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

D-α-SPEKT-MSEDI-01

Authors:

S. Schmied
A. Meyer
I. Goroncy
J. Herrmann

Federal coordinating office for sea water, suspended particulate matter and sediment

(Leitstelle für Meerwasser, Meeresschwebstoff und -sediment)

ISSN 1865-8725 Version June 2019

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 plutonium, americium and curium in sea sediment by alpha spectrometry

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 IMIS routine operation mode.

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 procedure is designed for dry masses of five to ten grams, whereby 10 grams are usually used.

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

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 sea 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 A mass of 10 g of dried sea sediment is weighed into a 250-ml-beaker. To determine the chemical yield, known activities of about 17 mBq to 34 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.

3.3.7 Afterwards, the precipitate is mixed with 100 ml to 150 ml of distilled water and heated for at least 15 minutes while stirring on a heating plate.

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

3.3.12 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.

3.3.13 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 Equations

The specific activity a_r of the radionuclide r is calculated according to equation (1) (a decay correction on the time of sampling is neglected due to the long half-lives of the plutonium and americium isotopes):

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

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;

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

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

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

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

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

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

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

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

The standard uncertainty u(ar) of the specific activity is calculated according to equation (2):

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

with

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

Herein are:

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

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

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

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

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

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

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

t_m duration of measurement, in s;

t_0 duration of the background measurement, in s.

For the calculation of the chemical yield η_r and its standard uncertainty $u(\eta_r)$ is referred to procedure D-α-SPEKT-MWASS-01.

5.2 Worked example

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

$A_{Pu\text{-}242}$ = 0,0432 Bq; $u_{rel}(A_{Pu\text{-}242})$ = 0,02;

$R_{n,Pu\text{-}242}$ = 0,0043 s^{-1}; $u_{rel}(R_{n,Pu\text{-}242})$ = 0,01;

$p_{\alpha,Pu\text{-}242}$ = 0,9997; $u_{rel}(p_{\alpha,Pu\text{-}242})$ = 0,002;

$p_{\alpha,\text{Pu-238}}$ = 1,000;
m_{TM} = 0,01 kg;
$R_{\text{g,Pu-238}}$ = 0,00055 s^{-1};
t_{m} = 1559663 s;
φ = 1004,350 Bq·s·kg^{-1};
$u_{\text{rel}}(p_{\alpha,\text{Pu-238}})$ = 0,002;
$u_{\text{rel}}(m_{\text{TM}})$ = 0,01;
$R_{0,\text{Pu-238}}$ = 0,00001 s^{-1};
t_0 = 1559663 s;
$u_{\text{rel}}(\varphi)$ = 0,025.

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

$$a_{\text{Pu}-238} = \frac{0{,}0432\ \text{Bq}}{0{,}0043\ \text{s}^{-1}} \cdot \frac{0{,}9997}{1{,}000} \cdot \frac{1}{0{,}01\ \text{kg}} \cdot (0{,}00055\ \text{s}^{-1} - 0{,}00001\ \text{s}^{-1}) =$$

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

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

$$u(a_{\text{Pu}-238}) = \sqrt{0{,}542^2 \cdot 0{,}000608 + 1004{,}350^2 \cdot \left(\frac{0{,}00055}{1559663} + \frac{0{,}00001}{1559663}\right)}\ \text{Bq} \cdot \text{kg}^{-1} =$$

$$= 0{,}0233\ \text{Bq} \cdot \text{kg}^{-1}$$

with

$$u_{\text{rel}}^2(\varphi) = 0{,}02^2 + 0{,}002^2 + 0{,}002^2 + 0{,}01^2 + 0{,}01^2 = 0{,}000608$$

The specific activity for Pu-238 is thus:

$$a_{\text{Pu}-238} = (0{,}542 \pm 0{,}023)\ \text{Bq} \cdot \text{kg}^{-1}$$

5.3 Consideration of uncertainties

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 ISO 11929.

An Excel spreadsheet (see section 7.3.1) as well as a project file for the software UncertRadio (see section 7.3.2) 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 these procedures manuals.

6.1 Equations

6.1.1 Decision threshold

The decision threshold a_r^* is determined according to equation (3):

$$a_\mathrm{r}^* = k_{1-\alpha} \cdot \varphi \cdot \sqrt{R_{0,r} \cdot \left(\frac{1}{t_\mathrm{m}} + \frac{1}{t_0}\right)} \tag{3}$$

Herein are:

a_r^* decision threshold of the radionuclide r, in $\mathrm{Bq \cdot kg^{-1}}$;

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

6.1.2 Detection limit

The detection limit $a_\mathrm{r}^\#$ is calculated according to the implicit equation (4):

$$a_\mathrm{r}^\# = a_\mathrm{r}^* \cdot k_{1-\beta} \cdot \sqrt{a_\mathrm{r}^{*2} \cdot u_\mathrm{rel}^2(\varphi) + \varphi^2 \cdot \left(\frac{a_\mathrm{r}^\#}{t_\mathrm{m} \cdot \varphi} + \frac{R_{0,r}}{t_\mathrm{m}} + \frac{R_{0,r}}{t_0}\right)} \tag{4}$$

Herein are:

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

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

After implementation of the auxiliary quantities Ψ and θ, the detection limit $a_\mathrm{r}^\#$ is calculated according to equation (5):

$$a_\mathrm{r}^\# = \frac{a_\mathrm{r}^* \cdot \Psi}{\theta} \cdot \left\{1 + \sqrt{1 - \frac{\theta}{\Psi^2} \cdot \left(1 - \frac{k_{1-\beta}^2}{k_{1-\alpha}^2}\right)}\right\} \tag{5}$$

with

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

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

6.1.3 Confidence intervals

The calculation of the upper and lower confidence intervals is not required in this case.

6.2 Worked example

With the values from section 5.2 and the following values

$k_{1-\alpha}$	=	3;	$k_{1-\beta}$	=	1,645;
φ	=	1004,350 Bq·s·kg^{-1};	$u_{\mathrm{rel}}^2(\varphi)$	=	0,000608.

the following decision threshold $a_{\text{Pu-238}}^*$ is obtained according to equation (3):

$$a_{\text{Pu}-238}^* = 3 \cdot 1004{,}350 \ \cdot \ \sqrt{0{,}00001 \ \cdot \left(\frac{1}{1559663} + \frac{1}{1559663}\right)} \mathrm{Bq} \cdot \mathrm{kg}^{-1} =$$

$$= 0{,}01078 \ \mathrm{Bq} \cdot \mathrm{kg}^{-1}$$

For the detection limit $a_{\text{Pu-238}}^\#$ the following value is determined according to equation (4):

$$a_{\text{Pu}-238}^\# = \frac{0{,}011 \ \cdot 1{,}079}{0{,}998} \cdot \left\{1 + \sqrt{1 - \frac{0{,}998}{1{,}079^2} \cdot \left(1 - \frac{1{,}645^2}{3^2}\right)}\right\} \mathrm{Bq} \cdot \mathrm{kg}^{-1} =$$

$$= 0{,}0194 \ \mathrm{Bq} \cdot \mathrm{kg}^{-1}$$

with

$$\theta = 1 - 1{,}645^2 \cdot 0{,}0006 = 0{,}998$$

$$\Psi = 1 + \frac{1{,}645^2}{2 \cdot 0{,}011 \ \mathrm{Bq} \cdot \mathrm{kg}^{-1}} \cdot 1004{,}350 \ \mathrm{Bq} \cdot \mathrm{s} \cdot \mathrm{kg}^{-1} \cdot \frac{1}{1559663 \ \mathrm{s}} = 1{,}0792$$

7 Catalogue of chemicals and equipment

7.1 Chemicals

The required chemicals are listed in procedure D-α-SPEKT-MWASS-01.

In addition, ice cubes made of distilled water are needed.

7.2 Equipment

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

7.3 Software supported calculation

7.3.1 Example of an Excel spreadsheet

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

D-α-SPEKT-MSEDI-01 Version June 2019

Procedures manual for monitoring of radioactive substances in the environment and of external radiation (ISSN 1865-8725)

SAMPLE IDENTIFICATION: Sea sediment and particulate matter

#Number of parameters p	9
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:

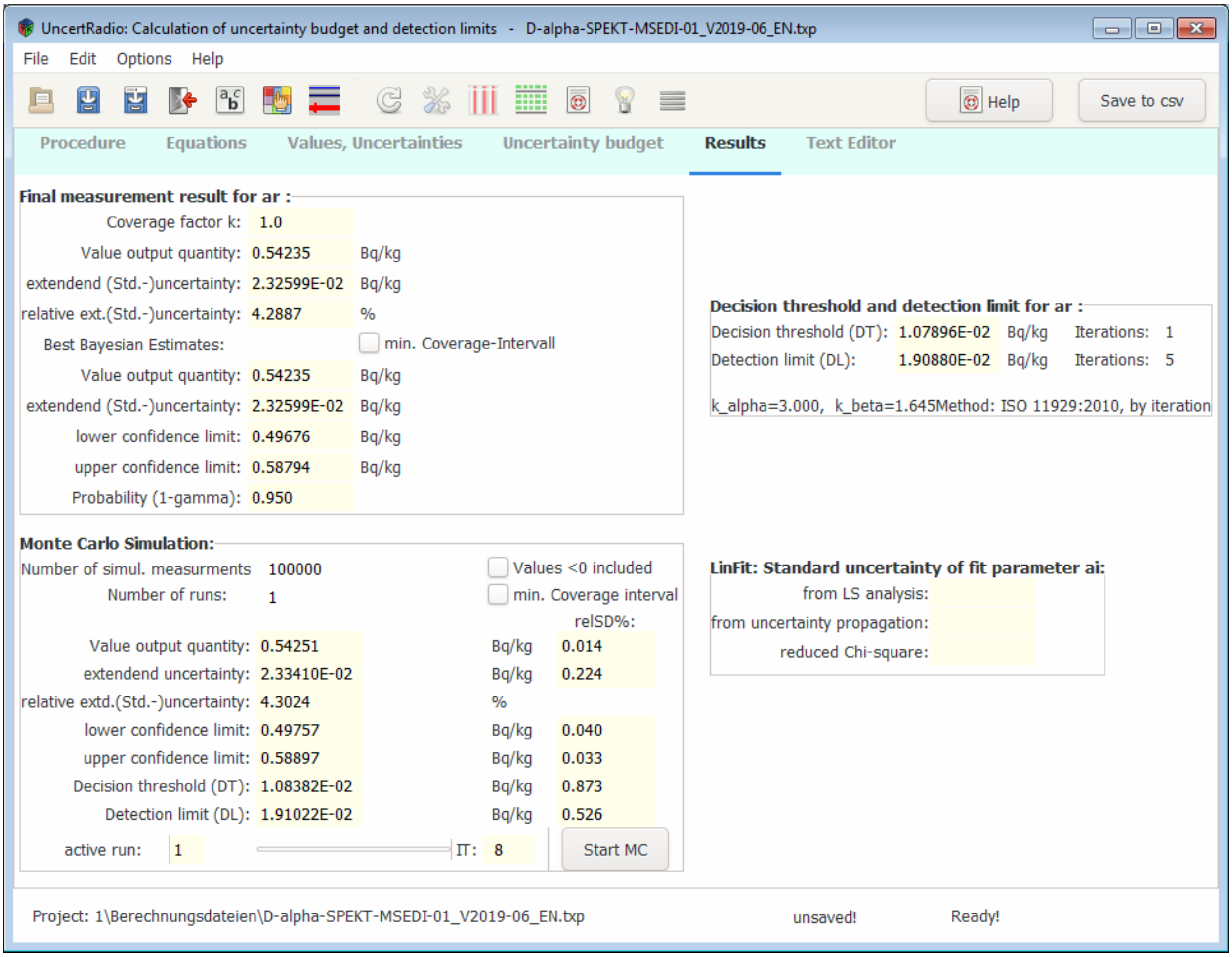
	#Values of parameters p	Unit	Excel variable	Input values	StdDev	partial derivatives	uncertainty budget:	budget in %
p 1	#Number of gross counts Ng		Ng	857,81	29,29	0,00064395	0,01886035	56,74108566
p 2	Added activity of the tracer nuclide	Bq	ATr	0,0432	0,000864	12,5543028	0,01084692	18,76768869
p 3	Net count rate of the tracer	1/s	RnTr	4,3000E-03	4,3000E-05	-126,126823	0,00542345	4,69191279
p 4	Background count rate	1/s	R0r	1,0000E-05	2,5321E-06	-1004,34977	0,00254314	1,031661701
p 5	Sum emission intensities (tracer)		pαTr	9,9970E-01		0,54250863	0	0
p 6	Sum emission intensities (radionuclide)		pαr	1		-0,54234534	0	0
p 7	Dry mass of the sample	kg	mTM	1,0000E-02	2,0000E-04	-54,2345338	0,01084691	18,76765116
p 8	Duration of measurement	s	tm	1559663		-3,5417E-07	0	0
p 9	Duration of background measurement	s	_t0	1559663		0	0	0
	(List can be continued here)							

	Model section		**c = phix * Rn**		
	Auxiliary equations h			(Formulae)	
h 1	#Gross count rate Rg	1/s	Rg	0,000549997	
	(List can be continued here)				
	#Net count rate Rn	1/s	Rn	5,4000E-04	
	#Calibration factor, proc.dep.	Bq*s/m³	phix	1004,349767	
	#Value output quantity	Bq/m³	Erg	5,4235E-01	0,01910753 <-- output value modifiable by VBA
	#Combined standard uncertainty	Bq/m³	uErg	2,5038E-02	
	#Decision threshold	Bq/m³		1,0790E-02	
	#Detection limit	Bq/m³		1,9108E-02	
	further derived values				
	Auxiliary quantity Omega		Omega	1	
	Best estimate	Bq/m³	BestEst	5,4235E-01	
	Uncertainty best estimate	Bq/m³		2,5038E-02	
	Lower confidence limit	Bq/m³		4,9327E-01	
	Upper confidence limit	Bq/m³		5,9142E-01	

Calculate!

The corresponding Excel spreadsheet is available on the website of this procedures manual.

7.3.2 Example of an UncertRadio project



The corresponding UncertRadio project file is available on the website of this procedures manual.

References

(1) Murray, C. N., Statham, G.: *Application of Solvent Extraction Procedure using Di-2-Ethyl Hexyl Phosphoric Acid (HDEHP) to the Separation of some Transuranic Elements in Environmental Samples*. Deutsche Hydrographische Zeitung, 1976, Band 29, S. 69 – 75.

(2) Kluge, S.: *Messung von Thorium mit Hilfe der alphaspektrometrischen Isotopenverdünnungsanalyse nach extraktionschromatographischer Abtrennung von der Probenmatrix*. Universität Regensburg, 1997, Dissertation.