# Procedure for determining the activity concentration of caesium-137 in seawater by proportional counting

D-Cs-137-MWASS-01

Authors:

A. Meyer

S. Schmied

A. Gottschalk

J. Herrmann

Federal coordinating office for seawater, suspended particulate matter and sediment

(Leitstelle für Meerwasser, Meeresschwebstoff und -sediment)

# Procedure of determining the activity concentration of caesium-137 in seawater by proportional counting

# 1 Scope

The procedure described in the following is suitable for determining the activity concentration of caesium-137 (Cs-137) in seawater according to the IMIS-routine programme [1].

The procedure is appropriate for activity concentrations of Cs-137 of a few becquerels per cubic metres of seawater.

#### Note:

If the presence of Cs-134 cannot be excluded, its activity concentration has to be considered in calculating to avoid an overestimation of the activity concentration of Cs-137. Therefore, a gamma spectrometric measurement has to be carried out.

# 2 Sampling

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

# 3 Analysis

# 3.1 Principle of the procedure

The procedure is designed for sample volumes of 20 l to 100 l [2]; usually, a sample volume of 45 l of seawater is used.

After adding stable caesium carrier, caesium is precipitated together with potassium by adding an aqueous solution of sodium hexanitrocobaltate. The precipitate obtained is dissolved and caesium is precipitated after various purification steps. The counting source thus obtained is measured by a low-level proportional counter.

# 3.2 Sample preparation

The acidified seawater sample is decanted into a 50-l-precipitation container with volume scale and the volume read off is noted.

# 3.3 Radiochemical separation

**3.3.1** A volume of 20 ml of caesium carrier solution (100 mg Cs<sup>+</sup>) are added to the sample by means of a volumetric pipette. Then the sample is thoroughly mixed by a stirrer motor with a propeller stirrer. Compressed air can be passed through the sample for better mixing during steps 3.3.1 to 3.3.5.

#### Note:

Water samples with a salinity below 30 PSU (Practical Salinity Unit) additionally have to be supported with 2,2 ml of potassium carrier solution (110 mg  $K^+$ ) before precipitation, below 15 PSU there have to be added 3,5 ml of potassium carrier solution (175 mg  $K^+$ ) per litre water sample.

- **3.3.2** First, concentrated ammonia solution (13,3 mol·l<sup>-1</sup>) is added till a pH-value between 9 and 10 is reached.
- **3.3.3** Afterwards, a pH-value of 5,5 is set with concentrated acetic acid (18 mol· $l^{-1}$ ).
- **3.3.4** Per litre sample, 1,6 g of sodium hexanitrocobaltate are dissolved in a small amount of distilled water in a beaker and added to the sample.
- **3.3.5** Then, 0,4 g of sodium hexanitrocobaltate per litre sample are added. In so doing, caesium is precipitated as cobaltate by co-precipitation of potassium.
- **3.3.6** The precipitation container is left to stand at best overnight to allow the precipitate to settle down.
- **3.3.7** The supernatant clear solution is siphoned. About 1 l of the siphoned solution is stored as wash water.
- **3.3.8** The precipitate is transferred quantitatively into a 2-I-beaker. For this purpose, the precipitation container is rinsed with the wash water from step 3.3.7.
- **3.3.9** The precipitate transferred has to settle down. The supernatant solution is removed by suction with a minimum loss of precipitate.
- **3.3.10** Afterwards, about 200 ml of concentrated hydrochloric acid (12 mol·l<sup>-1</sup>) are added and the solution is reduced to just below 100 ml on a hot plate in a fume hood.

#### Note:

The formation of nitrous gases has to be considered during heating.

- **3.3.11** The now blue coloured solution is transferred into a 600-ml-beaker and the 2-l-beaker is rinsed with distilled water. The combined solutions are evaporated almost to dryness, thus forming a smooth surface residue. During the evaporation process the solution is stirred occasionally with a glass rod.
- **3.3.12** The residue is rubbed under continuous stirring with a glass rod to produce a homogeneous powder. If necessary, the beaker is heated again.
- **3.3.13** The produced powder is dissolved in as little distilled water maximum 100 ml as possible.

#### Note:

If the powder cannot be dissolved completely in 100 ml of distilled water at first, the suspension is heated. The solution has to be cooled to room temperature before further processing.

**3.3.14** For the precipitation of potassium chloride, 500 ml of ethanol are added to the aqueous solution and the beaker is cooled in a water/ethanol ice bath or with an immersion cooler for 4 hours at approx. -5 °C.

- **3.3.15** The precipitated potassium chloride is collected under suction on a filter of the type white ribbon on a Büchner funnel.
- **3.3.16** The ethanol is separated from the filtrate.

#### Note:

The separation can be carried out using a rotary evaporator if the ethanol should be recovered. Alternatively, a heatable magnetic stirrer is used.

- **3.3.17** The remaining aqueous solution of 90 ml to 100 ml is filtered again by a filter of type white ribbon and a fast mode funnel into a 400 ml beaker.
- **3.3.18** To the filtrate, concentrated acetic acid (18 mol·l<sup>-1</sup>) is added in a volume ratio of 3 to 1 (three parts solution and one part acetic acid).
- **3.3.19** To this solution, 30 ml of iodobismuthate solution are added. The solution is then cooled in an ice bath to approx. -5 °C. The formation of the precipitate of caesium iodobismuthate (Cs<sub>3</sub>Bi<sub>2</sub>l<sub>9</sub>) is initiated by rubbing with a glass rod on the inner wall of the beaker. The caesium iodobismuthate precipitates in the form of red-light crystals. The solution is left in the ice bath to stand overnight to allow completion of the precipitation.
- **3.3.20** The supernatant solution is decanted. The precipitate is collected under suction on a G4-glass filter crucible and is washed with only a few millilitres of acetic acid (9 mol·l<sup>-1</sup>) and ethanol one by one.
- **3.3.21** The precipitate is dried in a drying cabinet for four hours at approx. 60 °C.
- **3.3.22** The dried precipitate is transferred as quantitatively as possible from the glass filter crucible on a pre-weighed counting tray.

#### Note:

A 2"-counting tray is suitable.

- **3.3.23** Afterwards, the precipitate is suspended in a small amount of distilled water in the counting tray and a homogeneous, flat counting source is produced. The counting source is dried again in a drying cabinet at approx. 60 °C until a constant weight is reached.
- **3.3.24** The counting source is weighed after cooling to determine the chemical yield and surface area.

#### Note:

The counting sources are not hygroscopic and therefore do not have to be cooled or stored in a desiccator.

# 4 Measuring the activity

#### 4.1 General

The Cs-137 activity is measured with a low-level proportional counter.

#### 4.2 Calibration

A nuclide specific calibration depending on the layer thickness is needed because of the self-absorption of the beta radiation of Cs-137 within the counting source.

The calibration sources are produced by using aqueous solutions of Cs-137 of a traceable standard of known activity concentration together with different volumes of caesium carrier solution (10 mg to 300 mg Cs<sup>+</sup>) in a beaker. Every calibration solution is filled to 100 ml with distilled water. The further processing is continued from step 3.3.18.

The detection efficiency depending on the mass distribution is determined from the measured values of the calibration sources. The obtained calibration function is linear in good approximation.

#### 4.3 Measurement

Every counting source is measured three times for 360 minutes in each case in a proportional counter. The mean value of the three obtained net count rates is used for calculation of the results.

#### 5 Calculation of the results

## 5.1 Equations

#### 5.1.1 Output quantity

The activity concentration of Cs-137, c, in seawater at the time of sampling is calculated according to Equation (1):

$$c = R_{\rm n} \cdot \varphi = R_{\rm n} \cdot \frac{f_{\rm A}}{\varepsilon \cdot \eta \cdot V} = R_{\rm n} \cdot \frac{e^{\lambda \cdot t_{\rm A}}}{\varepsilon \cdot \eta \cdot V} \tag{1}$$

with

$$R_{\rm n} = \bar{R}_{\rm g} - R_0$$

Herein are:

c Cs-137 activity concentration, in Bq·m $^{-3}$ ;

 $f_{\rm A}$  correction factor for the decay;

 $\lambda$  decay constant of Cs-137, in s<sup>-1</sup>;

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

 $R_{\rm n}$  net count rate, in s<sup>-1</sup>;

 $\bar{R}_{\rm g}$  mean gross count rate m measurements of the counting source, in s<sup>-1</sup>,

with 
$$\bar{R}_{g} = \frac{1}{m} \cdot \sum_{i=1}^{m} R_{g,i}$$

 $R_0$  background count rate, in s<sup>-1</sup>;

 $\varphi$  procedural calibration factor, in Bq·s·m<sup>-3</sup>;

 $\varepsilon$  detection efficiency depending on mass distribution, in Bq<sup>-1</sup>·s<sup>-1</sup>;

 $\eta$  chemical yield;

V volume of the sample, in  $m^3$ .

From experience, the count rates of the blank value  $R_{\rm BL}$  do not differ significantly from the background count rates. Therefore, the background count rate is used.

# 5.1.2 Standard uncertainty of the output quantity

The standard uncertainty of the activity concentration is calculated according to Equation (2):

$$u(c) = c \cdot \sqrt{\frac{1}{m} \cdot \frac{\bar{R}_{g}}{t_{m}} + \frac{R_{0}}{t_{0}} + u_{rel}^{2}(\varphi)} =$$

$$= c \cdot \sqrt{\frac{1}{m} \cdot \frac{\bar{R}_{g}}{t_{m}} + \frac{R_{0}}{t_{0}} + u_{rel}^{2}(f_{A}) + u_{rel}^{2}(\varepsilon) + u_{rel}^{2}(\eta) + u_{rel}^{2}(V)}$$
(2)

Herein are:

u(c) standard uncertainty of the Cs-137 activity concentration, in Bq·m<sup>-3</sup>;

 $t_{
m m}$  duration of measurement, in s;

 $t_0$  duration of the background measurement, in s;

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

 $u_{\rm rel}(f_{\rm A})$  relative standard uncertainty of the correction factor for the decay;

 $u_{\rm rel}(\varepsilon)$  relative standard uncertainty of the detection efficiency;

 $u_{\mathrm{rel}}(\eta)$  relative standard uncertainty of the chemical yield;

 $u_{\rm rel}(V)$  relative standard uncertainty of the volume.

In general, the contribution of the relative standard uncertainty of the correction factor for the decay  $u_{\rm rel}(f_{\rm A})$  can be neglected for the calculation of the combined relative standard uncertainty.

# 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.

$$R_{g,1} = 0,676 \text{ s}^{-1};$$
  $u(R_{g,1}) = 0,0056 \text{ s}^{-1};$   $R_{g,2} = 0,677 \text{ s}^{-1};$   $u(R_{g,2}) = 0,0056 \text{ s}^{-1};$   $u(R_{g,3}) =$ 

The activity concentration c is calculated with

$$\bar{R}_{\rm g} = \frac{1}{3} \cdot (0.676 \, {\rm s}^{-1} + 0.677 \, {\rm s}^{-1} + 0.678 \, {\rm s}^{-1}) = 0.6770 \, {\rm s}^{-1}$$

according to Equation (1):

$$c = (0.6770 \text{ s}^{-1} - 0.01 \text{ s}^{-1}) \cdot \frac{e^{0.73 \cdot 10^{-9} \text{ s}^{-1} \cdot 15.8 \cdot 10^{6} \text{ s}}}{0.31 \text{ Bq}^{-1} \cdot \text{s}^{-1} \cdot 0.77 \cdot 0.045 \text{ m}^{3}} = 62.82 \text{ Bq} \cdot \text{m}^{-3}$$

The standard uncertainty of the activity concentration, u(c), is determined according to Equation (2):

$$u(c) = 62,82 \text{ Bq} \cdot \text{m}^{-3} \cdot \sqrt{\frac{1}{3} \cdot \frac{0,6770 \text{ s}^{-1}}{21600 \text{ s}} + \frac{0,01 \text{ s}^{-1}}{21600 \text{ s}} + 0,05^2 + 0,05^2 + 0,02^2} =$$

$$= 62,82 \text{ Bq} \cdot \text{m}^{-3} \cdot 0,07356 = 4,621 \text{ Bq} \cdot \text{m}^{-3}$$

Thus, the activity concentration is:

$$c = (62.82 \pm 4.621) \text{ Bg} \cdot \text{m}^{-3}$$

#### 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 standard uncertainty of the analysis takes into consideration the standard uncertainties of the statistical counting, of the calibration, of the chemical yield and of the volume of the sample. The standard uncertainties of the duration of measurement and of the decay constant are neglected.

# 6 Characteristic limits of the procedure

The calculation of the characteristic limits follows the standard series ISO 11929 [3].

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  $c^*$  is determined using Equation (3):

$$c^* = k_{1-\alpha} \cdot \varphi \cdot \sqrt{R_0 \cdot \left(\frac{1}{m \cdot t_{\rm m}} + \frac{1}{t_0}\right)}$$
 (3)

Herein are:

 $c^*$  decision threshold of the activity concentration, in Bq·m<sup>-3</sup>;

 $k_{1-\alpha}$  quantile of the normal distribution for  $\alpha = 0.0014$ .

#### 6.1.2 Detection limit

The detection limit  $c^{\#}$  is calculated according to the implicit Equation (4):

$$c^{\#} = c^{*} + k_{1-\beta} \cdot \sqrt{(c^{\#})^{2} \cdot u_{\text{rel}}^{2}(\varphi) + \varphi^{2} \cdot \left(\frac{c^{\#}}{\varphi \cdot t_{\text{m}}} + \frac{R_{0}}{m \cdot t_{\text{m}}} + \frac{R_{0}}{t_{0}}\right)}$$
(4)

In Equations (3) and (4) are:

 $c^{\#}$  detection limit of the activity concentration, in Bq·m<sup>-3</sup>;

 $k_{1-\beta}$  quantile of the normal distribution for  $\beta = 0.05$ .

After transformation of Equation (4) and implementation of the auxiliary quantities  $\Psi$  and  $\theta$  the detection limit  $c^{\#}$  is calculated using Equation (5):

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

with

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

$$\Psi = 1 + \frac{k_{1-\beta}^2}{2 \cdot c^*} \cdot \varphi \cdot \frac{1}{t_m} \tag{7}$$

#### 6.1.3 Limits of the coverage interval

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

# 6.2 Worked examples

Besides the values of Section 5.2, the following additional values are considered:

$$k_{1-\alpha} = 3;$$
  $k_{1-\beta} = 1,645;$   $u_{\text{rel}}^2(\varphi) = 0,0054.$ 

The value of the decision threshold  $c^*$  is calculated according to Equation (3):

$$c^* = 3.94,18 \text{ Bq} \cdot \text{s} \cdot \text{m}^{-3} \cdot \sqrt{0,01 \text{ s}^{-1} \cdot \left(\frac{1}{3.21600 \text{ s}} + \frac{1}{21600 \text{ s}}\right)} = 0,2220 \text{ Bq} \cdot \text{m}^{-3}$$

The value of the decision threshold  $c^*$  is calculated according to Equation (5):

$$c^{\#} = \frac{0,2220 \text{ Bq} \cdot \text{m}^{-3} \cdot 1,0266}{0,9854} \cdot \left[ 1 + \sqrt{1 - \frac{0,9854}{1,0266^2} \cdot \left( 1 - \frac{1,645^2}{3^2} \right)} \right] = 0,3674 \text{ Bq} \cdot \text{m}^{-3}$$

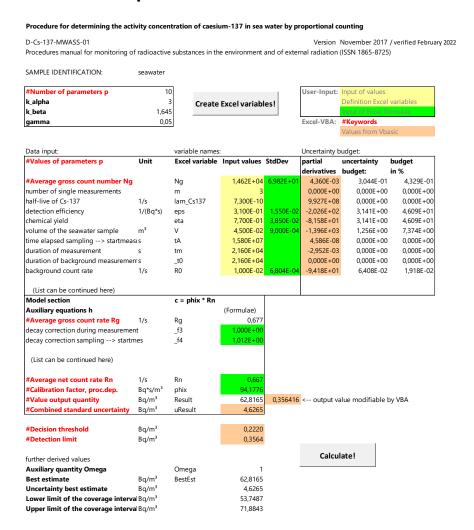
with

$$\theta = 1 - 1.645^2 \cdot 0.0054 = 0.9854$$

$$\Psi = 1 + \frac{1,645^2}{2 \cdot 0,2220 \text{ Bq} \cdot \text{m}^{-3}} \cdot 94,18 \text{ Bq} \cdot \text{s} \cdot \text{m}^{-3} \cdot \frac{1}{21600 \text{ s}} = 1,0266$$

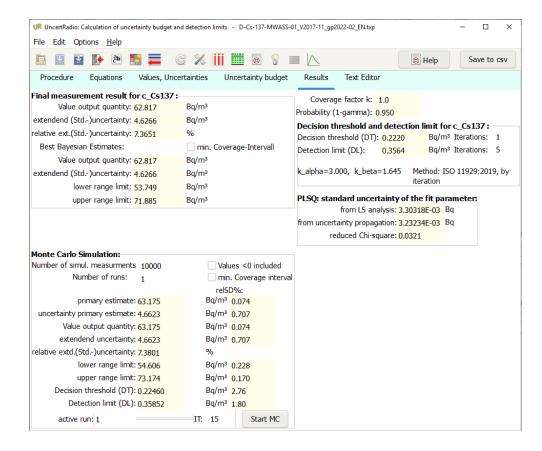
# 7 Software supported calculation

# 7.1 View of the Excel spreadsheet



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.

— acetic acid: 9 mol·l $^{-1}$ , 18 mol·l $^{-1}$ ;

— ammonia, NH₃: 13,3 mol·l⁻¹;

bismuth oxynitrate, BiNO<sub>4</sub>
 (alkaline bismuth nitrate);

— caesium chloride, CsCl;

— caesium carrier solution: 5 mg Cs+ per ml solution:

dissolve 6,334 g of caesium chloride in distilled

water and fill to 1 l;

— ethanol: denatured;

hydrochloric acid, HCl:
 12 mol·l<sup>-1</sup>.

— iodobismuthate solution: 24,7 g of bismuth oxynitrate are added slowly

while continuous stirring to a saturated solution of 90,4 g of sodium iodide in 50 ml of distilled and just before boiling heated water. Afterwards, the solution is taken off the hot plate and 125 ml of concentrated acetic acid (18 mol·l-1) are added in

portions;

potassium chloride, KCl;

potassium carrier solution:
 50 mg K+ per ml solution:

dissolve 95,348 g of potassium chloride in distilled water and fill to 1 l;

— sodium hexanitrocobaltate(III), Na<sub>3</sub>[Co(NO<sub>2</sub>)<sub>6</sub>];

sodium iodide, Nal.

# 8.2 Equipment

The following equipment is used for the procedure beside the usual equipment of a radiochemical laboratory:

- water sampling rosette or special scoop with volumes of 50 l to 500 l;
- precipitation container with volume scale, at least 20 l;
- stirrer motor with propeller stirrer, optionally compressed air;
- water/ethanol ice bath or immersion cooler;
- Büchner funnel, Ø 70 mm;
- heatable magnetic stirrer, optionally rotary evaporator;
- circular filter, Ø 70 mm and 110 mm, type white ribbon or comparable;
- glass filter crucible, type G4;
- drying cabinet;
- counting trays made of stainless steel;
- low-level proportional counter.

#### 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, S. 4-80.

- [2] Schmitt, D. E., Kautsky, H.: *Ein Verfahren zur Bestimmung des* <sup>137</sup>Cs-Gehaltes im *Meerwasser*. Deutsche Hydrografische Zeitschrift, 1961, Vol. 14 (5), S. 194-197.
- [3] 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).