

Procedure for determining the specific activity of strontium-90 in fish by proportional counting

G-Sr-90-FISCH-01

Authors:

M.-O. Aust

B. Klug

G. Kanisch

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

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

Procedure for determining the specific activity of strontium-90 in fish by proportional counting

1 Scope

The procedure described in the following is used for determining the specific activity of strontium-90 (Sr-90) in fish flesh and whole fish in the IMIS routine programme [1] under the directive of the Federal Radiation protection Act (StrlSchG) [2]. The procedure can similarly be used for monitoring of the specific Sr-90 activity according to the Guideline concerning Emission and Immission Monitoring of Nuclear Facilities (REI) in normal operation mode [3]. The procedure may only be used, when it is ensured that a radioactive equilibrium between Sr-90 and its progeny yttrium-90 (Y-90) is present at the time of the radiochemical strontium separation.

2 Sampling

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

The required sample size depends on whether fish flesh or whole fish is to be analysed, because strontium is mainly enriched in bone and skin of fish. This means that the strontium content in samples containing skin and bones has to be expected at least magnitude larger compared to those of pure fish flesh. The analysis of Sr-90 in fish flesh requires a filleted original sample of at least 2 kg, while 1 kg from whole fish samples is sufficient.

3 Analysis

3.1 Principle of the procedure

Fish ash is leached after addition of strontium-, barium-, caesium- and yttrium carrier solutions using hydrochloric acid. The ingrown Y-90 is extracted with bis-(2-ethylhexyl)-hydrogen phosphate (HDEHP, $0,45 \text{ mol}\cdot\text{l}^{-1}$) in n-heptane and afterwards re-extracted using hydrochloric acid and trioctylmethyl ammonium chloride in toluene. A counting source is received after an oxalate-precipitation, whose Y-90 activity is determined by low level beta anticoincidence counting. The chemical yield of yttrium is determined by complexometric measurement.

3.2 Sample preparation

The ash obtained from the Procedure G- γ -SPEKT-FISCH-01 is used for subsequent radiochemical separation. For this purpose, residues of stable carbon compounds such as collagens must be removed by ashing for eight days at a final temperature of 600 °C. The ash should then be almost white in colour. It is preferably stored in a desiccator, as fish ash can be very hygroscopic.

3.3 Radiochemical separation

The separation process described below is designed for ash masses between 50 g (whole fish) and 100 g (fish flesh).

3.3.1 The fish ash is dried at 110 °C for one hour and placed in a desiccator to cool.

3.3.2 The ash is weighed into a 1000 ml beaker (tall form); the exact weight is noted.

3.3.3 The ash is moistened with distilled water until the sample no longer darkens.

3.3.4 Then 5,0 ml of yttrium carrier solution (10 mg·ml⁻¹ Y³⁺), 1,5 ml of strontium carrier solution (40 mg·ml⁻¹ Sr²⁺), 2,5 ml of barium carrier solution (20 mg·ml⁻¹ Ba²⁺) and 2,0 ml of caesium carrier solution (30 mg·ml⁻¹ Cs⁺).

Note:

Strontium, caesium and barium are used as retention carriers, yttrium additionally for yield determination.

3.3.5 Per gram of weighed ash, 1 ml of hydrochloric acid (12,1 mol·l⁻¹) is added. The slurry is heated to boiling point and left to boil for 30 minutes.

3.3.6 The mixture is cooled to room temperature in an ice bath.

3.3.7 The mixture is transferred with hydrochloric acid (6 mol l⁻¹; 1 ml per gram of weighed ash) to a sufficiently large centrifuge tube and is centrifuged for 30 minutes at 21 °C at 2560×g. The clear supernatant is transferred to a 1000 ml beaker.

3.3.8 The residue in the centrifuge tube is treated twice more according to Step 3.3.7. The respective clear supernatants are combined in the 1000 ml beaker.

3.3.9 The solutions combined in the 1000 ml beaker are adjusted to a pH of 1 to 1,5 with sodium hydroxide solution (10 mol·l⁻¹).

3.3.10 The solution stands until it has reached room temperature. A slight turbidity in the solution is acceptable, but no visible precipitate.

Note:

- At this point, the radiochemical separation may be interrupted without negative effects on the analysis result.
- If salt crystals or precipitate are visible, the pH value of the solution is too high. It must be adjusted to the required pH value with hydrochloric acid (6 mol·l⁻¹) to dissolve the residue, if necessary, by stirring.

3.3.11 The cooled solution is transferred to a sufficiently large separating funnel (usually 1000 ml).

3.3.12 Afterwards, 100 ml of bis-(2-ethylhexyl)-hydrogen phosphate (HDEHP, 0,45 mol·l⁻¹) in n-heptane is added to the separatory funnel.

3.3.13 The date and time of the Y-90 separation is recorded immediately prior to the start of Step 3.3.14.

3.3.14 The solution in the separatory funnel is shaken for ten minutes on a horizontal shaker at a shaking frequency of 200 min⁻¹.

3.3.15 After removing the separatory funnel from the horizontal shaker, a waiting time of at least ten minutes has to be maintained until the aqueous and organic phases clearly separated.

3.3.16 The aqueous (lower) phase is transferred to a 1000 ml beaker and the organic phase drained into a 250 ml beaker.

3.3.17 Steps 3.3.12 and 3.3.14 to 3.3.16 are repeated once with the aqueous phase. The organic phases are combined in a 1000 ml shaking funnel. The aqueous phase is stored in the 1000 ml beaker.

Note:

The aqueous solution is kept as a reserve sample until a plausible result of the activity determination is available. If necessary, the analysis can be repeated from Step 3.3.11 after adding 5,0 ml yttrium carrier solution to the retain sample.

3.3.18 The organic phase is shaken five times in the 1000 ml separating funnel with 100 ml hydrochloric acid (1 mol·l⁻¹) for two minutes each time using the horizontal shaker at a shaking frequency of 200 min⁻¹. After phase separation, the aqueous (lower) phase is drained off and discarded.

Note:

At this stage, a source holder is prepared together with a filter paper according to Section 8.3.

3.3.19 To extract yttrium, 50 ml of hydrochloric acid (9 mol·l⁻¹) are added to the organic phase. The solution in the separatory funnel is shaken for two minutes with the horizontal shaker at a shaking frequency of 200 min⁻¹.

3.3.20 After removal of the separatory funnel from the horizontal shaker and a subsequent waiting time of at least two minutes, the lower, hydrochloric acid phase is transferred to a 500 ml separatory funnel.

3.3.21 Steps 3.3.19 and 3.3.20 are repeated four times, collecting the hydrochloric acid phases in the same separatory funnel.

3.3.22 To the hydrochloric acid solution in the separatory funnel, 200 ml of tri-octyl-methyl ammonium chloride (ADOGEN[®] 464, 0,65 mol·l⁻¹) in toluene are added. The

separatory funnel is shaken for ten minutes with the horizontal shaker at a shaking frequency of 200 min⁻¹.

3.3.23 After removal of the separatory funnel from the horizontal shaker and a waiting time of at least ten minutes, the phase separation should be complete and the aqueous phase clear and colourless.

Note:

If this is not the case, the solution is shaken briefly by hand up to five times and is waited until phase separation is complete.

3.3.24 The lower aqueous phase is drained into a 1000 ml beaker into which 200 ml of distilled water has already been added. The organic phase is collected in a waste container for halogenated solvents.

Note:

To avoid contamination of glassware with HDEHP and ADOGEN[®]464, the respective glassware is firstly rinsed with ethanol, followed by tap water. Afterwards, it is completely filled with a mixture of commercially available dish detergent and water and left to stand overnight. The glassware is then emptied, rinsed again with tap water and decontaminated with the remaining glassware in a rinsing solution (see Section 8.1).

3.3.25 Then, 400 ml of ammonia solution (13,4 mol·l⁻¹) is slowly added while stirring. The pH value of the solution should be in the range of 8,5 to 9,5. A turbidity is formed by colloiddally precipitating yttrium hydroxide.

3.3.26 The solution is heated to boiling in a water bath and then cooled to room temperature in an ice bath.

3.3.27 After the solution has cooled and the precipitate has settled, the supernatant is decanted down to about 200 ml or sucked off, for example with a water jet pump.

Note:

This step requires the utmost care in order to avoid loss of yield.

3.3.28 The remaining solution with the precipitate is quantitatively transferred to a 250 ml centrifuge tube.

3.3.29 After centrifugation for 30 minutes at 21 °C at 2560×g, the supernatant is discarded.

3.3.30 The precipitate is completely dissolved in a few drops of nitric acid (7,2 mol·l⁻¹). The solution in the centrifuge tube is heated until boiling in a water bath. Then, the water bath is immediately switched off and ice is added to the water bath.

Note:

A 250 ml beaker with about 35 ml water on a hotplate may be used as a water bath.

3.3.31 Afterwards, 20 ml distilled water and 3 ml saturated oxalic acid solution are added for yttrium oxalate precipitation.

3.3.32 Ammonia solution ($13,4 \text{ mol}\cdot\text{l}^{-1}$) is added dropwise until a pH between 1,0 and 1,5 is reached to ensure completeness of precipitation.

Note:

If no more turbidity is visible at the drop-in point, the precipitation of yttrium oxalate is complete.

3.3.33 After the precipitate has cooled and settled, it is transferred to a suitable, previously weighed filter paper (Section 8.3) using a glass vacuum filtration unit. Any precipitate remaining in the centrifuge tube or adhering to the filtration unit is rinsed onto the filter with as little ammoniacal water as possible. The precipitate on the filter paper is washed off with a little ethanol.

3.4 Preparation of the counting source

3.4.1 The glass vacuum filtration unit is opened. Any yttrium oxalate residue adhering to the glass parts is removed with a spatula and added to the precipitate on the filter.

3.4.2 The filter with the precipitate is dried at $110 \text{ }^\circ\text{C}$ for 30 minutes.

3.4.3 After cooling to room temperature in the desiccator, the filter with the precipitate is weighed.

3.4.4 The source holder prepared according to Section 8.3 is removed from the desiccator.

3.4.5 The loaded filter is then placed on the plastic disc and covered with Mylar[®] film. It is carefully fixed in place with a fixing ring, but tension of the Mylar[®] film must be avoided.

3.4.6 In order to achieve an even and thin coating of yttrium oxalate on the filter, the precipitate is evenly distributed on the surface by slightly circular movements with a stamp, for example a polytetrafluoroethylene plug with a suitable diameter.

3.4.7 The Mylar[®] film is then smoothed out without creases and the fixing ring is pushed to the lower edge of the plastic disc. The Mylar[®] film protruding beyond the lower edge of the fixing ring and plastic disc is cut off and any surface charges are equalised using an ion blower.

3.4.8 The counting source prepared in this way is measured immediately in order to minimise decay of the Y-90 activity.

3.5 Determination of the chemical yield of yttrium

The chemical yield of yttrium is determined by complexometry after the activity has been measured. Therefore, the counting source needs to be destroyed prior to the yield determination.

3.5.1 The yttrium oxalate precipitate together with the Mylar[®] film and filter paper are placed in a 300 ml Erlenmeyer flask and brought into solution with 10 ml Titriplex III solution (0,1 mol·l⁻¹) and 20 ml borate buffer (0,1 mol·l⁻¹) under heat.

3.5.2 A spatula tip of indicator mixture is added.

3.5.3 The titration is carried out with zinc sulphate solution (0,1 mol·l⁻¹) until the transition point from blue to violet is reached.

3.5.4 For comparison, 5 ml yttrium carrier solution (10 mg·ml⁻¹ Y³⁺) is added in a 300 ml Erlenmeyer flask, mixed with 10 ml Titriplex III solution (0,1 mol·l⁻¹) and 20 ml borate buffer (0,1 mol·l⁻¹) as well as a spatula tip of indicator and again titrated with zinc sulphate solution (0,1 mol·l⁻¹) up to the transition point.

3.5.5 The chemical yield of yttrium η_Y is calculated from the consumption of Titriplex III solution (0,1 mol·l⁻¹) in the solution with known yttrium concentration (Step 3.5.4) and the consumption in the solution with unknown yttrium content (Step 3.5.3) according to Equation (1).

$$\eta_Y = \frac{V_{\text{EDTA},1} - V_{\text{Zn,Pr}}}{V_{\text{EDTA},2} - V_{\text{Zn,Tr}}} \quad (1)$$

Herein are:

$V_{\text{EDTA},k}$ volume of added Titriplex III solution (0,1 mol·l⁻¹) with $k = 1, 2$, in ml;

$V_{\text{Zn,Pr}}$ consumption of zinc sulphate solution (0,1 mol·l⁻¹) for the solution with unknown yttrium concentration, in ml;

$V_{\text{Zn,Tr}}$ consumption of zinc sulphate (0,1 mol·l⁻¹) for the solution with a known yttrium concentration, in ml.

The square of the relative uncertainty of the yttrium yield is calculated using Equation (2):

$$u_{\text{rel}}^2(\eta_Y) = \frac{u^2(V_{\text{EDTA},1}) + u^2(V_{\text{Zn,Pr}})}{(V_{\text{EDTA},1} - V_{\text{Zn,Tr}})^2} + \frac{u^2(V_{\text{EDTA},2}) + u^2(V_{\text{Zn,Pr}})}{(V_{\text{EDTA},2} - V_{\text{Zn,Tr}})^2} \quad (2)$$

4 Measuring the activity

4.1 General

With a proportional counter, the pulses of all kind of ionising radiation in a sample are recorded in an integral count rate. In order to be able to use this count rate directly for activity determination, only the radionuclide to be determined must be present in the sample. In real counting sources of fish samples, impurities with beta- and gamma emitting radionuclides often occur, which must be taken into account when determining the activity of Sr-90 (see Section 4.3). In the present case, a decay curve adapted to the

net count rates of the Y-90 sample obtained at different measurement times is used for this purpose.

4.2 Calibration

To calibrate the low level beta anticoincidence counting system for oxalate precipitation, a Y-90 calibration source is prepared. For this purpose, Y-90 is separated from a solution with precisely known Sr-90 activity, which is also in radioactive equilibrium and has been mixed with the carriers according to Step 3.3.4, by means of hydroxide precipitation according to Step 3.3.25. The resulting yttrium hydroxide is then precipitated according to Step 3.3.25. The yttrium hydroxide obtained is then purified according to Steps 3.3.27 to 3.3.30 and Y-90 is precipitated as oxalate. The calibration source is prepared and measured as described in Steps 3.3.33 to 3.4.8. The chemical yield for each calibration source is determined according to Section 3.5.

The detection efficiency is calculated according to Equation (3):

$$\varepsilon_{Y-90} = \frac{R_{n,Y-90}}{A_{Y-90}} \cdot e^{\lambda_{Y-90} \cdot t_1} \cdot \frac{(1 - e^{-\lambda_{Y-90} \cdot t_m})}{\lambda_{Y-90} \cdot t_m} \quad (3)$$

Herein are:

ε_{Y-90} detection efficiency for Y-90, in $\text{Bq}^{-1} \cdot \text{s}^{-1}$;

A_{Y-90} activity of Y-90, in Bq;

$R_{n,Y-90}$ net count rate of Y-90, in s^{-1} ;

t_{Y-90} half time of Y-90, in s;

t_m measurement duration, in s;

t_1 time difference between Sr/Y separation and start of measurement, in s;

λ_{Y-90} decay constant of Y-90, in s^{-1}

$$\text{with } \lambda_{Y-90} = \frac{\ln 2}{t_{Y-90}} .$$

The masses determined before and after precipitation are used to calculate the area density according to Equation (4) in order to be able to take the self-absorption effects in the calibration source into account:

$$\rho_F = \frac{m_{bF} - m_{lF}}{F} \quad (4)$$

Herein are:

ρ_F area density of the calibration source, in $\text{g} \cdot \text{cm}^{-2}$;

m_{bF} mass of the filter including precipitation, in g;

- m_{IF} mass of the empty filter, in g;
 F effective surface area of the counting source calculated from the inner diameter of the fixing ring, in cm^2 .

Correction of the self-absorption can be omitted if the area densities of the calibration sources correspond to those of the counting sources. Otherwise, a calibration curve for the self-absorption must be established.

The square of the relative uncertainty of the detection efficiency is calculated according to Equation (5), whereby the uncertainties of the decay corrections can be neglected:

$$u_{\text{rel}}^2(\varepsilon_{Y-90}) = u_{\text{rel}}^2(R_{n,Y-90}) + u_{\text{rel}}^2(A_{Y-90}) \quad (5)$$

To reduce random uncertainty contributions from the determination of the chemical yield, the preparation of the counting source, etc., a set of different calibration sources should be used.

A beta emitting reference calibration source, e. g. a Sr-90/Y-90 source in radioactive equilibrium, is used for long-term monitoring of the detection efficiency of the detector.

4.3 Background

The background effect considered here corresponds to the blank count rate R_{BL} , which includes both impurities from the analysis and the specific background effect of the measurement system. The background count rate is determined from a large number of measurements of different inactive yttrium oxalate precipitates.

4.4 Measurement

The Y-90 activity in the sample is measured using a low-level beta anti-coincidence counting system whose central detector is operated in anti-coincidence with a screen detector. To further reduce the background effect, the detector system should also be surrounded on all sides by at least 10 cm of lead in order to achieve background counting rates of around $1,7 \cdot 10^{-3} \text{ s}^{-1}$.

To record the decay curve of Y-90, the counting source is measured several times with a single measurement duration of two hours each. Significant count rate increases can occur due to other radionuclides that may be co-extracted:

- Actinium-228 (Ac-228): This interference occurs in particular in the first measurements carried out directly after the preparation of the counting source.
- Radon progenies: These can accumulate from the ambient air in the precipitate during filtering through a glass vacuum filtration unit (see Step 3.3.27 in Section 3.3) and interfere with the first measurements carried out.

- Radionuclides with half-lives significantly longer than one hour, such as cerium-144 (Ce-144) with a half-life of 285 days and cerium-141 (Ce-141) with a half-life of 32,5 days: These radionuclides increase the measured count rates during the entire measurement. This extraneous contribution to the count rate can only be reliably recognised if the decay curve of a given counting curve is recorded over a period of at least three days.

5 Calculation of the results

5.1 Output quantity

The time-dependent measured net count rates, $R_n(t_i)$, are calculated according to Equation (6):

$$R_n(t_i) = g(t_i) - R_{BL} \quad (6)$$

Herein are:

$R_g(t_i)$ gross count rate at the time t_i , in s^{-1} ;

R_{BL} background count rate, in s^{-1} .

As explained in Section 4.4, interfering nuclides may be present in the sample. In this case, the gross count rates of the k individual measurements are made up of the contributions of the Y-90, the interfering nuclides and the background effect. The time-dependent net count rate $R_n(t_i)$ is calculated according to Equation (7).

$$R_n(t_i) \approx R_{n,Y-90}(t_i = 0) \cdot \left[e^{-\lambda_{Y-90} \cdot t_i} \cdot \frac{(1 - e^{-\lambda_{Y-90} \cdot t_{m,i}})}{\lambda_{Y-90} \cdot t_{m,i}} \right] + \sum_{j=1}^m R_{n,St,j}(t_i = 0) \cdot e^{-\lambda_{St,j} \cdot t_i} \quad (7)$$

Herein are:

$R_{n,Y-90}(t_i = 0)$ net count rate of Y-90 at the time of the Sr-/Y-separation, in s^{-1} ;

$R_{n,St,j}(t_i = 0)$ net count rate of the interfering radionuclide ($j = 1, \dots, m$) at the time of the Sr/Y-separation, in s^{-1} ;

t_i time difference between the Y-90-precipitation and begin of the i^{th} measurement ($i = 1, \dots, k$), in s;

$t_{m,i}$ measurement duration of the i^{th} measurement, in s;

$\lambda_{St,j}$ decay constant of the interfering radionuclide ($j = 1, \dots, m$), in s^{-1} .

Note:

After the decay curve has been recorded, chi-square values are determined for various assumptions of interfering nuclides (see General Chapter CHAGR-ISO-02, Annex D, of this Procedures' Manual). If a

comparison of these values leads to the conclusion that a long-lived interfering nuclide is present in the sample, a half-life of 10^{14} s is assumed for this initially unknown interfering nuclide, which is further optimised during the fit procedure and checked for plausibility.

Using the value $R_{n,Y-90}(t_i = 0)$ obtained from the linear deconvolution, the specific Sr-90 activity related to the sampling date is calculated according to Equation (8):

$$a_{\text{Sr-90}} = \frac{e^{\lambda_{\text{Sr-90}} \cdot t_A}}{\varepsilon_{Y-90} \cdot \eta_Y \cdot m_A \cdot q_F} \cdot R_{n,Y-90}(t_i = 0) = \varphi \cdot R_{n,Y-90}(t_i = 0) \quad (8)$$

Herein are:

- $a_{\text{Sr-90}}$ specific Sr-90-activity at the time of sampling, in $\text{Bq}\cdot\text{kg}^{-1}$;
 t_A time difference between sampling and Sr-/Y-separation, in s;
 m_A ash mass used for the analysis, in kg;
 q_F ratio between fresh mass and ash mass;
 $\lambda_{\text{Sr-90}}$ decay constant of Sr-90, in s^{-1}
 with $\lambda_{\text{Sr-90}} = \frac{\ln 2}{t_{\text{Sr-90}}}$
 φ procedural calibration factor, in $\text{Bq}\cdot\text{s}\cdot\text{kg}^{-1}$.

5.2 Standard uncertainty of the output quantity

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

The standard uncertainty of the net count rate is calculated according to Equation (9):

$$u^2(R_n(t_i)) = \frac{R_n(t_i)}{t_{m,i}} + R_{\text{BL}} \cdot \left(\frac{1}{t_{m,i}} + \frac{1}{t_0} \right) + u^2(R_{\text{BL}}) \quad (9)$$

Herein is:

- t_0 duration of the background measurement, in s.

The square of the relative uncertainty of the specific Sr-90 activity is calculated according to Equation (10), whereby the uncertainties of the decay correction are negligible:

$$u_{\text{rel}}^2(a_{\text{Sr-90}}) = u_{\text{rel}}^2(R_{n,Y-90}(t_i = 0)) + u_{\text{rel}}^2(\varphi) \quad (10)$$

with

$$u_{\text{rel}}^2(\varphi) = u_{\text{rel}}^2(f_2) + u_{\text{rel}}^2(\varphi_A) + u_{\text{rel}}^2(\eta_{\text{Sr}}) + u_{\text{rel}}^2(V) \quad (11)$$

The relative standard uncertainty of the net count rate of Y-90 at the time of the Sr/Y separation ($t_i = 0$) also includes the standard uncertainties of the count rates of any interfering nuclides present. These standard uncertainties are mapped, for example, using the results of the fit function for the decay curve determined with the UncertRadio software.

Experience has shown that the combined standard uncertainty is in the range of 10 % to 15 %.

6 Characteristic limits of the procedure

The characteristic limits are calculated in accordance with the ISO 11929 series of standards [4]. For further considerations, it is referred to the General Chapter CHAGR-ISO-01 of this Procedures' Manual [5].

The calculation of the decision threshold of the specific Sr-90 activity of the radionuclide $a_{\text{Sr-90}}^*$ and the detection limit $a_{\text{Sr-90}}^\#$ can only be solved by numerical iteration with a software, e. g. UncertRadio.

6.1 Decision threshold

The decision threshold $a_{\text{Sr-90}}^*$ is calculated according to Equation (12):

$$a_{\text{Sr-90}}^* = k_{1-\alpha} \cdot u(a_{\text{Sr-90}} = 0) \quad (12)$$

Herein are:

$a_{\text{Sr-90}}^*$ decision threshold, in $\text{Bq}\cdot\text{kg}^{-1}$ (FM);

$k_{1-\alpha}$ quantile of the normal distribution for the probability of the type I error α .

Note:

Equation (12) deviates from the usual scheme in the measurement instructions, in which the detection limit is directly related to the nuclide-specific background count rate. In the present case, the specific Sr-90 activity is determined indirectly via the net count rate of the Y-90 at the time of Sr/-separation, so that the detection limit is calculated only via the uncertainty of the specific Sr-90 activity, which is set equal to zero.

6.2 Detection limit

The value of the detection limit $a_{\text{Sr-90}}^\#$ is calculated using the implicit equation (14).

$$a_{\text{Sr-90}}^\# = a_{\text{Sr-90}}^* + k_{1-\beta} \cdot \tilde{u}(a_{\text{Sr-90}}^\#) \quad (13)$$

Herein are:

$k_{1-\beta}$ quantile of the normal distribution for the probability of the type II error β .

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.

The calculation of the specific Sr-90 activity according to Equations (6) to (11) can only be solved using linear deconvolution, as a decay curve of the Y-90 activity in the counting source is measured here. The specific activity of Sr-90 is determined from this. For this purpose, it is necessary to use software such as UncertRadio (see Section 7.2.2 and General Chapter CHAGR-ISO-02, Annex D, of this Procedures' Manual).

7.1 Manual evaluation

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

The specific Sr-90 activity is calculated as an example for 5,7 kg fresh mass of a herring sample taken from the Baltic Sea on 10th April 2012, whereby the following numerical values were obtained.

Sr-90/Y-90 separation date: 01.11.2012, 7:45 am:

R_0	=	0,0014 s ⁻¹ ;	$u_{\text{rel}}(R_0)$	=	0,0585;
R_{BL}	=	46,67·10 ⁻³ s ⁻¹ ;	$u_{\text{rel}}(R_{\text{BL}})$	=	0,6071;
m_{A}	=	0,07784 kg;	$u_{\text{rel}}(m_{\text{A}})$	=	51,39·10 ⁻⁶ ;
q_{F}	=	73,42;	$u_{\text{rel}}(q_{\text{F}})$	=	0,02;
$\varepsilon_{\text{Y-90}}$	=	0,4104 s ⁻¹ ·Bq ⁻¹ ;	$u_{\text{rel}}(\varepsilon_{\text{Y-90}})$	=	0,029;
η_{Y}	=	0,8897;	$u_{\text{rel}}(\eta_{\text{Y}})$	=	0,02;
$t_{\text{Y-90}}$	=	0,2307·10 ⁶ s;	$u_{\text{rel}}(t_{\text{Y-90}})$	=	0,4858·10 ⁻³ ;
$t_{\text{Ac-228}}$	=	22,140·10 ³ s;	$u_{\text{rel}}(t_{\text{Ac-228}})$	=	4,878·10 ⁻³ .

The standard uncertainties of the following input quantities are omitted:

t_{A}	=	17,69·10 ⁶ s;	t_0	=	208,694·10 ³ s;
$t_{\text{m,i}}$	=	72·10 ³ s;			
$t_{\text{Sr-90}}$	=	0,9088·10 ⁹ s.			

The data used as basis of the Y-90 decay curve are listed in Table 1.

Tab. 1: For each measurement i of the series, start date and start time, the time difference t_i between the Sr/Y-separation and beginning of the measurement as well as the gross count number are shown; the measurement duration of each cycle is two hours.

measurement i	start of measurement	time difference t_i in s	gross count number N_g
1	01.11.2012 15:34	28 140	554
2	02.11.2012 11:34	100 140	280
3	03.11.2012 07:34	172 140	238
4	04.11.2012 03:34	244 140	188
5	04.11.2012 23:34	316 140	200
6	05.11.2012 19:34	388 140	164

Due to the measurement data, it is assumed that a contamination of the counting source with a short-lived radionuclide, e. g. Ac-228, occurred. This assumption is verified using Figure 1.

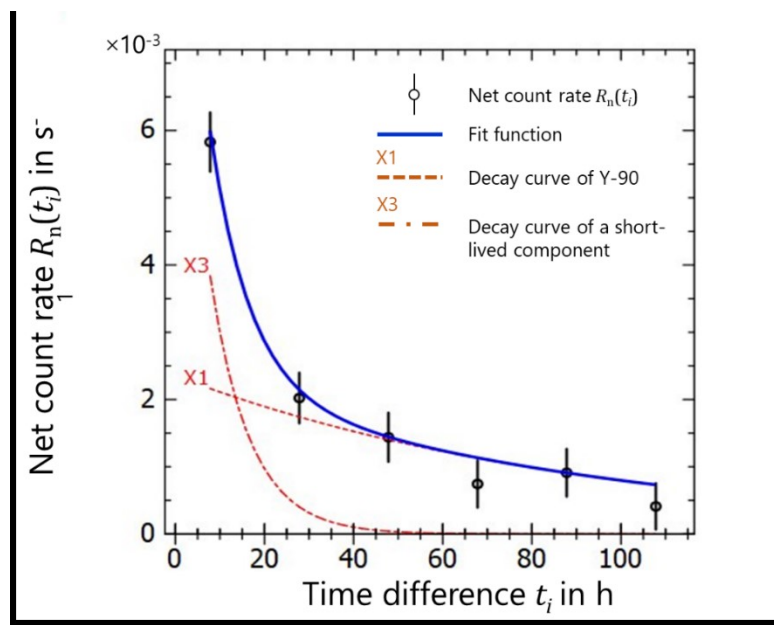


Fig. 1: Visualisation of the measured net count rates and their standard uncertainties; **blue:** decay curve fitted to the measured net count rates; **red:** calculated decay curves of the individual components: Y-90 (X1) and the short-lived interfering radionuclide (X3).

The specific Sr-90 activity and the assigned standard uncertainty are calculated according to Equations (8) and (10):

$$a_{\text{Sr-90}} = (1,27 \pm 0,26) \cdot 10^{-3} \text{ Bq} \cdot \text{kg}^{-1}(\text{FM})$$

The decision threshold of the specific Sr-90-activity $a_{\text{Sr-90}}^*$ using the quantile of the type I error of the normal distribution $k_{1-\alpha} = 3$ results in:

$$a_{\text{Sr-90}}^* = 0,673 \cdot 10^{-3} \text{ Bq} \cdot \text{kg}^{-1}(\text{FM})$$

The detection limit of the specific Sr-90-activity $a_{\text{Sr-90}}^\#$ using the quantile of the type II error of the normal distribution $k_{1-\beta} = 1,645$ results in:

$$a_{\text{Sr-90}}^\# = 1,100 \cdot 10^{-3} \text{ Bq} \cdot \text{kg}^{-1}(\text{FM})$$

The use of 1 kg fresh mass leads to a detection limit of approximately $3,4 \text{ mBq} \cdot \text{kg}^{-1}$ (FM), at 2 kg fresh mass $1,7 \text{ mBq} \cdot \text{kg}^{-1}$ (FM) are achievable.

7.2 Software supported evaluation

7.2.1 View of the Excel® spreadsheet

Procedure for determining the specific activities of strontium-90 in fish by proportional counting

G-Sr-90-FISCH-01

Version March 2024

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

Sample Identifier: Herring, Filet

ANALYTE: Sr-90

Number of result variables: 1
 Number of all fitparameters: 2
 Number of measurement channels: 1
 Number of measurements per channel: 6
 Number of parameters p: 2
 Number of parameters q: 6
 Number of parameters without uncertainty: 0
 k_alpha: 3
 k_beta: 1,644854
 Probability gamma: 0,05

Preparation of the count rates:

	tstart(i)	tmess(i)	Nb(i)	Rb(i)	tnull(i)	NO(i)	RO(i)	Rn(i)	u_Rn(i)
1	469	72000	554	0,00769	208694	292,1716	0,00140	0,005828	0,00044
2	1669	72000	280	0,00389	208694	292,1716	0,00140	0,002022	0,00038
3	2869	72000	238	0,00331	208694	292,1716	0,00140	0,001439	0,00036
4	4069	72000	188	0,00261	208694	292,1716	0,00140	0,000744	0,00035
5	5269	72000	200	0,00278	208694	292,1716	0,00140	0,000911	0,00035
6	6469	72000	164	0,00228	208694	292,1716	0,00140	0,000411	0,00034

Values of the Parameters p:

Value: modifiable StdDev:
 HwzY90 230550 112
 HWZAc228 22140 108

Values of the Parameters q:

Value: StdDev:
 epsY 0,4104 0,0119016
 etaY 0,8897 0,017794
 m 77,84 0,004
 qF 73,42 1,4684
 tA 204,8 0,2
 HWZs-90 10519 26

Backgroundcount rate:

Rb1 4,67E-04 2,83E-04

Values of parameters without uncertainties:

Values

Matrix Amat (transposed):

	Y-90	Ac-228
1	0,826227716	0,164531929
2	0,665409643	0,017269941
3	0,535893416	0,001821723
4	0,431586402	0,000190271
5	0,347581845	1,99718E-05
6	0,279928048	2,0963E-06

Vektor x, modified: Vektor x:

	Rn(i):
1	0,00601503
2	0,002150639
3	0,001449302
4	0,001137531
5	0,000913006
6	0,00073497

Kovar-Matrix U_x

	1	2	3	4	5	6
1	1,93852E-07	8,69843E-08	8,69843E-08	8,69843E-08	8,69843E-08	8,69843E-08
2	8,69843E-08	1,40997E-07	8,69843E-08	8,69843E-08	8,69843E-08	8,69843E-08
3	8,69843E-08	8,69843E-08	1,32895E-07	8,69843E-08	8,69843E-08	8,69843E-08
4	8,69843E-08	8,69843E-08	8,69843E-08	1,2325E-07	8,69843E-08	8,69843E-08
5	8,69843E-08	8,69843E-08	8,69843E-08	8,69843E-08	1,25565E-07	8,69843E-08
6	8,69843E-08	8,69843E-08	8,69843E-08	8,69843E-08	8,69843E-08	1,1862E-07

Solution vector y:

	modifizierbar:
1	0,002625393
2	0,023374536

Kovar-Matrix U_y:

1	2,77797E-07	-8,39861E-07
2	-8,39861E-07	6,81078E-06

StdDevs:

0,000527064
0,002609747

Reduced Chisquare:

0,609158558

Matrix Phi:

0,485727579	0
0	1

Solution vector y':

0,001275226
0,023374536

Sensitivity coefficients:

	Matrix Qsmat:	Y-90	Ac-228
p+q-Vektor:			
HwzY90	-2,34727E-09	2,61343E-08	
HWZAc228	-2,88638E-08	-1,51893E-06	
epsY	-0,003107272	0	
etaY	-0,00143332	0	
m	-1,63036E-05	0	
qF	-1,73689E-05	0	
tA	8,40307E-08	0	
HWZs-90	-1,63604E-09	0	

Budgets%:

0,00010131
0,01424453
2,004757159
0,953511134
6,29477E-06
0,953511134
4,14027E-07
2,65232E-06

Kovarianzmatrix U_pq:

	1	2	3	4	5	6	7	8
1	12544	0	0	0	0	0	0	0
2	0	11664	0	0	0	0	0	0
3	0	0	0,000141648	0	0	0	0	0
4	0	0	0	0,000316626	0	0	0	0
5	0	0	0	0	0,000016	0	0	0
6	0	0	0	0	0	2,15619856	0	0
7	0	0	0	0	0	0	0,04	0
8	0	0	0	0	0	0	0	676

Matrix Jmat (transposed):

0,485727579	0
0	1

complete covariance matrix og y':

6,82193E-08	-4,07433E-07
-4,07433E-07	6,8377E-06

Standarddeviations of y':

0,000261188
0,002614899

Decision thresholds:

Y-90
 0,00067367
 detection limit 0,00109975
 result values 0,0012752
 result uncertainties 0,00026119
 derived values
 Omega's 0,99999948
 best estimator 0,00127523
 uncertainties of best estimator 0,00026119
 lower confidence interval 0,00076331
 upper confidence interval 0,00178715

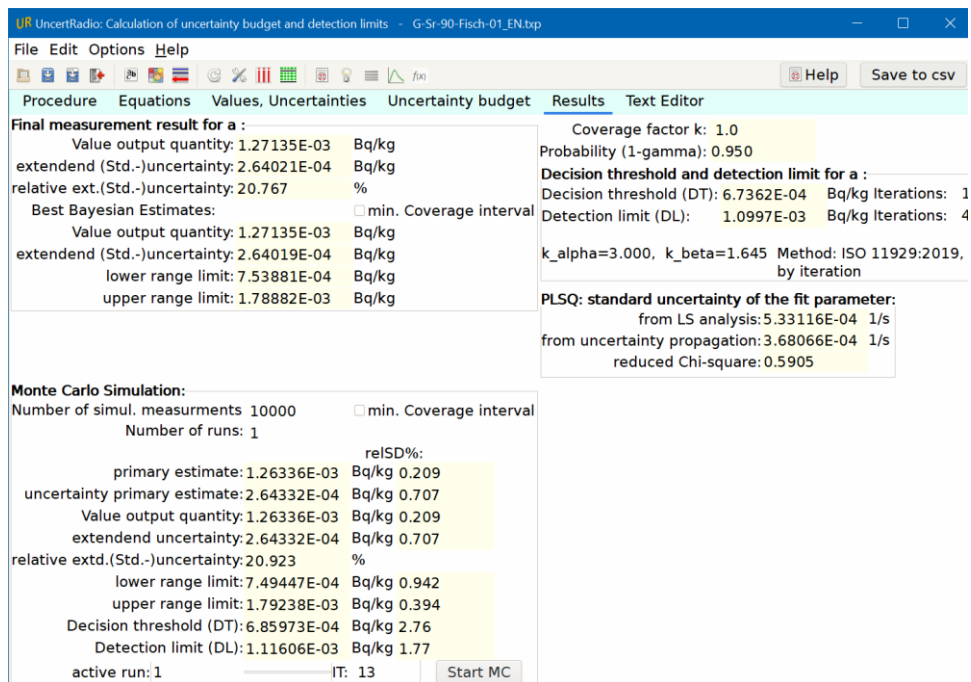
Calculate!

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

Note:

This Excel® spreadsheet is to be used for a decay curve of six measurements only.

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 shall be of analytically pure quality.

- Adogen[®] 464 in toluene: 0,65 mol l⁻¹:
Add 700 ml Toluene into a 1000 ml volumetric flask and fill up with 300 ml Adogen[®] 464 (trioctylmethyl ammonium chloride);
- ammonia-containing water distilled water with ammonia, pH ca. 8;
- ammonia solution, NH₃: 13,4 mol·l⁻¹;
- barium carrier solution: 20 mg·ml⁻¹ Ba²⁺:
Dissolve 9,51 g barium nitrate (Ba(NO₃)₂) in distilled water inside a 250 ml volumetric flask and fill up to 250 ml;
- borate buffer: 0,1 mol·l⁻¹:
Dissolve 38,1 g sodium tetraborate decahydrate (Na₂B₄O₇·10 H₂O) and 6,18 g boron acid (H₃BO₃) in distilled water in a 1000 ml volumetric flask and fill up to 1000 ml;

-
- | | |
|--|--|
| — caesium carrier solution: | 30 mg·ml ⁻¹ Cs ⁺ :
Dissolve 9,50 g caesium chloride (CsCl) in a 250 ml volumetric-flask in distilled water and fill up to 250 ml; |
| — HDEHP in n-heptane: | 0,45 mol·l ⁻¹ :
Add 850 ml n-heptane into a 1000 ml volumetric flask and fill up with 150 ml bis-(2-ethyl-hexyl)-hydrogen phosphate (HDEHP) to 1000 ml; |
| — hydrochloric acid, HCl: | 1 mol·l ⁻¹ :
Add 83 ml HCl (12,1 mol·l ⁻¹) in a 1000 ml volumetric flask and fill up with distilled water to 1000 ml; |
| — hydrochloric acid, HCl: | 6 mol·l ⁻¹ :
Give 500 ml HCl (12,1 mol·l ⁻¹) in a 1000 ml volumetric flask and fill up with distilled water to 1000 ml; |
| — hydrochloric acid, HCl: | 9 mol·l ⁻¹ :
Add 744 ml HCl (12,1 mol·l ⁻¹) in a 1000 ml volumetric flask and fillup with distilled water to 1000 ml; |
| — hydrochloric acid, HCl: | 12,1 mol·l ⁻¹ ; |
| — indicator mixture: | Mixture of sodium chloride (NaCl) and Eriochrome black T (indicator for metal titrations):
99 parts of NaCl are intensively mixed with 1 part Eriochrome black T using a mortar; |
| — nitric acid, HNO ₃ : | 14,4 mol·l ⁻¹ ; |
| — oxalic acid solution (saturated): | 0,81 mol·l ⁻¹ :
Distilled water is heated in a beaker until boiling. Oxalic acid dihydrate is added as solid until precipitation occurs. The supernatant is transferred into a bottle and closed. The saturated oxalic acid can be stored for a long time; |
| — rinsing solution: | e. g. RBS [®] solution, 2 %; |
| — sodium hydroxide, NaOH: | 10 mol l ⁻¹ :
Dissolve 400 g sodium hydroxide with distilled water in a 1000 ml volumetric flask and fill up with distilled water to 1000 ml; |
| — strontium carrier solution: | 40 mg·ml ⁻¹ Sr ²⁺ :
Weigh 24,15 g strontium nitrate (Sr(NO ₃) ₂) into a 250 ml volumetric flask and fill up with distilled water; |
| — Titriplex [®] III solution: | 0,1 mol·l ⁻¹ ; |
| — yttrium carrier solution: | 10 mg·ml ⁻¹ Y ³⁺ : |
-

Dissolve 8,54 g yttrium chloride hexahydrate ($\text{YCl}_3 \cdot 6\text{H}_2\text{O}$) in distilled water in a 250 ml volumetric flask and fill up with distilled water. In case of visible precipitation, a few drops of hydrochloric acid ($12,1 \text{ mol} \cdot \text{l}^{-1}$) are added for dissolving. The amount is determined by complexometry;

- zinc sulfate solution, ZnSO_4 : $0,1 \text{ mol} \cdot \text{l}^{-1}$.

8.2 Equipment

The following equipment is used for the procedure:

- analytical balance;
- low-level-beta-anticoincidence counting system;
- beaker (1000 ml, tall and/or broad form);
- burette;
- Erlenmeyer flasks (300 ml);
- desiccator;
- glass vacuum filtration unit: holder for 20 mm membrane filter with glass frit filter support and suction flask with tubing nozzle (ge. *Hahnsche Nutsche*);
- ion blower, e. g. Sartorius Stat-Fan YIB01;
- Mylar[®] film
- separation funnel (1000 ml, 500 ml);
- horizontal shaker;
- drying chamber;
- source holder, containing of a plastic disc and a fixing ring (POM, density approx. $1,41 \text{ g} \cdot \text{cm}^{-3}$). Total diameter 1 inch, plastic disc: height 6,1 mm, diameter 23,8 mm);
- filter paper: ashfree, slow draining, (mean retention capacity $2 \mu\text{m}$ bis $4 \mu\text{m}$), diameter 22 mm, e. g. Macherey-Nagel MN 640d.
- pH-meter;
- pH-test strips: ranges 0 to 6, 5 to 10 and 7,5 to 14;
- temperature controlled centrifuge;
- glass made centrifuge tubes (250 ml and/or 500 ml with round bottom).

8.3 Preliminary works

A source holder is dried together with a filter paper (see Figure 2) in a suitable vessel for at least 30 minutes at $110 \text{ }^\circ\text{C}$. After cooling in the desiccator, the three components are

weighed separately; the masses are recorded. The components are stored in the desiccator until use.



Fig. 2: a) Counting source, consisting of plastic disc, fixing ring and filter paper with precipitate and Mylar[®] film, in a Petri dish;
b) Plastic disc and fixing ring.

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] *Gesetz zum Schutz vor der schädlichen Wirkung ionisierender Strahlung (Strahlenschutzgesetz - StrlSchG) vom 27. Juni 2017 (BGBl. I S. 1966)*, zuletzt geändert durch die Bekanntmachung vom 3. Januar 2022 (BGBl. I S. 15).
- [3] *Richtlinie zur Emissions- und Immissionsüberwachung kerntechnischer Anlagen (REI)*. Gemeinsames Ministerialblatt, 2024, Nr. 6-9, p. 102.
- [4] 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)*.
- [5] 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: Bundesministerium für Umwelt, Naturschutz, nukleare Sicherheit und Verbraucherschutz, (ed.): *Messanleitungen für die Überwachung radioaktiver Stoffe in der Umwelt und externer Strahlung*. ISSN 1865-8725. Available at: <https://www.bmu.de/WS1517>. [Last access 27.10.2023].