 minutes.

3.3.2.23 Three phases form in the separating funnel. The aqueous phase (lower phase) is discarded.

3.3.2.24 The solutions inside the separating funnel are washed twice using 20 ml nitric acid (12 mol·l^{-1}), each, and shaking for one minute, each. The aqueous phase (lower phase) is always discarded.

3.3.2.25 For back-extraction of the americium and the curium, 5 ml xylole and 20 ml nitric acid (2 mol·l^{-1}) are added to the separation funnel. The separating funnel is shaken for 2 minutes. The nitric acid phase (lower phase) is drained to a 100 ml beaker.

Note:
Thorium and iron are coextracted in this step. Traces of plutonium remain in the organic phase.

3.3.2.26 The back-extraction is repeated by addition of 10 ml to 20 ml nitric acid (2 mol·l^{-1}) and shaking for 2 minutes. Both nitric acid solutions are combined with that in the 100 ml beaker from step 3.3.2.25. The other solutions are discarded.

3.3.2.27 The nitric acid solution is precisely reduced to dryness on a heating plate at temperatures between 100 °C bis 150 °C.

Note:
Caution: The danger of formation of a smelt exists, which leads to high loss of americium. Therefore, the evaporation starts at 150 °C and is reduced to a temperature smaller than 100°C when the process is going to end.

3.3.2.28 The residue is redissolved in 20 ml nitric-acid-methanol-solution (1 mol·l^{-1} HNO_3 / 93 % CH_3OH).

3.3.2.29 The solution is loaded on a prepared anion extraction column (see Section Fehler! Verweisquelle konnte nicht gefunden werden.) and percolated through it at a rate of 1 ml per minute. The column must not run dry. The percolate is discarded.

3.3.2.30 The column is washed three times with 20 ml nitric-acid-methanol-solution (1 mol·l^{-1} HNO_3 / 93 % CH_3OH), each, at a flow rate of 1 ml per minute to remove rests from iron. The percolate is discarded.

3.3.2.31 Rare earth metals are washed from the columns by addition of three times 20 ml methanol-ammoniumthiocyanate-hydrchloric-solution (80 % CH_3OH / 20 % 0,5 mol·l^{-1} NH_4SCN in 0,1 mol·l^{-1} HCl). The percolate is discarded.

3.3.2.32 Afterwards, americium and curium are eluted from the column by addition of four times 20 ml hydrochloric-acid-methanol-solution (1,5 mol·l^{-1} HCl / 86 % CH_3OH) at a flow rate of 1 ml per minute. The leachate is collected in a 150 ml crystallizing dish.

3.3.2.33 The solution is gently evaporated to dryness at a temperature around 100 °C, which results in formation of a white residue from ion exchange particles.

3.3.2.34 The residue is gently vaporised using 10 ml nitric acid (14,4 mol·l^{-1}) and afterwards a mixture of 1 ml hydrochloric acid (12,1 mol·l^{-1}) and 1 ml nitric acid (14,4 mol·l^{-1}). The vaporisation step with the mixture of nitric and hydrochloric acid is repeated until no residue is visible, any more.

Note:
Caution! Formation of nitrous gases. Therefore, the counting source must not get too hot.

3.3.2.35 If no white residue is visible any more, one last vaporisation step is carried out using 1 ml hydrochloric acid (12,1 mol·l^{-1}). The counting source must not get too hot.

3.4 Preparation of the counting sources

The stainless steel disks and the electrodepositon apparatus required for preparation of the counting source are pretreated according the Sections 8.3.3 and 8.3.4.

3.4.1 The dry residue inside the crystallizing dish is dissolved in 0,4 ml hydrochloric acid (4 $mol \cdot l^{-1}$); the solution is quantitatively transferred into a prepared electrolysis vessel.

3.4.2 Afterwards, the crystallizing dish is rinsed three times using 1 ml ammoniumoxalate solution (0,32 $mol \cdot l^{-1}$) and once with 0,6 ml destilled water. These solutions are unified with the americium solution of step 3.4.1.

3.4.3 The electrodeposition on prepared stainless steel disks is carried out for 4 hours at a constant current of 300 mA. The electrolysis vessel (see Figure 1) is covered with a single bulb condenser to recover evaporated solution.

3.4.4 Before the current is switched off, 1 ml ammonia solution (13,4 $mol \cdot l^{-1}$) is added and the electrodeposition is continued for 1 minute.

3.4.5 The solution is discarded, the current is switched off, afterwards.

3.4.6 The platinum electrode is removed and washed with distilled water.

Note:
Afterwards, it is stored in nitric acid (14,4 $mol \cdot l^{-1}$).

3.4.7 Finally, the electrolysis vessel containing the counting source is washed with slight ammonia containing water (pH 8).

3.4.8 The counting source is removed from the electrolysis vessel and thoroughly washed with slight ammonia containing water (pH 8), first, followd by ethanol.

Afterwards, the counting source is dried on a heating plate.

4 Measuring the activity

4.1 General

Basics of alpha spectrometry, such as calibration, measurement and evaluation of results are described in the General Chapter α-SPEKT/GRUNDL of this Procedures Manual. For procedure specific informations, it is referred to the Procedure G-α-SPEKT-FISCH-01.

Considering the estimated low activities of Am-241 and the curiumisotopes in samples obtained for analysis in the IMIS routine mode [1], a distance of 1 mm between counting source and detector is recommended. In the pulse height spectrum, full-width-at-half-maximum between 30 keV and 70 keV are achievable using this set-up and considering the properties of the counting sources prepared in Section 0. The lines of the curium

isotopes Cm-243 and Cm-244 are very close in the pulse height spectrum and overlay, so only the sum of their activities is determined.

Due to the low estimated activity in the analysed samples, measurement durations of several days up to three weeks are required. The estimated specific activity of Am-241 is considerably smaller than 1 mBq kg^{-1} fresh mass.

A validation of the procedure using certified standard reference material from the marine environment, e. g. available from the International Atomic Energy Agency (IAEA), is recommended.

4.2 Calibration

For procedure specific informations to the calibration, it is referred to the Procedure G-α-SPEKT-FISCH-01.

4.3 Measurement

For procedure specific informations to the measurement, it is referred to the Procedure G-α-SPEKT-FISCH-01.

5 Calculation of the results

5.1 Equations

5.1.1 Output quantity

The calculation of specific activity of Am-241, Cm-242 and Cm-(243+244) with reference to the fresh mass (FM) is calculated according to Equation (1):

$$a_{\mathrm{r}} = \varphi \cdot R_{\mathrm{n,r}} \tag{1}$$

The procedural calibration factor φ is calculated using Equation (2), while Equation (3) calculates the net count rate of the analyte $R_{\mathrm{n,r}}$ in the selected region of the impulse height spectrum:

$$\varphi = \frac{A_{\mathrm{Tr}}}{m_{\mathrm{A}} \cdot q_{\mathrm{F}}} \cdot \frac{p_{\alpha,\mathrm{Tr}}}{p_{\alpha,\mathrm{r}}} \cdot \frac{f_1 \cdot f_3}{R_{\mathrm{n,Tr}}} \tag{2}$$

$$R_{\mathrm{n,r}} = R_{\mathrm{g,r}} - R_{0,\mathrm{r}} - R_{\mathrm{BL,r}} - R_{\mathrm{n,Tr}} \cdot \frac{q_1 \cdot f_7}{f_3} \tag{3}$$

According to Equation (3), different count rates have to be considered when calculating the net count rate of the analyte $R_{\mathrm{n,r}}$. These are defined in Equations (4) to (6):

$$R_{\mathrm{BL,r}} = A_{\mathrm{BL,r}} \cdot \varepsilon \cdot p_{\alpha,\mathrm{r}} \quad (4)$$

$$R_{\mathrm{n,Tr}} = R_{\mathrm{g,Tr}} - R_{0,\mathrm{Tr}} - R_{\mathrm{BL,Tr}} \quad (5)$$

$$R_{\mathrm{BL,Tr}} = A_{\mathrm{BL,Tr}} \cdot \varepsilon \cdot p_{\alpha,\mathrm{Tr}} \quad (6)$$

In Equations (1) to (6) are:

a_{r} specific activity of radionuclide r, with reference to fresh mass, in Bq·kg^{-1} (FM);

A_{Tr} added activity of the tracer, e. g. Am-243, referenced to the tracer solution certificate, in Bq;

$A_{\mathrm{BL,r}}$ activity of the radionuclide r in the blank counting source, in Bq;

$A_{\mathrm{BL,Tr}}$ activity of the tracers in the blank counting source, in Bq;

f_1 correction factor for radioactive decay of the analyte r between sampling and beginning of the analysis:
$f_1 = \mathrm{e}^{\lambda_{\mathrm{r}} \cdot t_{\mathrm{A}}}$

f_3 correction factor for radioactive decay of the tracer between certification of the tracer solution and beginning of the measurement:
$f_3 = \mathrm{e}^{-\lambda_{\mathrm{Tr}} \cdot t_{\mathrm{Tr}}}$

f_7 correction factor for radioactive decay of the analyte in the tracer solution beween certification of the tracer solution and beginning of the measurement:
$f_7 = \mathrm{e}^{-\lambda_{\mathrm{r}} \cdot t_{\mathrm{Tr}}}$

m_{A} mass of the ash used for analysis in kg;

$p_{\alpha,\mathrm{Tr}}$ sum of the emission intensities of the alpha lines of the tracer;

$p_{\alpha,\mathrm{r}}$ sum of the emission intensities of the alpha lines of radionuclide r.

q_1 proportion of the analyte (radionuclide r) in the tracer solution at the time of certification of the solution;

q_{F} ratio of fresh mass to ash mass;

$R_{\mathrm{BL,r}}$ count rate of radionuclide r in the blank counting source, in s^{-1};

$R_{\mathrm{BL,Tr}}$ count rate of the tracer in the blank counting source, in s^{-1};

$R_{\mathrm{g,r}}$ gross count rate of the radionuclide r, in s^{-1};

$R_{\mathrm{g,Tr}}$ gross count rate of the tracers, in s^{-1};

$R_{\mathrm{n,r}}$ net count rate of radionuclide r, in s^{-1};

$R_{\mathrm{n,Tr}}$ net count rate of the tracer, in s^{-1};

$R_{0,\mathrm{r}}$ background count rate of radionuclide r, in s^{-1};

$R_{0,\mathrm{Tr}}$ background count rate of the tracer, in s^{-1};

t_{m} duration of measurement, in s;

t_0 duration of background measurement, in s;

t_{A} time period between sampling and beginning of the measurement, in s;

t_{Tr} time period between certification of the tracer solution and beginning of the measurement, in s;

ε detection efficiency of the measuring system, in $Bq^{-1}{\cdot}s^{-1}$;

λ_{r} decay constant of radionuclide r, in s^{-1};

λ_{Tr} decay constant of the tracer, in s^{-1};

φ procedural calibration factor, in $Bq{\cdot}kg^{-1}$ s.

The equations described above are almost identical to those from Procedure G-α-SPEKT-FISCH-01 for the analysis of plutonium isotopes.

The basic difference in the present procedure is the term $R_{\mathrm{n,Tr}} \cdot q_1 \cdot f_7/f_3$ in Equation (3), considering a contamination of the tracer solution with the analyte Am-241. This causes covariances with the procedural calibration factor φ in Equation (2).

Note:

If there is no contamination of the tracer with Am-241, the equations may be simplified by omission of the last term, $R_{\mathrm{n,Tr}} \cdot q_1 \cdot f_7/f_3$, in Equation (3) and the corresponding covariances. The latter is considered in the calculation of the standard uncertainties by assigning the value zero to the variable q_1 in the respective equations.

The corrections for the radioactive decay of the radionuclides during measurement may be omitted. In the recent procedure the correction factor f_3 equals one due to the long half life of the tracer Am-243. This is also valid for the correction factor f_7. The sum of the alpha emission intensities is also almost one.

The chemical yield η, which is not occurring explicitly in Equation (2), can also be calculated according to Equation (7) and is usable as quality criterion:

$$\eta = \frac{R_{\mathrm{n,r}}}{\varepsilon \cdot A_{\mathrm{Tr}}} \tag{7}$$

5.1.2 Standard uncertainty of the output quantity

The standard uncertainty of the procedural calibration factor, $u(\varphi)$, and the standard uncertainty of the net count rate of radionuclide r, $u(R_{\mathrm{n,r}})$, are required to determine the standard uncertainty of the specific activity of radionuclide r.

The relative standard uncertainty of the procedural calibration factor, $u_{\mathrm{rel}}(\varphi)$, is calculated from the relative standard uncertainties of the input quantities:

$$u_{\mathrm{rel}}^2(\varphi) = u_{\mathrm{rel}}^2(A_{\mathrm{Tr}}) + u_{\mathrm{rel}}^2(m_{\mathrm{A}}) + u_{\mathrm{rel}}^2(q_{\mathrm{F}}) + u_{\mathrm{rel}}^2\left(R_{\mathrm{n,Tr}}\right) + u_{\mathrm{rel}}^2\left(p_{\alpha,\mathrm{r}}\right) + u_{\mathrm{rel}}^2\left((p_{\alpha,\mathrm{Tr}}\right) \quad (8)$$

To calculate the standard uncertainty of the net count rate of radionuclide r, $u(R_{\mathrm{n,r}})$, the standard uncertainties of count rates described in Equations (4) to (6) are needed. These uncertainties are specified in Euations (9) to (11):

$$u\left(R_{\mathrm{BL,Tr}}\right) = R_{\mathrm{BL,Tr}} \cdot \sqrt{u_{\mathrm{rel}}^2\left(A_{\mathrm{BL,Tr}}\right) + u_{\mathrm{rel}}^2(\varepsilon) + u_{\mathrm{rel}}^2(p_{\alpha,\mathrm{Tr}})} \quad (9)$$

$$u^2\left(R_{\mathrm{n,Tr}}\right) = \frac{R_{\mathrm{n,Tr}}}{t_{\mathrm{m}}} + R_{0,\mathrm{Tr}} \cdot \left(\frac{1}{t_m} + \frac{1}{t_0}\right) + \frac{R_{\mathrm{BL,Tr}}}{t_{\mathrm{m}}} + u^2\left(R_{\mathrm{BL,Tr}}\right) \quad (10)$$

$$u\left(R_{\mathrm{BL,r}}\right) = R_{\mathrm{BL,r}} \cdot \sqrt{u_{\mathrm{rel}}^2\left(A_{\mathrm{BL,r}}\right) + u_{\mathrm{rel}}^2(\varepsilon) + u_{\mathrm{rel}}^2(p_{\alpha,\mathrm{r}})} \quad (11)$$

The combined standard uncertainty of the net count rate of radionuclide r, $u(R_{\mathrm{n,r}})$, is calculated according to Equation (12):

$$u^2\left(R_{\mathrm{n,r}}\right) = \mu_0 \cdot R_{\mathrm{n,r}}^2 + \mu_1 \cdot R_{\mathrm{n,r}} + \mu_2 \quad (12)$$

For the auxiliary quantities μ_0, μ_1 and μ_2, the relations according to Equations (13) to (15) apply:

$$\mu_0 = 0 \quad (13)$$

$$\mu_1 = \frac{1}{t_{\mathrm{m}}} \quad (14)$$

$$\mu_2 = R_{0,\mathrm{r}} \cdot \left(\frac{1}{t_{\mathrm{m}}} + \frac{1}{t_0}\right) + \frac{R_{\mathrm{BL,r}} + R_{\mathrm{n,Tr}} \cdot q_1 \cdot \frac{f_7}{f_3}}{t_{\mathrm{m}}} + u^2\left(R_{\mathrm{BL,r}}\right) + u^2\left(R_{\mathrm{n,Tr}} \cdot \frac{q_1 \cdot f_7}{f_3}\right) \quad (15)$$

With these, Equation (12) converts to Equation (16):

$$u^2(R_{\mathrm{n,r}}) = \frac{R_{\mathrm{n,r}}}{t_{\mathrm{m}}} + R_{0,\mathrm{r}} \cdot \left(\frac{1}{t_m} + \frac{1}{t_0}\right) + \frac{R_{\mathrm{BL,r}} + R_{\mathrm{n,Tr}} \cdot q_1 \cdot \frac{f_7}{f_3}}{t_{\mathrm{m}}} + u^2(R_{\mathrm{BL,r}}) + \\ + u^2\left(R_{\mathrm{n,Tr}} \cdot \frac{q_1 \cdot f_7}{f_3}\right) \tag{16}$$

The standard uncertainty representing the last term in Equation (16) is calculated according to Equation (17):

$$u^2\left(R_{\mathrm{n,Tr}} \cdot \frac{q_1 \cdot f_7}{f_3}\right) = \left(R_{\mathrm{n,Tr}} \cdot \frac{q_1 \cdot f_7}{f_3}\right)^2 \cdot \left[u_{\mathrm{rel}}^2(R_{\mathrm{n,Tr}}) + u_{\mathrm{rel}}^2(q_1) + u_{\mathrm{rel}}^2(f_7) + u_{\mathrm{rel}}^2(f_3)\right] \tag{17}$$

The calculation of the standard uncertainty of the specific activity of radionuclide r, $u(a_{\mathrm{r}})$, requires that the covariance of the two input quantities φ and $R_{\mathrm{n,r}}$ due to the quantities f_3 and $R_{\mathrm{n,Tr}}$ included in both input quantitiest, is considered. It is calculated according to Equation (18) under the assumption that the standard uncertainty of f_3 is omittable:

$$\mathrm{cov}\left(\varphi, R_{\mathrm{n,r}}\right) = \frac{\partial \varphi}{\partial R_{\mathrm{n,Tr}}} \cdot \frac{\partial R_{\mathrm{n,r}}}{\partial R_{\mathrm{n,Tr}}} \cdot u^2(R_{\mathrm{n,Tr}}) = \frac{\varphi \cdot q_1 \cdot f_7}{R_{\mathrm{n,Tr}} \cdot f_3} \cdot u^2(R_{\mathrm{n,Tr}}) \tag{18}$$

It is used to calculate the standard uncertainty of the specific activity $u(a_{\mathrm{r}})$ according to Equation (19):

$$u(a_{\mathrm{r}}) = \sqrt{\left(\frac{\partial a_{\mathrm{r}}}{\partial \varphi}\right)^2 \cdot u^2(\varphi) + \left(\frac{\partial a_{\mathrm{r}}}{\partial R_{\mathrm{n,r}}}\right)^2 \cdot u^2(R_{\mathrm{n,r}}) + 2 \cdot \frac{\partial a_{\mathrm{r}}}{\partial \varphi} \cdot \frac{\partial a_{\mathrm{r}}}{\partial R_{\mathrm{n,r}}} \cdot \mathrm{cov}\left(\varphi, R_{\mathrm{n,r}}\right)} = \\ = \sqrt{R_{\mathrm{n,r}}^2 \cdot u^2(\varphi) + \varphi^2 \cdot u^2(R_{\mathrm{n,r}}) + 2 \cdot a_{\mathrm{r}} \cdot \mathrm{cov}(\varphi, R_{\mathrm{n,r}})} = \\ = \sqrt{a_{\mathrm{r}}^2 \cdot u_{\mathrm{rel}}^2(\varphi) + \varphi^2 \cdot u^2(R_{\mathrm{n,r}}) + 2 \cdot a_{\mathrm{r}} \cdot \mathrm{cov}(\varphi, R_{\mathrm{n,r}})} \tag{19}$$

5.2 Worked example

In the worked examples of the Sections 5.2 and 6.2, the interim results and the result are given with four significant digits. Deviations from the calculated values are possible when using another number of significant digits.

The specific activity of Am-241 is calculated in the following. For the analysis, 1,56 kg fish flesh (FM) and Am-243 as tracer are used. The calculation bases in the following values:

m_{A}	=	52,93·10^{-3} kg;	$u_{\mathrm{rel}}(m_{\mathrm{A}})$	=	3,7786·10^{-3};
$R_{\mathrm{g,Am\text{-}241}}$	=	41,446·10^{-6} s^{-1};	$u(R_{\mathrm{g,Am\text{-}241}})$	=	4,779·10^{-6} s^{-1};
$R_{0,\mathrm{Am\text{-}241}}$	=	2,205·10^{-6} s^{-1};	$u(R_{0,\mathrm{Am\text{-}241}})$	=	1,05·10^{-6} s^{-1};
$A_{\mathrm{BL,Am\text{-}241}}$	=	5,62·10^{-6} Bq;	$u_{\mathrm{rel}}(A_{\mathrm{BL,Am\text{-}241}})$	=	0,929153;
$p_{\alpha,\mathrm{Am\text{-}241}}$	=	1,0016;	$u_{\mathrm{rel}}(p_{\alpha,\mathrm{Am\text{-}241}})$	=	7,887·10^{-3};
$A_{\mathrm{Am\text{-}243}}$	=	49,475·10^{-3} Bq;	$u_{\mathrm{rel}}(A_{\mathrm{Am\text{-}243}})$	=	10,439·10^{-3};
$A_{\mathrm{BL,Am\text{-}243}}$	=	30·10^{-6} Bq;	$u_{\mathrm{rel}}(A_{\mathrm{BL,Am\text{-}243}})$	=	0,5;
$R_{\mathrm{g,Am\text{-}243}}$	=	13,9506·10^{-3} s^{-1};	$u(R_{\mathrm{g,Am\text{-}243}})$	=	87,686·10^{-6} s^{-1};
$R_{0,\mathrm{Am\text{-}243}}$	=	5,5115·10^{-6} s^{-1};	$u(R_{0,\mathrm{Am\text{-}243}})$	=	1,66·10^{-6} s^{-1};
$p_{\alpha,\mathrm{Am\text{-}243}}$	=	0,9998;	$u_{\mathrm{rel}}(p_{\alpha,\mathrm{Am\text{-}243}})$	=	0,69·10^{-3};
ε	=	0,3537 Bq^{-1}·s^{-1};	$u_{\mathrm{rel}}(\varepsilon)$	=	0,013288;
q_{F}	=	29,53;	$u_{\mathrm{rel}}(q_{\mathrm{F}})$	=	0,02;
q_1	=	0,294·10^{-3};	$u_{\mathrm{rel}}(q_1)$	=	0,075.

The standard uncertainty of the following input quantities are omittable:

t_{m}	=	1,8144·10^{6} s;	f_1	=	1,000439;
t_0	=	2,0·10^{6} s;	f_3	=	0,99944;
t_{A}	=	8,640·10^{6} s;	f_7	=	0,9905 ;
t_{Tr}	=	1,878·10^{8} s.			

The Equations (4) to (6) are used to calculate the respective net count rates:

$$R_{\mathrm{BL,Am-243}} = 30 \cdot 10^{-6}\ \mathrm{Bq} \cdot 0{,}3537\ \mathrm{Bq^{-1} \cdot s^{-1}} \cdot\ 0{,}9998 =\ 10{,}61 \cdot 10^{-6}\ \mathrm{s^{-1}}$$

$$R_{\mathrm{n,Am-243}} = (13{,}9506 \cdot 10^{-3} - 5{,}5115 \cdot 10^{-6} - 10{,}61 \cdot 10^{-6})\ \mathrm{s^{-1}} = 13{,}93 \cdot 10^{-3}\ \mathrm{s^{-1}}$$

$$R_{\mathrm{BL,Am-241}} = 5{,}62 \cdot 10^{-6}\ \mathrm{Bq} \cdot 0{,}3537\ \ \mathrm{Bq^{-1} \cdot s^{-1}} \cdot\ 1{,}0016 =\ 1{,}991 \cdot 10^{-6}\ \mathrm{s^{-1}}$$

The net count rate of Am-241 is calculated according to Equation (3)

$$R_{\mathrm{n,Am-241}} = 41{,}446 \cdot 10^{-6}\ \mathrm{s^{-1}} - 2{,}205 \cdot 10^{-6}\ \mathrm{s^{-1}} - 1{,}991 \cdot 10^{-6}\ \mathrm{s^{-1}} -$$

$$-13{,}93 \cdot 10^{-3}\ \mathrm{s^{-1}} \cdot \frac{0{,}294 \cdot 10^{-3} \cdot 0{,}9905}{0{,}99944} = 33{,}19 \cdot 10^{-6}\ \mathrm{s^{-1}}$$

and leads via the procedural calibration factor calculated by using Equation (2)

$$\varphi = \frac{49{,}475 \cdot 10^{-3}}{52{,}93 \cdot 10^{-3} \cdot 29{,}53} \cdot \frac{0{,}99980}{1{,}0016} \cdot \frac{1{,}000439 \cdot 0{,}99944}{13{,}93 \cdot 10^{-3}}\ \mathrm{Bq \cdot s \cdot kg^{-1}} =$$

$$= 2{,}268\ \mathrm{Bq \cdot s \cdot kg^{-1}}$$

to the specific activity of Am-241 according to Equation (1):

$$a_{\mathrm{Am-241}} = 2{,}268\ \mathrm{Bq \cdot s \cdot kg^{-1}} \cdot 33{,}19 \cdot 10^{-6}\ \mathrm{s^{-1}} =$$
$$= 75{,}27 \cdot 10^{-6}\ \mathrm{Bq \cdot kg^{-1}}$$

The standard uncertainties of the count rates from the blank counting source are calculated according to Equations (9) and (11) result in:

$$u\left(R_{\mathrm{BL,Am-243}}\right) = 10{,}61 \cdot 10^{-6}\ \mathrm{s^{-1}} \cdot \sqrt{0{,}50^2 + 0{,}013288^2 + 0{,}00069^2} =$$
$$= 5{,}307 \cdot 10^{-6}\ \mathrm{s^{-1}}$$

$$u\left(R_{\mathrm{BL,Am-241}}\right) = 1{,}991 \cdot 10^{-6} \cdot \sqrt{0{,}929153^2 + 0{,}013288^2 + 0{,}007887^2} =$$
$$= 1{,}850 \cdot 10^{-6}\ \mathrm{s^{-1}}$$

For calculation of the standard uncertainty of the net count rate of the Am-243 tracer according to Equation (10) requires the calulation of the single terms, first:

$$\frac{R_{\mathrm{n,Am-243}}}{t_{\mathrm{m}}} = \frac{13{,}93 \cdot 10^{-3}}{1{,}8144 \cdot 10^{6}}\ \mathrm{s^{-1}} = 7{,}677 \cdot 10^{-9}\ \mathrm{s^{-1}}$$

$$R_{0,\mathrm{Am-243}} \cdot \left(\frac{1}{t_{\mathrm{m}}} + \frac{1}{t_0}\right) = 5{,}5115 \cdot 10^{-6} \cdot \left(\frac{1}{1{,}8144 \cdot 10^{6}} + \frac{1}{2{,}0 \cdot 10^{6}}\right)\ \mathrm{s^{-1}} =$$
$$= 5{,}793 \cdot 10^{-12}\ \mathrm{s^{-1}}$$

$$\frac{R_{\mathrm{BL,Am-243}}}{t_{\mathrm{m}}} = \frac{10{,}61 \cdot 10^{-6}}{1{,}8144 \cdot 10^{6}}\ \mathrm{s^{-1}} = 5{,}848 \cdot 10^{-12}\ \mathrm{s^{-1}}$$

$$u^2\left(R_{\mathrm{BL,Am-243}}\right) = (5{,}307 \cdot 10^{-6})^2\ \mathrm{s^{-1}} = 28{,}16 \cdot 10^{-12}\ \mathrm{s^{-1}}$$

The standard uncertainty of the net count rate of the tracer Am-243 $u(R_{\mathrm{n,Am\text{-}243}})$ is calculated using Equation (10) and results in:

$$u\left(R_{\mathrm{n,Am-243}}\right) = \sqrt{7{,}677 \cdot 10^{-9} + (5{,}793 + 5{,}848 + 28{,}16) \cdot 10^{-12}}\ \mathrm{s^{-1}} = 87{,}85 \cdot 10^{-6}\ \mathrm{s^{-1}}$$

For calculation of the standard uncertainty of the net count rate Am-241 according to Equation (16), first of all the five values of the single terms and finally the last term of Equation (17) are calculated:

$$\frac{R_{\mathrm{n,Am-241}}}{t_{\mathrm{m}}} = \frac{33{,}19 \cdot 10^{-6}}{1{,}8144 \cdot 10^{6}}\ \mathrm{s}^{-2} = 18{,}29 \cdot 10^{-12}\ \mathrm{s}^{-2}$$

$$R_{0,\mathrm{Am-241}} \cdot \left(\frac{1}{t_{\mathrm{m}}} + \frac{1}{t_0}\right) = 2{,}205 \cdot 10^{-6} \cdot \left(\frac{1}{1{,}8144 \cdot 10^{6}} + \frac{1}{2{,}0 \cdot 10^{6}}\right)\mathrm{s}^{-2} = 2{,}318 \cdot 10^{-12}\ \mathrm{s}^{-2}$$

$$\frac{R_{\mathrm{BL,Am-241}} + R_{\mathrm{n,Am-243}} \cdot q_1 \cdot \frac{f_7}{f_3}}{t_{\mathrm{m}}} =$$

$$= \frac{1{,}991 \cdot 10^{-6} + 13{,}93 \cdot 10^{-3} \cdot 0{,}294 \cdot 10^{-3} \cdot \frac{0{,}9905}{0{,}99944}}{1{,}8144 \cdot 10^{6}}\ \mathrm{s}^{-2} = 3{,}334 \cdot 10^{-12}\ \mathrm{s}^{-2}$$

$$u^2\left(R_{\mathrm{BL,Am-241}}\right) = (1{,}850 \cdot 10^{-6})^2\ \mathrm{s}^{-2} = 3{,}423 \cdot 10^{-12}\ \mathrm{s}^{-2}$$

$$u^2\left(R_{\mathrm{n,Am-243}} \cdot \frac{q_1 \cdot f_7}{f_3}\right) = \left(\frac{13{,}93 \cdot 10^{-3} \cdot 0{,}294 \cdot 10^{-3} \cdot 0{,}9905}{0{,}99944}\right)^2 \cdot$$

$$\cdot \left[\left(\frac{87{,}85 \cdot 10^{-6}}{13{,}93 \cdot 10^{-3}}\right)^2 \mathrm{s}^{-2} + 0{,}075^2\right]\mathrm{s}^{-2} = 9{,}333 \cdot 10^{-14}\ \mathrm{s}^{-2}$$

This results in a standard uncertainty of the net count rate of Am-241 $u(R_{\mathrm{n,Am\text{-}241}})$ of:

$$u^2\left(R_{\mathrm{n,Am-241}}\right) = (18{,}29 + 2{,}318\ + 3{,}334 + 3{,}423) \cdot 10^{-12}\ \mathrm{s}^{-2} + 9{,}333 \cdot 10^{-14}\ \mathrm{s}^{-2} =$$

$$= 27{,}46 \cdot 10^{-12}\ \mathrm{s}^{-2}$$

$$u\left(R_{\mathrm{n,Am-241}}\right) = \sqrt{27{,}46178 \cdot 10^{-12}}\ \mathrm{s}^{-1} = 5{,}240 \cdot 10^{-6}\ \mathrm{s}^{-1}$$

The relative standard uncertainty of the procedural calibration factor $u_{\mathrm{rel}}(\varphi)$ calculated by Equation (8) results in:

$$u_{\mathrm{rel}}(\varphi) = \{10{,}439^2 \cdot 10^{-6} + 3{,}7786^2 \cdot 10^{-6} + 0{,}02^2 + 6{,}307^2 \cdot 10^{-6} +$$

$$+ 7{,}887^2 \cdot 10^{-6} + 0{,}69^2 \cdot 10^{-6}\}^{\frac{1}{2}} = 25{,}01 \cdot 10^{-3}$$

In the following, the conbtriburion of the covariance calculated by Equation (18) results in:

$$\operatorname{cov}\left(\varphi, R_{\mathrm{n,Am-241}}\right) = \frac{2{,}268 \cdot 0{,}294 \cdot 10^{-3} \cdot 0{,}9905}{13{,}93 \cdot 10^{-3} \cdot 0{,}99944} \cdot 87{,}85^2 \cdot 10^{-12}\ \mathrm{Bq \cdot kg^{-1}} =$$
$$= 0{,}3661 \cdot 10^{-9}\ \mathrm{Bq \cdot kg^{-1}}$$

For the final calculation of the standard uncertainty of the specific activity of Am-241 $u(a_{\mathrm{Am\text{-}241}})$ with Equation (19), the three values of the single terms need to be calculated, first:

$$a_{\mathrm{Am-241}}^2 \cdot u_{\mathrm{rel}}^2(\varphi) = (75{,}27 \cdot 10^{-6})^2 \cdot (25{,}01 \cdot 10^{-3})^2\ \mathrm{Bq^2 \cdot kg^{-2}} =$$
$$= 3{,}544 \cdot 10^{-12}\ \mathrm{Bq^2 \cdot kg^{-2}}$$

$$\varphi^2 \cdot u^2\left(R_{\mathrm{n,Am-241}}\right) = 2{,}268^2 \cdot (5{,}240 \cdot 10^{-6})^2\ \mathrm{Bq^2 \cdot kg^{-2}} =$$
$$= 0{,}1412 \cdot 10^{-9}\ \mathrm{Bq^2 \cdot kg^{-2}}$$

$$2 \cdot a_{\mathrm{Am-241}} \cdot \operatorname{cov}\left(\varphi, R_{\mathrm{n,Am-241}}\right) = 2 \cdot 75{,}27 \cdot 10^{-6} \cdot 0{,}3661 \cdot 10^{-9}\ \mathrm{Bq^2 \cdot kg^{-2}} =$$
$$= 5{,}511 \cdot 10^{-14}\ \mathrm{Bq^2 \cdot kg^{-2}}$$

Therewith, the standard uncertainty of the specific activity of Am-241 $u(a_{\mathrm{Am\text{-}241}})$ by using Equation (19) results in:

$$u(a_{\mathrm{Am-241}}) = \sqrt{3{,}544 \cdot 10^{-12} + 0{,}1412 \cdot 10^{-9} + 5{,}511 \cdot 10^{-14}}\ \mathrm{Bq \cdot kg^{-1}} =$$
$$= 12{,}03 \cdot 10^{-6}\ \mathrm{Bq \cdot kg^{-1}}$$

The specific activity of Am-241 in fish flesh related to fresh mass $a_{\mathrm{Am\text{-}241}}$ results to:

$$a_{\mathrm{Am-241}} = (75{,}27 \pm 12{,}03) \cdot 10^{-6}\ \mathrm{Bq \cdot kg^{-1}}$$

5.3 Consideration of the uncertainties

Uncertainty contributions arising from sampling are not taken into account in the frame–work of this Procedures Manual, as these can depend on many different and often not quantifiable factors.

The activities of Am-241 and the curium isotopes are normally in the range of the decision threshold, so the proportion of the counting statistics is dominating. The combined standard uncertainy normally amounts between 10 % and 30 %.

The examination of the components of the uncertainty budget (see Section 7.1) shows that the blank value of the analyte is in many cases the second important contribution to the uncertainty. Another contribution to the uncertainty may become dominant, when the counting source is relatively thick or contaminated. This leads to overlapping alphalines of the interesting radionuclides due to strong tailing; an estimation of this uncertainty contribution may be possible using linear unfolding.

6 Characteristic limits of the procedure

The calculation of the characteristic limits follows the standard series ISO 11929 [2].

An Excel spreadsheet (see Section 7.1) as well as a project file for the software Uncert-Radio (see Section 7.2) are available on the website of this Procedures Manual.

Further considerations concerning the characteristic limits are to be found in the General Chapters ERK/NACHWEISGR-ISO-01 and ERK/NACHWEISGR-ISO-02 of this Procedures Manual.

6.1 Equations

6.1.1 Decision threshold

The decision threshold a_r^* is calculated from the auxiliary quantitiy μ_2 using equation (15) and the quantile of the standard normal distribution to the type I error α, $k_{1-\alpha}$, according to Equation (20):

$$a_r^* = k_{1-\alpha} \cdot \varphi \cdot \sqrt{\mu_2} = k_{1-\alpha} \cdot \sqrt{\varphi^2 \cdot \mu_2} \tag{20}$$

6.1.2 Detection limit

Equation (21) for calculation of the detection limit $a_r^\#$ reads:

$$a_r^\# = \frac{a_r^* \cdot \psi}{\theta} \cdot \left[1 + \sqrt{1 - \frac{\theta}{\psi^2} \cdot \left(1 - \frac{k_{1-\beta}^2}{k_{1-\alpha}^2} \right)} \right] \tag{21}$$

with the auxiliary quantities

$$\theta = 1 - k_{1-\beta}^2 \cdot \left(u_{rel}^2(\varphi) + \mu_0 \right) \tag{22}$$

$$\psi = 1 + \frac{k_{1-\beta}^2}{2 \cdot a_r^*} \cdot \varphi \cdot \mu_1 \tag{23}$$

and the quantile, $k_{1-\beta}$, of the standard normal distribution to the type II error β.

The additionally required auxiliary quanities μ_0, μ_1 und $u_{\mathrm{rel}}(\varphi)$ are calculated according to Equations (13), (14) and as root of the results of Equation (8).

6.1.3 Limits of the coverage interval

The calculation of limits of the coverage interval is not required.

6.2 Worked example

Using the values calculated in Section 5.2 and application of $k_{1\text{-}\alpha}$ = 3 and the value of the auxiliary quantity obtained with Equation (15)

$$\mu_2 = (2{,}318 + 3{,}334 + 3{,}423) \cdot 10^{-12}\ \mathrm{s}^{-2} + 9{,}333 \cdot 10^{-14}\ \mathrm{s}^{-2} = 9{,}168 \cdot 10^{-12}\ \mathrm{s}^{-2}$$

the decision threshold according Equation (20) calculates to:

$$a^{*}_{\mathrm{Am-241}} = 3 \cdot 2{,}268 \cdot \sqrt{9{,}168 \cdot 10^{-12}}\ \mathrm{Bq \cdot kg^{-1}} = 20{,}6 \cdot 10^{-6}\ \mathrm{Bq \cdot kg^{-1}}$$

The following values for the auxiliary quantities calculated with Equations (22) and (23) using $k_{1\text{-}\beta}$ = 1,645 lead to:

$$\theta = 1 - 1{,}645^2 \cdot (25{,}01 \cdot 10^{-3})^2 = 0{,}9983$$

$$\psi = 1 + \frac{1{,}645^2}{2 \cdot 20{,}6 \cdot 10^{-6}} \cdot 2{,}268 \cdot \frac{1}{1{,}8144 \cdot 10^{6}} = 1{,}082$$

Therewith, the detection limit of the specific activity $a^{\#}_{\mathrm{Am\text{-}241}}$ according to Equation (21) calculates to:

$$a^{\#}_{\mathrm{Am-241}} = \frac{20{,}6 \cdot 10^{-6} \cdot 1{,}082}{0{,}9983} \cdot \left[1 + \sqrt{1 - \frac{0{,}9983}{1{,}082^{\,2}} \cdot \left(1 - \frac{1{,}645^2}{3^2}\right)}\right] \mathrm{Bq \cdot kg^{-1}} =$$

$$= 36{,}51 \cdot 10^{-6}\ \mathrm{Bq \cdot kg^{-1}}$$

7 Software supported calculation

7.1 View of the Excel spreadsheet

Procedure for determining the specific activities of americium-241 and curium isotopes in fish by alpha spectrometry

G-α-SPEKT-FISCH-02 Version February 2022
Procedures Manual for monitoring of radioactive substances in the environment and of external radiation
(Messanleitungen für die „Überwachung radioaktiver Stoffe in der Umwelt und externer Strahlung“, ISSN 1865-8725)

SAMPLE IDENTIFICATION: Cod ANALYTE: **Am-241**

#Number of parameters p	18
k_alpha	3
k_beta	1,645
gamma	0,05

Create Excel variables!

User-Input: Input of values
Definition Excel variables
Input of Excel Formulae
Excel-VBA: **#Keywords**
Values from Vbasic

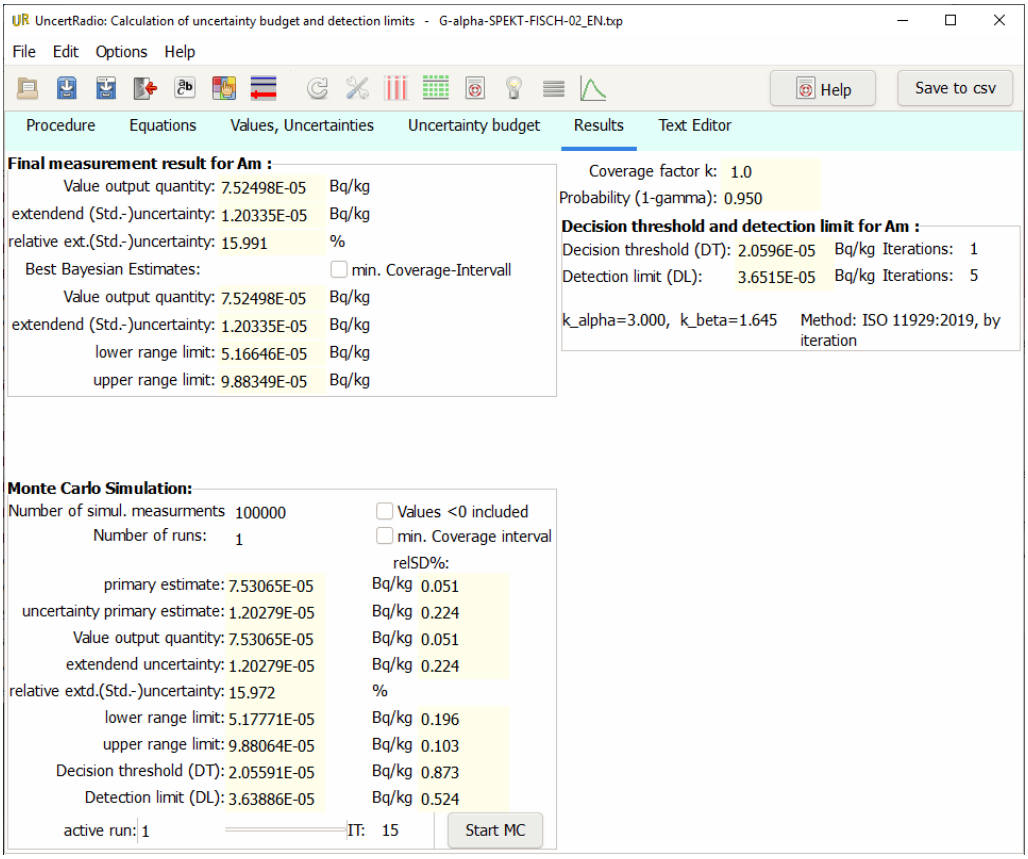
	Data input:		variable names:			Uncertainty budget:		
	#Values of parameters p	Unit	Excel variable	**Input values**	**StdDev**	**partial derivatives**	**uncertainty budget**	**budget in %**
p 1	**#Number of gross counts Ng**		Ng	7,520E+01	8,672E+00	1,250E-06	1,084E-05	8,109E+01
p 2	background count rate in the lines the analyte (Am-241)	1/s	R0	2,205E-06	1,050E-06	-2,267E+00	2,381E-06	3,914E+00
p 3	gross count rate of the tracer (Am-243)	1/s	RgTr	1,395E-02	8,769E-05	-6,061E-03	5,315E-07	1,951E-01
p 4	background count rate in the line of the tracer	1/s	R0Tr	5,512E-06	1,660E-06	6,061E-03	1,006E-08	6,990E-05
p 5	duration of measurement	s	tm	1,814E+06		-5,179E-11	0,000E+00	0,000E+00
p 6	activity of the analyte in the blank couting source	Bq	ABL	5,620E-06	5,222E-06	-8,032E-01	4,194E-06	1,215E+01
p 7	activity of the tracer in the blank counting source	Bq	ABLT	3,000E-05	1,500E-05	2,143E-03	3,215E-08	7,138E-04
p 8	added activity of the tracer	Bq/mL	_CT1	1,979E-01	1,999E-03	3,802E-04	7,600E-07	3,989E-01
p 9	added volumen of tracer solution	mL	_VT1	2,500E-01	6,600E-04	3,010E-04	1,987E-07	2,725E-02
p 10	Impurity ratio analyte/tracer in the tracer solution		_q1	2,940E-04	2,205E-05	-3,131E-02	6,904E-07	3,292E-01
p 11	mass of the ash used for analysis	kg	ma	5,293E-02	2,000E-04	-1,422E-03	2,843E-07	5,583E-02
p 12	ratio of fresh mass to ash mass		qF	2,953E+01	5,906E-01	-2,548E-06	1,505E-06	1,564E+00
p 13	sum of the emission intensities of the tracer		PaT	9,998E-01	6,900E-04	7,533E-05	5,198E-08	1,866E-03
p 14	sum of the emission intensities of the analyte		PaA	1,002E+00	7,900E-03	-7,964E-05	6,291E-07	2,733E-01
p 15	detection efficiency		eps	3,537E-01	4,700E-03	-1,258E-05	5,913E-08	2,414E-03
p 16	decay correction factor f1		_f1	1,000E+00	0,000E+00	7,522E-05	0,000E+00	0,000E+00
p17	decay correction factor f3		_f3	9,994E-01	0,000E+00	8,450E-05	0,000E+00	0,000E+00
p18	decay correction factor f7		_f7	9,905E-01	0,000E+00	-9,293E-06	0,000E+00	0,000E+00
	(List can be continued here)							
	Model section		**c = phix * Rn**					
	Auxiliary equations h			(Formulae)				
h 1	**#Gross count rate Rg**	1/s	RgA	4,145E-05				
h 2	count rate in the alpha lines of Am-241 in a blank counting source	1/s	RBL	1,991E-06				
h 3	count rate in the alpha lines of the Am-243 tracer in a blank counting source	1/s	RBLT	1,061E-05				
h 4	net count rate of the tracer Am-243	1/s	RnT	1,393E-02				
h 5	added activity of the Am-243 tracer	Bq	Atr	4,948E-02				
h 6	chemical yield		eta	7,963E-01				
h 7	impurity factor		QIMP	2,914E-04				
	(List can be continued here)							
	#Net count rate Rn	1/s	Rn	3,319E-05				
	#Calibration factor, proc.dep.	Bq*s/kg	phix	2,267E+00				
	#Value output quantity	Bq/kg	Result	7,525E-05	3,65147E-05	<-- output value modifiable by VBA		
	#Combined standard uncertainty	Bq/kg	uResult	1,203E-05				
	#Decision threshold	Bq/kg		2,060E-05				
	#Detection limit	Bq/kg		3,651E-05				

Calculate!

further derived values (DIN ISO 11929):			
Auxiliary quantity Omega		Omega	1,000E+00
Best estimate	Bq/kg	BestEst	7,525E-05
Uncertainty best estimate	Bq/kg		1,203E-05
Lower confidence limit	Bq/kg		5,166E-05
Upper confidence limit	Bq/kg		9,883E-05

The corresponding Excel spreadsheet is available on the website of this Procedures Manual.

7.2 View of the UncertRadio result page



The corresponding UncertRadio project file is available on the website of this Procedures Manual.

8 Catalogue of the chemicals und equipment

8.1 Chemicals

The chemicals used should be of analytically pure quality.

- Am-243-tracer solution: ca. 200 mBq·ml^{-1} in HNO_3 (8 mol·l^{-1});
- ammonia, NH_3: 13,4 mol·l^{-1};
- slight ammonia-containing water: dest. water with ammonia solution, pH ca. 8
- ammonium oxalate solution: 0,32 mol·l^{-1}
  dissolve 4,6 g $(NH_4)_2C_2O_4 \cdot H_2O$ in destilled water and fill up with dest. water to 100 ml;
- anion exchange resin 1: 1 X 4, 100 mesh – 200 mesh, Cl^--Form;
- anion exchange resin 2: 1 X 8, 100 mesh – 200 mesh, Cl^--Form;
- cation exchange resin: 50 W X 8, 100 mesh – 200 mesh, H^+-Form;

— cyclohexane;

— di-n-butyl N,N-diethylcarbamoyl-phosphonate (DDCP) in n-heptane: 0,5 mol·l^{-1}
fill up 146,68 g DDCP with n–heptane to 1000 ml;

— hydrofluoric acid, HF: 22,6 mol·l^{-1}

— cleansing agent: e. g. RBS-50®-liquid concentrate, 2 % in destilled water;

— methanol;

— sodium nitrite, $NaNO_2$;

— n-heptane;

— nitric acid, HNO_3: 14,4 mol·l^{-1};

— nitric acid, HNO_3: 12 mol·l^{-1}
fill up 833 ml HNO_3 (14,4 mol·l^{-1}) with dest. water to 1000 ml;

— nitric acid, HNO_3: 8 mol·l^{-1}
fill up 554 ml HNO_3 (14,4 mol·l^{-1}) with dest. water to 1000 ml;

— nitric acid, HNO_3: 2 mol·l^{-1}
fill up 139 ml HNO_3 (14,4 mol·l^{-1}) with dest. water to 1000 ml;

— nitric acid, HNO_3: 0,1 mol·l^{-1}
fill up 6,95 ml HNO_3 (14,4 mol·l^{-1}) with dest. water to 1000 ml;

— nitric acid, HNO_3, in methanol: 0,1 mol·l^{-1}
fill up 69 ml HNO_3 (14,4 mol·l^{-1}) with 931 ml methanol to 1000 ml;

— hydrochloric acid, HCl: 12,1 mol·l^{-1};

— hydrochloric acid, HCl: 9 mol·l^{-1}
fill up 744 ml HCl (12,1 mol·l^{-1}) with dest. water to 1000 ml;

— hydrochloric acid, HCl: 4 mol·l^{-1}
fill up 331 ml HCl (12,1 mol·l^{-1}) with dest. water to 1000 ml;

— hydrochloric acid, HCl: 1 mol·l^{-1}
fill up 83 ml HCl (12,1 mol·l^{-1}) with dest. water to 1000 ml;

— hydrochloric acid, HCl, in methanol: 0,1 mol·l^{-1}
fill up 124 ml HCl (12,1 mol·l^{-1}) with dest. water to 1000 ml;

— tri-n-octylphosphinoxid (TOPO): 0,2 mol·l^{-1}
fill up 77,13 g TOPO with cyclohexane to 1000 ml;

— xylole.

8.2 Equipment

8.2.1 Laboratory equipment

The following equipment is used for the procedure:

— laboratory balance and/or analytical balance;
— drying oven;
— exsiccator;
— magnetic stirrer with heating plate;
— ultrasonic bath;
— sand bath;
— diverse variable volume micropipettors;
— glass beakers (250 ml, 600 ml, 1000 ml);
— centrifuge, equipped with beakers made of polyethylene (400 ml);
— separating funnel (250 ml, 1000 ml);
— chromatography columns with reservoir and teflon valve (length 10 cm, inner diameter 8 mm) to hold the anion exchange resin;
— 0,45 µm glass fibre filter, adapted to the inner diameter of the chromatography column used;
— crystallizing dish;
— stainless steel plates (diameter 25 mm, V2A-steel, material identifier 1.4301g);
— electrolysis apparatus (see Figure 1);
— constant current power supply (max. 30 V, 5 A).
— bulb condenser

8.2.2 Measuring devices

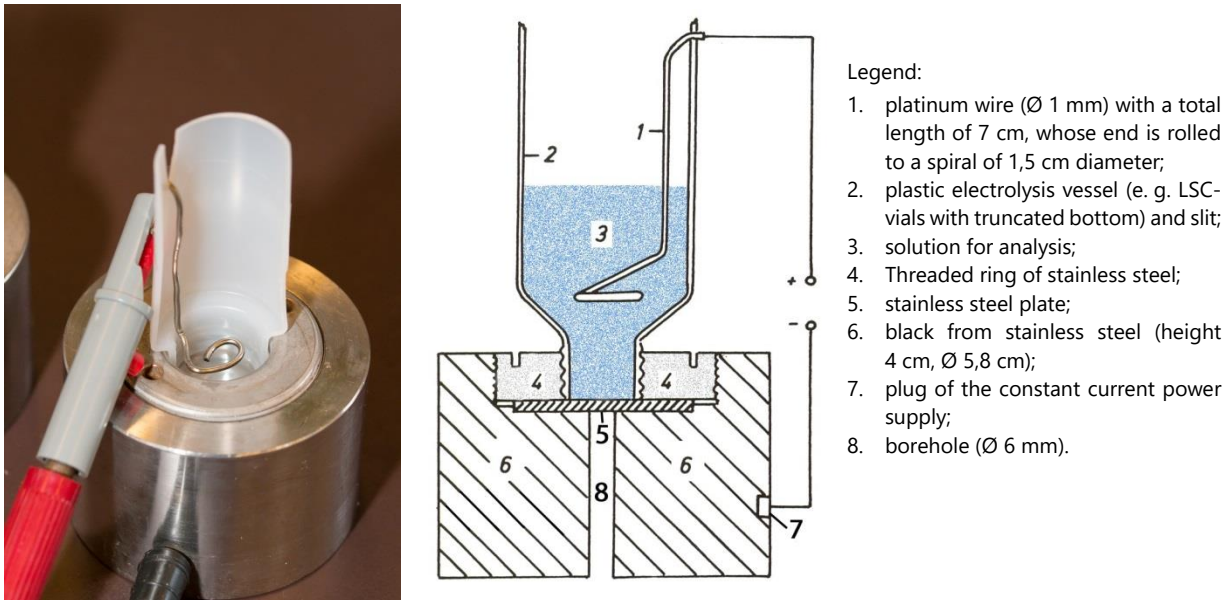
— alpha spectrometer with ion-implanted Si-semiconductor detector (300 mm^2 or 450 mm^2, approx. 20 keV full width at half peak maximum);
— measurement electronics;

— vaccuum system;

— measurement and evaluation software.

8.2.3 Electrodeposition apparatus

The eletrodeposition apparatus is presented schematically in Figure 1.



Legend:

1. platinum wire (Ø 1 mm) with a total length of 7 cm, whose end is rolled to a spiral of 1,5 cm diameter;
2. plastic electrolysis vessel (e. g. LSC-vials with truncated bottom) and slit;
3. solution for analysis;
4. Threaded ring of stainless steel;
5. stainless steel plate;
6. black from stainless steel (height 4 cm, Ø 5,8 cm);
7. plug of the constant current power supply;
8. borehole (Ø 6 mm).

Fig. 1: Apparatus for electrochemical deposition of plutonium, (not in scale)

A new electrolysis vessel is used for each electrodeposition procedure in order to avoid cross contamination. Stainless steel plates prepared according to Section 8.3.3.2 must be connected tight fitting to the stainless steel plate and must be connected tot he minus-pole of the constant current power supply. The platinum electrode taken out of the nitric acid is rinsed with distilled water and attached in the slit of the electrolysis vessel at a distance of approximately 10 mm to stainless steel plate.

A central borehole of 6 mm allows to lift the prepared counting soure to the top of the stainless steel block by pushing a bar from the bottom.

The analysis solution is thoroughly mixed via gas formation and process heat during electrolysis. The plastic electrolysis vessel is covered by a suitable single bulb condenser (not included in Figure 1) to reduce losses through evaporation.

8.3 Preliminary work

8.3.1 Preparation of glassware

All glassware used is placed in 70 °C warm 2 % solution of a laboratory cleansing agent overnight. Afterwards, the are thoroughly rinsed with tap water, shortly put into hydrochloric acid (1 mol l^{-1}) and thoroughly rinsed with distilled water.

8.3.2 Preparation of the ion exchange columns

If only chromatography columns without a frit are available, a glass wool plug is inserted into the column. A glass-fibre filter with 0,45 µm pore size is placed on its top and the required ion exchange resin is filled into the column as outlined in Sections 8.3.2.1 or 8.3.2.4.

8.3.2.1 Packing the 2-layer ion exchange column

On the glass-fibre filter, a 4 cm high layer of anion exchange resin 2 is filled into the column. An additional layer of 8 cm cation exchange resin is placed on top of it and covered by an additional glass-fibre filter.

8.3.2.2 Conditioning of the 2-layer ion exchange column

The 2-layer ion exchange resin is washed with 20 ml hydrochloric acid (9 mol l^{-1}) at a flow rate of 1 ml per minute.

Note:
The two-layer ion exchange resin must remain moistened througout the workflow. The column loaded with resin must not run dry.

8.3.2.3 Conversion of the anion exchange resin from chloride into nitrate form

The anion exchange resin 1 is converted into the nitrate form by placing it in nitric acid (8 mol·l^{-1}) for at least 24 hours.

After that, the resin is rinsed two or three times with approx. 1,5 bed volumes of nitric acid (8 mol·l^{-1}). The rinsing solution is either sucked up or decanted, depending on the quality of the resin. The prepared resin is stored in 1,5 bed volumes of distilled water.

8.3.2.4 Packing of the anion exchange column

On top of the glass fibre filter, the converted anion exchange resin 1 prepared according to Section 8.3.2.3 is filled to a height of 5 cm into the column and is covered by an additional glass-fibre filter.

8.3.2.5 Conditioning of the anion exchange resin

The packed anion exchange column is conditioned using 20 ml methanol-nitric-acid-mixture (1 mol·l^{-1} HNO_3 / 93 % CH_3OH) at a flow rate of 1 ml per minute.

Note:
The anion exchange resin must remain moistened througout the workflow. The column loaded with redin must not run dry.

8.3.3 Preparation of the electrodeposition

8.3.3.1 Cleaning and functional test of the electrodeposition apparatus

The stainless steel block of the electrodeposition apparatus is cleaned as described in Section 8.3.1 for glassware.

A cleaning electrodesposition (see Section 3.4) without tracer is frequently carried out for one hour to test the stainless steel block and the platinum electrode for potential contamination. The resulting stainless steel plate is analysed as control. Is the cleaning electrolysis carried out as operational test, only, the stainless steel plate may be discarded.

8.3.3.2 Preparation of the stainless steel plates

The stainless steel plates are treated with 2 % RBS-50-solution in an ultrasonic bath at 50 °C for 5 minutes, first. Afterwards, they are thoroughly cleaned with destilled water and onece with ethanol before stored in ethanol. Before use, prepared stainless steel plates are removed out oft he storage solution and dried at approximately 70 °C on a heating plate.

References

[1] *Allgemeine Verwaltungsvorschrift zum integrierten Mess- und Informationssystem zur Überwachung der Radioaktivität in der Umwelt (IMIS) nach dem Strahlenschutz-vorsorgegesetz (AVV-IMIS)*. Bundesanzeiger, 2006, Nr. 244a from 13.12.2006, S. 4-80.

[2] Standard series ISO 11929:2019, *Determination of the characteristic limits (decision threshold, detection limit and limits of the coverage interval) for measurements of ionizing radiation — Fundamentals and application (Parts 1 to 3)*.