Procedure for determining the specific activities of plutonium, americium and curium in marine sediment by alpha spectrometry

D-α-SPEKT-MSEDI-01

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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")

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1 Scope

The procedure outlined in the following is suitable for determining the specific activities of plutonium, americium and curium in marine sediment according to the Radiation Protection Act (Strahlenschutzgesetz, StrlSchG) in accordance with the routine operation mode of the General Administrative Provision „Integrated Measurement and Information System for monitoring the environmental radioactivity (IMIS) according to the Radiation Protection Precautionary Act" (AVV-IMIS) [1].

2 Sampling

A detailed description of sampling is given in procedure D-γ-SPEKT-MSEDI-01.

3 Analysis

3.1 Principle of the procedure

The principle of the procedure is described in the procedure D-α-SPEKT-MWASS-01; the procedure itself is designed for dry masses of five grams to ten grams.

3.2 Sample preparation

Sampling preparation is carried out according to procedure D-γ-SPEKT-MSEDI-01. After the gamma spectrometric measurement of the dried marine sediments a representative subsample with a mass of usually 10 g is taken for the radiochemical separation of the transuranic elements

3.3 Radiochemical separation

3.3.1 The representative subsample is weighed into a 250-ml-beaker. To determine the chemical yield, known activities of about 15 mBq to 40 mBq of the radioactive tracers Pu-242 and Am-243, which are traceable to national primary standards, are added.

3.3.2 After addition of 20 ml to 30 ml of concentrated nitric acid (about 15 $mol \cdot l^{-1}$), the suspension is heated for at least 15 minutes while stirring on a heating plate.

3.3.3 After cooling, the suspension is transferred to a 500-ml-centrifuge tube and centrifuged until complete separation at about 1510 times of acceleration of gravity (1510 *g*) for three minutes. The supernatant is decanted into a 2-l-beaker.

Note:
If the centrifuge shows only revolutions per minute, the manual for the centrifuge/rotor should to be checked.

3.3.4 The precipitate is mixed with 100 ml to 150 ml of concentrated hydrochloric acid (12 mol·l^{-1}) and heated for at least 15 minutes while stirring on a heating plate.

3.3.5 After cooling, centrifugation is carried out according to step 3.3.3. The supernatant is added to the nitric acid extract from step 3.3.3 in the 2-l-beaker.

3.3.6 Steps 3.3.4 and 3.3.5 are repeated once, but without heating.

3.3.7 Afterwards, the precipitate is mixed with 100 ml to 150 ml of distilled water and stirred for at least 15 minutes.

3.3.8 After cooling, centrifugation is carried out according to step 3.3.3. The supernatant is combined with the solution in the 2-l-beaker.

3.3.9 10 ml of ferric chloride solution (0,5 g of Fe^{3+}) are added to the combined solutions.

3.3.10 After addition of a few ice cubes, a pH value of 9 to 10 is adjusted with concentrated ammonia (13,3 mol·l^{-1}) while stirring. The transuranic elements coprecipitate with iron hydroxide.

3.3.11 After settling of the precipitate, the supernatant is sucked off as far as possible without loss of precipitate, e.g. with a water jet pump.

Note:
The volume of the suspension in the 2-litre beaker should be about 400 ml after removing of the supernatant solution.

3.3.12 The precipitate is centrifuged according to step 3.3.3. The supernatant is discarded.

3.3.13 The precipitate is dissolved in as little nitric acid as possible (8 mol·l^{-1}) and transferred lossless into a 250-ml-beaker, rinsing the centrifuge tube with as little nitric acid as possible (8 mol·l^{-1}). The total volume of the solution should be 100 ml.

3.3.14 Further steps are described in procedure D-α-SPEKT-MWASS-01 beginning at step 3.3.1.16

4 Measuring the activity

The activity measurement is described in procedure D-α-SPEKT-MWASS-01.

5 Calculation of the results

5.1 Output quantity

The specific activity a_{r} of the radionuclide r is calculated according to Equation (1); the decay correction on the time of sampling is neglected due to the long half-lives of the plutonium and americium isotopes:

$$a_{\mathrm{r}} = \frac{A_{\mathrm{Tr}}}{R_{\mathrm{n,Tr}}} \cdot \frac{p_{\alpha,\mathrm{Tr}}}{p_{\alpha,\mathrm{r}}} \cdot \frac{1}{m_{\mathrm{TM}}} \cdot \left(R_{\mathrm{g,r}} - R_{0,\mathrm{r}}\right) = \frac{A_{\mathrm{Tr}}}{R_{\mathrm{n,Tr}}} \cdot \frac{p_{\alpha,\mathrm{Tr}}}{p_{\alpha,\mathrm{r}}} \cdot \frac{1}{m_{\mathrm{TM}}} \cdot R_{\mathrm{n,r}} = \varphi \cdot R_{\mathrm{n,r}} \quad (1)$$

Herein are:

a_{r} specific activity of radionuclide r, in Bq·kg^{-1};

A_{Tr} activity of the tracer nuclide at the beginning of the measurement, in Bq;

m_{TM} dry mass of the weighed marine sediment, in kg;

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

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

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

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

$R_{0,\mathrm{r}}$ background count rate of the alpha line of the radionuclide r to be determined (blank source), in s^{-1};

$R_{\mathrm{n,r}}$ net count rate of the alpha line of the radionuclide r to be determined, in s^{-1};

φ procedural calibration factor, in Bq·s·kg^{-1}.

For the calculation of the chemical yield and its associated standard uncertainty is referred to procedure D-α-SPEKT-MWASS-01.

5.2 Standard uncertainty of the output quantity

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 standard uncertainty $u(a_{\mathrm{r}})$ of the specific activity is calculated according to Equation (2):

$$u(a_{\mathrm{r}}) = \sqrt{a_{\mathrm{r}}^2 \cdot u_{\mathrm{rel}}^2(\varphi) + \varphi^2 \cdot \left(\frac{R_{\mathrm{g,r}}}{t_{\mathrm{m}}} + \frac{R_{0,\mathrm{r}}}{t_0}\right)} \quad (2)$$

with

$$u_{\mathrm{rel}}^2(\varphi) = u_{\mathrm{rel}}^2(A_{\mathrm{Tr}}) + u_{\mathrm{rel}}^2(p_{\alpha,\mathrm{Tr}}) + u_{\mathrm{rel}}^2(p_{\alpha,\mathrm{r}}) + u_{\mathrm{rel}}^2(R_{\mathrm{n,Tr}}) + u_{\mathrm{rel}}^2(m_{\mathrm{TM}}) \quad (3)$$

In the Equations (2) and (3) are:

t_{m} duration of measurement, in s;

t_0 duration of the background measurement (blank source), in s;

$u(a_{\mathrm{r}})$ standard uncertainty of the specific activity of the radionuclide r, in Bq·kg^{-1};

$u_{\mathrm{rel}}(A_{\mathrm{Tr}})$ relative standard uncertainty of the tracer activity;

$u_{\mathrm{rel}}(m_{\mathrm{TM}})$ relative standard uncertainty of the dry mass;

$u_{\mathrm{rel}}(p_{\alpha,\mathrm{Tr}})$ relative uncertainty of the emission intensities of the tracer;

$u_{\mathrm{rel}}(p_{\alpha,\mathrm{r}})$ relative standard uncertainty of the emission intensities of the radionuclide r;

$u_{\mathrm{rel}}(R_{\mathrm{n,Tr}})$ relative uncertainty of the net count rate of the tracer;

$u_{\mathrm{rel}}(\varphi)$ relative standard uncertainty of the procedural calibration factor.

The standard uncertainty of the analysis includes the standard uncertainties of the statistical counting, of the tracer activity, of the emission intensities and of the dry mass of the sample. The standard uncertainty of the duration of measurement is neglected.

6 Characteristic limits of the procedure

The calculation of the characteristic limits follows the standard series ISO 11929 [2]. For further considerations concerning the characteristic limits, it is referred to the General Chapter CHAGR-ISO-01 of this Procedures' Manual [3].

6.1 Decision threshold

The decision threshold a_{r}^* is determined according to Equation (4):

$$a_{\mathrm{r}}^* = k_{1-\alpha} \cdot \varphi \cdot \sqrt{R_{0,\mathrm{r}} \cdot \left(\frac{1}{t_{\mathrm{m}}} + \frac{1}{t_0}\right)} \quad (4)$$

Herein are:

a_{r}^* decision threshold of the specific activity of the radionuclide r, in Bq·kg^{-1};

$k_{1-\alpha}$ quantile of the normal distribution for α = 0,0014.

6.2 Detection limit

The detection limit $a_{\mathrm{r}}^{\#}$ is determined according to Equation (5):

$$a_{\mathrm{r}}^{\#} = a_{\mathrm{r}}^{*} \cdot k_{1-\beta} \cdot \sqrt{a_{\mathrm{r}}^{*2} \cdot u_{\mathrm{rel}}^{2}(\varphi) + \varphi^{2} \cdot \left(\frac{a_{\mathrm{r}}^{\#}}{t_{\mathrm{m}} \cdot \varphi} + \frac{R_{0,\mathrm{r}}}{t_{\mathrm{m}}} + \frac{R_{0,\mathrm{r}}}{t_{0}} \right)} \tag{5}$$

Herein are:

$a_{\mathrm{r}}^{\#}$ detection limit of the specific activity of the radionuclide r, in Bq·kg^{-1};

$k_{1-\beta}$ quantile of the normal distribution for β = 0,05.

Using the auxiliary quantities Ψ and θ according to the Equations (6) and (7)

$$\theta = 1 - k_{1-\beta}^{2} \cdot u_{\mathrm{rel}}^{2}(\varphi) \tag{6}$$

$$\Psi = 1 + \frac{k_{1-\beta}^{2}}{2 \cdot a_{\mathrm{r}}^{*}} \cdot \varphi \cdot \frac{1}{t_{\mathrm{m}}} \tag{7}$$

the detection limit $a_{\mathrm{r}}^{\#}$ is calculated by Equation (8):

$$a_{\mathrm{r}}^{\#} = \frac{a_{\mathrm{r}}^{*} \cdot \Psi}{\theta} \cdot \left\{ 1 + \sqrt{1 - \frac{\theta}{\Psi^{2}} \cdot \left(1 - \frac{k_{1-\beta}^{2}}{k_{1-\alpha}^{2}} \right)} \right\} \tag{8}$$

6.3 Limits of the coverage interval

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

7 Worked examples

The evaluation can be carried out either manually (see Section 7.1) or software supported by Excel® or by the software UncertRadio (see Section 7.2). An Excel® spreadsheet as well as a project file for the software UncertRadio are available on the website of this Procedures' Manual.

For the worked example with Pu-238, the following values are used:

$R_{\mathrm{g,Pu\text{-}238}}$	=	0,55·10^{-3} s^{-1};	t_{m}	=	1559663 s;
$R_{0,\mathrm{Pu\text{-}238}}$	=	0,01·10^{-3} s^{-1};	t_{0}	=	1559663 s
$R_{\mathrm{n,Pu\text{-}242}}$	=	4,3·10^{-3} s^{-1};	$u_{\mathrm{rel}}(R_{\mathrm{n,Pu\text{-}242}})$	=	0,01;
$A_{\mathrm{Pu\text{-}242}}$	=	43,2·10^{-3} Bq^{-1};	$u_{\mathrm{rel}}(A_{\mathrm{Pu\text{-}242}})$	=	0,05;

$p_{\alpha,\text{Pu-238}}$	=	1,000;	$u_{\text{rel}}(p_{\alpha,\text{Pu-238}})$	=	0,002;
$p_{\alpha,\text{Pu-242}}$	=	0,9997;	$u_{\text{rel}}(p_{\alpha,\text{Pu-242}})$	=	0,002;
m_{TM}	=	0,01 kg;	$u_{\text{rel}}(m_{\text{TM}})$	=	0,01;
φ	=	1004,35 Bq·s·kg^{-1};	$u_{\text{rel}}(\varphi)$	=	0,052.

7.1 Manual evaluation

In the manual evaluation, the interim results and the result are given rounded with four significant digits.

The specific activity $a_{\text{Pu-238}}$ is calculated according to Equation (1):

$$a_{\text{Pu-238}} = \frac{43{,}2 \cdot 10^{-3}\ \text{Bq}}{4{,}3 \cdot 10^{-3}\ \text{s}^{-1}} \cdot \frac{0{,}9997}{1{,}000} \cdot \frac{1}{0{,}01\ \text{kg}} \cdot (0{,}55 \cdot 10^{-3}\ \text{s}^{-1} - 0{,}01 \cdot 10^{-3}\ \text{s}^{-1}) \approx$$

$$\approx 0{,}5423\ \text{Bq} \cdot \text{kg}^{-1}$$

The standard uncertainty of the specific activity $u(a_{\text{Pu-238}})$ is calculated according to the Equations (2) and (3):

$$u(a_{\text{Pu-238}}) = \sqrt{0{,}542^2 \cdot 2{,}708 \cdot 10^{-3} + 1004{,}35^2 \cdot \left(\frac{0{,}55 \cdot 10^{-3}}{1559663} + \frac{0{,}01 \cdot 10^{-3}}{1559663}\right)}\ \text{Bq} \cdot \text{kg}^{-1} \approx$$

$$\approx 0{,}0340\ \text{Bq} \cdot \text{kg}^{-1}$$

mit $u_{\text{rel}}^2(\varphi) = 0{,}05^2 + 0{,}002^2 + 0{,}002^2 + 0{,}01^2 + 0{,}01^2 = 2{,}708 \cdot 10^{-3}$

The specific activity for Pu-238 is for this worked example:

$$a_{\text{Pu-238}} = (0{,}5423 \pm 0{,}0340)\ \text{Bq} \cdot \text{kg}^{-1}$$

For calculating the characteristic limits, the value of the quantile $k_{1\text{-}\alpha}$ of 3 and the value of the quantile $k_{1\text{-}\beta}$ of 1,645, respectively, are used. For the decision threshold $a^*_{\text{Pu-238}}$, the following value is obtained using Equation (4):

$$a^*_{\text{Pu-238}} = 3 \cdot 1004{,}35 \cdot \sqrt{0{,}01 \cdot 10^{-3} \cdot \left(\frac{1}{1559663} + \frac{1}{1559663}\right)}\ \text{Bq} \cdot \text{kg}^{-1} \approx$$

$$\approx 10{,}79 \cdot 10^{-3}\ \text{Bq} \cdot \text{kg}^{-1}$$

For calculating the detection limit, $a^{\#}_{\text{Pu-238}}$, the values of the auxiliary quantities Ψ and θ are determined by the Equations (6) and (7):

$$\theta \approx 1 - 1{,}645^2 \cdot 2{,}708 \cdot 10^{-3} \approx 0{,}993$$

$$\Psi \approx 1 + \frac{1{,}645^2}{2 \cdot 10{,}79 \cdot 10^{-3}\ \text{Bq} \cdot \text{kg}^{-1}} \cdot 1004{,}35\ \text{Bq} \cdot \text{s} \cdot \text{kg}^{-1} \cdot \frac{1}{1559663\ \text{s}} \approx 1{,}081$$

The detection limit itself is calculated by Equation (8):

$$a^{\#}_{\text{Pu-238}} \approx \frac{10{,}79 \cdot 10^{-3} \cdot 1{,}081}{0{,}993} \cdot \left\{1 + \sqrt{1 - \frac{0{,}993}{1{,}081^2} \cdot \left(1 - \frac{1{,}645^2}{3^2}\right)}\right\} \text{Bq} \cdot \text{kg}^{-1} \approx$$

$$\approx 19{,}23 \cdot 10^{-3}\ \text{Bq} \cdot \text{kg}^{-1}$$

7.2 Software supported evaluation

7.2.1 View of the Excel® spreadsheet

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SAMPLE IDENTIFICATION: Marine sediment ANALYTE: Pu-238

#Number of input quantities	9
k_alpha	3
k_beta	1,645
gamma	0,05

Create Excel variables!

User-Input: definition quantities/Excel variables
Input of Excel formulae
Input of values of quantities
Excel-VBA: #Keywords
Values from Vbasic

	DATA INPUT					UNCERTAINTY BUDGET		
	#Values of input quantities	Unit	Excel variable	Input values	StdDev	partial derivatives	uncertainty budget:	budget in %
p 1	#Number of gross counts Ng		Ng	857,81465	29,288473	0,000643953	0,018860402	30,69895259
p 2	Added activity of the tracer nuclide	Bq	ATr	4,3200E-02	2,1600E-03	12,55437209	0,027117444	63,4627908
p 3	Net count rate of the tracer	1/s	RnTr	4,3000E-03	4,3000E-05	-126,127519	0,005423483	2,538506555
p 4	Background count rate	1/s	R0r	1,0000E-05	2,5321E-06	-1004,34976	0,002543136	0,558162765
p 5	Sum emission intensities (tracer)		paTr	0,99970	1,9994E-03	0,542511628	0,001084698	0,101540465
p 6	Sum emission intensities (radionuclide)		par	1,00000	2,0000E-03	-0,54234833	0,001084697	0,101540262
p 7	Dry mass of the sample	kg	mTM	1,0000E-02	1,0000E-04	-54,2348332	0,005423483	2,538506555
p 8	Duration of measurement	s	tm	1,5597E+06	0	-3,5417E-07	0	0
p 9	Duration of background measurement	s	_t0	1,5597E+06	0	0	0	0
	(List can be continued here)							

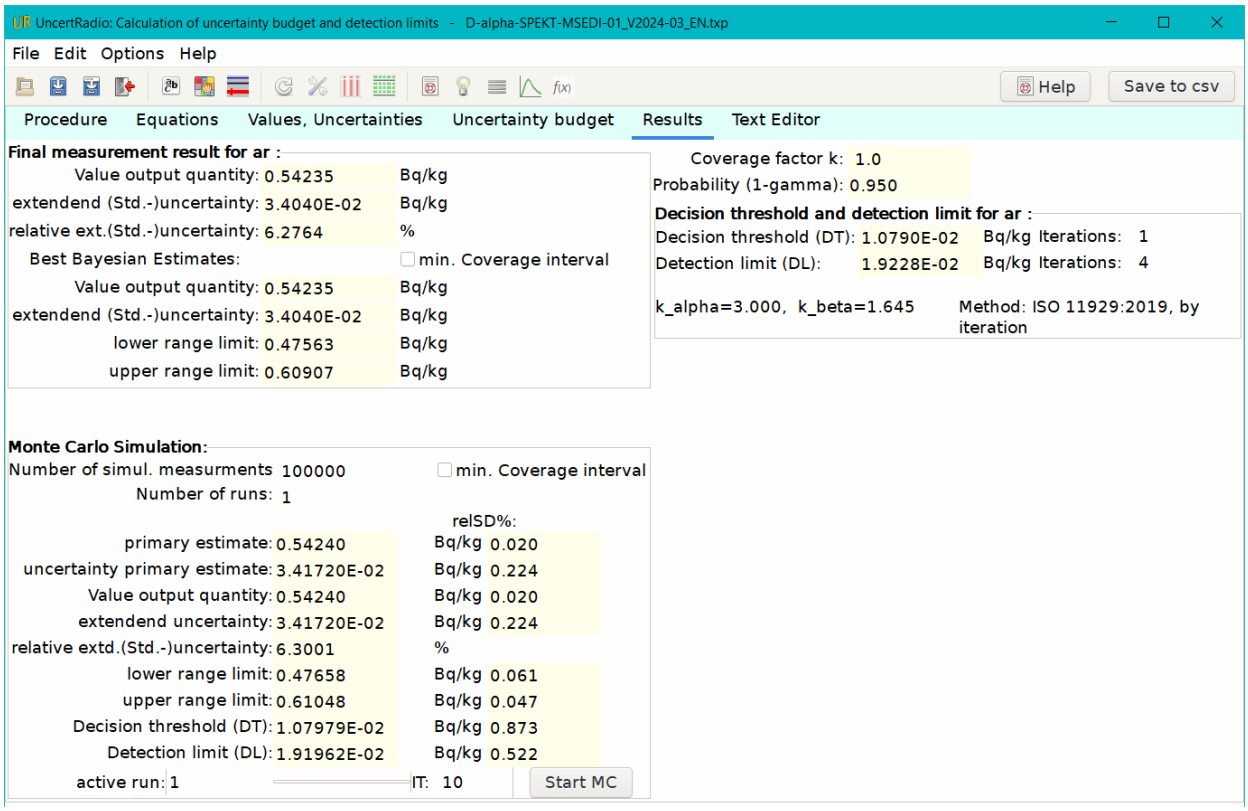
	MODEL SECTION		Result = phi * Rn			
	Derived quantities			(Formulae)		
h 1	#Gross count rate Rg	1/s	Rg	5,5000E-04		
	(List can be continued here)					
	#Net count rate Rn	1/s	Rn	5,4000E-04		
	#Calibration factor, proc.dep.	Bq*s/kg	phi	1,0043E+03		
	#Value output quantity	Bq/kg	Result	5,4235E-01	0,01922877	<-- output value modifiable by VBA
	#Standard uncertainty output quantity	Bq/kg	uResult	3,4040E-02		
	#Decision threshold	Bq/kg		1,0790E-02		
	#Detection limit	Bq/kg		1,9229E-02		

FURTHER DERIVED QUANTITIES			
Auxiliary quantity Omega		Omega	1,0000E+00
Best estimate	Bq/kg	BestEst	5,4235E-01
Standard uncertainty best estimate	Bq/kg		3,4040E-02
Coverage interval (lower limit)	Bq/kg		4,7563E-01
Coverage interval (upper limit)	Bq/kg		6,0907E-01

Calculate!

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

7.2.2 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.

The required chemicals are listed in procedure D-α-SPEKT-MWASS-01. In addition, ice cubes made of distilled water are needed.

8.2 Equipment

The required equipment is listed in procedure D-α-SPEKT-MWASS-01.

References

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

[3] Kanisch, G., Aust, M.-O., Bruchertseifer, F., Dalheimer, A., Heckel, A., Hofmann, S., et al.: *Bestimmung der charakteristischen Grenzen bei der Aktivitätsbestimmung radioaktiver Stoffe – Teil 1: Grundlagen*. Version Mai 2022. In: Messanleitungen für die Überwachung radioaktiver Stoffe in der Umwelt und externer Strahlung. ISSN 1865-8725. Available at: https://www.bmuv.de/WS1517. [Last access 27.10.2023].