

Procedure for determining the activity concentrations of plutonium, americium and curium in sea water by alpha spectrometry

D- α -SPEKT-MWASS-01

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1 Scope

The procedure outlined in the following is suitable for determining the activity concentrations of plutonium isotopes and other transuranic elements in seawater above $2,5 \text{ mBq}\cdot\text{m}^{-3}$ according to the Radiation Protection Act (Strahlenschutzgesetz, StrlSchG) in the IMIS routine operation mode.

2 Sampling

A detailed description of sampling is given in procedure D-Cs-MWASS-01.

The usual sample volume is 100 l. If the analysis is already started at sea, acidification of the seawater is not required. Otherwise, 3 ml of concentrated hydrochloric acid ($12 \text{ mol}\cdot\text{l}^{-1}$) per liter of seawater are added beforehand to the sample containers in order to avoid adsorption of the transuranic elements to the container walls.

Note:

In case of non-acidified seawater samples stored at the pH value of the seawater of eight, a quantitative determination of the activity concentration of plutonium is not possible any more.

3 Analysis

3.1 Principle of the procedure

The procedure is designed for sample volumes from 80 l to 200 l; usually a sample volume of 100 l is used.

Plutonium, americium and curium are co-precipitated with iron hydroxide together with the added tracers Pu-242 and Am-243, which serve as internal standards for determining the chemical yield.

Afterwards, plutonium is separated from americium and curium by liquid-liquid extraction with diisooctyl hydrogen phosphate in n-heptene (HDEHP). After re-extraction of plutonium, further impurities are removed by ion exchange on AG 1X8.

Americium and curium are purified by further liquid-liquid extractions with dibutyl-N,N-diethylcarbamyolphosphonate (DDCP). After re-extraction with xylene, further impurities are removed by ion exchange on AG 1X4.

The separated radionuclides are deposited by means of electrodeposition on stainless steel plates. Their activities are determined by alpha spectrometry using silicon based surface barrier detectors.

3.2 Sample preparation

The seawater sample is filled into a 100 l or 200 l plastic container and the volume is noted.

3.3 Radiochemical separation

Figure 1 shows schematically the radiochemical separation, which will be described in detail in the following.

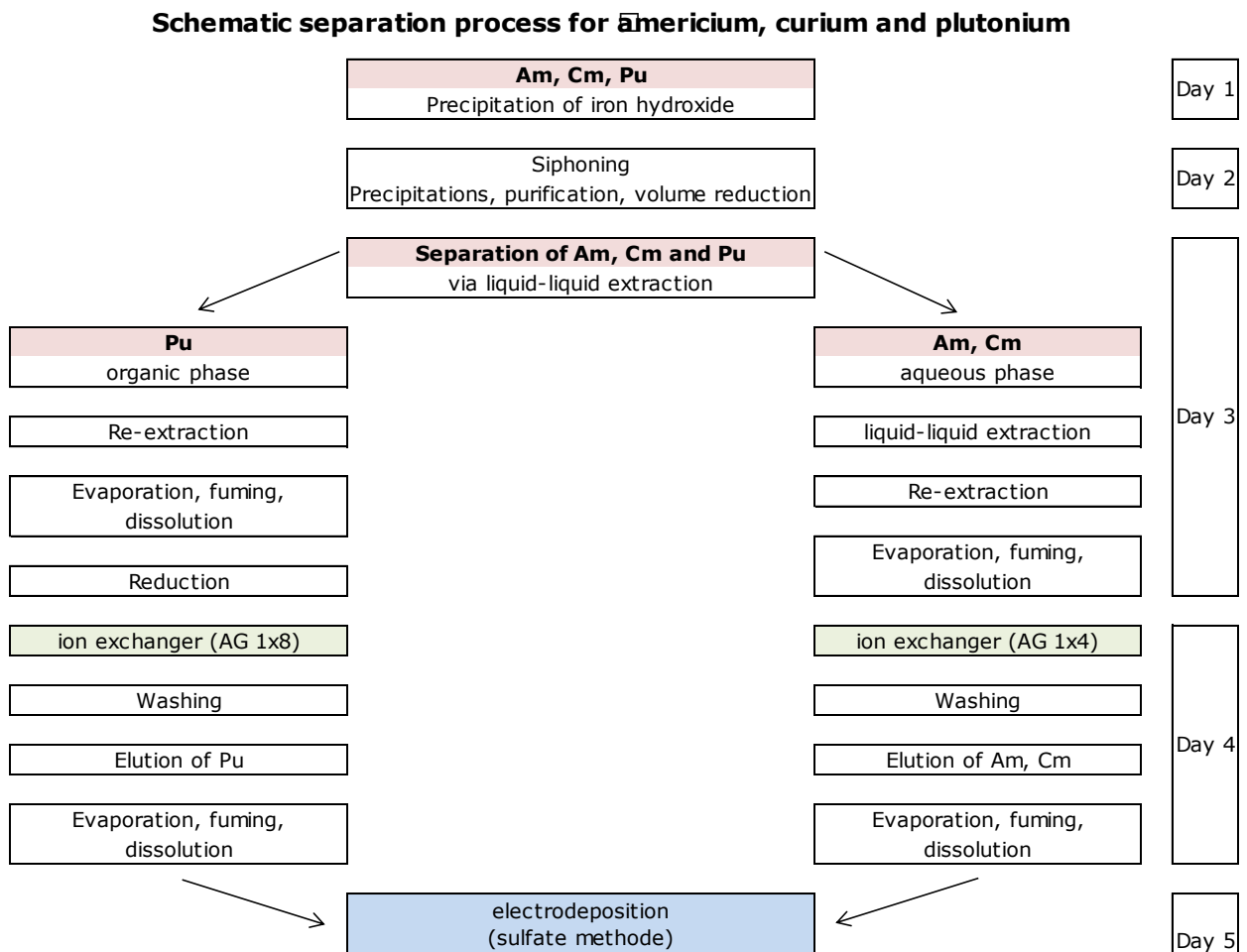


Fig. 1: Schematic description of the radiochemical separation

3.3.1 Separation of the matrix by means of iron hydroxide precipitation

3.3.1.1 While thoroughly mixing with a stirring motor with propeller stirrer, 20 ml of ferric chloride solution (1 g Fe³⁺) are added to the sample.

3.3.1.2 Afterwards, 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 for determining the chemical yield. The solution is thoroughly mixed for further 10 minutes.

Note:

The tracer activities should correspond to the expected activities of the radionuclides to be determined.

3.3.1.3 Concentrated ammonia (13,3 mol·l⁻¹) is used to adjust the pH value from 9,2 to 9,7 for the precipitation of iron as hydroxide. Plutonium, as well as americium and curium precipitate together with the iron hydroxide precipitate. The solution is allowed to stand overnight.

Note:

If the analysis is carried out at sea, the duration for settling down is reduced to four to six hours.

3.3.1.4 The supernatant is siphoned to about 4 liters.

3.3.1.5 The precipitate is drained into a 5-l-beaker. The precipitate which is still adhering to the inner walls of the plastic container is rinsed with hydrochloric acid (6 mol·l⁻¹) into the beaker. Finally, it is rinsed with distilled water into the beaker.

Note:

If the hydroxide precipitate in the beaker has not completely dissolved, hydrochloric acid (6 mol·l⁻¹) is added until it is completely dissolved.

3.3.1.6 Again, the solution is adjusted to a pH value between 9,2 and 9,7 with concentrated ammonia (13,3 mol·l⁻¹) in order to precipitate iron hydroxide.

3.3.1.7 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:

At sea, this precipitate is transferred into a 1-l-glass bottle for storage and for transport with as little hydrochloric acid (6 mol·l⁻¹) as possible. The beaker is rinsed with hydrochloric acid (6 mol·l⁻¹) and distilled water into the glass bottle. The precipitate has to be completely dissolved; otherwise additional hydrochloric acid (6 mol·l⁻¹) has to be added. All further analysis steps take place on land.

3.3.1.8 The precipitate from step 3.3.1.7 is dissolved with as little hydrochloric acid (6 mol·l⁻¹) as possible. This solution or the solution from the 1-l-glass bottle from the note to step 3.3.1.7 is filtered through a Büchner funnel combined with a witt jar into a 1-l-glass beaker in order to remove any suspended particulate matter remaining in the solution.

3.3.1.9 The filtered solution is adjusted to a pH value between 9,2 and 9,7 with concentrated ammonia (13,3 mol·l⁻¹) in order to precipitate iron hydroxide again.

3.3.1.10 After visible settling of the precipitate the clear supernatant is sucked off as far as possible without loss of precipitate.

3.3.1.11 The suspension remaining in the beaker is transferred to centrifuge tubes and centrifuged for three minutes until complete separation at about 1510 times of acceleration of gravity (1510 g).

Note:

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

3.3.1.12 The beaker is rinsed with a little amount of nitric acid (8 mol·l⁻¹). The rinsing solution is stored.

3.3.1.13 The supernatant is sucked off and discarded.

3.3.1.14 The precipitate is completely dissolved in the rinsing solution from step 3.3.1.12 while swiveling; if necessary, additional nitric acid (8 mol·l⁻¹) is added.

3.3.1.15 The solution is transferred lossless into a 250-ml-beaker, whereby the centrifuge tube is rinsed with nitric acid (8 mol·l⁻¹). The total volume of the solution should be 100 ml.

3.3.1.16 The solution is evaporated on a heating plate to a volume of about 50 ml and further treated according to section 3.3.2.

Note:

By concentrating the solution to about 50 ml, the nitric acid concentration is already close to the desired one. This simplifies the adjustment of the nitric acid concentration described in step 3.3.2.1.

3.3.2 Separation of Plutonium

3.3.2.1 The nitric acid concentration of the solution has to be between 7,4 mol·l⁻¹ and 7,6 mol·l⁻¹ and is adjusted as described in the following:

- A volume of 0,5 ml of the solution from step 3.3.1.16 is transferred into a 100-ml-glass beaker and about 20 ml of distilled water are added.
- A few drops of methyl red are added to the solution until a noticeable pink color is visible.
- The pink solution is titrated with sodium hydroxide solution (1 mol·l⁻¹) until its colour changes towards orange-yellow.
- The nitric acid concentration is calculated from the volume of sodium hydroxide solution used according to equation (1):

$$c_{\text{HNO}_3} = c_{\text{NaOH}} \cdot \frac{V_{\text{NaOH}}}{V_{\text{Lösung}}} \quad (1)$$

Note:

If the acid concentration of the solution is not within the desired range, concentrated nitric acid (about 15 mol·l⁻¹) or distilled water has to be added again and the determination of the acid concentration has to be repeated.

3.3.2.2 The solution is then transferred into a 250-ml-separating funnel. The beaker is rinsed with a little amount of nitric acid (8 mol·l⁻¹) and the rinsing solution is also transferred into the separating funnel.

3.3.2.3 Afterwards, 25 ml of HDEHP solution (0,5 mol·l⁻¹) are added to the separating funnel.

3.3.2.4 The separating funnel is shaken for at least two minutes. After phase separation, the plutonium is in the upper, organic phase.

3.3.2.5 The lower, aqueous phase is drained off into a 250-ml-beaker and is stored if an americium/curium determination has to be carried out in accordance with the section 3.3.3.

3.3.2.6 The organic phase is washed twice with 25 ml of concentrated hydrochloric acid ($12 \text{ mol}\cdot\text{l}^{-1}$) in each case for at least two minutes. The aqueous phases are discarded in each case.

3.3.2.7 The re-extraction of the plutonium from the organic phase into the aqueous phase is carried out by shaking with the freshly prepared ammonium iodide/hydrochloric acid solution (1:9) for at least two minutes. The colour of the organic phase thereby turns dark brown.

3.3.2.8 The lower, aqueous phase is drained off into a 100-ml-beaker and, with the addition of a few drops of concentrated nitric acid (about $15 \text{ mol}\cdot\text{l}^{-1}$), is evaporated until dryness.

3.3.2.9 The dry residue is again fumed with 1 ml to 5 ml of concentrated hydrochloric acid ($12 \text{ mol}\cdot\text{l}^{-1}$) and concentrated nitric acid (about $15 \text{ mol}\cdot\text{l}^{-1}$), each, in the same volume ratio.

Note:

The volumes of hydrochloric and nitric acid depend on the mass of the residue.

3.3.2.10 Afterwards, 20 ml of nitric acid ($8 \text{ mol}\cdot\text{l}^{-1}$) are added to the residue and the suspension is heated gently on a heating plate until complete dissolution.

3.3.2.11 After the solution has cooled down, 200 mg to 300 mg of sodium nitrite are added in portions. The solution is allowed to stand overnight.

Note:

With the addition of sodium nitrite violent reactions can occur with the formation of nitrogen oxides.

3.3.2.12 The solution is loaded onto the ion exchanger preconditioned as described in section 7.4.1, whereby the plutonium is adsorbed on the ion exchanger. The rinse is discarded.

Note:

The flow rate results automatically by the design of the column and is not regulated.

3.3.2.13 The ion exchanger is rinsed consecutively with 40 ml of nitric acid ($8 \text{ mol}\cdot\text{l}^{-1}$), 20 ml of concentrated hydrochloric acid ($12 \text{ mol}\cdot\text{l}^{-1}$) and 60 ml of concentrated hydrochloric acid ($12 \text{ mol}\cdot\text{l}^{-1}$). The rinses are discarded. Between the individual rinsing operations, the ion exchanger shall not fall dry.

3.3.2.14 The elution of plutonium is carried out consecutively with the freshly prepared ammonium iodide/hydrochloric acid solution (1:18) and 20 ml of concentrated hydrochloric acid ($12 \text{ mol}\cdot\text{l}^{-1}$) into a 100-ml-beaker.

3.3.2.15 The eluate is evaporated on a heating plate almost to dryness.

3.3.2.16 To the damp residue, a few drops of concentrated nitric acid (about $15 \text{ mol}\cdot\text{l}^{-1}$) are added to oxidise the iodide to iodine. Afterwards, the residue is evaporated to dryness, whereby the iodine volatilizes.

3.3.2.17 The dry residue is mixed with 1 ml to 5 ml of concentrated hydrochloric acid ($12 \text{ mol}\cdot\text{l}^{-1}$) and concentrated nitric acid (approximately $15 \text{ mol}\cdot\text{l}^{-1}$), each, in the same volume ratio and evaporated in order to remove the ammonium salts.

Note:

After this wet incineration step, a crystalline residue should be no longer visible.

3.3.2.18 Afterwards, 1 ml to 5 ml of concentrated hydrochloric acid ($12 \text{ mol}\cdot\text{l}^{-1}$) are added into the beaker. The solution is gently evaporated to dryness on a heating plate.

3.3.2.19 Further processing is carried out in accordance with the section 3.4.

3.3.3 Separation of americium and curium

3.3.3.1 The aqueous phase from step 3.3.2.5 is evaporated to half the volume on a heating plate.

Note:

In this case, a white precipitate of poorly soluble calcium and strontium salts and silicates may occur, which does not interfere with the subsequent steps.

3.3.3.2 The nitric acid concentration of the solution shall be about $12 \text{ mol}\cdot\text{l}^{-1}$. This will be checked according to step 3.3.2.1 and adjusted accordingly, if necessary.

3.3.3.3 The solution is transferred into a 250-ml-separating funnel. The beaker is rinsed with a little amount of nitric acid ($12 \text{ mol}\cdot\text{l}^{-1}$) and the rinse is also transferred into the separating funnel.

3.3.3.4 A volume of 10 ml of DDCP solution ($0,5 \text{ mol}\cdot\text{l}^{-1}$) are added to the 250-ml-separating funnel and the solution is extracted with shaking for at least 2 minutes. In this case, three phases are formed.

3.3.3.5 The lower, aqueous phase is discarded.

3.3.3.6 The remaining phases are washed twice with 20 ml of nitric acid ($12 \text{ mol}\cdot\text{l}^{-1}$) in each case for at least two minutes. In each case, the lower, aqueous phase is discarded.

3.3.3.7 Then 5 ml of xylene and another 20 ml of nitric acid ($2 \text{ mol}\cdot\text{l}^{-1}$) are added to the separating funnel. Americium and curium are extracted into the lower phase by shaking for at least two minutes.

Note:

Thorium and iron are also extracted.

3.3.3.8 The lower, aqueous phase is drained into a 100-ml-beaker. The solution is evaporated to dryness on a heating plate whereby brown bubbles are formed.

Note:

The beaker with the concentrated residue has to be removed from the heating plate before the residue turns black. Otherwise, very high yield losses have to be expected. This note also refers to step 3.3.3.9.

3.3.3.9 A volume of 1 ml of concentrated nitric acid (approximately $15 \text{ mol}\cdot\text{l}^{-1}$) is added to the residue and again gently evaporated to dryness.

3.3.3.10 The residue is dissolved in 20 ml of methanol-nitric acid solution (1:14,6).

3.3.3.11 The solution is loaded onto the ion exchanger preconditioned in accordance with the section 7.4.2, whereby americium and curium are adsorbed to the ion exchanger. The rinse is discarded.

Note:

The flow rate results automatically by the design of the column and is not regulated.

3.3.3.12 The exchanger is washed three times with 20 ml of a methanol-nitric acid solution (1:14,6), each, to remove residual iron. The rinses are discarded.

3.3.3.13 The remaining rare earths are removed three to four times with 20 ml of methanol-ammonium thiocyanate-hydrochloric acid mixture (1:1:8) from the ion exchanger. The rinses are discarded.

3.3.3.14 The elution of americium and curium is carried out by adding four times 20 ml of a mixture of methanol and hydrochloric acid (1:7,1), each. The eluates are collected in a 100-ml-beaker.

3.3.3.15 The eluate is concentrated on a heating plate until a white residue appears.

3.3.3.16 Afterwards, the moist residue is evaporated with 1 ml to 5 ml of concentrated hydrochloric acid ($12 \text{ mol}\cdot\text{l}^{-1}$) and concentrated nitric acid (about $15 \text{ mol}\cdot\text{l}^{-1}$), each, in the same volume ratio.

Note:

Beware of nitrous gases!

3.3.3.17 If there is still a white residue after evaporation, step 3.3.3.16 is repeated up to twice.

3.3.3.18 To the residue, 1 ml to 5 ml of concentrated hydrochloric acid ($12 \text{ mol}\cdot\text{l}^{-1}$) are added into the beaker. The solution is gently evaporated to dryness on a heating plate.

3.3.3.19 Further processing is carried out in accordance with the section 3.4.

3.4 Preparation of the counting source

3.4.1 A volume of 300 μl concentrated sulfuric acid (about $18 \text{ mol}\cdot\text{l}^{-1}$) is added into the beaker containing the residue from step 3.3.2.19 (plutonium) or step 3.3.3.19 (americium/curium). The beaker is covered with a watch glass and heated on a heating plate until white vapours occur.

3.4.2 The resulting solution shall be colorless. If not, one drop of hydrogen peroxide ($9,8 \text{ mol}\cdot\text{l}^{-1}$) is added and the solution is heated until bubbling stops and white vapours appear. If the solution is still coloured, this step is repeated once.

3.4.3 After cooling down, 5 ml of distilled water and one drop of mixed indicator 5 are added.

3.4.4 This solution is treated with concentrated ammonia ($13,3 \text{ mol}\cdot\text{l}^{-1}$) until the colour changes to green and afterwards with sulfuric acid ($2 \text{ mol}\cdot\text{l}^{-1}$) until the colour changes to pink. In addition, it is acidified with one more drop of sulfuric acid ($2 \text{ mol}\cdot\text{l}^{-1}$).

3.4.5 The solution is transferred into an electrolysis cell prepared according to section 7.4.4. The beaker is washed twice with 2,5 ml of distilled water, each, and the rinses are also transferred into the electrolysis cell.

3.4.6 The electrolysis cell is placed in a water-cooled copper tube (see figure 2) and the plutonium is electrodeposited onto a stainless steel disc at a constant current of 500 mA for two hours.

3.4.7 Then 1 ml of concentrated ammonia solution ($13,3 \text{ mol}\cdot\text{l}^{-1}$) is added and the electrolysis is continued for another minute.

3.4.8 Afterwards, the power is turned off first and then the cell is removed from the apparatus.

3.4.9 The electrolyte is discarded.

3.4.10 The stainless steel disc is removed from the cell, rinsed with a little amount of distilled water and dried on a heating plate. The counting source is now ready for alpha spectrometric measurement.

4 Measuring the activity

4.1 General

To measure the activity concentrations of plutonium, americium and curium, a commercially available silicon based surface barrier detector is used.

4.2 Calibration

The detection efficiency of the detector is determined by measurement of calibration sources of known activity traceable to national primary standards. The detection efficiency can be considered constant in the energy range of interest.

The energy calibration of the spectral region is carried out using calibration sources with known nuclide composition.

The background in the respective peak areas is detected by measurement of blank sources. These usually have count rates that differ only slightly from the background of the alpha spectrometer. Further information can be found in the general chapter RAD-CHEM/GRUNDL of these procedure manuals.

4.3 Measurement

The duration of measurement of the counting source is adapted to the expected activity and is usually one week for routine measurements. The counting source is measured at the same distance to the detector as the calibration and blank source.

5 Calculation of the results

5.1 Equations

The activity concentration c_r of the nuclide r is calculated according to equation (2) (a decay correction on the time of sampling is neglected due to the long half-lives of the plutonium and americium isotopes):

$$c_r = \frac{A_r}{V} = \frac{A_{Tr}}{R_{n,Tr}} \cdot \frac{p_{\alpha,Tr}}{p_{\alpha,r}} \cdot \frac{1}{V} \cdot (R_{g,r} - R_{0,r}) = \frac{A_{Tr}}{R_{n,Tr}} \cdot \frac{p_{\alpha,Tr}}{p_{\alpha,r}} \cdot \frac{1}{V} \cdot R_{n,r} = \varphi \cdot R_{n,r} \quad (2)$$

Herein are:

- c_r activity concentration of the radionuclide r in Bq·m⁻³;
- 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;
- V volume of the sample, in m³;
- φ procedural calibration factor in Bq·s·m³.

The standard uncertainty $u(c_r)$ of the activity concentration is calculated according to equation (3):

$$u(c_r) = \sqrt{c_r^2 \cdot u_{rel}^2(\varphi) + \varphi^2 \cdot \left(\frac{R_{b,r}}{t_m} + \frac{R_{0,r}}{t_0} \right)} \quad (3)$$

with

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

Herein are:

- $u(c_r)$ standard uncertainty of the activity concentration of the radionuclide r, in Bq·m⁻³;
- $u_{rel}(\varphi)$ 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;
- $u_{rel}(V)$ relative standard uncertainty of the volume;
- t_m duration of measurement, in s;
- t_0 duration of the background measurement, in s.

The chemical yield is not necessary for the calculation of the activity concentration, but can be used to evaluate the radiochemical separation. The chemical yield and the associated standard uncertainty are calculated according to equations (4) and (5):

$$\eta_r = \frac{10000 \cdot R_{0,Tr} \cdot t_0}{t_m \cdot A_{Tr} \cdot \varepsilon_{Tr}} \quad (4)$$

$$u(\eta_r) = \eta_r \cdot \sqrt{u_{rel}^2(R_{0,Tr}) + u_{rel}^2(A_{Tr}) + u_{rel}^2(\varepsilon_{Tr})} \quad (5)$$

Herein are:

- η_r chemical yield of the radionuclide r;
- ε_{Tr} detection efficiency of the detector in the energy range of the tracer peak, in $\text{Bq}^{-1} \cdot \text{s}^{-1}$;
- $R_{0,Tr}$ background count rate of the tracer peak of the blank source, in s^{-1} ;
- $u_{rel}(\eta_r)$ relative standard uncertainty of the chemical yield;
- $u_{rel}(\varepsilon_{Tr})$ relative standard uncertainty of the detection efficiency;
- $u_{rel}(R_{0,Tr})$ relative standard uncertainty of the background count rate.

5.2 Worked example

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

$A_{\text{Pu-242}} = 0,038 \text{ Bq};$	$u_{rel}(A_{\text{Pu-242}}) = 0,02;$
$R_{n,\text{Pu-242}} = 0,009 \text{ s}^{-1};$	$u_{rel}(R_{n,\text{Pu-242}}) = 0,01;$
$\rho_{\alpha,\text{Pu-242}} = 0,9997;$	$u_{rel}(\rho_{\alpha,\text{Pu-242}}) = 0,002;$
$\rho_{\alpha,\text{Pu-238}} = 1,000;$	$u_{rel}(\rho_{\alpha,\text{Pu-238}}) = 0,002;$
$V = 0,101 \text{ m}^3;$	$u_{rel}(V) = 0,02;$
$R_{g,\text{Pu-238}} = 0,00055 \text{ s}^{-1};$	$R_{0,\text{Pu-238}} = 0,00001 \text{ s}^{-1};$
$t_m = 1559663 \text{ s};$	$t_0 = 1210843 \text{ s};$
$\varphi = 41,792 \text{ Bq} \cdot \text{s} \cdot \text{m}^{-3};$	$u_{rel}(\varphi) = 0,03.$

The activity concentration of Pu-238 $c_{\text{Pu-238}}$ is calculated according to equation (2):

$$c_{\text{Pu-238}} = \frac{0,038}{0,009} \cdot \frac{0,9997}{1,000} \cdot \frac{1}{0,101} \cdot (0,00055 - 0,00001) \text{ Bq} \cdot \text{m}^{-3} = 0,0226 \text{ Bq} \cdot \text{m}^{-3}$$

The standard uncertainty of the activity concentration $u(c_{\text{Pu-238}})$ is calculated according to equation (3):

$$\begin{aligned} u(c_{\text{Pu-238}}) &= \sqrt{0,0226^2 \cdot 0,0009 + 41,792^2 \cdot \left(\frac{0,00055}{1559663} + \frac{0,00001}{1210843} \right)} \text{ Bq} \cdot \text{m}^{-3} = \\ &= 0,001 \text{ Bq} \cdot \text{m}^{-3} \end{aligned}$$

with

$$u_{rel}^2(\varphi) = 0,02^2 + 0,002^2 + 0,002^2 + 0,01^2 + 0,02^2 = 0,0009$$

The activity concentration for Pu-238 is thus:

$$c_{\text{Pu-238}} = (0,0226 \pm 0,001) \text{ Bq} \cdot \text{m}^{-3}$$

5.3 Consideration of uncertainties

The standard uncertainty of the analysis result includes the standard uncertainties of the statistical counting, of the tracer activities, of the emission intensities and of the volume of the sample. The standard uncertainties of the duration of measurement are 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 c_r^* is determined according to equation (6):

$$c_r^* = k_{1-\alpha} \cdot \varphi \cdot \sqrt{R_{0,r} \cdot \left(\frac{1}{t_m} + \frac{1}{t_0} \right)} \quad (6)$$

Herein are:

c_r^* decision threshold of the radionuclide r in, $\text{Bq} \cdot \text{m}^{-3}$;

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

6.1.2 Detection limit

The detection limit $c_r^\#$ can be calculated after introducing the auxiliary quantities Ψ and θ with equation (7):

$$c_r^\# = \frac{c_r^* \cdot \Psi}{\theta} \cdot \left\{ 1 + \sqrt{1 - \frac{\theta}{\Psi^2} \cdot \left(1 - \frac{k_{1-\beta}^2}{k_{1-\alpha}^2} \right)} \right\} \quad (7)$$

with:

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

$$\Psi = 1 + \frac{k_{1-\beta}^2}{2 \cdot c_r^*} \cdot \varphi \cdot \frac{1}{t_m}$$

Herein are:

$c_r^{\#}$ detection limit of the radionuclide r , in $\text{Bq} \cdot \text{m}^{-3}$;

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

6.1.3 Confidence intervals

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

6.2 Worked example

For Pu-238, the decision threshold $c_{\text{Pu-238}}^*$ is calculated using the values given in Section 5.2 and the values for the quantiles

$$k_{1-\alpha} = 3; \quad k_{1-\beta} = 1,645;$$

according to equation (6):

$$\begin{aligned} c_{\text{Pu-238}}^* &= 3 \cdot 41,792 \text{ Bq} \cdot \text{s} \cdot \text{m}^{-3} \cdot \sqrt{0,00001 \text{ s}^{-1} \cdot \left(\frac{1}{1559663 \text{ s}} + \frac{1}{1210843 \text{ s}} \right)} = \\ &= 0,00048 \text{ Bq} \cdot \text{m}^{-3} = 0,48 \cdot 10^{-3} \text{ Bq} \cdot \text{m}^{-3} \end{aligned}$$

The detection limit $c_{\text{Pu-238}}^{\#}$ is determined according to equation (7):

$$\begin{aligned} c_{\text{Pu-238}}^{\#} &= \frac{0,48 \cdot 10^{-3} \text{ Bq} \cdot \text{m}^{-3} \cdot 1,0755}{0,998} \cdot \left\{ 1 + \sqrt{1 - \frac{0,998}{1,0755^2} \cdot \left(1 - \frac{1,645^2}{3^2} \right)} \right\} = \\ &= 0,00084 \text{ Bq} \cdot \text{m}^{-3} = 0,84 \cdot 10^{-3} \text{ Bq} \cdot \text{m}^{-3} \end{aligned}$$

with:

$$\theta = 1 - 1,645^2 \cdot 0,0009 = 0,998$$

$$\Psi = 1 + \frac{1,645^2}{2 \cdot 0,48 \cdot 10^{-3} \text{ Bq} \cdot \text{m}^{-3}} \cdot 41,792 \text{ Bq} \cdot \text{s} \cdot \text{m}^{-3} \cdot \frac{1}{1559663 \text{ s}} = 1,0755$$

7 Catalogue of chemicals and equipment

7.1 Chemicals

The chemicals used shall be of analytically pure quality.

- Am-243-tracer: from a traceable standard of activity, a solution containing an Am-243 activity of about $0,17 \text{ Bq}\cdot\text{ml}^{-1}$ is prepared by dilution with nitric acid ($1 \text{ mol}\cdot\text{l}^{-1}$);
- ammonia, NH_3 : $13,3 \text{ mol}\cdot\text{l}^{-1}$;
- ammonium iodide solution: $1 \text{ mol}\cdot\text{l}^{-1}$;
dissolve 3,625 g ammonium iodide, NH_4I , in 25 ml distilled water (prepared **weekly**);
- ammonium iodide-hydrochloric acid-solution (1:9): mix 2 ml ammonium iodide solution ($1 \text{ mol}\cdot\text{l}^{-1}$) with 18 ml concentrated hydrochloric acid ($12 \text{ mol}\cdot\text{l}^{-1}$) (freshly prepared **before use**);
- ammonium iodide-hydrochloric acid-solution (1:18): mix 2 ml ammonium iodide solution ($1 \text{ mol}\cdot\text{l}^{-1}$) with 36 ml concentrated hydrochloric acid ($12 \text{ mol}\cdot\text{l}^{-1}$) (freshly prepared **before use**);
- anion exchanger, each in the chloride form: AG 1X4, 100 mesh - 200 mesh, and AG 1X8, 100 mesh - 200 mesh;
- cleaning solution: 2 %, commercial concentrate, e.g. Mucosol®;
- DDCP-solution: $0,5 \text{ mol}\cdot\text{l}^{-1}$;
dissolve 73,34 g dibutyl-N,N-diethylcarbamyolphosphonate in 500 ml n-heptane;
- dimethylbenzene, C_8H_{10} (xylene, Imixed isomeres);
- ferric chloride solution: 50 mg Fe^{3+} per ml solution:
dissolve 242 g ferric chloride hexahydrate, $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$, in 500 ml concentrated hydrochloric acid ($12 \text{ mol}\cdot\text{l}^{-1}$) and fill to 1 l with concentrated hydrochloric acid ($12 \text{ mol}\cdot\text{l}^{-1}$);
- HDEHP-solution: $0,5 \text{ mol}\cdot\text{l}^{-1}$;
fill 322 g Di-isooctyl-hydrogen phosphonate to 2 l with n-heptane;
- hydrochloric acid, HCl: $1 \text{ mol}\cdot\text{l}^{-1}$, $6 \text{ mol}\cdot\text{l}^{-1}$, $12 \text{ mol}\cdot\text{l}^{-1}$;
- hydrogen peroxide, H_2O_2 : $9,8 \text{ mol}\cdot\text{l}^{-1}$.
- indicator solution: mix 0,2 g methyl red in 100 ml ethanol (60 %);
- methanol-ammonium thiocyanate-hydrochloric acid-solution (1:1:8): mix 40 ml hydrochloric acid ($1 \text{ mol}\cdot\text{l}^{-1}$), 40 ml ammonium thiocyanate solution ($5 \text{ mol}\cdot\text{l}^{-1}$, prepared of ammonium thiocyanate, NH_4SCN) and 320 ml methanol (98 %);
- methanol-nitric acid-solution (1:14,6): mix 32 ml nitric acid (about $15 \text{ mol}\cdot\text{l}^{-1}$) with 468 ml methanol (98 %);

- methanol-hydrochloric acid-solution (1:7,1): mix 61 ml hydrochloric acid ($12 \text{ mol}\cdot\text{l}^{-1}$) with 430 ml methanol (98 %);
- mixed indicator 5;
- nitric acid, HNO_3 : $2 \text{ mol}\cdot\text{l}^{-1}$, $8 \text{ mol}\cdot\text{l}^{-1}$, $12 \text{ mol}\cdot\text{l}^{-1}$, $15 \text{ mol}\cdot\text{l}^{-1}$;
- Pu-242-tracer: from a traceable standard of activity, a solution containing a Pu-242 activity of about $0,17 \text{ Bq}\cdot\text{ml}^{-1}$ is prepared by dilution with nitric acid ($1 \text{ mol}\cdot\text{l}^{-1}$);
- sodium hydroxide: $1 \text{ mol}\cdot\text{l}^{-1}$;
- sodium nitrite, NaNO_2 ;
- sulphuric acid, H_2SO_4 : $2 \text{ mol}\cdot\text{l}^{-1}$, $18 \text{ mol}\cdot\text{l}^{-1}$;

7.2 Equipment

- plastic container with volume graduation, 100 l and 200 l, respectively;
- stirring motor with propeller stirrer;
- pH meter;
- beaker (100 ml, 250 ml, 1 l, 5 l);
- 1-l-glass bottle with screw cap and plastic seal;
- separating funnel (250 ml);
- burette;
- usual equipment of a radiochemical laboratory;
- laboratory centrifuge with centrifuge tubes (500 ml, 600 ml);
- suction devices (witt jar, buchner funnel (\varnothing 125 mm), water jet pump);
- filter paper (\varnothing 125 mm);
- glass columns (inner diameter 11 mm);
- electrolysis apparatus with electroysis cells (see section 7.4.4);
- stainless steel discs (\varnothing 18 mm);
- alpha spectrometer with silicon based surface barrier detectors, e.g. area 300 mm^2 , layer thickness $100 \mu\text{m}$, peak width at half height 20 keV.

7.3 Software supported calculation

7.3.1 Example of an Excel spreadsheet

Procedure for determining the activity concentrations of plutonium, americium and curium in sea water by alpha spectrometry

D- α -SPEKT-MWASS-01

Version June 2019

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

SAMPLE IDENTIFICATION: Sea water

#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	29,2883936	2,6795E-05	0,00078479	56,57295008
p 2	Added activity of the tracer nuclide	ATr	0,038	0,00076	0,59387791	0,00045135	18,71207614
p 3	Net count rate of the tracer	RnTr	9,0000E-03	0,00009	-2,507482	0,00022567	4,67800968
p 4	Background count rate	R0r	1,0000E-05	2,8738E-06	-41,7916389	0,0001201	1,324925381
p 5	Sum emission intensities (tracer)	p α Tr	9,9970E-01		0,02257413	0	0
p 6	Sum emission intensities (radionuclide)	p α r	1		-0,02256734	0	0
p 7	Volume of the sample	V	1,0100E-01	2,0200E-03	-0,22343899	0,00045135	18,71203872
p 8	Duration of measurement	tm	1559663		-1,4737E-08	0	0
p 9	Duration of background measurement	_t0	1210843		0	0	0
(List can be continued here)							
Model section		c = phix * Rn					
Auxiliary equations h		(Formulae)					
h 1	#Gross count rate Rg	Rg	0,000549997				
(List can be continued here)							
	#Net count rate Rn	Rn	5,4000E-04				
	#Calibration factor, proc.dep.	phix	41,79163916				
	#Value output quantity	Erg	2,2567E-02		0,00084388	--> output value modifiable by VBA	
	#Combined standard uncertainty	uErg	1,0434E-03				
	#Decision threshold	Bq/m ³	4,8021E-04				
	#Detection limit	Bq/m ³	8,4388E-04				
further derived values							
	Auxiliary quantity Omega	Omega	1				
	Best estimate	BestEst	0,022567361				
	Uncertainty best estimate		0,001043397				
	Lower confidence limit		0,020522339				
	Upper confidence limit		0,024612382				

Calculate!

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

7.3.2 Example of an UncertRadio project

The screenshot shows the UncertRadio software interface with the following data:

Final measurement result for cr :

- Coverage factor k: 1.0
- Value output quantity: 2.25675E Bq/m³
- extendend (Std.-)uncertainty: 1.04535E-03 Bq/m³
- relative extd.(Std.-)uncertainty: 4.6321 %
- Best Bayesian Estimates: min. Coverage-Intervall
- Value output quantity: 2.25675E-02 Bq/m³
- extendend (Std.-)uncertainty: 1.04535E-03 Bq/m³
- lower confidence limit: 2.05186E-02 Bq/m³
- upper confidence limit: 2.46163E-02 Bq/m³
- Probability (1-gamma): 0.950

Decision threshold and detection limit for cr :

- Decision threshold (DT): 4.78430E-04 Bq/m³ Iterations: 1
- Detection limit (DL): 8.41881E-04 Bq/m³ Iterations: 5
- k_alpha=2.989, k_beta=1.645 Method: ISO 11929:2010, by iteration

Monte Carlo Simulation:

- Number of simul. measurments: 100000
- Number of runs: 1
- Values <0 included:
- min. Coverage interval:
- reISD%:
 - Value output quantity: 2.25743E-02 Bq/m³ 0.015
 - extendend uncertainty: 1.04696E-03 Bq/m³ 0.224
 - relative extd.(Std.-)uncertainty: 4.6378 %
 - lower confidence limit: 2.05630E-02 Bq/m³ 0.043
 - upper confidence limit: 2.46647E-02 Bq/m³ 0.036
 - Decision threshold (DT): 4.78186E-04 Bq/m³ 0.863
 - Detection limit (DL): 8.41192E-04 Bq/m³ 0.521
- active run: 1 IT: 11 Start MC

LinFit: Standard uncertainty of fit parameter ai:

- from LS analysis:
- from uncertainty propagation:
- reduced Chi-square:

Project: 1\Berechnungsdateien\D-alpha-SPEKT-MWASS-01_V2019-06_EN.bxp Ready!

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

7.4 Preparing work

7.4.1 Anion exchange column for plutonium

If a glass column with frit is not available, a suitable support material for the ion exchange resin is introduced into a glass column. The anion exchange resin AG 1X8 is slurried with distilled water into the column. After settling, the height of the ion exchange resin shall be 10 cm. The supernatant is drained and the ion exchanger is conditioned with about 20 ml of nitric acid (8 mol·l⁻¹).

7.4.2 Anion exchange column for americium/curium

If a glass column with frit is not available, a suitable support material for the ion exchange resin is introduced into a glass column. The anion exchange resin AG 1X4 is slurried into the column with the methanol-nitric acid solution (1:14,6). After settling, the height of the ion exchange resin shall be 8 cm. The column can be used without further conditioning.

7.4.3 Electrolysis discs

The stainless steel discs are cleaned with a 2 % cleaning solution.

7.4.4 Electrolysis cell

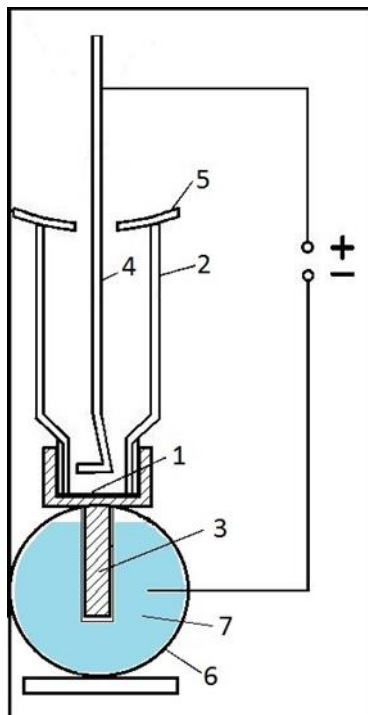
To eliminate contamination, disposable cells made from polyethylene scintillation vials of 20 ml capacity are used. The cell body (2) is cleaned with a 2 % cleaning solution. The vial bottom is cut off.

A stainless steel disc is heated by means of a holder on a heating plate and then adhered to the vial neck of the scintillation vial by pressing firmly with this stainless steel disc (1).

This cell is electroconductively connected by screwing into a brass bottle cap (3). A leak test with distilled water is recommended, since the electrolysis plate can loosen. The anode (4) consists of a 120 mm long and 2 mm thick platinum wire, which is formed at the lower end into a circular loop. In order to avoid losses by spraying during electrolysis, the cell body is covered with a slotted cover (5) made of Teflon.

The electrolysis cell thus prepared is placed in a water-cooled copper tube (6 and 7).

The apparatus used for the electrodeposition is shown schematically in figure 2 and its design in figure 3.



Key:

- 1 stainless steel disc (cathode)
- 2 cell body
- 3 brass bottle cap
- 4 platinum wire (anode)
- 5 slotted cover
- 6 copper tube
- 7 water cooling

Fig. 2: Scheme of the apparatus for the electrodeposition

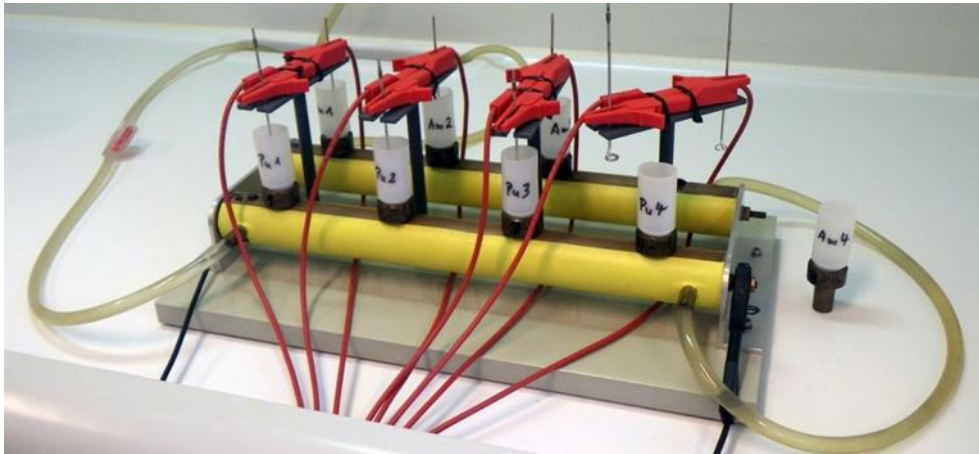


Fig. 3: Design of the apparatus used for electrodeposition.

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.