

Procedure for determining strontium-89 and strontium-90 in surface water in cases of normal conditions

C-Sr-89/Sr-90-OWASS-01

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1 Scope

The described procedure is suitable for determining strontium isotopes Sr-89 and Sr-90 in surface water in normal scenarios. In order to increase the sensitivity of the method, the nuclides are enriched from sample volumes of 50 litres prior to the actual measurement. For measurement periods of 100 minutes per sample, it can still detect concentrations of $0,1 \text{ Bq}\cdot\text{m}^{-3}$ (Sr-90) and $1 \text{ Bq}\cdot\text{m}^{-3}$ (Sr-89), respectively.

This procedure facilitates to monitor in great detail the contamination of a water body with Sr-89 and Sr-90 and demonstrate the impact of the various sources on the nearer and farther surroundings of emitters (1).

2 Sampling

The collection of samples is described in procedure C- γ -SPEKT-OWASS-01.

3 Analysis

3.1 Principle of the method

Determining the two strontium isotopes, Sr-89 and Sr-90, contained in surface water at concentrations of $0,1 \text{ Bq}\cdot\text{m}^{-3}$ to $100 \text{ Bq}\cdot\text{m}^{-3}$ is a two-step process:

3.1.1 Enrichment

Enrichment of Sr-89 and Sr-90 from sample volumes of 50 litres through co-precipitation on strontium hydrogen phosphate with the aid of bentonitic flocculation aids and subsequent acid elution (2).

Alternatively, the surface water sample may be concentrated with a rotary evaporator or similar apparatus and the residue admitted to acid.

3.1.2 Radiochemical separation

Fission and activation products are separated through repetitive precipitation of the alkaline earth nitrates in highly concentrated, cold ($< 0 \text{ }^\circ\text{C}$) nitric acid ("nitrate method"). Ba-140 and possibly present contributions of Ra-226 and Ra-228, which commonly accompany Sr-89 and Sr-90 at this stage of separation, are extracted via chromate precipitation. Remnants of subsequently generated Y-90 are removed by inserting an yttrium hydroxide scavenger precipitation step.

Once equilibrium between Sr-90/Y-90 has established (after about 14 days), the sample is measured as strontium carbonate in a proportional counter at time t_G . The sample to be measured is then dissolved in acid and the subsequently formed Y-90 extracted from the weakly acidic solution on a filter medium impregnated with bis-(2-ethylhexyl) phosphate (HDEHP), eluted with concentrated hydrochloric acid, precipitated as yttrium oxalate, and measured at time t_Y . The count rate of the parent nuclide $R_{\text{Sr-90}}$ is calculated on the basis of the count rate $R_{\text{Y-90}}(t_G)$ at the time

of separation t_M or of the gross measurement t_B , also taking into account the degree of equilibrium between Sr-90 and Y-90 (2).

The contribution to the count rate by Sr-89, R_{Sr-89} , is determined by subtracting the now-known contributions of R_{Sr-90} , $R_{Y-90}(t_G)$ and R_0 from the gross activity count rate, R_g taken at time t_G . Based on the known efficiency, ε_{Sr-89} , R_{Sr-90} is converted into the activity to be determined, A_{Sr-89} (Bq), and the activity concentration, c_{Sr-89} (Bq·l⁻¹), respectively. The corresponding activity concentration, c_{Sr-90} (Bq·l⁻¹) may be obtained in the same manner. Determination of the individual activity components requires that the times of the separation of Y-90 during the final yttrium hydroxide scavenger precipitation, t_F , the gross measurement, t_G , the separation of Y-90 on the HDEHP filter medium, t_M , and the measurement(s) of Y-90, t_Y , be recorded and taken into account for the specification of the equilibrium factors and the compensation for radioactive decay.

3.2 Sample Preparation

The random sample taken or collected mixed water sample is processed without any filtering or other preceding preparation.

3.3 Radiochemical separation

3.3.1 Enrichment through precipitation according to the bentonite method (2)

The following description of the procedure for enriching Sr-89 and Sr-90 according to the bentonite method supposes a sample volume of $V = 50$ litres. If a smaller or larger sample volume is used and so leads to a reduced or increased sensitivity of detecting nuclides, respectively, the following procedure has to be adapted accordingly. The procedure is executed as follows:

3.3.1.1 A portion of about 15 l of the unfiltered and unprepared sample is filled into a plastic container (60 l), mixed with 10 ml of a strontium chloride solution (100 mg of Sr²⁺), replenished with the sample balance of ca. 35 l, and stirred for ca. 15 minutes.

Note

- If the chemical yield, η_{Sr} , is to be determined with the aid of Sr-85, a precisely dosed amount of this tracer has to be added, too. This necessitates that two gamma spectrometric measurements be taken of the gamma emitter Sr-85 ($E_\gamma = 514,01$ keV; $t_{Sr-85} = 64,849$ d). In addition, the contribution, R_{Sr-85} , of this nuclide must be taken into account when determining the gross activity, R_g , at t_G ; this requires knowing the beta efficiency, ε_{Sr-85} , of Sr-85. Be aware that determining Sr-85 on the basis of the gamma line at 514,01 keV may be compromised by the ever-present line at 511,0 keV.
- The concentrations of stable strontium (Sr²⁺) in typical inland waters range from 0,02 mg·l⁻¹ to 0,05 mg·l⁻¹ (5). They can therefore usually be neglected vis-à-vis the addition of 2 mg·l⁻¹ of the carrier added.

3.3.1.2 Now, 60 g of di-sodium hydrogen phosphate (Na₂HPO₄·12 H₂O) are dissolved in a small measure of distilled water and added to the sample under stirring.

3.3.1.3 Then, 400 ml of a Flygtol A solution (activated montmorillonite) are added, followed by 100 ml to 150 ml of a concentrated ammoniac solution (18 mol·l⁻¹) until the alkaline reaction sets in (pH > 8), and the mix is stirred for 30 minutes.

3.3.1.4 Thereafter, 300 ml of a Kerafloc solution (poly-electrolyte) are added and stirred for 3 minutes. The precipitate is left to settle for at least 1 hour.

Note

This precipitation process will separate/flocculate ca. 90 % of the Sr-89 and Sr-90 contained.

3.3.1.5 Once the precipitation has settled, the stand-over is siphoned or sucked off and discarded. The precipitate is now transferred to a centrifuge insert (1000 ml) and centrifuged at 3000 revolutions per minute for 30 minutes. The supernate is decanted and again discarded.

Note

If a gamma spectrometric measurement of individual nuclides is to follow the determination of the two strontium isotopes, the residue left after step 3.3.1.12 of the procedure C- γ -SPEKT-OWASS-01 may be processed further as follows:

3.3.1.6 The residue is now eluted with 100 ml of concentrated hydrochloric acid ($10 \text{ mol}\cdot\text{l}^{-1}$) in a centrifugal insert (1000 ml). The eluate is separated by means of centrifuging and transferred to a 1000 ml-glass beaker.

3.3.1.7 The elution process is repeated with 100 ml of concentrated hydrochloric acid ($10 \text{ mol}\cdot\text{l}^{-1}$) and centrifuged once more.

3.3.1.8 Finally, the residue is eluted with 100 ml of hydrochloric acid ($2 \text{ mol}\cdot\text{l}^{-1}$) and centrifuged again. The individual eluates from steps 3.3.1.6 through 3.3.1.8 are united.

3.3.1.9 The united eluates are now adjusted to pH 1 using a concentrated ammoniac solution ($18 \text{ mol}\cdot\text{l}^{-1}$).

3.3.1.10 Adding a saturated sodium carbonate solution in excess will now precipitate the alkaline earth carbonates. The precipitate is centrifuged off at 3000 revolutions per minute for 15 minutes and the supernate discarded. The precipitate is now processed further as described in section 3.3.3.

Note

Concentrating the two strontium isotopes by means of a rotary evaporator or evaporation collector is possible as well. This approach will require significant time and energy for samples of 50 litres, however (6).

3.3.2 Separation of Y-90 on a filter medium impregnated with HDEHP

The method of separating Y-90 on a filter medium impregnated with HDEHP is superior to an extraction by means of a liquid/liquid two-phase system (hydrochloric acid $0,1 \text{ mol}\cdot\text{l}^{-1}$)/HDEHP in petrol ether) insofar as high precipitation quota will already be achieved with contact periods of less than one second. Further advantages are that the filter medium can be reused several times and that once impregnated, the filter medium in its solid state can be stored almost indefinitely (2, 4).

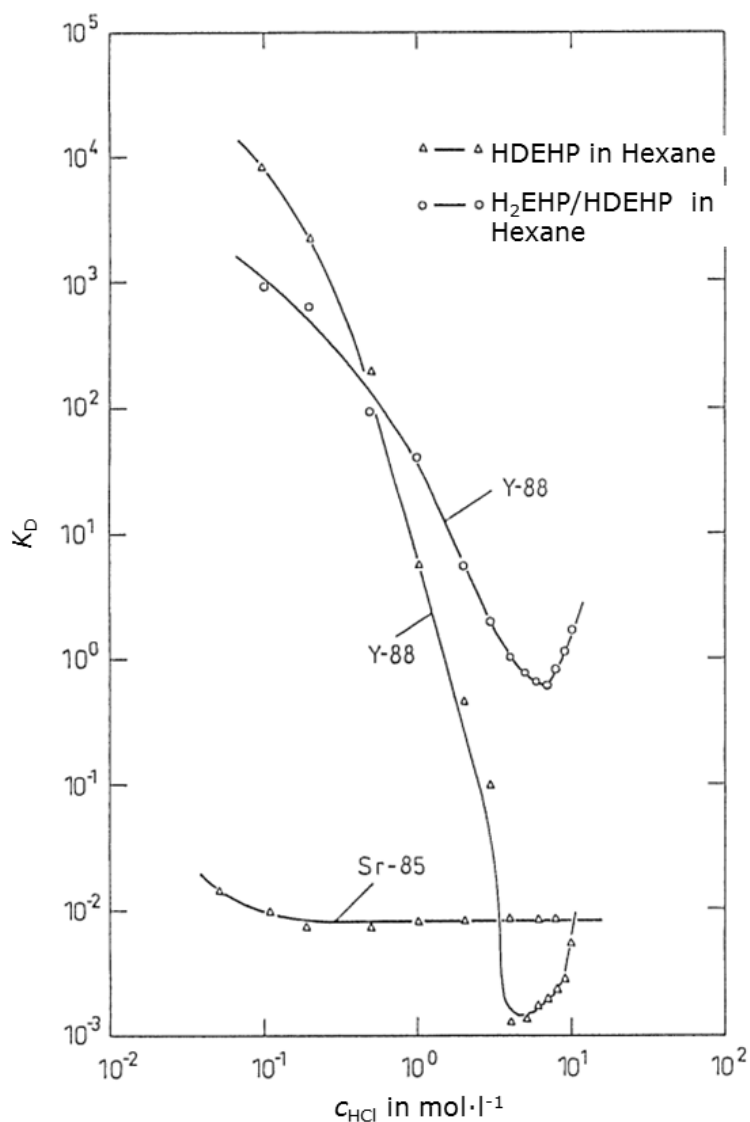


Fig. 1: Distribution coefficients K_D of Y-88 and Sr-85 in the two-phased system hydrochloric acid/HDEHP and H₂DEHP, respectively, vs. the concentration of hydrochloric acid, c_{HCl} (2).

The extraction behaviour of strontium and yttrium in the two-phased system, hydrochloric acid/HDEHP, is illustrated in the functional dependency of the distribution coefficients, K_D , for concentration range from $0,1 \text{ mol}\cdot\text{l}^{-1}$ to $10 \text{ mol}\cdot\text{l}^{-1}$ in Figure 1. The respective measurements were taken using the two radionuclides Sr-85 and Y-88 as tracers (2).

This suggests that the highest separation factors of ca. 10^6 and thus the most advantageous separation conditions for strontium/yttrium can be expected at an acid concentration of $0,1 \text{ mol}\cdot\text{l}^{-1}$.

For the preparation of the HDEHP filter medium, 3 parts by weight of Voltalef 300 (poly-fluorochlorethylene) are mixed under vigorous stirring in a ceramic dish with 1 part by weight of HDEHP (dissolved in acetone) and left to dry on air under a fume hood. Voltalef 300 may also be substituted with a chemically identical product, Voltalef 302, which will need to be crushed in a ball-mill to a grain size that is suitable for the filter medium. Further details on processing can be obtained from the Bundesanstalt für Gewässerkunde.

For the production of the actual filter medium, the impregnated filter material is turned into a paste in distilled water and sucked off via glass fibre filters in a Hahn's suction apparatus (nutsch filter). The optimal area fill is $1 \text{ g}\cdot\text{cm}^{-2}$ to $1,5 \text{ g}\cdot\text{cm}^{-2}$. In order to avoid losses from turbulences during the sucking-through of the actual solutions, the filter medium needs to be covered with a glass fibre filter. Attention should be paid on the filter medium being packed tightly. The separation of Y-90 from Sr-90 then requires that the weakly hydrochloric-acidic solution (pH 1,5) be sucked through the filter medium at maximum suction speed. Under realistic conditions, the achievable extraction yields amount to $> 90 \%$. Following the extraction of Y-90 with concentrated hydrochloric acid ($10 \text{ mol}\cdot\text{l}^{-1}$) and washing it with diluted hydrochloric acid ($0,1 \text{ mol}\cdot\text{l}^{-1}$), the filter medium can be reused (2).

Note

Commercially available products of HDEHP sometimes contain significant amounts of mono-(2-ethylhexyl) phosphate (H_2DEHP) that may interfere significantly with the separation of Y-90. These products are therefore unsuited for the intended purpose.

3.3.3 Radiochemical separation process (2, 3, 6)

3.3.3.1 The residue obtained from step 3.3.1.10 is dissolved in 20 ml to 30 ml of nitric acid ($4 \text{ mol}\cdot\text{l}^{-1}$). The solution is then cooled to $< 0 \text{ }^\circ\text{C}$ in a thermostat-controlled cooler.

3.3.3.2 This solution is then fortified under stirring with 100 ml of smoking nitric acid ($24 \text{ mol}\cdot\text{l}^{-1}$) that has been cooled to $< 0 \text{ }^\circ\text{C}$. Use an fume exhaust!

Note

Smoking nitric acid reacts violently with easily oxidised substances (ethanol, turpentine, wood wool, cellulose and others) and has a seriously caustic effect on the skin, respiratory system and mucous membranes. The relevant directives of the ordinance on hazardous materials need to be observed.

3.3.3.3 The precipitated alkaline earth nitrates are now centrifuged off in 250 ml-inserts made of Teflon in a cooler centrifuge at 3000 revolutions per minute for 15 minutes. The supernate is decanted and discarded.

3.3.3.4 The residue is dissolved in 10 ml of nitric acid ($1 \text{ mol}\cdot\text{l}^{-1}$) and the solution is again cooled to $< 0 \text{ }^\circ\text{C}$ in a thermostat-controlled cooler.

3.3.3.5 After it has been cooled to $< 0 \text{ }^\circ\text{C}$, the solution is once more fortified with 40 ml of smoking nitric acid ($24 \text{ mol}\cdot\text{l}^{-1}$) that has also been cooled to $< 0 \text{ }^\circ\text{C}$ and stirred with a glass rod. The precipitate is centrifuged off and the supernate discarded.

Note

If the sample contains further fission and activation products, adequate retainer carriers (10 mg of the carrier per nuclide) have to be added at this stage (nitrate precipitation) in order to improve separation efficiency.

3.3.3.6 Steps 3.3.3.4 and 3.3.3.5 have to be repeated four times.

Note

Precipitating the alkaline earth nitrates five times in succession makes it possible to separate strontium (and barium) with a chemical yield of 80 % to 90 % even if calcium is present at an excess factor of 100 (6). The calcium content in the strontium nitrate precipitate will not exceed a maximum of 3 % if all steps have been executed with care. Barium, radium and lead accompany strontium during the nitrate precipitation. The chemical yields for barium likewise range between 80 % and 90%. Like the daughter nuclide Y-90, all other fission and activation products are practically separated quantitatively. Experience shows

that the separation effect can be improved during the first two nitrate precipitations by adding carriers for the nuclides that are to be separated.

3.3.3.7 Following the nitrate precipitation processes, the alkaline earth nitrates are dissolved in 20 ml of distilled water.

3.3.3.8 The aqueous solution of the alkaline earth nitrates is now fortified with:

- 5 ml of a barium chloride solution (50 mg of Ba²⁺)
- 1 ml of acetic acid (6 mol·l⁻¹)
- 2 ml of an ammonium acetate solution (6 mol·l⁻¹)

3.3.3.9 Using hydrochloric acid (1 mol·l⁻¹) or an ammoniac solution (1 mol·l⁻¹), the pH of the solution is adjusted to 5,5, using a pH-meter for accuracy.

3.3.3.10 The solution is then heated to 95 °C on a hotplate and fortified, drop by drop, with 1 ml to 2 ml of a sodium chromate solution (0,3 mol·l⁻¹). Once the barium chromate precipitate has settled, the completeness of the precipitation process has to be verified by adding a few drops of a Na₂CrO₄ solution (0,3 mol·l⁻¹): the supernate must turn slightly yellow.

3.3.3.11 After having allowed the solution to cool, the precipitates (Ba-140 and others) are filtered off via blue ribbon filters, and the filtrate containing Sr-89 and Sr-90 is transferred to a 400 ml-glass beaker. The barium chromate precipitate is discarded.

Note

The barium chromate precipitation process requires that the pH be maintained with great precision. If the solution is more acidic, barium will precipitate incompletely while a more alkaline pH will see strontium precipitate as well. The content of Ba-140 that accompanies Sr-89/Sr-90 will not exceed a maximum of 3 % if all steps are executed with care. The amount of Sr-89/Sr-90 that will precipitate together with the barium chromate varies from 5 % to 10 %. If the sample has an elevated content of Ba-140 it is recommendable to repeat the barium chromate precipitation process in the filtrate after step 3.3.3.11.

3.3.3.12 The chrome-rich solution of Sr-89 and Sr-90 is fortified, drop by drop, with hydrazine hydroxide for the reduction of its Cr⁶⁺ and Cr³⁺ contents and warmed.

Note

If it is sufficiently certain that the sample does not contain Ba-140 or other unwanted nuclides (e. g., Ra-228), steps 3.3.3.8 through 3.3.3.12 may be skipped. In this case, work may proceed as follows:

3.3.3.13 The solution containing the Sr-89 and Sr-90 is fortified with 10 ml of an yttrium chloride solution (100 mg Y³⁺) and well mixed. By adding drops of a concentrated ammoniac solution (18 mol·l⁻¹) until the alkaline reaction sets in (pH > 8,5), yttrium hydroxide is precipitated. The suspension is transferred to a centrifuge insert (250 ml) and centrifuged at 3000 revolutions per minute for 5 minutes. The time of the separation of the phases, t_F , must be recorded. The supernate containing the Sr-90 and Sr-89 is decanted and the residue (yttrium hydroxide and possibly chrome hydroxide) discarded.

3.3.3.14 The solution containing the Sr-89/Sr-90 is now heated in a glass beaker (400 ml) to boiling point, and strontium carbonate is precipitated through the addition of ammonium carbonate in excess.

3.3.3.15 After having allowed it to cool, the strontium carbonate precipitate is filtered off on a previously weighed membrane filter (pore size: 0,45 µm), dried at 105 °C for 1 hour, and then weighed (m_{Sr}^g) for determining the chemical yield, η_{Sr} .

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Note

If the determination of the chemical yield, η_{Sr} , is to be based on Sr-85, the counting source obtained after step 3.3.3.15 needs to be measured by gamma spectrometry. The yield to be quantified, η_{Sr} , is calculated from the measured count rate, R_{Sr-85} , and the count rate, $R_{Sr-85}(St)$, obtained from a standard source measured under the same conditions. If η_{Sr} is to be determined with the aid of Sr-85, the relatively high beta efficiency of the gamma emitter Sr-85 ($\epsilon_{Sr-85} = 0,05$ to $0,10$) has to be taken into account in the subsequent total activity measurement at t_G . Applying a high dosage of Sr-85 in order to shorten the measuring period will substantially raise the decision threshold for Sr-90. In this case, the gravimetric determination of η_{Sr} may be of advantage. Be aware of the possibility that the gamma spectrometric determination of Sr-85 at 514,01 keV may be compromised by the ever-present line at 511,0 keV.

3.3.3.16 The strontium carbonate sample obtained after step 3.3.3.15 is left standing for ca. 14 days to equilibrium between Sr-90 and Y-90. The total activity, R_G , is determined at time t_G . The measure of equilibrium can be specified exactly via the equilibrium factor, f_2 . After the measurement, the sample is ashed at 450 °C.

Note

If it is sufficiently certain that the sample is free of Sr-89, the measurement of the total activity, R_G , can be omitted. In this case, work may proceed as follows:

3.3.3.17 The strontium carbonate sample is dissolved in portions in a total of ca. 30 ml of hydrochloric acid ($1 \text{ mol}\cdot\text{l}^{-1}$). The hydrochlorated solution is fortified with 10 ml of an yttrium chloride solution (100 mg Y^{3+}).

3.3.3.18 The hydrochlorated solution of Sr-90/Y-90 and, as the case may be, Sr-89 and Sr-85 is adjusted to a pH of 1,5 by adding an ammoniac solution ($1 \text{ mol}\cdot\text{l}^{-1}$) and then sucked over an adequately prepared HDEHP filter medium (for the manufacturing of the filter medium see section 3.1.2). The time of the extraction of Y-90 on the filter medium, t_M , must be recorded.

Note

The separation of Y-90 by means of extraction on a HDEHP filter medium may also be executed already 5 days after the yttrium hydroxide scavenger precipitation (t_F), which will shorten the processing time. At this time, the equilibrium between Sr-90 and Y-90 will be ca. 75 % complete. This can be taken into account via the equilibrium factor, f_2 .

3.3.3.19 The Y-90 deposited in the HDEHP filter medium is successively eluted five times with 10 ml of concentrated hydrochloric acid ($10 \text{ mol}\cdot\text{l}^{-1}$) each.

3.3.3.20 The united eluates are adjusted to a pH of between 1 and 2 with a concentrated ammoniac solution ($18 \text{ mol}\cdot\text{l}^{-1}$), then heated to 95 °C on a hotplate, and the yttrium hydroxide contained is precipitated by adding drops of the ammoniac solution until the alkaline reaction sets in ($\text{pH} > 8,5$). The supernate is decanted and discarded; the yttrium hydroxide residue is dissolved in a few ml of glacial acetic acid ($17 \text{ mol}\cdot\text{l}^{-1}$) and the solution diluted with 25 ml of distilled water.

3.3.3.21 The Y-90 solution is now heated to 95 °C on a hotplate, and by adding drops of saturated oxalic acid, the yttrium is precipitated as yttrium oxalate on reaching a pH of 2 to 3.

3.3.3.22 After having been left to cool, the precipitate is filtered off on blue ribbon filters, flushed with a little distilled water, and dried at 105 °C in a drying oven for 1 hour.

3.3.3.23 The sample present on blue ribbon filters is transferred to a measuring dish (diameter: 50 mm or 60 mm), covered with adhesive foil, and then measured in a proportional counter. The times of the measurement(s), t_Y , is (are) to be recorded, and the count rate(s), $R_{Y-90}(t_Y)$, need to be converted relative to the time of the separation, t_M , after the possible background count rate, R_u , has been subtracted (Fig. 4).

Note

For determining $R_{Y-90}(t_M)$, it is necessary to measure the reduction in Y-90 activity for a minimum of 5 days – corresponding to 2 half-lives of Y-90 – in order to determine as precisely as possible the potential background count rate, R_u , of long-lived interfering emitters (e. g., Sr-90, Ra-226 and others). This analysis can very substantially increase the selectivity of the Y-90 determination (Figure 4).

3.3.3.24 Following the activity measurement of Y-90, the sample including its adhesive foil cover is ashed at 800 °C in a crucible furnace for 2 hours and re-weighed as Y_2O_3 (m_Y^g). This will produce the chemical yield, η_Y , from the separation of Y-90 on the HDEHP filter medium.

4 Measuring the activity

The determination of the two strontium isotopes necessitates a well-shielded, calibrated beta measurement setup. Workstations with an automatic sample exchanger or simultaneous operation in conjunction with computer-supported data processing are of advantage. Proportional counters running on argon/methane are superior to Geiger-Müller counting tubes in that they facilitate higher and coincidence-free count rates.

The long-term consistency of the workstation and the efficiencies are to be verified at adequate intervals by measuring Sr-90 standard sources. The background effect needs to be monitored continuously in order to become aware of possible contamination or other negative impacts in time. Further details can be found in chapter V. of this procedures manual.

4.1 Calibration

The measurement setup is calibrated on the basis of calibration sources with known specific activities measured under the same conditions as the actual samples. These sources are produced from solutions of Sr-90 and Sr-89 with known activity concentrations that are available from the Phys.-Tech. Bundesanstalt, Brunswick.

Sr-89 is precipitated with strontium carbonate and then measured. Sr-90 is separated from the Y-90 on an HDEHP filter medium, then also precipitated with strontium carbonate and measured. The rise in the regenerating daughter nuclide Y-90 is extrapolated to the time of the separation, t_M , and will so reveal the count rate, R_{Sr-90} , of pure Sr-90. The Y-90 deposited on the HDEHP filter medium is eluted with concentrated hydrochloric acid, precipitated as yttrium oxalate and measured. The count rate, R_{Y-90} , is again related to the time of the separation, t_M . The specific activity of the sources present at the time of the measurement or the separation, respectively, can be calculated from the certified data for the standard solutions.

The directly obtained (R_{Sr-89}) count rates (s^{-1}) of the known activity concentrations of the standard solutions, C_{Sr-89} and C_{Sr-90} ($Bq \cdot ml^{-1}$), respectively those extrapolated to the time of separation (R_{Sr-90} , R_{Y-90}), as well as the sample volume, V (ml), used for the production of measuring sources, permit to calculate the beta efficiencies

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($\varepsilon_{\text{Sr-89}}$, $\varepsilon_{\text{Sr-90}}$ and $\varepsilon_{\text{Y-90}}$) of the three nuclides. That the separation and precipitation processes have been complete needs to be verified by weighing the standard sources. If necessary, a correction must be applied via the chemical yields, η_{Sr} and η_{Y} .

$$\varepsilon_{\text{Sr-89}} = \frac{R_{\text{Sr-89}}}{C_{\text{Sr-89}} \cdot V \cdot \eta_{\text{Sr}}} \quad (1)$$

$$\varepsilon_{\text{Sr-90}} = \frac{R_{\text{Sr-90}}(t_M)}{C_{\text{Sr-90}} \cdot V \cdot \eta_{\text{Sr}}} \quad (2)$$

$$\varepsilon_{\text{Y-90}} = \frac{R_{\text{Y-90}}(t_M)}{C_{\text{Y-90}} \cdot V \cdot \eta_{\text{Y}}} \quad (3)$$

The chemical yields are determined by weighing the carbonates (Sr-89, Sr-90) or the yttrium oxide following the annealing of the yttrium oxalate precipitate (Y-90). The chemical yields, η , are then obtained from the predetermined mass (m^V) and the re-weighed mass after the separation process (m^g):

$$\eta_{\text{Sr}} = \frac{m_{\text{Sr}}^g}{m_{\text{Sr}}^V} \quad (4)$$

$$\eta_{\text{Y}} = \frac{m_{\text{Y}}^g}{m_{\text{Y}}^V} \quad (5)$$

The chemical yields of river water samples are then determined analogously. Alternatively, determination of the chemical yield in the analysis of Sr-90 may use the aid of Sr-85. The following relation applies:

$$\eta_{\text{Sr}} = \frac{R_{\text{Sr-85}}^g}{R_{\text{Sr-85}}^V} \quad (6)$$

In this case, two additional gamma spectrometric measurements need to be taken.

Owing to the absorption of emitted beta particles within the actual sample (self-absorption) that is to be expected in the measurement of Sr-90/Y-90, the efficiencies always need to be related to a certain area fill, d . If the actual samples are metered at other values of d than those applied for the standard sources used for calibration, this impact may need to be compensated for by a self-absorption factor, f_s . Such a necessity may be encountered, for example, when the chemical yields are subject to major fluctuation during the processing of the samples.

For the purpose of illustration, the impact of self-absorption on the efficiency, ε , is demonstrated in the shape of the self-absorption factor, f_s ($= \varepsilon/\varepsilon_0$), plotted for Sr-89, Y-90 as well as Sr-90/Y-90 in relation to the area fill of the sample to be metered in Figure 2. This indicates that corrections will usually be required only in the case of extreme fluctuations of d .

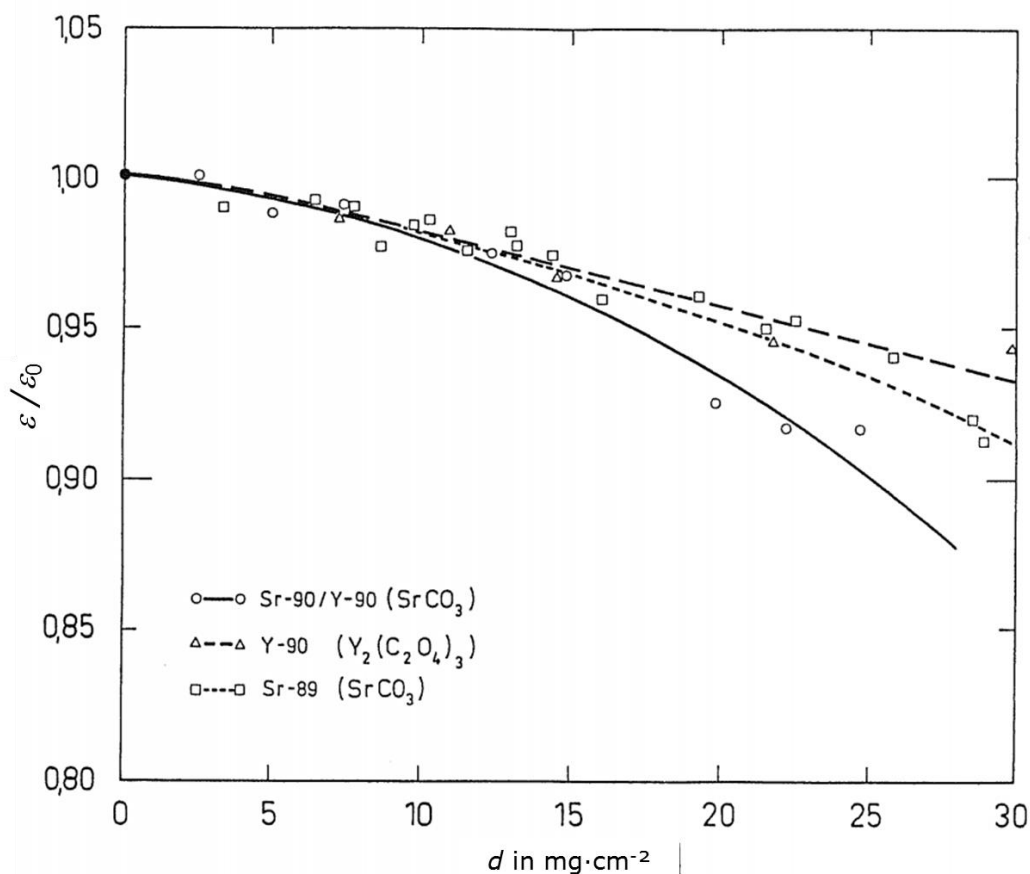


Fig. 2: Dependency of the self-absorption factor, $f_s (= \varepsilon/\varepsilon_0)$, on the area fill, d

4.2 Interferences

Interferences to the measurement process of Sr-89 must be expected when the strontium nitrate is insufficiently separated during nitrate precipitation as a result of complex nuclide mixtures so that interfering nuclides in significant amounts feign the presence of Sr-89 in the gross measurement, t_B . In this case, the number of precipitation processes needs to be increased accordingly. Crosschecking the sample by gamma spectrometry is called for here as well.

In determining Sr-90, falsified results may be obtained if the Y-90 content is determined after separation on the basis of merely one measurement at t_T , thus leaving the background of a long-lived interfering emitter unidentified. To avoid the possibility of such a disturbance it is recommended to measure the decay of Y-90 over at least two half-lives (ca. 5 days) (see Figure 4).

If the precipitation processes for strontium nitrate are executed at temperatures above 0 °C, considerable losses and as a consequence, reduced chemical yields, η_{Sr} , as well as smaller separation factors must be expected.

5 Calculation of the results

The separation and determination of the two strontium isotopes, Sr-89 and Sr-90, in large-volume water samples extend over a series of steps at which a variety of measurements need to be taken and calculations made: Following the enrichment of Sr-89 and Sr-90 from 50 litres of river water according to the bentonite method, washing of the alkaline earth fraction through repeated precipitation of the nitrates contained ("nitrate method"), possibly present Ba-140 is extracted by means of a barium chromate precipitation process. Sr-89 and Sr-90 are then precipitated as strontium carbonate. The daughter nuclide Y-90 is left to regenerate to an almost perfect radioactive equilibrium. For determining the Sr-89 content, the gross activity, R_g , is measured at time t_G (Figure 3).

After R_g has been determined, the precipitate containing Sr-90, Y-90, Sr-89 and possibly also Sr-85 is turned into a solution from which Y-90 is extracted on an HDEHP filter medium at t_M , processed and continuously measured at $t_{Y1}, t_{Y2} \dots t_Y^{\max}$. From the count rate of the Y-90 activity, $R_{Y-90}(t_{Y1})$, measured at time t_{Y1} , the Y-90 activity that is regenerated by Sr-90 at time t_M can be calculated. Taking into account the beta-efficiencies of the individual nuclides, the equivalent count rate R_{Sr-90} is calculated. The difference between the gross activity, R_g , measured at time t_G and the count rates of Sr-90 and Y-90 then yields the Sr-89 content and that of Sr-85, as the case may be. Based upon the individual efficiencies, ε , and taking into account the degree of equilibrium between Sr-90 and Y-90 as well as the corresponding chemical yields, η , the individual count rates are converted into equivalent units of activity concentration, c_r . The nuclide contents, c_r , always need to be related to the time the sample was taken, t_p .

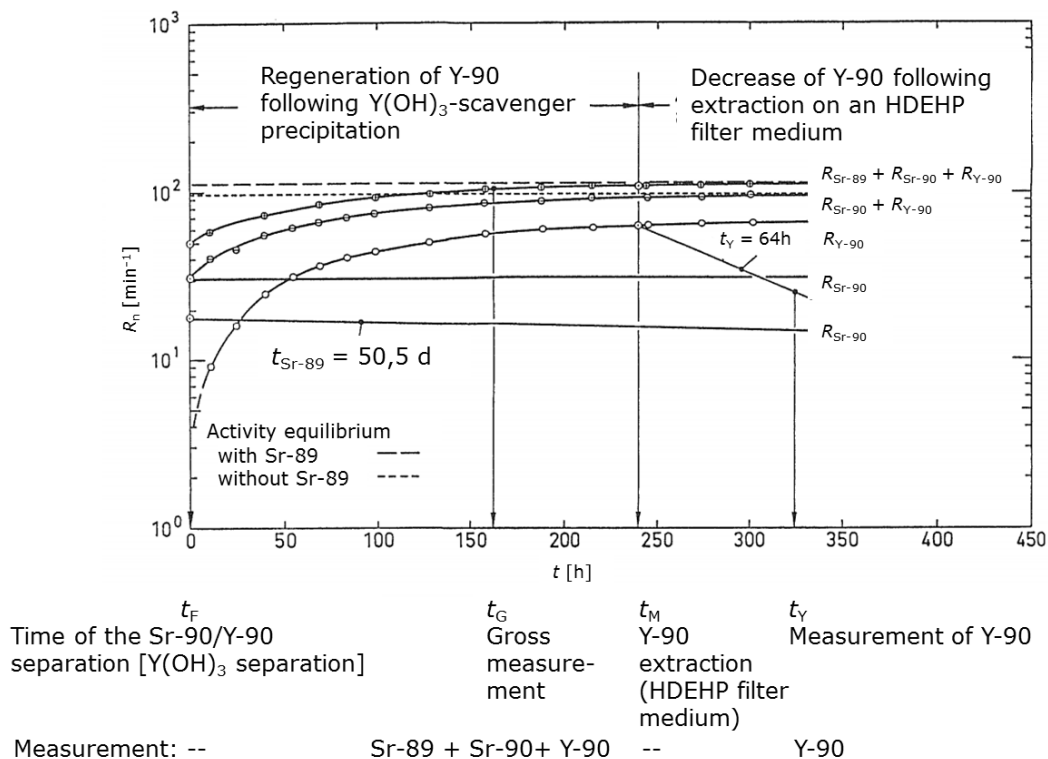


Fig. 3: Example for count rate rates vs. time of Sr-90, Sr-89 and Y-90 following yttrium hydroxide scavenger precipitation at t_F , extraction of Y-90 on an HDEHP filter medium at time t_M , and a gross count at time t_G . Reference time: $t_F = 0$

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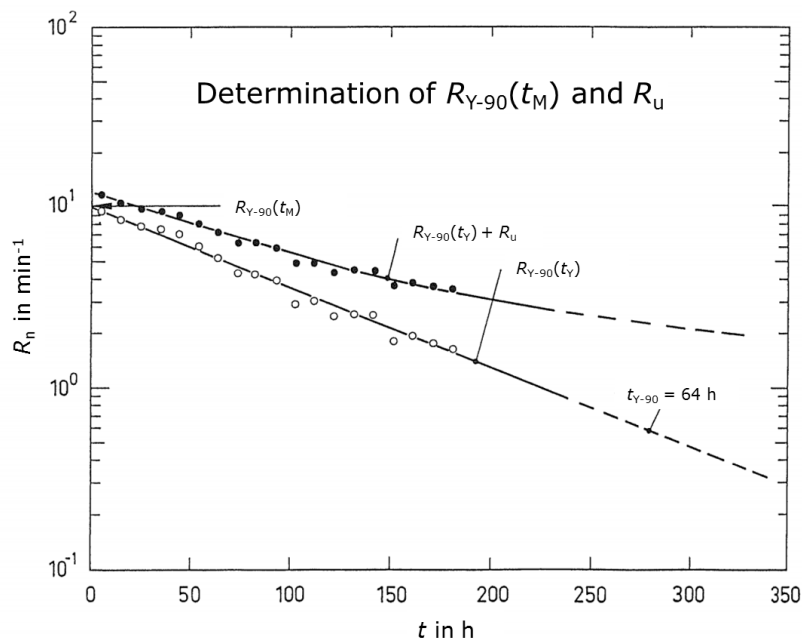


Fig. 4: Count rate $R_{Y-90}(t_M)$ extrapolated to the time of separation, t_M , and subtraction of the constant background count rate, R_U , of long-lived interfering emitters

Following the separation of Y-90 on an HDEHP filter medium and its precipitation as yttrium oxalate, the counting source is continuously measured with measurement periods of $t_m = 100$ minutes each over a period of at least 5 days (Figure 4). Marked with time stamps, the continuously taken results, $R_{Y-90}(t_Y)$, are analysed either as graphic plots or, employing computer support, with the aid of a suitable least-squares-fit algorithm: Subtraction of a possible background, R_U , and extrapolation of the count rate to the time of separation on an HDEHP filter medium. Therefore,

$$R_{Y-90}(t_M) = R_{Y-90}(t_Y) \cdot e^{\lambda_{Y-90} \cdot (t_Y - t_M)} \quad (7)$$

with

$$\lambda_{Y-90} = 0,0108 \text{ h}^{-1} \text{ and } (t_Y - t_M) \text{ in hours}$$

The measure of equilibrium between Sr-90 and Y-90 at time t_M can be deduced from the equilibrium factor, f_1 , taken at time t_F , which will produce the count rate for the Y-90 activity, $R_{Y-90}(t_\infty)$, which is overall in equilibrium with Sr-90, from:

$$R_{Y-90}(t_\infty) = \frac{R_{Y-90}(t_M)}{\eta_Y \cdot [1 - e^{\lambda_{Y-90} \cdot (t_F - t_M)}]} \quad (8)$$

$$R_{Y-90}(t_\infty) = \frac{R_{Y-90}(t_M)}{\eta_Y \cdot f_1} \quad (8a)$$

where

$$f_1 = 1 - e^{\lambda_{Y-90} \cdot (t_F - t_M)}$$

The count rate, $R_{Y-90}(t_\infty)$, which is in equilibrium with Sr-90, in conjunction with the chemical yield from the strontium separation, η_{Sr} , the efficiency, ε_{Y-90} , and the self-absorption factor, f_S , will then produce the activity concentration, c_{Sr-90} (Bq·l⁻¹) of the sample from its volume, V (l), from:

$$c_{Sr-90} = \frac{R_{Y-90}(t_\infty)}{\varepsilon_{Y-90} \cdot \eta_{Sr} \cdot f_S \cdot V} \quad (9)$$

The count rate, $R_{Sr-89}(t_F)$ at time t_F can be calculated from the total activity count rate, $R_g(t_G)$, measured at time t_G as follows:

$$R_{Sr-89}(t_F) = \frac{R_g(t_G) - R_0 - R_{Y-90}(t_G) - R_{Sr-90}}{e^{\lambda_{Sr-89} \cdot (t_F - t_G)}} \quad (10)$$

$R_{Y-90}(t_G)$ is calculated as follows:

$$R_{Y-90}(t_G) = R_{Y-90}(t_\infty) \cdot [1 - e^{\lambda_{Y-90} \cdot (t_F - t_G)}] \quad (11)$$

$$R_{Y-90}(t_G) = R_{Y-90}(t_\infty) \cdot f_2 \quad (11a)$$

with

$$f_2 = 1 - e^{\lambda_{Y-90} \cdot (t_F - t_G)}$$

$R_{Y-90}(t_\infty)$ is obtained from equations (7) and (8) as:

$$R_{Y-90}(t_\infty) = R_{Y-90}(t_Y) \cdot \frac{e^{\lambda_{Y-90} \cdot (t_Y - t_M)}}{\eta_Y \cdot [1 - e^{\lambda_{Y-90} \cdot (t_F - t_M)}]} \quad (12)$$

$$R_{Y-90}(t_\infty) = R_{Y-90}(t_Y) \cdot f_3 \quad (12a)$$

with

$$f_3 = \frac{e^{\lambda_{Y-90} \cdot (t_Y - t_M)}}{\eta_Y \cdot [1 - e^{\lambda_{Y-90} \cdot (t_F - t_M)}]}$$

and therefore:

$$R_{Y-90}(t_G) = R_{Y-90}(t_Y) \cdot f_2 \cdot f_3 \quad (12b)$$

R_{Sr-90} can be calculated as follows:

$$R_{Sr-90} = R_{Y-90}(t_\infty) \cdot \frac{\varepsilon_{Sr-90}}{\varepsilon_{Y-90}} \quad (13)$$

$$R_{Sr-90} = R_{Y-90}(t_Y) \cdot f_3 \cdot \frac{\varepsilon_{Sr-90}}{\varepsilon_{Y-90}} = R_{Y-90}(t_Y) \cdot f_3 \cdot f_4 \quad (13a)$$

with

$$f_4 = \frac{\varepsilon_{Sr-90}}{\varepsilon_{Y-90}}$$

Rearranging, equation (10) reads:

$$R_{\text{Sr-90}}(t_F) = \frac{R_g(t_G) - R_0 - R_{\text{Y-90}}(t_Y) \cdot (f_2 \cdot f_3 + f_3 \cdot f_4)}{e^{\lambda_{\text{Sr-89}} \cdot (t_F - t_G)}} \quad (13b)$$

The activity concentration, $c_{\text{Sr-89}}(t_F)$, taken at time t_F is obtained from:

$$c_{\text{Sr-89}}(t_F) = \frac{R_{\text{Sr-89}}(t_F)}{\varepsilon_{\text{Sr-89}} \cdot \eta_{\text{Sr}} \cdot f_S \cdot V} \quad (14)$$

and at the time of sampling, t_P , from

$$c_{\text{Sr-89}}(t_P) = c_{\text{Sr-89}}(t_F) \cdot e^{\lambda_{\text{Sr-89}} \cdot (t_F - t_P)} \quad (15)$$

The statistical counting uncertainty of Sr-90 is determined mainly by the standard deviation of the Y-90 measurement, $s[R_{\text{Y-90}}(t_Y)]$. In the case of a measurement of a single nuclide, the statistical counting uncertainty of $R_{\text{Y-90}}(t_Y)$ is given by:

$$s[R_{\text{Y-90}}(t_Y)] = \sqrt{\frac{R_{\text{Y-90}}(t_Y) + R_0 \cdot (1 + t_m/t_0)}{t_m}} \quad (16)$$

This produces the relative standard deviation, $s[R_{\text{Y-90}}(t_Y)]/R_{\text{Y-90}}(t_Y)$ (variation coefficient) as:

$$\frac{s[R_{\text{Y-90}}(t_Y)]}{R_{\text{Y-90}}(t_Y)} = \frac{s(c_{\text{Sr-90}})}{c_{\text{Sr-90}}} = \frac{\sqrt{\frac{R_{\text{Y-90}}(t_Y) + R_0 \cdot (1 + t_m/t_0)}{t_m}}}{R_{\text{Y-90}}(t_Y)} \quad (17)$$

In order to enhance the selectivity of the Sr-90 measurement, the decay of Y-90 should be measured continuously over a minimum of 5 days (Fig. 4). This will make it possible to reduce the statistical counting uncertainty even further. In doing so, the data obtained from the measurements between t_M and t_Y^{max} with measurement periods of t_m and the graphically or computer-converted count rate, $R_{\text{Y-90}}(t_M)$ at time t_M will produce the relative standard deviation:

$$\frac{s[R_{\text{Y-90}}(t_Y)]}{R_{\text{Y-90}}(t_Y)} = \frac{s(c_{\text{Sr-90}})}{c_{\text{Sr-90}}} = \frac{\sqrt{\frac{R_{\text{Y-90}}(t_Y) + R_0 \cdot (1 + n \cdot t_m/t_0)}{n \cdot t_m}}}{R_{\text{Y-90}}(t_Y)} \quad (18)$$

with

$$\overline{R_{\text{Y-90}}(t_Y)} = \frac{R_{\text{Y-90}}(t_M)}{(t_Y^{\text{max}} - t_M) \cdot \lambda_{\text{Y-90}}} \cdot \left(1 - e^{\lambda_{\text{Y-90}} \cdot (t_Y^{\text{max}} - t_M)}\right) \quad (19)$$

With the count rate, $R_{\text{Y-90}}(t_M)$, being known and the count rate $\overline{R_{\text{Y-90}}(t_Y)}$ averaged over the period $(t_Y^{\text{max}} - t_M)$, the corresponding mean time \bar{t}_Y can be easily calculated, taking into account the radioactive decay of Y-90.

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The statistical counting uncertainty in Sr-89 is impacted by various individual sources of error, which are combined by the law of error propagation as follows:

$$s(R_{\text{Sr-89}}) = \sqrt{\{s[R_g(t_G)]\}^2 + [s(R_0)]^2 + \{s[R_{\text{Y-90}}(t_G)]\}^2 + [s(R_{\text{Sr-90}})]^2} \quad (20)$$

Applying equations (12b) and (13a) will now alter equation (20) to the following form:

$$s(R_{\text{Sr-89}}) = \sqrt{\frac{R_g + R_0 \cdot (1 + t_g/t_0)}{t_g} + \{s[R_{\text{Y-90}}(t_Y)]\}^2 \cdot (f_2^2 \cdot f_3^2 + f_3^2 \cdot f_4^2)} \quad (21)$$

Y-90 may be determined either by a singular measurement or by n repeated measurements. The statistical count uncertainties $s[R_{\text{Y-90}}(t_Y)]$ and $s[\bar{R}_{\text{Y-90}}(t_Y)]$, respectively, encountered in the process can be quantified according to equations (17) and (18) and incorporated into equation (21). This will produce:

$$s(R_{\text{Sr-89}}) = \sqrt{\frac{R_g + R_0 \cdot (1 + t_g/t_0)}{t_g} + \frac{R_{\text{Y-90}}(t_Y) + R_0 \cdot (1 + t_m/t_0)}{t_m} \cdot (f_2^2 \cdot f_3^2 + f_3^2 \cdot f_4^2)} \quad (22)$$

and

$$s(R_{\text{Sr-89}}) = \sqrt{\frac{R_g + R_0 \cdot (1 + t_g/t_0)}{t_g} + \frac{R_{\text{Y-90}}(t_Y) + R_0 \cdot (1 + n \cdot t_m/t_0)}{n \cdot t_m} \cdot (f_2^2 \cdot f_3^2 + f_3^2 \cdot f_4^2)} \quad (22a)$$

which again makes it easy to calculate the relative standard deviation, $s(R_{\text{Sr-89}})/R_{\text{Sr-89}}$, and thus that of the Sr-89 quantification:

$$\frac{s(R_{\text{Sr-89}})}{R_{\text{Sr-89}}} = \frac{s(c_{\text{Sr-89}})}{c_{\text{Sr-89}}} \quad (23)$$

It needs to be pointed out that the analytical preparation errors that are encountered in reality during the determination of Sr-89 and Sr-90 and are usually difficult to assess regarding their impacts, dominate and therefore diminish the significance of statistical counting uncertainty.

5.1 Worked example

Determining the activity concentrations $c_{\text{Sr-89}}$ and $c_{\text{Sr-90}}$ in surface water

| | | |
|---|----------------------|--------------------------------|
| Time of sampling | : t_P | = 1 Jul 1991/8 ⁰⁰ |
| Time of Y(OH) ₃ precipitation | : t_F | = 15 Jul 1991/8 ⁰⁰ |
| Time of gross measurement | : t_G | = 29 Jul 1991/8 ⁰⁰ |
| Time of Y-90 extraction | : t_M | = 30 Jul 1991/8 ⁰⁰ |
| Time of Y-90 individual measurement | : t_Y | = 30 Jul 1991/12 ⁰⁰ |
| Time of the last repeat measurement of Y-90 | : t_{max}^Y | = 06 Aug 1991/20 ⁰⁰ |
| Mean time of the repeat measurement of Y-90 | : \bar{t}_Y | = 02 Aug 1991/12 ⁰⁰ |
| Measurement period for gross measurement | : t_g | = 6000 s |
| Measurement period for Y-90 measurement | : t_m | = 6000 s |

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| | | |
|---|--------------------------------|----------------------------|
| Number of repeat measurements | : n | = 19 |
| Efficiency of Sr-90 | : $\varepsilon_{\text{Sr-90}}$ | = 0,20 |
| Efficiency of Y-90 | : $\varepsilon_{\text{Y-90}}$ | = 0,40 |
| Efficiency of Sr-89 | : $\varepsilon_{\text{Sr-89}}$ | = 0,30 |
| Volume of the water sample | : V | = 50 l |
| Chemical yield of strontium | : η_{Sr} | = 0,80 |
| Chemical yield of yttrium | : η_{Y} | = 0,90 |
| Decay constant of Sr-89 | : $\lambda_{\text{Sr-89}}$ | = 0,000572 h ⁻¹ |
| Decay constant of Y-90 | : $\lambda_{\text{Y-90}}$ | = 0,0108 h ⁻¹ |
| Background count rate | : R_0 | = 0,017 s ⁻¹ |
| Measuring period of the background effect | : t_0 | = 60 000 s |
| Count rate of Y-90 at t_Y | : $R_{\text{Y-90}}(t_Y)$ | = 0,163 s ⁻¹ |
| Count rate of gross measurement | : $R_g(t_B)$ | = 1,80 s ⁻¹ |
| Self-absorption factor | : f_S | = 1,0 |

According to equation (7), the count rate, $R_{\text{Y-90}}(t_Y)$, measured at time t_Y , is converted to the count rate, $R_{\text{Y-90}}(t_M)$, at time t_M as follows:

$$R_{\text{Y-90}}(t_M) = 0,163 \cdot e^{0,0108 \cdot 4,0} \text{ s}^{-1} = 0,170 \text{ s}^{-1}$$

Following equation (8), the count rate of the daughter nuclide, $R_{\text{Y-90}}(t_\infty)$, which is in equilibrium with the mother nuclide, Sr-90, can be calculated, taking into account the chemical yield from the Y-90 extraction process:

$$R_{\text{Y-90}}(t_\infty) = \frac{0,170}{0,9 \cdot (1 - e^{-0,0108 \cdot 360})} \text{ s}^{-1} = 0,193 \text{ s}^{-1}$$

Now applying equation (9), the activity concentration, $c_{\text{Sr-90}}$, in the sample is:

$$c_{\text{Sr-90}} = \frac{0,193}{0,40 \cdot 0,80 \cdot 1,0 \cdot 50} \text{ Bq} \cdot \text{l}^{-1} = 0,0121 \text{ Bq} \cdot \text{l}^{-1}$$

The count rate, $R_{\text{Sr-89}}(t_F)$ to be expected at time t_F can be obtained from the gross activity measurement, $R_g(t_G)$, at time t_G by applying equations (11) through (13) as follows:

$$R_{\text{Sr-89}}(t_F) = \frac{1,80 - 0,017 - 0,163 \cdot (0,974 \cdot 1,18 + 0,50 \cdot 1,18)}{e^{-0,000572 \cdot 336}} \text{ s}^{-1} = 1,82 \text{ s}^{-1}$$

This produces the activity concentration, $c_{\text{Sr-89}}$, of the sample at the point of time t_F from equation (14) as:

$$c_{\text{Sr-89}}(t_F) = \frac{1,82}{0,30 \cdot 0,80 \cdot 1,0 \cdot 50} \text{ Bq} \cdot \text{l}^{-1} = 0,152 \text{ Bq} \cdot \text{l}^{-1}$$

and at the time of sampling, t_P , after equation (15) as:

$$c_{\text{Sr-89}}(t_P) = 0,152 \cdot e^{0,000572 \cdot 336} \text{ Bq} \cdot \text{l}^{-1} = 0,184 \text{ Bq} \cdot \text{l}^{-1}$$

In the case of a single measurement of the Y-90 contribution, the relative statistical counting error associated to Sr-90 can be calculated according to equation (17):

$$\frac{s[R_{Y-90}(t_Y)]}{R_{Sr-90}(t_Y)} = \frac{s(c_{Sr-90})}{c_{Sr-90}} = \frac{\sqrt{0,163 + 0,017 \cdot (1 + 0,10)}}{6000} = 0,034$$

In the case that Y-90 has been determined by means of n repeat measurements (Figure 4), the relative statistical counting uncertainty associated with Sr-90 is obtained from equations (18) and (19) as:

$$\frac{s[R_{Y-90}(t_Y)]}{R_{Y-90}(t_Y)} = \frac{s(c_{Sr-90})}{c_{Sr-90}} = \frac{\sqrt{0,0749 + 0,017 \cdot (1 + 1,9)}}{19 \cdot 6000} = 0,014$$

with

$$R_{Y-90}(t_Y) = \frac{0,170}{0,0108 \cdot 180} \cdot (1 - e^{0,0108 \cdot 180}) s^{-1} = 0,0749 s^{-1}$$

In analogy, if Y-90 has been determined by means of a single measurement, the relative statistical counting uncertainty associated with Sr-89 can be calculated according to equations (22) and (23) as follows:

$$\frac{s(c_{Sr-89})}{c_{Sr-89}} = \frac{\sqrt{\frac{1,80 + 0,017 \cdot (1 + 0,10)}{6000} + \frac{0,163 + 0,017 \cdot (1 + 0,10)}{6000}} \cdot 1,67}{1,80 - 0,017 - 0,187 - 0,096} = 0,012$$

with

$$f_2^2 \cdot f_3^2 + f_3^2 \cdot f_4^2 = 1,67$$

In the case Y-90 has been determined by n repeat measurements:

$$\frac{s(c_{Sr-89})}{c_{Sr-89}} = \frac{\sqrt{\frac{1,80 + 0,017 \cdot (1 + 0,10)}{6000} + \frac{0,163 + 0,017 \cdot (1 + 1,9)}{19 \cdot 6000}} \cdot 1,67}{1,80 - 0,17 - 0,187 - 0,096} = 0,012$$

The result of determining the activity concentrations of the two strontium isotopes Sr-89 and Sr-90 in surface water with the statistical counting uncertainty, at the time of sampling, t_P , therefore reads:

Sr- 89: $c_{Sr-89}(t_P) = (184 \pm 2,2) \text{ mBq} \cdot \text{l}^{-1}$
 $c_{Sr-89}(t_P) = 184 \text{ Bq} \cdot \text{l}^{-1} \pm 1,2 \%$

Sr-90: $c_{Sr-90}(t_P) = (12,1 \pm 0,41) \text{ mBq} \cdot \text{l}^{-1}$
(single measurement) $c_{Sr-90}(t_P) = 12,1 \text{ mBq} \cdot \text{l}^{-1} \pm 3,4 \%$

Sr-90: $c_{Sr-90}(t_P) = (12,1 \pm 0,17) \text{ mBq} \cdot \text{l}^{-1}$
(repeat measurement) $c_{Sr-90}(t_P) = 12,1 \text{ mBq} \cdot \text{l}^{-1} \pm 1,4 \%$

6 Characteristic limits of the procedure

6.1 Decision thresholds

The decision threshold, g_{Sr-90}^* , that can be achieved in the measurement of Sr-90 contained in surface water depends both on analytical quantities (η_{Sr} , η_Y , ε_{Y-90} , V etc.) as well as the statistical count error, ($s[R_{Y-90}(t_Y)]$), associated with the count rate, $R_{Y-90}(t_Y)$ at time t_Y . If Sr-90 is determined via a single measurement of Y-90 with a measuring period t_m , g_{Sr-90}^* can be estimated in good approximation from the following relationship:

$$g_{Sr-90}^* = \frac{k_{1-\alpha} \cdot \sqrt{\frac{R_0}{t_m} \cdot \left(1 + \frac{t_m}{t_0}\right)}}{\varepsilon_Y \cdot \eta_{Sr} \cdot \eta_Y \cdot f_S \cdot V \cdot [1 - e^{\lambda_{Y-90} \cdot (t_F - t_M)}] \cdot e^{\lambda_{Y-90} \cdot (t_M - t_Y)}} \quad (24)$$

If, on the other hand, Sr-90 is determined on the basis of several successive measurements of Y-90 and $R_{Y-90}(t_M)$ according to the method of the least-square-fit (Fig. 4), g_{Sr-90}^* may be reduced further. In this case, the decision threshold, g_{Sr-90}^* , should be based on the standard deviation, $s[\overline{R_{(Y-90)}}(t_Y)]$ (see section 5). If Sr-90 is determined on the basis of n repeat measurements, $R_{Y-90}(t_Y)$, the decision threshold, g_{Sr-90}^* , that can be achieved, can be estimated from the following relationship:

$$g_{Sr-90}^* = \frac{k_{1-\alpha} \cdot \sqrt{\frac{R_0}{n \cdot t_m} \cdot \left(1 + \frac{n \cdot t_m}{t_0}\right)}}{\varepsilon_{Y-90} \cdot \eta_{Sr} \cdot \eta_Y \cdot f_S \cdot V \cdot [1 - e^{\lambda_{Y-90} \cdot (t_F - t_M)}] \cdot e^{\lambda_{Y-90} \cdot (t_M - t_Y)}} \quad (25)$$

Hence, a single measurement with $t_m = 6000$ s and standard conditions (see section 5.1), a confidence coefficient of $k_{1-\alpha} = 3$ and a sample volume of $V = 50$ l performed with a conventional low-level measurement setup will yield a decision threshold of $g_{Sr-90}^* = 0,40$ mBq·l⁻¹. If Sr-90 is determined on the basis of $n = 19$ individual measurements, and conditions are otherwise the same, the decision threshold can be reduced to $g_{Sr-90}^* = 0,11$ mBq·l⁻¹.

The decision threshold, g_{Sr-89}^* , that can be achieved in the determination of Sr-89 is determined mainly by the standard deviation, $s[R_{Sr-89}(t_G)]$, associated with the measurement of the gross count rate, R_g (equation (22)). The concentrations of Sr-90 and Y-90 have a particularly severe impact on the sensitivity of the determination of Sr-89. Here, g_{Sr-89}^* evaluated at time t_G can be estimated according the following relationship:

$$g_{Sr-89}^* = \frac{k_{1-\alpha} \cdot \sqrt{\frac{R_{Y-90}(t_Y) \cdot (f_2 \cdot f_3 + f_3 \cdot f_4) + R_0 \cdot \left(1 + \frac{t_g}{t_0}\right)}{t_g} + \frac{\left[R_{Y-90}(t_Y) + R_0 \cdot \left(1 + \frac{t_m}{t_0}\right)\right] \cdot (f_2^2 \cdot f_3^2 + f_3^2 \cdot f_4^2)}{t_m}}}{\varepsilon_{Sr-89} \cdot \eta_{Sr} \cdot f_S \cdot V} \quad (26)$$

To calculate the decision threshold at time t_p , it is necessary to correct the radioactive decay of Sr-89 accordingly:

$$g_{\text{Sr-89}}^*(t_p) = \frac{g_{\text{Sr-89}}^*(t_G)}{e^{\lambda_{\text{Sr-89}} \cdot (t_p - t_G)}} \quad (27)$$

Equation (26) indicates that the decision threshold, $g_{\text{Sr-89}}^*$, that can be achieved for Sr-89 is determined to a large extent by the Sr-90 and Y-90 concentrations in the same sample. If, for example, the Sr-90 content amounts to $12 \text{ mBq} \cdot \text{l}^{-1}$ in a conventional measurement setup under the commonly applied conditions (see section 5.1), the decision threshold that can be achieved for a confidence coefficient of $k_{1-\alpha} = 3$ and a sample volume of $V = 50 \text{ l}$ is $g_{\text{Sr-89}}^*(t_G) = 1,5 \text{ mBq} \cdot \text{l}^{-1}$.

6.2 Detection limits

The detection limits $g_{\text{Sr-89}}$ and $g_{\text{Sr-90}}$ in determining Sr-89 and Sr-90, respectively, can be calculated on the basis of the decision thresholds $g_{\text{Sr-89}}^*$ and $g_{\text{Sr-90}}^*$, according to the described procedure by including the confidence coefficient $k_{1-\beta}$ for the type II error as follows (see chapter IV.5 of this procedures manual):

$$g_{\text{Sr-89}} = \frac{k_{1-\alpha} + k_{1-\beta}}{k_{1-\alpha}} \cdot g_{\text{Sr-89}}^* \quad (28)$$

$$g_{\text{Sr-90}} = \frac{k_{1-\alpha} + k_{1-\beta}}{k_{1-\alpha}} \cdot g_{\text{Sr-90}}^* \quad (28a)$$

This means that for a confidence coefficient of $k_{1-\beta} = 1,645$, the detection limit for Sr-89 is calculated as being $g_{\text{Sr-89}} = 3,9 \text{ mBq} \cdot \text{l}^{-1}$ and that for Sr-90 as $g_{\text{Sr-90}} = 0,62 \text{ mBq} \cdot \text{l}^{-1}$ (single measurement) and $g_{\text{Sr-90}} = 0,17 \text{ mBq} \cdot \text{l}^{-1}$ (repeat measurements), respectively, under the specified measuring conditions (see section 5.1). Attention is explicitly drawn to particulars of the conditions that limit the probability of the error β (type II error) occurring and ensure a predetermined power of $1 - \beta$.

It needs to be pointed out, though, that the decision thresholds and detection limits that can be achieved in determining Sr-89 and Sr-90 are particularly dependent on analytical parameters (η_{Sr} , η_{Y} , $\varepsilon_{\text{Sr-90}}$, $\varepsilon_{\text{Sr-89}}$ etc.) that are prone to fluctuations and therefore usually difficult to describe mathematically. The calculation of the decision thresholds and detection limits of the two strontium isotopes Sr-89 and Sr-90, respectively, as performed above therefore represents an estimate that is intended to provide an idea of the sensitivity of a procedure under realistic measurement conditions. It indicates in any case that the detection limit of $10 \text{ mBq} \cdot \text{l}^{-1}$ demanded by the routine measurement programme for the determination of Sr-89 and Sr-90 in surface water according to the StrVG can easily be complied with.

7 Catalogue of chemicals and equipment

7.1 Chemicals

- Flygtol A solution (activated montmorillonite) (20 g Flygtol A/l distilled water by Erbslöh GmbH, 65366 Geisenheim);
- Kerafloc A 4005 (poly-electrolyte) (0,2 g of Kerafloc A 4005/l distilled water by Zschimmer & Schwarz GmbH & Co., Chemische Fabriken, Max-Schwarz-Str. 4-5, 56112 Lahnstein);
- Ammoniac solution, NH_4OH , 2 mol·l⁻¹, 4 mol·l⁻¹, 10 mol·l⁻¹ and 18 mol·l⁻¹;
- Hydrochloric acid, HCl , 1 mol·l⁻¹, 2 mol·l⁻¹, 4 mol·l⁻¹, and 10 mol·l⁻¹;
- Nitric acid, HNO_3 , 1 mol·l⁻¹, 4 mol·l⁻¹, 10 mol·l⁻¹ and 24 mol·l⁻¹;
- Acetic acid, CH_3COOH , 6 mol·l⁻¹ and 17 mol·l⁻¹;
- Strontium chloride solution, $\text{SrCl}_2 \cdot 6 \text{H}_2\text{O}$, 30,6 g·l⁻¹ in distilled water;
- Yttrium chloride solution, $\text{YCl}_3 \cdot \text{H}_2\text{O}$, 34,0 g·l⁻¹ in diluted hydrochloric acid (0,1 mol·l⁻¹);
- Barium chloride solution, $\text{BaCl}_2 \cdot 6 \text{H}_2\text{O}$, 17,9 g·l⁻¹ in distilled water;
- Sodium carbonate solution, $\text{Na}_2\text{CO}_3 \cdot 10 \text{H}_2\text{O}$, saturated solution from distilled water;
- Oxalic acid, $(\text{COOH})_2$, saturated solution from distilled water;
- Sodium chromate solution, Na_2CrO_4 , 48,6 g·l⁻¹ in distilled water;
- Ammonium acetate solution, $\text{CH}_3\text{COONH}_4$, 460 g·l⁻¹ in distilled water;
- Ammonium carbonate solution, $(\text{NH}_4)_2\text{CO}_3$, 200 g·l⁻¹ in distilled water;
- Hydrazine hydroxide, $\text{N}_2\text{H}_5\text{OH}$, solution 24 %;
- Bis-(2-ethylhexyl) phosphate (HDEHP), free of monoester content;
- Ethanol/water mix (1:1) (v/v);
- Voltalef 300 or 302 (poly-fluorochlorethylene) (can be obtained from Lehmann & Voß, Alsterufer 13, 20354 Hamburg);
- Sodium carbonate, $\text{Na}_2\text{CO}_3 \cdot 10 \text{H}_2\text{O}$, solid;
- Di-sodium hydrogen phosphate, $\text{Na}_2\text{HPO}_4 \cdot 12 \text{H}_2\text{O}$, solid;
- Standard solution (activity standards) of Sr-89, Sr-90 and Sr-85 (optional) from the Phys.-Tech. Bundesanstalt, 38116 Brunswick.

7.2 Equipment

- Low-level measuring station with proportional counter and screen counter set to anti-coincidence for 50 mm- and 60 mm-measuring dishes and computer-supported data processing;
- Rotary evaporator, 10 l (optional);
- Cooled centrifuge with 1000 ml- and 250 ml-inserts (Teflon);
- Water jet pumps;
- Hotplates with magnetic stirrer;
- Thermostat-controlled cooler with cooling bath liquid on the basis of per-fluorinated hydrocarbon (e. g., bath liquid FC-77 manufactured by 3M Deutschland GmbH, D-41453 Neuss);
- Hahn's suction apparatus, G2, diameter: 40 mm;
- Crucible furnace;
- Muffle furnace;

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- 2 plastic bottles, 60 l, with lateral tap;
- Blue ribbon filter, membrane filter (0,46 µm), glass fibre filter (e.g., glass fibre filter No. 8 by Schleicher & Schüell, 37586 Dassel).

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