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Water quality — Determination of the activity concentration of radionuclides by high resolution gamma-ray spectrometry

Qualité de l'eau — Détermination de l'activité volumique des radionucléides par spectrométrie gamma à haute résolution

Reference number
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Foreword

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Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

International Standard ISO 10703 was prepared by Technical Committee ISO/TC 147, *Water quality*, Subcommittee SC 3, *Radiological methods*.

Annexes A and B of this International Standard are for information only.

International Organization for Standardization
Case Postale 56 • CH-1211 Genève 20 • Switzerland

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Introduction

This International Standard allows, after proper sampling, sample handling and, when necessary or desirable, sample preparation, the simultaneous determination of the activity concentration of several gamma-ray emitting radionuclides in water samples by gamma-ray spectrometry using high purity germanium or lithium drifted germanium [Ge(Li)] detectors. Gamma-ray emitting radionuclides are widespread both as naturally occurring and as man-made radionuclides. Therefore, environmental samples usually contain a multitude of different gamma-ray emitters and high resolution gamma-ray spectrometry provides a useful analytical tool for environmental measurements.

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Water quality — Determination of the activity concentration of radionuclides by high resolution gamma-ray spectrometry

1 Scope

This International Standard specifies a method for the simultaneous determination of the activity concentration of various radionuclides emitting gamma rays with energies 0,1 MeV $< E <$ 2 MeV in water samples, by gamma-ray spectrometry using germanium detectors with high energy resolution in combination with a multichannel analyser.

NOTE 1 The determination of the activity concentration of radionuclides emitting gamma rays with an energy 40 keV $< E <$ 100 keV and above 2 MeV is possible within the scope of this International Standard, provided both the calibration of the measuring system and the shielding are adapted to this purpose (see 6.2, 8.5 and 10.3).

This International Standard includes the procedures for energy calibration, determination of the energy dependent sensitivity of the measuring system, the analysis of the spectra and the determination of the activity concentration of the various radionuclides in the sample studied. It is only applicable to homogeneous samples. Samples with activities typically between 1 Bq and 10^4 Bq can be measured as such, i.e. without dilution or concentration of the sample Bq or special (electronic) devices.

Depending on different factors, such as the energy of the gamma rays and the emission probability per nuclear disintegration, the size and geometry of the sample and the detector, the shielding, the counting time and other experimental parameters, the sample should be concentrated by evaporation when activities below about 1 Bq have to be measured. Also, when the activity is considerably higher than 10^4 Bq, the sample should be either diluted or an aliquot of the sample should be taken, or the source to detector distance should be increased, or a correction for pile-up effects should be applied.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 5667-1:1980, *Water quality — Sampling — Part 1: Guidance on the design of sampling programmes.*

ISO 5667-2:1991, *Water quality — Sampling — Part 2: Guidance on sampling techniques.*

ISO 5667-3:1994, *Water quality — Sampling — Part 3: Guidance on the preservation and handling of samples.*

IEC 659:1979, *Test methods for multichannel amplitude analyzers.*

IEC 973:1989, *Test procedures for germanium, gamma-ray detectors.*

IEC 1151:1992, *Nuclear instrumentation — Amplifiers and preamplifiers used with detectors of ionizing radiation — Test procedures.*

3 Definitions

For the purposes of this International Standard, the following definitions apply.

3.1 counting efficiency: Under stated conditions of detection, the ratio of the number of detected gamma-photons to the number of gamma-photons of the same type emitted by the radiation source in the same time interval.

3.2 gamma cascade: Two or more different gamma-photons emitted successively within the resolution time from one nucleus when it de-excites through one or more intermediate energy levels.

3.3 gamma radiation: Electromagnetic radiation emitted in the process of nuclear transition or particle annihilation.

3.4 gamma-ray spectrometry: A method of measuring gamma rays yielding the energy spectrum of the gamma radiation.

3.5 energy resolution: A measure, at a given energy, of the smallest relative difference between the energy of two gamma rays which can be distinguished by the apparatus used for gamma-ray spectrometry.

NOTE 2 In this International Standard, the energy resolution is expressed by a factor which is the full peak width at half maximum height, divided by the energy at the peak of the distribution curve for monoenergic photons.

3.6 decay constant (λ): For a radionuclide in a particular energy state, the quotient of dP by dt, where dP is the probability of a given nucleus undergoing a spontaneous nuclear transition from that energy state in the time interval dt.

$$\lambda = \frac{\mathrm{d}P}{\mathrm{d}t} = -\frac{1}{N}\frac{\mathrm{d}N}{\mathrm{d}t}$$

where N is the number of nuclei of concern existing at time t.

3.7 dead time: The time interval which must elapse between the occurrence of two consecutive pulses or ionizing events for them to be recognized by the detection system as separate pulses or events.

3.8 dead time correction: Correction to be applied to the observed number of pulses in order to take into account the number of pulses lost during the dead time.

3.9 pile-up: The processing by a radiation spectrometer of pulses resulting from the simultaneous absorption of particles, or photons, originating from different decaying nuclei, in the radiation detector. As a result, they are counted as one single particle or photon with an energy between the individual energies and the sum of these energies.

3.10 full energy peak: The peak of the spectral response curve corresponding to the total absorption of the photon energy by the photoelectric effect.

3.11 transition probability: the fraction of the nuclei which disintegrates in a specific way.

4 Symbols and abbreviations

$A_i(t)$	is the activity of radionuclide i at time t, in becquerels;
C_i	is the activity concentration of radionuclide i, in becquerels per litre;

$f_{\mathrm{d},i}$	is the correction factor to correct the activity or activity concentration of radionuclide i for physical decay between the time of sampling and the time of the measurement (dimensionless);
$f_{\mathrm{s},i}$	is the correction factor for coincidence summing of the multi-line photon emitting radionuclide i at energy E;
g_i	is the limit of detection for radionuclide i, as specified in this International Standard, in becquerels per litre;
g'_i	is the lower limit of decision for radionuclide i, as specified in this International Standard, in becquerels per litre;
$k_{1-\alpha}$ and $K_{1-\beta}$	are the confidence coefficients according to the errors of the first kind (α) and second kind (β);
$P_{i,E}$	is the transition probability of radionuclide i giving rise to the emission of a gamma ray with energy E, also referred to as the branching fraction for energy E (dimensionless);
$R_{\mathrm{n},E}$	is the net counting rate per second, under the full energy peak corresponding to energy E;
$R_{\mathrm{n},i}$	is the net counting rate per second, under the full energy peak corresponding to radionuclide i;
$\overline{R}_{\phi}$	is the median background counting rate, per second per kilo- electronvolt;
t_{m}	is the measurement time of the sample, in seconds;
v_i	is the coefficient of variation of the activity concentration, due to the stochastic character of nuclear decay, in percent;
V	is the volume of the sample, in litres;
ε_E	is the energy-specific counting efficiency for gamma rays with energy E (dimensionless);
ε_i	is the radionuclid-specific counting efficiency for radionuclide i at a given energy (dimensionless);
λ_i	is the decay constant of radionuclide i, per second.

5 Principle

Gamma rays cause ionizations when interacting with matter. When a voltage is applied across a semiconductor detector, these ionizations are, after proper amplification, detected as current pulses. The pulse height is related to the energy absorbed from the gamma-photon or photons in the resolving time of the detector and electronics. By discriminating between the height of the pulses, a gamma-ray pulse height spectrum is obtained. After analysis of the spectrum, the various peaks are assigned to the radionuclides which emitted the corresponding gamma rays. The concentration of the radionuclides present in the sample is calculated using the previously obtained energy-dependent detector efficiency.

6 Reference sources

All reference sources shall be traceable to a national standard.

6.1 Reference source(s) for energy calibration

One or more reference sources emitting gamma rays with accurately known energies covering the entire energy range to be studied shall be used.

NOTE 3 It is recommended that photon-emitting sources be used which cover the energy region of interest. Choose the source so that at least nine full energy peaks uniformly divided throughout the energy range of interest are available; sources containing long-lived radionuclides (europium-152, americium-241, cobalt-60, caesium-137) are reommended for this purpose. For a periodical control on the energy calibration, a smaller number of energy peaks may be used.

6.2 Reference source(s) for determination of the energy-dependent counting efficiency

One or more reference sources, traceable to national or International Standards, for which the total uncertainty of the activity is stated shall be used. Multi-radionuclide sources may also be used. The energies of the emitted gamma rays shall be distributed over the entire energy range to be analysed, in such a way that the energy-dependent efficiency of the measuring apparatus can be determined in a sufficiently accurate way. For most purposes, the accuracy is sufficient if the difference in counting efficiency between two subsequent energies is smaller than 10 % of the counting efficiency at 120 keV, if the required radionuclides are available. For determining the activity of radionuclide-emitting gamma rays in the energy region 40 keV $< E <$ 100 keV, the counting efficiency for these gamma rays shall be determined by calibration with this particular radionuclide.

NOTE 4 For the energy range 100 keV $< E <$ 2 000 keV, the following radionuclides can be used: manganese-54, cobalt-57, zinc-65, strontium-85, yttrium-88, cadmium-109, tin-113, caesium-137, cerium-139, mercury-203. Radionuclides with cascade transitions (e.g. cobalt-60 and caesium-134) should be applied with caution (see 10.6.1).

7 Reagents

The following reagents shall be used when the sample is concentrated by evaporation with iodine retention. Use only reagents of recognized analytical grade and only demineralized water or water of equivalent purity.

7.1 Concentrated nitric acid (HNO_3), $\rho = 1{,}42$ g/ml

7.2 Concentrated sulfuric acid (H_2SO_4), $\rho = 1{,}84$ g/ml.

7.3 Silver nitrate solution, $\rho = 3{,}2$ g/l.

Dissolve 3,2 g of silver nitrate ($AgNO_3$) in water acidified with 0,1 ml of nitric acid (7.1) and dilute to a total volume of 1 litre with water.

7.4 Potassium iodide solution, $\rho = 1{,}3$ g/l.

Dissolve 1,3 g of potassium iodide (KI) in 1 litre of water.

7.5 Sodium sulfite (Na_2SO_3).

7.6 Hydrogen peroxide solution (H_2O_2), $\rho = 0{,}3$ g/l.

7.7 Sodium carbonate solution (Na_2CO_3), saturated at 20°C.

8 Apparatus

Basically the measuring apparatus consists of two parts, the detector and the device which handles, stores and analyses the signals from the detector. Traditionally, the output of the detector is fed into a multichannel analyser (MCA). MCA's have been mostly replaced by multichannel buffers (MCB) and all handling, display, storage and analysis of data is done by a microprocessor with software and peripheral hardware. For the purposes of this International Standard either of the possibilities can be used, but data analysis is executed using the computer (8.8).

The apparatus shall consist of the following necessary parts.

8.1 High purity germanium or lithium drifted germanium [Ge(Li)] crystal.

The performance of the detector shall be tested according to IEC 973.

NOTE 5 The detectors can be obtained mainly in three different shapes, each having its own advantage depending on the circumstances: planar, coaxial and well-type detectors are commercially available. For example, coaxial detectors are generally used when large volumes of sample are available, whereas the well-type detectors are most efficient for small volumes. More detailed information on the detectors is given in reference [1] in annex B.

8.2 High voltage power supply.

WARNING — Take necessary safety precautions according to the manufacturer's instructions.

8.3 Preamplifier, which determines to a high degree the quality of the entire measuring system, as both noise and energy resolution depend on the characteristics of the preamplifier.

NOTE 6 Usually the preamplifier is located very close to the detector. Cooling the input stage (FET) of the preamplifier decreases the noise level and improves the energy resolution.

8.4 Cryostat, capable of keeping the detector close to the temperature of liquid nitrogen.

Operation at a low temperature is required to reduce the leakage current and electronic noise level of the detector and preamplifier; it is recommended that an automatic switch off and an alarm signal be installed which are activated in the case of an increase of temperature (e.g. caused by malfunctioning of the cryostat or loss of liquid nitrogen). A Ge(Li) detector will be damaged when allowed to warm up.

A high purity germanium detector may be stored at room temperature, however, it shall be cooled when bias voltage is applied.

8.5 Shielding

The detector shall be shielded from all sides (including the bottom) with lead or iron, to reduce background signals originating mainly from naturally occurring radionuclides. If measurements in the energy region 40 keV $< E <$ 100 keV are to be made, the internal casing shall consist of three successive layers of cadmium, copper and polymethylmethacrylate to achieve a low and constant background by attenuating the X-ray produced in the shielding.

Shielding is important to reduce background levels, especially if low activity levels are to be measured. The following measures can be taken:

— use of low activity lead; no shielding should be close to the detector if at all possible:

— ventilation, air filtration and the construction and other materials of the system should be chosen carefully, in order to reduce activity concentrations to achieve low levels of background radiation.

8.6 Main amplifier

The main amplifier shall have linear characteristics with respect to input and output signals, shall have pulse-shaping capacities and shall be equipped with a pole-zero network and a DC-restorer. The conformity of the actual characteristic parameters with the manufacturer's specifications shall be tested according to IEC 1151.

NOTE 7 When high counting rates ($> 5\,000\ s^{-1}$), are to be expected, a pulse pile-up rejection circuit may be useful. The correct use of pile-up rejection requires considerable expertise.

8.7 Multichannel analyser (MCA) or multichannel buffer (MCB)

The multichannel analyser shall have at least 1 024 channels. For a good resolution, 2 048 channels are advisable. The performance of the multichannel analyser shall be tested according to IEC 659.

8.8 Computer, including peripherical devices and software

The computer, in combination with the available hardware and software, should be able to:

- read the data from the MCA or MCB;
- reproduce these data on a video display, a plotter or a printer and store them;
- determine the relation between channel number and corresponding energy over the entire energy range to be studied, by making use of the appropriate reference source (see 6.1);
- determine the energy-dependent counting efficiency over the entire energy range to be studied, by making use of the appropriate reference source (see 6.2);
- detect peaks, determine the characteristics of the detected peaks such as the centroid, the full peak width at half maximum height, the number of net counts collected under the peak, and determine the uncertainty of this number;
- identify the radionuclides responsible for the observed full energy peaks by making use of radionuclide references (e.g. [2] to [6] in annex B);
- calculate the activity of the respective radionuclides on the basis of the number of counts, the counting time, the counting efficiency and the data given in radionuclide references (e.g. [2] to [6] in annex B);
- calculate the standard deviation of the activity of the identified radionuclides, or the detection limit of radionuclides to be measured but not found in the sample. Whenever necessary, calculations and identification may be performed manually.

It is recommended that the results of the computer analysis of the spectrum be visually checked regularly for obvious anomalies or errors. To check the performance of the apparatus, the use of a laboratory standard is recommended. Participation in intercomparison runs can also help to test the performance of the apparatus and analysis.

9 Sampling

The sample shall be collected and preserved according to ISO 5667-1, ISO 5667-2 and ISO 5667-3. Particular attention shall be given to the following:

- sample identification (place, time and procedure followed);
- the time elapsed between the moment of sampling and the measurement of the sample;
- homogeneity of the sample; if any particulate matter is present which can cause inhomogeneity, this shall be removed by filtration, and the residue shall be measured separately if necessary (see also 10.1.1);
- for the sampling, polyethylene bottles shall be used which have been cleaned with 1 mol/l hydrochloric acid, followed by leaching with dilute nitric acid solution and rinsing with distilled or deionized water;
- immediately after collection, the sample shall be acidified to pH < 2 with nitric acid; if particulate matter is removed by filtration or centrifugation, this shall be carried out before acidification (see 10.1.1);
- between acidification and measurement, the sample shall be transported and/or stored in the absence of light and at a temperature $0\ °C < t < 5\ °C$;

If radio-iodine is to be determined, hydrochloric acid should be used instead of nitric acid for acidification of the sample.

NOTE 8 In some cases, it may be desirable to add a carrier solution to the sample. For instance, when waste water from a nuclear power plant is measured, a carrier solution as described in annex A can be used.

10 Procedure

10.1 Sample preparation

In this International Standard, three different ways of preparing the water sample are described. In the test report, the method of sample preparation actually used shall be referred to as described in 10.1.1 to 10.1.3.

The choice of method depends on the limit of detection required (see 10.1.1 or 10.1.2). However, if radionuclides of iodine have to be determined, the choice is between 10.1.1 and 10.1.3, depending on the limit of detection required.

10.1.1 Direct measurement

Direct measurement is to be used when relatively high activity concentrations are to be expected, i.e. for emission monitoring or in accident situations. After filtration through a membrane filter (pore size 0,45 µm), acidify the sample (see clause 9) and measure directly, (see 10.4) preferably in a Marinelli beaker.

The residue on the filter shall be measured separately. In the test report, the method shall be referred to as "direct measurement", giving the results for "liquid" and for "solid" both referring to the volume of the sample. The mass concentration of suspended solids shall also be given.

NOTE 9 Homogenization of the sample during measurement, for example by stirring or by adding a gelling agent, is possible. In this case, the results should be reported as "total".

10.1.2 Evaporation without iodine retention

Evaporate the sample until a small amount of water with solid material remains. Transfer the concentrated sample to a small dish, evaporate the remaining water and dry the sample at 105 °C for 30 min. Determine the mass of the residue and measure it. In the test report, the method shall be referred to as "evaporation without iodine retention". The results shall be given as "total", unless the suspended solids are counted separately.

10.1.3 Evaporation with iodine retention

Add to the sample, while stirring, 10 ml of potassium iodide solution (7.4), 0,1 g of sodium sulfite (7.5) and 5 ml of concentrated sulfuric acid (7.2) per litre of unfiltered water sample. After stirring for 5 min, add 10 ml of silver nitrate solution (7.3) and 10 ml of hydrogen peroxide solution (7.6) per litre. Adjust the pH to a value of 9, using saturated sodium carbonate solution (7.7).

Evaporate and dry the sample according to 10.1.2. In the test report, the method shall be referred to as "evaporation with iodine retention". The results shall be given as "total", unless the suspended solids are counted separately.

10.2 Energy calibration

Place the reference source for energy calibration (6.1) in the measuring apparatus (see clause 8). Adjust the amplifier and the Analog Digital Converter (ADC) in such a way that the first channel corresponds to an energy between 0 keV and 30 keV and that each channel corresponds to 0,5 keV, assuming that 4 096 channels are used.

In the equipment systems, the relationsphip between energy and channel number is approximately linear. For analysis of the spectrum, it is however necessary to attribute to each channel the corresponding energy accurately, for example by fitting the experimental points with a polynomial.

Determine the relationship between energy and channel number with a mathematical expression which expresses this relationship with an accuracy of 0,1 keV or better. Repeat the energy calibration weekly. Check the correct relationship between energy and channel number daily.

10.3 Determination of the counting efficiency

The counting efficiency is affected by the following factors:

— the detector used;

— the geometry of the sample with respect to the detector;

— the density of the sample and the sample container.

Taking these factors into account, the counting efficiency shall be determined under the same conditions as the sample. When one of these factors is changed, the counting efficiency shall be re-evaluated for the new conditions. The same algorithms for analysis of the spectrum shall also be used for both the sample and reference. Depending on the purpose of the measurement (single radionuclide or multi-radionuclide determination, the counting efficiency can be determined in two different ways, i.e. as a function of energy or for the single radionuclide.

Radionuclide-specific counting efficiency can be used when the purpose of the measurement is to determine a single radionuclide and as to be used when the energy region 40 keV $\leq E <$ 100 keV is to be analysed. The radionuclide-specific counting efficiency can be used for that particular radionuclide and for cases where the radionuclide under investigation emits gamma radiation from cascade transitions (see 10.3.2). It might also be necessary when random summing corrections become important, i.e. in well-type detectors.

10.3.1 Procedure

Place the reference source (6.2) in the measuring apparatus (see clause 8) and record a spectrum until the net counting rate under the full energy peak can be determined with a variation coefficient of 1 % or less (see 10.6.3). To avoid errors due to pile-up, the activity of the reference source in combination with the measuring geometry shall be such that the real counting time of the measurement does not differ by more than 10 % from the live time. A pulse pile-up rejection circuit may also be used (see note 7).

Determine the number of net counts under the relevant peaks for all energies (E) to be used. Use the same peak area calculation procedure when measuring samples. Correct the activity of the reference source for radioactive decay since the calibration date of the source using the equation:

$$A_i(t) = A_i(0) \times e^{-\lambda_i t} \qquad \ldots (1)$$

where

$A_i(t)$ is the activity of radionuclide i at the time of measurement t, in becquerels;

$A_i(0)$ is the activity if radionuclide i at the time of certification of the reference source, in becquerels;

λ_i in the decay constant of radionuclide i, per second;

t is the time elapsed between the time of certification and the time of measurement, in seconds.

10.3.2 Counting efficiency as a function of energy

Determine the counting efficiency at energy E for all the peaks to be used from the equation:

$$\varepsilon_E = \frac{R_{\mathrm{n},E}}{A_i(t) \times P_{i,E}} \qquad \ldots (2)$$

where

ε_E	is the energy-specific counting efficiency for gamma rays with energy E;
$R_{\text{n},}E$	is the net counting rate per second, under the full energy peak corresponding to energy E;
$A_i(t)$	is the activity of radionuclide i at the time of calibration t in becquerels;
$P_{i,E}$	is the transition probability of radionuclide i giving rise to the emission of a gamma ray with energy E (or branching fraction).

Determine the energy-dependent detection efficiency by finding the best fitting line or mathematical expression which relates the experimental data of the efficiency to the energy. All experimental points shall not deviate by more than 5 % from the line or the expression.

Repeat the procedure described in 10.3.1 regularly as a check, but in any case for each different measuring geometry and for each different density of the sample; this assumes that the detection efficiency only depends each on the sample density and not on the effective average atomic number.

For radionuclides with cascade transitions, counting losses due to coincidence summing are to be expected, especially at high counting efficiencies.

The necessity of correction for coincidence summing shall be checked as follows.

The dependency of counting efficiency on energy shall be established with single-line photon-emitting radionuclides. For a multi-line photon-emitting radionuclide (e.g. cobalt 60 or coesium-134) the deviation of the measured "apparent" efficiency from the "real" efficiency for the energies under consideration (obtained from measurements of single-line photon-emitting radionuclides) shall be determined. If the deviation for the main lines of this radionuclide exceeds 20 %, correction factors for coincidence summing of the multi-line photon-emitting radionuclides, $f_{\text{s},i}$ shall be determined individually from the equation:

$$f_{\text{s},i} = \frac{\varepsilon_E}{\varepsilon_i} \qquad \text{. . . (3)}$$

where

$f_{\text{s},i}$	is the correction factor for coincidence summing of the multi-line photon-emitting radionuclide i at energy E;
ε_E	is the counting efficiency as a function of energy determined with single-line photon-emitting radionuclides at energy E;
ε_i	is the counting efficiency for the multi-line photon-emitting radionuclide i at energy E.

If the deviation between "apparent" and "real" efficiency is less than 20 % and the multiline photon-emetting radionuclide to be determined is not available for calibration, the correction factors for coincidence summing of the multiline photon-emitting radionuclides, $f_{\text{s},i}$, can be estimated approximately using the following procedure [8] in annex B). Establish the counting efficiency of an available multi-line photon-emitting radionuclides i (e.g. cobalt-60) at energy E of one of the main full energy peaks and calculate the correction factor $f_{\text{s},j}$. This correction factor shall be compared with a value given literature for a similar detector and a similar source geometry. The same relation can be applied to a distinct line of the multi-line photon-emitting radionuclide i to be determined and a value given in the literature, which gives the following equation:

$$\frac{f_{\text{s},i} - 1}{f_{\text{s},i}(\text{lit}) - 1} = \frac{f_{\text{s},j}(\text{meas}) - 1}{f_{\text{s},j}(\text{lit}) - 1} \qquad \text{. . . (4)}$$

where

$f_{\text{s},i}$	is the correction factor for coincidence summing of radionuclide i, to be estimated approximately;
$f_{\text{s},i}(\text{lit})$	is the correction factor for coincidence summing of radionuclide i given in the literature;

$f_{s,j}$(meas) is the correction factor for coincidence summing of radionuclide j available for calibration and determined experimentally;

$f_{s,j}$(lit) is the correction factor for coincidence summing of radionuclide j given in the literature.

It is recommended to use the most recent correction factor tables available from internationally accepted sources ([7] and [8] in annex B).

The values of the correction factors $f_{s,i}$ shall be incorporated into the calculation of the activity concentration (see 10.6.1) and into the calculation of the lower limit of decision and the lower limit of detection (see 10.6.4).

If a more correct approximation is sought, sophisticated computer programmes [7] and [9] in annex B) could be applied.

10.3.3 Radionuclide-specific counting efficiency

Determine the counting efficiency for each specific radionuclide i using the equation:

$$\varepsilon_i = \frac{R_{n,i}}{A_{i(t)}} \quad \ldots (5)$$

where

ε_i is the radionuclide-specific counting efficiency for radionuclide i at a given energy;

$R_{n,i}$ is the net counting rate per second, under the full energy peak corresponding to radionuclide i;

$A_i(t)$ is the activity of radiunuclide i at the time of calibration t, in becquerels.

NOTE 10 Several radionuclides yield more than one full energy peak, which facilitates the use of higher sensitivity and accuracy. Multiple counting efficiency for a single radionuclide gives higher sensitivity and better accuracy. See also note 11.

10.4 Recording of a gamma-ray pulse height spectrum of the sample

Place the sample in the measuring apparatus (see clause 8) reset the MCA (8.7) and record a spectrum. Note the time and date. Count for a sufficiently long time to reach the desired detection limit of the various radionuclides (see 10.6.4).

The detector, the sample container or the detector surroundings can be contaminated or can contain naturally occurring radionuclides. This can give rise to peaks in the spectrum, not originating from the sample. For this reason, record a background spectrum regularly as a check, using a container of an identical composition filled with demineralized water and counting for the same time as for the sample. Only non-contaminated containers should be re-used. Wen low detection limits have to be obtained and long counting times are necessary, take into account in the analysis the peaks from the background spectrum.

10.5 Analysis of the spectrum

Detect the peaks which have evolved in the spectrum, determine the energies to which the maxima correspond and the net number of counts collected undet the peaks, in the same way as for the determination of the energy-dependent detection efficiency. For each peak, determine to which radionuclide it has to be assigned, taking into account the possible X-ray emission and the occurrence of summation and pile-up.

Very small, very big and double peaks can cause problems in the spectrum analysis. It is highly preferable to check visually the agreement between the peaks that have been detected by the program and the measured spectrum.

If the counting time has been sufficiently long for peaks to evolve in the background spectrum, the number of counts under these peaks shall be subtracted from the corresponding sample peak counts. If necessary, correct for a difference in counting time between sample and blank.

10.6 Expression of results

10.6.1 Calculation of the activity concentration using the counting efficiency as a function of energy

For all peaks, calculate the activity concentration of each radionuclide i present in the sample using the equation:

$$c_i = \frac{R_{\mathrm{n},E} \times f_{\mathrm{d},i} \times f_{\mathrm{s},i}}{\varepsilon_E \times P_{i,E} \times V} \qquad \ldots (6)$$

where

c_i	is the activity concentration of radionuclide i, in becquerels per litre;
$R_{\mathrm{n},E}$	is the net counting rate per second, under the peak with energy E which has been assigned to radionuclide i;
ε_E	is the energy-specific counting efficiency at energy E to which the maximum of the peak corresponds (see 10.3.2);
$P_{i,E}$	is the transition probability of radionuclide i giving rise to the emission of a gamma ray with energy E;
V	is the volume of the sample, in litres; if the sample is solid material, V is the volume of the water from which the sample has been obtained;
$f_{\mathrm{s},i}$	is the correction factor for coincidence summing of the multi-line photon-emitting radionuclide i at energy E:
$f_{\mathrm{d},i}$	is the correction factor to correct for physical decay of radionuclide i between the time of sampling and the time of measurement, calculated using the equation:

$$f_{\mathrm{d},i} = \mathrm{e}^{\lambda_i t} \times \left[\frac{\lambda_i \times t_\mathrm{m}}{1 - e^{-\lambda_i t_\mathrm{m}}} \right] \qquad \ldots (7)$$

where

λ_i	is the decay constant of radionuclide i, per second;
t	is the time elapsed between the time of sampling and beginning of measurement, in seconds;
t_m	is the measurement time of the sample, in seconds.

NOTE 11 Several radionuclides yield more than one full energy peal. On one hand this facilitates the assignment of the peaks to the respective radionuclides, on the other hand this will yield, for a single radionuclide, more than one value of the activity. In this case, the activity concentration may be calculated using the equation:

$$\bar{c}_i = \frac{\sum\limits_j \frac{c_{i,j}}{V_j^2}}{\sum\limits_j \frac{1}{V_j^2}} \qquad \ldots (8)$$

where

$\bar{c}_i$	is the weighted mean of the activity concentration of radionuclide i, in becquerels per litre;
$c_{i,j}$	is the activity concentration of radionuclide i as calculated from full energy peak j, in becquerels per litre

v_j is the variation coefficient of $c_{i,j}$ (see 10.6.3);

For radionuclides with cascade transitions, counting losses due to summing are to be expected, especially at high counting efficiencies. Correct for counting losses by coincidence summing if necessary (see 10.3.2).

NOTE 12 As an alternative for correction for coincidence summing by means of an approximation, a radionuclide-specific calibration (see 10.3.3) is possible.

10.6.2 Calculation of the activity concentration using radionuclide-specific counting efficiency

For all peaks, calculate the activity concentration of each radionuclide i present in the sample using the equation:

$$c_i = \frac{R_{n,i} \times f_{d,i}}{\varepsilon_i \times V} \qquad \dots (9)$$

where

c_i is the activity concentration of radionuclide i, in becquerels per litre;

$R_{n,i}$ is the net counting rate per second, under the full energy peak which has been assigned to radionuclide i;

ε_i is the radionuclide-specific counting efficiency for radionuclide i;

V is the volume of the sample, in litres; if the sample is solid material, V is the volume of the water from which the sample has been obtained;

$f_{d,i}$ is the correction factor to correct for physical decay of radionuclide i between the time of sampling and the time of measurement; see equation (7) in 10.6.1 for the calculation of $f_{d,j}$.

See note 11.

10.6.3 Calculation of the coefficient of variation

Calculate the coefficient of variation v_i of the activity concentration of the radionuclide i, du to the stochastic character of the process of nuclear disintegration, using the equation:

$$v_i = \frac{s(R_n)}{R_n} \times 100 \qquad \dots (10)$$

with

$$s(R_n) = \sqrt{\frac{R_n + 2b \times \overline{R}_\phi}{t_m}} \qquad \dots (11)$$

where

v_i is the coefficient of the variation of the activity concentration of radionuclide i, in percent;

$s(R_n)$ is the standard deviation of the net counting rate per second, under the full energy peak of radionuclide i;

R_n is the net counting rate per second, under the full energy peak;

b is the full peak width of the full energy peak, calculated as 1,7 × h where h is the full peak width at half maximum of the photopeak at energy E, in kiloelectronvolts;

$\overline{R}_\phi$ is the median background counting rate of the spectrum in the region of the full energy peak, per second per kilo- electronvolt;

t_m is the measurement time of the sample, in seconds.

Equations (10) and (11) shall only be applied if the measurement of a blank with a measurement time $t_0 \geqslant t_m$ does not give rise to peaks in the regions of interest concerned. In this case, calculate the coefficient of variation v_i for radionuclide i using the equation (12) and (13).

$$v'_i = \frac{s(R'_n)}{R'_n} \times 100 \qquad \text{. . . (12)}$$

with

$$s(R'_n) = \sqrt{\frac{(R'_n + 2b \times \overline{R}_\phi)}{t_m} + \frac{\left(R_n^0 + 2b \times \overline{R}_\phi^0\right)}{t_0}} \qquad \text{. . . (13)}$$

where

v'_i	is the coefficient of variation of the activity concentration of radionuclide i, in percent;
$s(R'_n)$	is the standard deviation of the total net peak counting rate of radionuclide i, per second;
R'_n	is the total net peak counting rate, per second;
$\overline{R}_\phi^0$	is the median background counting rate of the spectrum of the blank in the region of the peak, in per second per kilo- electronvolt;
R_n^0	is the net counting rate per second of the spectrum of the blank in the region of the peak;
t_0	is the measurement time of the blank, in seconds.

10.6.4 Calculation of the lower limit of decision and the lower limit of detection

Calculate the lower limit of decision g'_i for radionuclide i using equation 14:

$$g'_i = \frac{k_1 - \alpha}{\varepsilon_i \times V} \times f_{d,i} \times f_{s,i} \sqrt{\frac{2b \times \overline{R}_\phi}{t_m}} \qquad \text{. . . (14)}$$

Calculate the lower limit of detection g_i for radionuclide i according to equation 12:

$$g_i = \frac{k_{1-\alpha} + k_{1-\beta}}{\varepsilon_i \times V} \times f_{d,i} \times f_{s,i} \times \sqrt{\frac{2b \times \overline{R}_\phi}{t_m}} \qquad \text{. . . (15)}$$

where

g'_i	is the lower limit of decision for radionuclide i, in becquerels per litre;
g_i	is the lower limit of detection for radionuclide i, in becquerels per litre;
$k_{1-\alpha}$ and $k_{1-\beta}$	are the confidence coefficients according to the errors of the first kind (α) and second kind (β); (For a confidence level of 95 %, $k_{1-\alpha}$ and $k_{1-\beta}$ equals 1,64;
b	is the full peak width of the full energy peak, calculated as 1,7 × h, where h is the full peak width at half maximum of the full energy peak at energy E, in kiloelectronvolts;
$\overline{R}_\phi$	is the median background counting rate of the spectrum in the region of the peak, per second per kiloelectronvolt;
ε_i	is the radionuclide-specific peak counting efficiency for radionuclide i, with $\varepsilon_i = \varepsilon_E \times P_{i,E}$ if the calibration is energy specific;
ε_E	is the energy-specific peak counting efficiency at energy E;

$P_{i,E}$	is the ratio of the transition probability of radionuclide i at which the photon with energy E decays to the total transition probability of decay;
V	is the volume of the sample, in litres;
t_m	is the measurement time of the sample, in seconds.

Equations (14) and (15) shall only be applied if the measurements of a blank with a duration of counting $t_0 \geqslant t_m$ does not give rise to peaks in the rgions of interest concerned. In this case, calculate the lower limit of decision g'_i and the lower limit of detection g_i for radionuclide i using equations 16 and 17, respectively:

$$g'_i = \frac{k_{1-\alpha}}{\varepsilon_i \times V} \times \sqrt{\frac{1}{t_\mathrm{m}} \times \left[2b \times \overline{R}_\phi + R_\mathrm{n}^0 + \frac{t_\mathrm{m}}{t_0} \times \left(R_\mathrm{n}^0 + 2b \times R_\phi^0\right)\right]} \times f_{\mathrm{d},i} \times f_{\mathrm{s},i} \quad \ldots (16)$$

$$g_i = \frac{k_{1-\alpha} + k_{1-\beta}}{\varepsilon_i \times V} \times \sqrt{\frac{1}{t_\mathrm{m}} \times \left[2b \times \overline{R}_\phi + R_\mathrm{n}^0 + \frac{t_\mathrm{m}}{t_0} \times \left(R_\mathrm{n}^0 + 2b \times R_\phi^0\right)\right]} \times f_{\mathrm{d},i} \times f_{\mathrm{s},i} \quad \ldots (17)$$

where

$\overline{R}_\phi^0$	is the median background counting rate of the spectrum of the blank in the region of the peak, per second per kiloelectronvolt;
R_n^0	is the net counting rate per second of the spectrum of the blank in the region of the peak;
t_0	is the measurement time of the blank, in seconds.

NOTES

13 The lower limit of decision of a single measurement is the net signal level above which an observed net rate may be recognized as to be detected at a given error probability (according to the error of the first kind α).

The lower limit of detection is the smallest contribution of the sample which may be recognized as to be detected at a given error probability (according to the error of the second kind β).

Observed values are to be compared with the lower limit of decision; given values of regulations etc. are to be compared with the lower limit of detection.

14 Equations (14) and (15) may only be applied,

- if the term $2b \times R_\phi \times t_\mathrm{m} > 10$;
- if the backround in the region of the peak allows the calculation of the net area of the peak by the trapezium method (commonly used method of linear approximation of the background; the background in the region of the peak is represented as trapezium);
- if the counts are governed by the Poisson distribution.

15 The required error probabilities $k_{1-\alpha}$ and $k_{1-\beta}$ cannot always be attained, especially if the term $2b \times \overline{R}_\phi \times t_\mathrm{m}$ is low.

In this case the application of the method is problematic.

11 Test report

The test report shall include the following information:

a) a reference to this International Standard;

b) reference and accuracy of the Standard solution used;

c) complete identification of the sample, and reference to its preparation;

d) the activity concentration of all radionuclides which have been identified, with the coefficient of variation in percent and the lower limit of detection;

e) the lower limit of detection for those radionuclides which have not been identified but for whose presence a check was required;

f) the geometry of the detector used;

g) the detection efficiency (relative to a NAI detector) and the energy resolution at 1 332 keV, expressed in kiloelectronvolts;

h) any unusual features noted during the determination;

i) any deviation from the procedures specified in this International Standard, or regarded as optional.