Procedure for determining radionuclides in surface water by gamma spectrometry

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1   Scope

The described procedure is suitable for determining fission and activation products in surface water in normal scenarios, where the sensitivity for detecting nuclides is increased by enriching nuclides from sample volumes of 50 litres prior to the actual gamma spectrometric measurement. For measurement periods of 1000 minutes, depending on the nuclide, concentrations of as little as 1 Bq·m^{-3} can be detected. Measurements of this type are necessary, amongst others, in the framework of radio-ecological studies. They provide information on long-term developments of the contamination with radioactive substances of bodies of water and reveal the effects of various emitters and sources on the basis of suitable indicator substances (1).

In contrast, a multitude of measurements need to be collected in the shortest possible time to rapidly obtain an overview of the extent of the contamination in bodies of surface water in cases of an accidental release of radioactive substances. This requires that direct measurements be taken in Marinelli beakers with a sample volume of 1 litre. Here, measurement periods of 100 minutes suffice to detect nuclide concentrations of as little as ca. 300 Bq·m^{-3}.

2   Sampling

The selection of sampling localities and the manner in which samples are collected must be effected as to ensure the samples are representative of the water body examined (2).

In the case of flowing water, mixed water samples are to be collected continually at the river bed profile at a depth not exceeding 1 m. The collection period should be commensurate to the half-life of the radionuclides of interest. In standing waters, it suffices to collect representative samples periodically with an adequate periodicity. In the case of an accidental release, daily mixed samples or spot samples are to be collected, respectively.

The monitoring focusses on:
— Areas of water bodies with current or potential uses (e. g., collection of drinking water through bank filtration/direct collection; irrigation of agriculturally used areas, etc.);
— Sections of rivers in cross-border regions;
— Mouths and estuaries of rivers;
— Coastal waters;
— Uncontaminated sections of rivers that serve as reference sites.

Under normal circumstances, the collected water samples are stored and transported for further processing in clean plastic containers. In the case of an accidental release of radioactive substances, it must be expected that the measurement and sampling containers have been contaminated as well. This makes verification checks obligatory. To exclude disturbances of this kind as far as possible, it is re-

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commended that measurement containers (Marinelli beakers) be stored in a manner that safely prevents their contamination through airborne activity.

Measurements are always performed on unfiltered water samples. This ensures that activity attached to suspended matter is quantified, too. By quantifying both the content of suspended matter and its specific activity, a distinction can be made between nuclides that are contained in the sample in dissolved and particulate states, respectively. For moderate concentrations of suspended matter of 25 g·m^{-3} and depending on the radionuclide involved, significant proportions may be found to be attached to suspended matter. Elevated concentrations of suspended matter of more than 100 g·m^{-3} may see the content of particulate nuclides rise to 90 % and above and will then need to be quantified separately. Measurements on filtered water samples should be avoided, as the separation of dissolved and particulate nuclide portions is problematic and the results obtained thus will produce an overly optimistic assessment when the exposure is evaluated, for example, for the exposure path 'Irrigation of agriculturally used land'.

3   Analysis

3.1   Principle of the method

3.1.1   Measurements in cases of normal conditions

To determine individual nuclides in water samples by gamma spectrometry, the nuclides to be determined are precipitated from larger sample volumes by adding bentonitic precipitants following a modified bentonite method (3, 4). While some fission and activation products are present as phosphates that are of low solubility, Cs-134 and Cs-137 attach readily to an ion exchanger of the potassium zirconyle hexacyano-ferrate-(II), $K_2ZrOFe(CN)_6$ type, while I-131 attaches to silver iodide (3, 5). The precipitates of low solubility are first performed in the sample by successively adding the precipitants. Preformed thus and partly colloidal, the compounds are then jointly precipitated in an adsorptive manner on activated montmorillonite ("Flygtol A") in combination with a poly-electrolyte ("Kerafloc A 4005"). The extracted precipitate can then be directly measured either in wet or dried form in ring dishes under defined counting conditions. The radiochemical yields of individual nuclides need to be quantified separately under realistic conditions.

An alternative to precipitating radionuclides that are present only in small concentrations is concentrating them by evaporating the sample under reduced pressure in a rotary evaporator or similar apparatus. The disadvantage of this method is the need for increased time and energy required for processing large volumes of water samples compared to the precipitation method.

3.1.2   Measurements in cases of accidental conditions

In the case of the accidental contamination of a water body with radioactive substances, water samples are to be measured directly in Marinelli beakers. To this end, 1 litre of the collected water sample is filled into a Marinelli beaker (volume: 1 litre) and measured directly. Possible adsorption and precipitation effects during the measurement are avoided by acidulating the sample with nitric acid (pH = 1).

3.2   Sample preparation

The water sample is processed unfiltered and without undergoing any pre-treatment.

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3.3 Radiochemical separation

3.3.1 Enrichment through precipitation according to the bentonite method (normal conditions)

For the enrichment of radionuclides according the bentonite method, the following refers to a sample volume of 50 litres. For smaller or larger sample volumes corresponding to lower or higher sensitivity for registering nuclides, respectively, the amount of chemicals to be added are to be adapted accordingly. The method is performed as follows:

3.3.1.1 A fraction of ca. 15 litres of the unfiltered sample is filled into a plastic container (60 litres) and the following additives are added as a mixed solution:

10 ml of potassium iodide solution (100 mg I$^-$)

10 ml of caesium chloride solution (100 mg Cs$^+$)

10 ml of cerium chloride solution (100 mg Ce^{3+})

[10 ml of barium chloride solution (100 mg Ba^{2+}); only if Ba-140 is to be determined subsequently]

[10 ml of strontium chloride solution (100 mg Sr^{2+}); only if Sr-89/Sr-90 is to be determined subsequently]

10 ml of cobalt chloride solution (100 mg Co^{2+})

20 ml of manganese chloride solution (100 mg Mn^{2+})

10 ml of zinc chloride solution (100 mg Zn^{2+})

Finally, 1 g of sodium sulphite (solid) and the remaining 35 litres of the sample are added while the mix is stirred.

3.3.1.2 10 ml of silver nitrate solution (100 mg Ag$^+$) are stirred in.

3.3.1.3 The ion exchanger of the potassium zirconyle hexacyano-ferrate-(II), $K_2ZrOFe(CN)_6$, type is produced:

50 ml of potassium hexacyano-ferrate-(II)-solution are stirred into 50 ml of zirconyl chloride solution in a 1000 ml-glass beaker and then diluted with 100 ml of distilled water.

3.3.1.4 The ion exchanger [$K_2ZrOFe(CN)_6$] freshly prepared thus is successively stirred into the sample. Stirring is continued for 30 minutes after it has been added.

3.3.1.5 Now, 60 g of di-sodium hydrogen phosphate ($Na_2HPO_4 \cdot 2\,H_2O$) are dissolved in a little distilled water and added under stirring.

3.3.1.6 Then, 400 ml of Flygtol A solution (activated montmorillonite) is added,

3.3.1.7 after which 100 ml – 150 ml of ammoniac solution (10 mol·l-1) are added until the alkaline reaction sets in (pH > 8); stirring is continued for 30 minutes.

3.3.1.8 Then, 200 ml of Kerafloc solution (poly-electrolyte) are added and stirred for ca. 3 minutes. Let precipitate settle for at least 1 hour.

3.3.1.9 Once the precipitate has settled, the supernate is siphoned or sucked off and discarded. The precipitate is now transferred to suitable centrifuge bottles (1000 ml) and centrifuged at 3000 revolutions per minute for 30 minutes. The supernatant is again decanted and discarded.

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3.3.1.10 The precipitate is transferred to a ceramic dish and dried at 105 ºC until its weight remains constant.

3.3.1.11 The remaining dry extract is crushed in an agate mortar and measured in a plastic container (e. g, a transparent plastic jar).

Note
— Because the mass of the dry extract may vary from one sample to the next, differences in filling height in the plastic containers used are to be levelled with solid sodium chloride and homogenized.
— If the gamma spectrometric analysis is to be complemented by a quantification of the Sr-89/Sr-90 and Ba-140 contents, step 3.3.1.9 above is to be followed by:

3.3.1.12 The extract is filled into a Marinelli beaker and measured while it is still in a moist state.

3.3.1.13 After it has been measured, the extract is transferred to a 1000 ml-centrifuge container and successively eluted with hydrochloric acid (10 mol·l^{-1}) (see also procedure C-Sr-89/Sr-90-OWASS-01).

Note
— If the sample is evaporated under reduced pressure by a rotary evaporator or similar device, the concentrate and possible salt residues are to be transferred to a ceramic dish and processed further according to step 3.3.1.10 ff.
— The chemical yields from precipitation need to be quantified separately from doped water samples under realistic circumstances. The co-precipitation quotas achieved by the bentonite method under the described circumstances are exemplary for some more important radionuclides and summarized in Table 1 (3, 4).

Tab. 1: Co-precipitation yields, η_r, with the respective standard deviation, $s(\eta_r)$, of the individual values, of various radionuclides precipitated according to the bentonite method from large-volume samples (3, 4)

Nuclide	$\eta_r \pm s(\eta_r)$ %	n
Mn-54	88,4 ± 5,8	13
Co-58	85,2 ± 8,5	13
Zn-65	85,8 ± 5,4	13
Y-88	89,8 ± 8,0	13
Cd-109	83,2 ± 10,0	13
Ba-133	90,8 ± 9,2	10
Cs-134	86,4 ± 4,1	5
Ce-144	86,6 ± 5,2	8
I-131	90,0 ± 4,2	10

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3.3.2 Direct measurement (cases of accidental conditions)

In the case of an accidental release, the unfiltered sample is measured in a Marinelli beaker:

3.3.2.1   The sample (volume: 1 litre) is filled into a ring dish and measured. The reference time is the start of the measurement process, t_m.

3.3.2.2   If the presence of I-131 – including I-131 in inorganic form – is suspected, the sample is fortified with 1 ml of potassium iodide solution (10 mg I⁻) and 0,2 g of sodium sulphite (solid), and acidulated with a little nitric acid (10 ml·l⁻¹) to a pH of 1.

Note
The acute risk of contamination has to be taken into particular consideration when water samples are examined in an event scenario. Depending on the situation, reference and verification measurements may have to be taken of uncontaminated ring dishes to an increased extent.

4   Measuring the activity

Semiconductor detectors made from high purity germanium (p-type) can detect radionuclides with gamma energies between 50 keV and 3000 keV. If gamma emitters with energies of less than 100 keV need to be determined, n-type semiconductor sensors or Si(Li)-detectors with a berryllium- or plastic window should be given preference.

Semiconductor detectors with a large volume of at least 100 cm³ and more than 25 % in relative efficiencies compared to a 3" x 3" NaI(Tl)-probe are to be used as detectors. Their maximum energy resolution should be 2 keV at 1,33 MeV (Co-60). To achieve the highest possible sensitivity in the measurement of the processed water samples, low-level type detectors should be purchased that have been manufactured from materials particularly low in activity. The analysis of gamma spectra and calculation of results should be effected with the aid of PC computer-supported measurement and analysis equipment. 2000 channels per spectrum are required at the least. Further details can be found in chapter IV.1.1 of this procedures manual.

Considering that the secondary scattering and fluorescent radiation of Pb may sometimes interfere with the determination of radionuclides with gamma energies of less than 100 keV, "graded shielding" must be made provision for in order to reduce this effect (7, 9):

<p style="text-align:center">Pb (10 cm) – Cd (0,2 cm) – Cu (0,5 cm) – acrylic glass (1 cm)</p>

In view of the toxic properties of Cd, this shielding material may be omitted. Complementing the Pb-shields with additional shields of copper and Perspex will effectively suppress the photo peaks between 70 keV and 80 keV that result from the fluorescent radiation of lead in particular (Figure 1). This will help to avoid taking incorrect measurements and consequent misinterpretations of photo peaks in this energy range of the kind encountered in the 1992 comparative analysis of doped sediment samples conducted by the Federal Institute of Hydrology (Bundesanstalt für Gewässerkunde) (14).
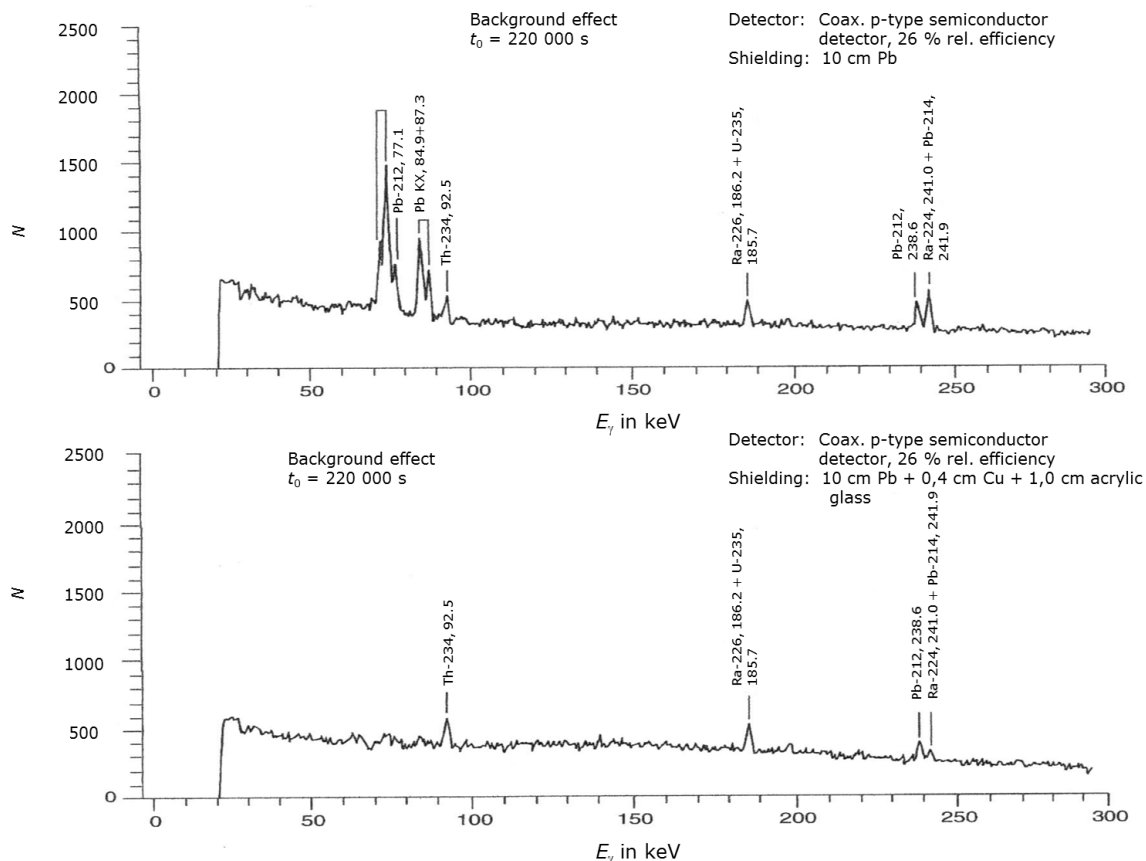
Fig. 1: Background spectrum below 300 keV of a semiconductor detector shielded with: 10 cm Pb (top) and 10 cm Pb + 0,4 cm Cu + 1,0 cm acrylic glass (bottom), respectively
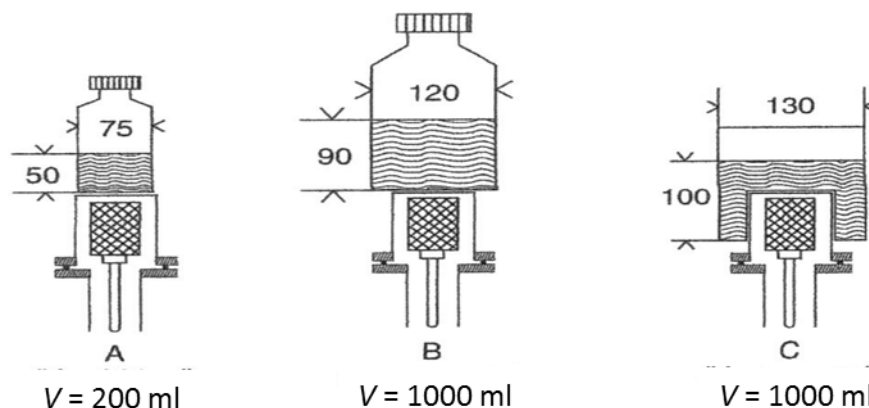

Counting configurations for water samples

Fig. 2: Various counting configurations for determining individual nuclides in water samples by gamma spectrometry (6, 7)

Considering that requirements will typically vary in practice it is recommended to calibrate the detector with several sample containers (6, 7). Three of the configurations commonly used in radiometric water analysis are illustrated in Figure 2. The highest sensitivity in nuclide detection is achieved by using commercially available Marinelli beakers with volumes of 0,5 l, 1 l, 2 l and 4 l.

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Long-term consistency of the efficiencies, in particular following repairs, is verified by measurements on standard sources at monthly intervals. To detect possible contamination, the background effect needs to be measured weekly with measurement periods of at least 10^5 s. The energy calibration should also be checked routinely on the basis of suitable standard sources in order to identify and adjust drift effects.

4.1 Calibration

4.1.1 Energy calibration

The energy calibration of the setup is to be effected for the spectral range in which radionuclides are to be determined. A channel/keV ratio of at least 1:1 is to be adhered to. Calibration should be based on long-lived radionuclides whose gamma energies are distributed over the entire energy range. Due to the high integral linearity of the presently available analog-to-digital converters, a three-point calibration procedure will usually suffice (e. g., Am-241: 59,5 keV; Cs-137: 661,6 keV; K-40: 1460,8 keV).

4.1.2 Quantification of nuclide-/energy-specific peak efficiencies

The photo peak efficiency, ε_γ, as a function of the gamma energy, E_γ, should be determined for each detector and each configuration separately by using standard sources with known nuclide contents. This requires that the same measurement conditions with regard to geometry, sample density, etc. be applied under which the actual environmental samples will also be measured.

The calibration of the measurement configuration may be nuclide-specific or energy-specific. To this end, standard sources solutions (activity standards) e. g. from the Physikalisch-Technische Bundesanstalt, Brunswick, may be used, but also other calibration sources that are certified with sufficient reliability.

The nuclide-specific photo peak efficiency, ε_r, results from the net peak count rate, R_n of the nuclide r, the activity concentration, c_r, either provided by, or known from, the standard source, and the volume, V:

$$\varepsilon_r = \frac{R_n}{c_r \cdot V} \tag{1}$$

Including the relative intensity (emission probability), p_γ, the energy-specific peak efficiency, ε_γ, is given by:

$$\varepsilon_\gamma = \frac{R_n}{c_r \cdot p_\gamma \cdot V} \tag{2}$$

The function of the energy-specific efficiency, ε_γ, is to be identified for the energy range within which radionuclides are to be determined. For this reason, gamma emitters with non-coincident transitions should be given preference (e.g., Am-241, Co-57, Ce-139, Ce-141, Hg-203, Cr-51, Sn-113, Be-7, Cs-137, Mn-54, Zn-65, Fe-59 and K-40). Figure 3 illustrates the energy-specific peak efficiency, ε_γ, vs. the gamma-energy for three commonly employed counting configurations (Figure 2) on a log-log scale (6, 7).

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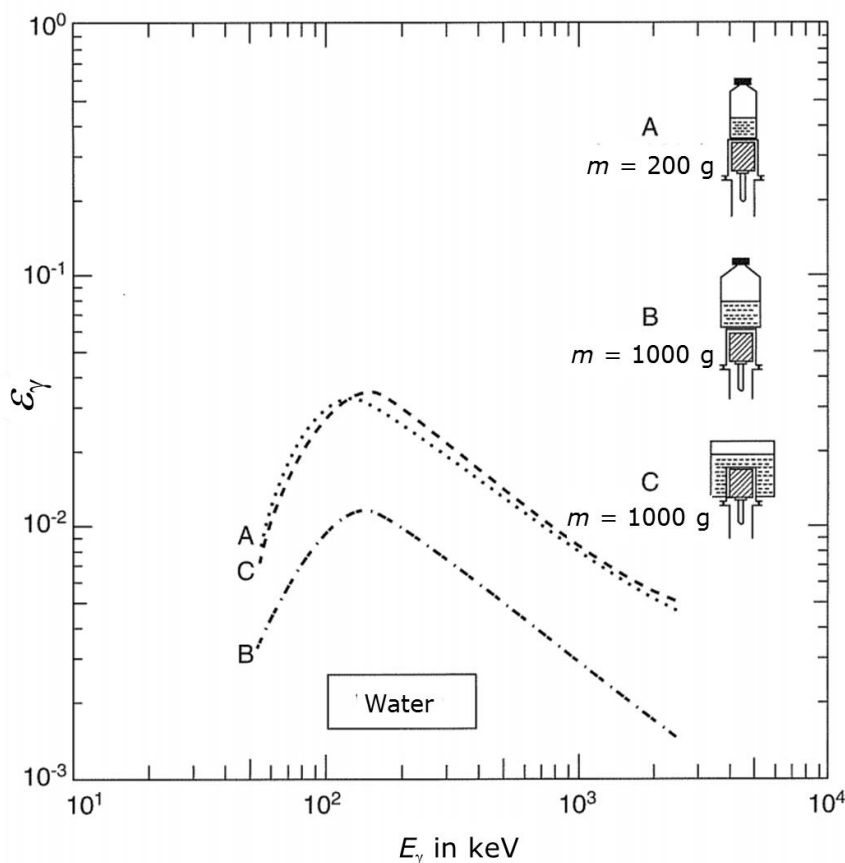
Fig. 3: Energy-specific peak efficiency, ε_γ, vs. the gamma energy for counting configurations A, B and C (measurement of water)

It demonstrates that the photo peak efficiencies of counting configurations A and C are almost identical throughout the entire energy range. But because configuration C uses 1000 ml (g) and thus five times the sample volume of configuration A [200 ml (g)], the decision threshold g_r^* of configuration C is a fifth, all other conditions remaining the same. Owing to the by far more advantageous geometry, ring dishes (counting configuration C) enable decision thresholds, g_r^*, throughout the entire energy range that are lower by a factor of about 3 as compared to the commonly used Kautex bottles (counting configuration B).

4.2   Compensation of coincidence losses of cascade emitters

Coincidence losses, which are particularly important in counting configurations of high measurement geometries and which arises from the formation of cumulative peaks caused by cascade gamma emitters (e. g., Co-60, Cs-134, Y-88 and others), needs to be taken into consideration.

The easiest option for compensating coincidence loss is to first determine the energy-specific photo peak efficiency ε_γ at energy E_γ, at which photo peaks of cascade emitters occur. This can be done with the help of gamma emitters with non-coincident transitions. Having thus obtained the ε_γ (without CL) for peak efficiencies from coincidence-free transitions, and ε_γ (with CL) obtained from the respective cascade emitter at the same energy E_γ, the correction factor, f_{CL}, can easily be calculated. It is used to correct lost counts of this cascade emitter for the respective measurement setup (11):

$$f_{CL} = \frac{\varepsilon_\gamma \left(\text{without} \quad CL \right)}{\varepsilon_\gamma \left(\text{with} \quad CL \right)} \tag{3}$$

To correct for coincidence losses, the correction factor f_{CL} (CL: coincidence loss) is then multiplied with the nuclide-specific contents, a_r, obtained from the measurement on cascade emitters. By associating f_{CL} with p_γ of the cascade emitter, a computer-supported analysis may produce ad-hoc corrected values. For ring dishes (volume: 1 litre), the loss rate amounts to ca. 5 % in the case of typical cascade emitters (e. g., Cs-134, Co-60, Y-88). Further details pertaining to the compensation of coincidence losses observed in cascade emitters are given elsewhere (6, 8, 10 as well as chapter IV.1.1 of this procedures manual).

4.3   Interferences

In spite of the high energy resolution of modern semiconductor detectors, intermediates of natural decay chains may sometimes fake the presence of fission and activation products with identical or very similar energies in the analysis of gamma spectra with many lines. Knowledge of the radionuclides and photo peaks, respectively, contained in the background effect spectrum of the measurement setup used is therefore crucial. The same interferences may also be caused by natural nuclides contained in individual samples, however. Further details on this subject can be found in chapters IV.1.2 and IV.1.3 of this procedures manual.

The density of the samples to be measured and that of the matrix used for calibration should be (at least nearly) matched. If not, a corresponding self-absorption correction is to be applied. Inhomogeneities that arise within the liquid sample during the measuring process (e. g., in measurements taken following an accident) impact the measuring geometry and therefore need to be avoided. The sedimentation of particulate constituents in an aqueous sample can be simply yet effectively prevented by stirring, but also by gelling the sample prior to the measurement.

The analysis of samples with elevated nuclide contents (accidental release) needs to take into account that counting loss remains uncorrected by live-time clocks and must be expected as a result of the limited temporal resolution of conventional measuring equipment (12). The extent of count losses is determined here to a critical extent by the time constant of the shaping time of the main amplifier. For example, count losses in the peak count rate, R_n, of Cs-137 at a time constant of 8 µs and an integral count rate of R_t = 17 000 s^{-1} amounted to ca. 20 %, whereas it was only 5 % at a time constant of 0,5 µs. Because the latter conditions reduce the energy resolution significantly, fixing the time constant requires finding a compromise. In practice, the time constant is typically set as 2 µs to 4 µs. In order to avoid count losses, the sum of the individual nuclide activities within the sample to be analysed should not exceed a value of 50 kBq, otherwise the sample needs to be diluted or an aliquot made from it must be used for taking measurements.

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5   Calculation of the results

In gamma spectrometric analyses, the calculation of the activity concentrations is usually performed automatically with the help of a computer. Here, c_r, of a nuclide, r, in a water sample with a certain volume, V, obeys the following relationship:

$$c_r(t_M) = \frac{R_n}{\varepsilon_\gamma \cdot p_\gamma \cdot \eta_r \cdot V} \cdot \frac{\lambda_r \cdot t_m}{1 - e^{-\lambda_r \cdot t_m}} \tag{4}$$

The beginning of the measurement is always set as a reference time t_M. The decay of very short-lived radionuclides during the measurement is taken into account according to equation (2.25) in chapter IV.5 of this procedures manual.

Extrapolation of the activity concentration to the time when the sample was collected, t_p, requires that equation (4) be expanded accordingly:

$$c_r(t_p) = \frac{R_n \cdot e^{-\lambda_r \cdot (t_m - t_p)}}{\varepsilon_\gamma \cdot p_\gamma \cdot \eta_r \cdot V} \cdot \frac{\lambda_r \cdot t_m}{1 - e^{-\lambda_r \cdot t_m}} \tag{5}$$

Count losses in the case of cascade emitters (Co-60, Cs-134 etc.) are to be compensated for according to section 4.2.

The statistical count uncertainty, s_n, of the net count rate, R_n (s^{-1}), that results from a gamma spectrometric measurement of an individual nuclide can be calculated from the mean background count rate per channel, $\bar{R}_0$ (s^{-1}), the half-width, h (number of channels), and the measuring period, t_m (s), as follows:

$$s_n = \sqrt{\frac{R_n + 3{,}40 \cdot h \cdot \bar{R}_0}{t_m}} \tag{6}$$

As the shape of photo peaks can be approximated by a normal distribution, an interval covering 95 % of the peak's area is used for the analysis. This produces the statistical uncertainty, $s(c_r)$ of a gamma spectrometric measurement of a single nuclide as:

$$s(c_r) = \frac{s_n}{\varepsilon_\gamma \cdot p_\gamma \cdot \eta_r \cdot V} = c_r \cdot \frac{s_n}{R_n} \tag{7}$$

and the relative standard deviation, $s(c_r)/c_r$ (variation coefficient) as:

$$\frac{s(c_r)}{c_r} = \frac{s_n}{\varepsilon_\gamma \cdot p_\gamma \cdot \eta_r \cdot V \cdot c_r} = \frac{s_n}{R_n} \tag{8}$$

5.1   Worked example

Determining the I-131 concentration in a water sample

Time of collectig the sample:	t_p	= 20 June 1991, 12.00 h
Begin of the measurement:	t_M	= 28 June 1991, 12.00 h
Duration of counting source measurement:	t_m	= 28 800 s
Detection efficiency at 364,5 keV:	ε_γ	= 0,0113
Relative intensity of I-131:	p_γ	= 0,816
Radiochemical yield:	η_r	= 0,80
Volume of the sample:	V	= 10 l
Decay constant of I-131:	$\lambda_{\text{I-131}}$	= 0,0864 d^{-1} (= 1,00·10^{-6} s^{-1})
Peak half-width in channels (364,5 keV):	h	= 4
Net count rate of I-131:	R_n	= 0,0073 s^{-1}
Mean background count rate per channel (364,5 keV):	$\overline{R}_0$	= 0,0010 s^{-1}

Following equation (4), this yields a I-131 concentration, $c_{\text{I-131}}$, of the sample at time t_M, of:

$$c_{\text{I-131}}(t_M) = \frac{0,0073}{0,0113 \cdot 0,816 \cdot 0,8 \cdot 10} \cdot \frac{0,0288}{1 - 0,972} \text{ Bq} \cdot \text{l}^{-1} = 0,102 \text{ Bq} \cdot \text{l}^{-1}$$

and, following equation (5), at the time when the sample was collected, t_p, as:

$$c_{\text{I-131}}(t_p) = 0,102 \cdot e^{0,0864 \cdot 8,0} \text{ Bq} \cdot \text{l}^{-1} = 0,204 \text{ Bq} \cdot \text{l}^{-1}$$

The respective statistical uncertainty for the time when the measurement, t_M, was taken is calculated using equations (6) and (7).

$$s(c_{\text{I-131}}) = \frac{\sqrt{\dfrac{0,0073 + 3,40 \cdot 4 \cdot 0,001}{28800}}}{0,0113 \cdot 0,816 \cdot 0,80 \cdot 10} \text{ Bq} \cdot \text{l}^{-1} = 0,012 \text{ Bq} \cdot \text{l}^{-1}$$

To quantify the statistical uncertainty of the result at time t_p, a conversion must be done analogous to equation (5).

The result of the I-131 concentration in a water sample at the time when the sample was collected with its statistical uncertainty based on the uncertainty of the count rate therefore reads:

$$c_{\text{I-131}}(t_p) = (0,20 \pm 0,024) \text{ Bq} \cdot \text{l}^{-1}$$

or

$$c_{\text{I-131}}(t_p) = 0,20 \text{ Bq} \cdot \text{l}^{-1} \pm 12 \text{ \%}$$

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6 Characteristic limits of the procedure

6.1 Decision thresholds

The nuclide and energy-specific decision thresholds, g_r^* and g_γ^* (Bq · l^{-1}), respectively, that can be obtained in the gamma spectrometric determination of individual nuclides, are largely determined by fixed parameters, such as:

— Spectral background, R_0, (depends on shielding, local dose rate, detector materials used, etc.);

— Half-width, h (depends on the detector as well as main and pre-amplifier);

— Detection efficiency, ε_γ (depends on detector size, measurement geometry, etc.).

as well as on quantities that might vary significantly:

— Volume of the sample, V;

— Measurement period, t_m;

— Composition of the sample to be measured.

As radionuclide contents always need to be associated with the time of sampling, t_p, the half-life of short-lived radionuclides also has an impact.

In order to be able to compare the sensitivity of various measurement configurations for given conditions, the calculation of decision thresholds, g_r^*, should always be based upon measurements taken of the background effect spectra without samples. The values g_γ^* and g_r^* obtained thus will then correspond to the achievable decision thresholds obtained in the actual measurement if the volumes of the measured counting sources are minimal and the gamma emitters of natural and artificial origins contained therein can be neglected. The nuclides found in real environmental samples, and natural ones in particular (K-40, U-238 and progeny, etc.), whose concentrations vary from sample to sample, increase the Compton background to an extent that cannot be foreseen, causing the decision thresholds for identical conditions to always be elevated and, moreover, to vary from one counting source to the next (see also procedure C-γ-SPEKT-SEDIM-01).

The literature contains a number of formulae for the calculation of decision thresholds, g_r^*, which are based on different decision criteria for identifying photo peaks. Following the "central channel method" (6, 7):

$$g_r^* = \frac{h \cdot k_{1-\alpha}}{\varepsilon_\gamma \cdot p_\gamma \cdot \eta_r \cdot V} \cdot \sqrt{\frac{\pi \cdot \overline{R}_0 \cdot (1 + 1/n)}{4 \cdot t_m \cdot \ln 2}} = \frac{1{,}064 \cdot h \cdot k_{1-\alpha}}{\varepsilon_\gamma \cdot p_\gamma \cdot \eta_r \cdot V} \cdot \sqrt{\frac{\overline{R}_0 \cdot (1 + 1/n)}{t_m}} \tag{9}$$

a photo peak of the nuclide r is regarded as having been detected if the channel-related differential peak count rate, $R(x_p)$, at the peak position, x_p (highest signal/background ratio), just reaches or exceeds $k_{1-\alpha}$ times the standard deviation of the background count rate, $\overline{R}_0$.

Whereas, following the relationship given in DIN 38404, C 15 (13) of:

$$g_r^* = \frac{k_{1-\alpha}}{\varepsilon_\gamma \cdot p_\gamma \cdot \eta_r \cdot V} \cdot \sqrt{\frac{2 \cdot 1{,}7 \cdot h \cdot \overline{R}_0}{t_m}} \tag{10}$$

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a photo peak of the nuclide r is considered to be detected if the count rate integrated over a region of the spectrum that covers 95 % – corresponding to 1,7 · h – of the photo peak just reaches or exceeds $k_{1-\alpha}$ times the standard deviation of the summed background count rate, $\Sigma R_{0,i,}$ over the same region. A very similar relationship is also given in chapter IV.5 of this procedures manual.

As an example, the decision threshold, $g^{*}_{\text{I-131}}$, for I-131 on the basis of the peak at 364,5 keV, with a half-width of h = 3 channels and otherwise fixed measurement conditions (ε_{γ} = 0,0113; t_{m} = 60 000 s; $\bar{R}_{0}$ = 0,0010 s^{-1}; V = 10 l; η_{r} = 0,80; p_{γ} = 0,816; n = 10; $k_{1-\alpha}$ = 3) can be calculated to be $g^{*}_{\text{I-131}}$ = 0,018 Bq·l^{-1} according to the central channel method, and $g^{*}_{\text{I-131}}$ = 0,017 Bq·l^{-1} according to DIN 38 404, C 16. If the peak region to be analysed is increased to b = 2,5 h in procedures following DIN 38 404, C 16, the corresponding value of $g^{*}_{\text{I-131}}$ = 0,020 Bq·l^{-1}. This demonstrates that the decision threshold will increase with the width of the peak region, b, to be analysed, and will reduce the sensitivity of the detection of the peak accordingly. Furthermore, since decision thresholds always have to be related to the time of sampling, t_{p}, the g^{*}_{r}-values of short-lived radionuclides will increase with the holding period of the sample prior to the actual measurement.

The two methods thus differ to a minor extent with regard to the sensitivity of their peak-detection capabilities, but these differences are of no concern for the requirements of measurements in practice. Given that individual values close to decision thresholds with $k_{1-\alpha}$ = 3 imply a standard deviation of at least 30 %, values of g^{*}_{r} should be employed for subsequent calculations (e. g., detailed assessments, averaging etc.) very cautiously for a negative decision.

6.2   Detection limits

The detection limit can be calculated from the decision threshold, g^{*}_{r} by including the confidence coefficient, $k_{1-\beta}$, for type II errors (see chapter IV.5 of this procedures manual):

$$g_{r} = \frac{k_{1-\alpha} + k_{1-\beta}}{k_{1-\alpha}} \cdot g^{*}_{r} \tag{11}$$

Tab. 2: Calculated decision thresholds, g_r^* ($k_{1-\alpha}$ = 3,0), and detection limits, g_r ($k_{1-\alpha}$ = 3,0 and $k_{1-\beta}$ = 1,64), for various relevant radionuclides that have been enriched according to the described procedure from 50 litres, supposing a background effect spectrum of a conventional semiconductor detector [25 % relative efficiency, compared to a 3″ x 3″ NaI(Tl)-detector and 2,2 keV half-width at 1332 keV] for two measurement periods, t_m.

Nuclide	E_γ (keV)	g_r^* Bq·l⁻¹ t_m = 6000 s	t_m = 60 000 s	g_r Bq·l⁻¹ t_m = 6000 s	t_m = 60 000 s
Cr-51	320,1	0,036	0,012	0,055	0,018
Mn-54	834,8	0,0055	0,0017	0,0085	0,0026
Fe-59	1099,3	0,011	0,0035	0,017	0,0055
Co-57	122,1	0,0037	0,0012	0,0060	0,0018
Co-58	810,8	0,0055	0,0017	0,0085	0,0026
Co-60	1332,5	0,0070	0,0022	0,011	0,0034
Zn-65	1115,6	0,012	0,0040	0,019	0,0060
Zr-95	756,7	0,0095	0,0029	0,014	0,0044
Nb-95	765,8	0,0050	0,0016	0,0080	0,0024
Ru-103	497,1	0,0043	0,0013	0,0065	0,0021
Ag-110m	884,7	0,0075	0,0023	0,011	0,0035
Sb-124	1691,0	0,011	0,0035	0,0017	0,0055
Sb-125	427,9	0,013	0,0040	0,020	0,0065
I-131	364,5	0,0045	0,0014	0,0070	0,0022
Cs-134	795,9	0,0060	0,0019	0,0090	0,0029
Cs-137	661,7	0,0055	0,0018	0,0090	0,0028
Ba-140	537,4	0,017	0,0055	0,027	0,0085
Ce-141	145,4	0,0070	0,0022	0,010	0,0034
Ce-144	133,5	0,030	0,0095	0,046	0,014

Attention is explicitly drawn to particulars in the measurement conditions that limit the probability of the error β (type-II error) occurring and ensure a power of 1−β.

The decision threshold, g_r^*, and detection limits, g_r, that can be achieved with the described procedure under realistic conditions for standard measurement periods are summarized as examples for a number of relevant radionuclides in Table 2. Leaving the short-lived radionuclides aside, this list indicates that detection limits of 0,01 Bq·l⁻¹ and 0,05 Bq·l⁻¹, respectively, demanded by routine measurement programmes in accordance with the StrVG as well as the guideline for the monitoring of emissions and immissions of nuclear installations can easily be complied with.

7   Catalogue of chemicals and equipment

7.1   Chemicals

— Standard solutions (activity standards) e. g. of the Physikalisch-Technische Bundesanstalt, Brunswick;

— Potassium iodide solution, KI, 13,1 $g\cdot l^{-1}$, in distilled water;

— Silver nitrate solution, $AgNO_3$, 15,7 $g\cdot l^{-1}$, in diluted nitric acid (0,05 $mol\cdot l^{-1}$);

— Caesium chloride solution, CsCl, 12,7 $g\cdot l^{-1}$, in distilled water;

— Cobalt chloride solution, $CoCl\cdot 6\ H_2O$, 40,4 $g\cdot l^{-1}$, in distilled water;

— Barium chloride solution, $BaCl_2\cdot 2\ H_2O$, 17,8 $g\cdot l^{-1}$, in distilled water;

— Cerium chloride solution, $CeCl_3\cdot 7\ H_2O$, 26,6 $g\cdot l^{-1}$, in diluted hydrochloric acid (0,1 $mol\cdot l^{-1}$);

— Manganese chloride solution, $MnCl_2\cdot 4\ H_2O$, 36,0 $g\cdot l^{-1}$, in distilled water;

— Zinc chloride solution, $ZnCl_2$, 20,8 $g\cdot l^{-1}$, in diluted hydrochloric acid (0,1 $mol\cdot l^{-1}$);

— Zircon oxide chloride, $ZrOCl_2\cdot 8\ H_2O$, 81,0 $g\cdot l^{-1}$, in diluted hydrochloric acid (0,1 $mol\cdot l^{-1}$);

— Potassium hexacyano-ferrate-(II), $K_4Fe(CN)_6\cdot 3\ H_2O$, 106 $g\cdot l^{-1}$, in distilled water;

— Flygtol A solution (activated montmorillonite) (20 g of Flygtol A/l dist. water; manufactured by Erbslöh GmbH, 65366 Geisenheim);

— Kerafloc A 4005 (poly-electrolyte) (0,2 g of Kerafloc A 4005/l dist. Water; man-ufactured by Zschimmer & Schwarz GmbH & Co., Chemische Fabriken, Max-Schwarz-Str. 4-5, 56112 Lahnstein);

— Sulphuric acid, H_2SO_4, 18 $mol\cdot l^{-1}$;

— Ammoniac solution, NH_4OH, 10 $mol\cdot l^{-1}$;

— Sodium chloride, NaCl, solid;

— Sodium sulphite, Na_2SO_3, solid;

— di-Sodium hydrogen phosphate, $Na_2HPO_4\cdot 2\ H_2O$;

— Nitric acid, HNO_3, 10 $mol\cdot l^{-1}$;

— Hydrochloric acid, HCl, 10 $mol\cdot l^{-1}$.

7.2   Equipment

— Computer-supported multi-channel analyser for analysis of gamma spectra in online mode, with tabulated and graphic data outputs;

— High-purity germanium semiconductor detector with a relative efficiency of > 25 % [relative to a 3" x 3" NaI(Tl) sensor] and an energy resolution of < 1,9 keV at 1,33 MeV;

— 3 plastic containers with tap, 60 litres;

— Cooling centrifuge with 1000 ml-inserts;

— 1 stirring apparatus;

— Drying oven;

— Analytic scale;

— Rotary evaporator (optional);

— Ring dishes (plastic) with volumes of 0,5 litre, 1 litre and 2 litres;

— General laboratory equipment.

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