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

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

Reference number
ISO 10703:2007(E)

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. 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.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 10703 was prepared by Technical Committee ISO/TC 147, *Water quality*.

This second edition cancels and replaces the first edition (ISO 10703:1997), which has been technically revised.

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 [HPGe] 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.

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

WARNING — Persons using this International Standard should be familiar with normal laboratory practice. This International Standard does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to ensure compliance with any national regulatory conditions.

IMPORTANT — It is absolutely essential that tests conducted in accordance with this International Standard be carried out by suitably trained staff.

1 Scope

This International Standard specifies a method for the simultaneous determination of the activity concentration of various radionuclides emitting gamma rays with energies $40\ \text{keV} < E < 2\ \text{MeV}$ in water samples, by gamma-ray spectrometry using germanium detectors with high energy resolution in combination with a multichannel analyser.

NOTE The determination of the activity concentration of radionuclides emitting gamma rays with energy below 40 keV and above 2 MeV is also possible within the scope of this International Standard, provided both the calibration of the measuring system and the shielding are adapted to this purpose.

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 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 referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 31-9, *Quantities and units — Part 9: Atomic and nuclear physics*

ISO 3696, *Water for analytical laboratory use — Specification and test methods*

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

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

ISO 5667-14, *Water quality — Sampling — Part 14: Guidance on quality assurance of environmental water sampling and handling*

ISO/IEC 17025, *General requirements for the competence of testing and calibration laboratories*

Guide to the expression of uncertainty in measurement (GUM), BIPM, IEC, IFCC, ISO, IUPAC, IUPAP, OIML

IEC 60973, *Test procedures for germanium gamma-ray detectors*

IEC 61151, *Nuclear instrumentation — Amplifiers and preamplifiers used with detectors of ionizing radiation — Test procedures*

IEC 61452, *Nuclear instrumentation — Measurement of gamma-ray emission rates of radionuclides — Calibration and use of germanium spectrometers*

3 Terms and definitions

For the purposes of this document, the definitions, symbols and abbreviations given in ISO 31-9 and the following apply.

3.1

blank sample

container of an identical composition to the one used for the water test sample filled with radon free demineralized water

3.2

dead time

time interval which must elapse between the occurrence of two consecutive pulses or ionising events for them to be recognized by the detection system as separate pulses or events

3.3

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

3.4

decay constant

λ

⟨radionuclide in a particular energy state⟩ 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

3.5

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

3.6
energy resolution
measure, at a given energy, of the smallest difference between the energy of two gamma rays which can be distinguished by the apparatus used for gamma-ray spectrometry

3.7
full energy peak
peak of spectral response curve corresponding to the total absorption of the photon energy in the sensitive detector volume by the photoelectric effect or by consecutive photon interactions of pair production (only for photon energy > 1 022 keV), Compton scattering and photoelectric absorption

3.8
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

3.9
gamma radiation
electromagnetic radiation emitted in the process of nuclear transition or particle annihilation

3.10
gamma-ray spectrometry
method of measuring gamma rays yielding the energy spectrum of the gamma radiation

3.11
pile-up
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.

NOTE 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.

3.12
transition probability
fraction of the nuclei which disintegrates in a specific way

4 Symbols and units

V	Volume of the water sample for test, in litres
A	Activity of each radionuclide in calibration source, at the calibration time, in becquerels
$c_A, c_{A,\text{c}}$	Activity concentration1) of each radionuclide, without and with corrections, expressed in becquerels per litre
t_g	Sample spectrum counting time, in seconds
t_0	Background spectrum counting time, in seconds
t_s	Calibration spectrum counting time, in seconds
$n_{N,E}, n_{N0,E}, n_{N\text{s},E}$	Number of counts in the net area of the peak, at energy E, in the sample spectrum, in the background spectrum and in the calibration spectrum, respectively
$n_{\text{g},E}, n_{\text{g0},E}, n_{\text{gs},E}$	Number of counts in the gross area of the peak, at energy E, in the sample spectrum, in the background spectrum and in the calibration spectrum, respectively
$n_{\text{b},E}, n_{\text{b0},E}, n_{\text{bs},E}$	Number of counts in the background of the peak, at energy E, in the sample spectrum in the background spectrum and in the calibration spectrum, respectively
ε_E	Efficiency of the detector at energy E at actual measurement geometry
P_E	Probability of the emission of a gamma ray with energy E of each radionuclide, per decay
λ	Decay constant of each radionuclide, in reciprocal seconds
$u(c_A), u(c_{A,\text{c}})$	Standard uncertainty associated with the measurement result, without and with corrections, in becquerels per litre
U	Expanded uncertainty calculated by $U = k \cdot u\left(c_A\right)$ with k = 1, 2..., in becquerels per litre
$c_A^*, c_{A,\text{c}}^*$	Decision threshold, without and with corrections, in becquerels per litre
$c_A^\#, c_{A,\text{c}}^\#$	Detection limit, without and with corrections, in becquerels per litre
$c_A^\triangleleft, c_A^\triangleright$	Lower and upper limits of the confidence interval, in becquerels per litre

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1) “Volumic activity” is an alternative name for “Activity concentration".

5 Principle

Gamma rays cause electron-hole pairs when interacting with matter. When a voltage is applied across a semiconductor detector, these electron hole-pairs 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 using the previously obtained energy detector calibration. The concentration of the radionuclides present in the sample is calculated using the previously obtained energy-dependent detector efficiency.

6 Reference sources

All certified reference sources shall be traceable to a national or international 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.

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 recommended for this purpose. For a periodical control on the energy calibration, a smaller number of energy peaks can be used.

6.2 Reference source(s) for efficiency calibration

One or more reference sources, traceable to national or international standards, for which the 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 should be determined by calibration with this particular radionuclide.

NOTE 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. Radionuclides with cascade transitions (e.g. cobalt-60 and caesium-134) are applied with caution. As mercury is volatile it cannot be incorporated in solid sources prepared by evaporation.

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 water complying with grade 3 of ISO 3696 shall be used for all applications.

7.1 Nitric acid, concentrated, $c(\mathrm{HNO_3}) = 15{,}8$ mol/l, 69 % volume fraction or w/w, [$\rho(\mathrm{HNO_3}) = 1{,}42$ g/ml].

7.2 Sulfuric acid, concentrated, $c(\mathrm{H_2SO_4}) = 17{,}9$ mol/l, 95 % volume fraction or w/w, [$\rho(\mathrm{H_2SO_4}) = 1{,}84$ g/ml].

7.3 **Silver nitrate solution**, $c(AgNO_3) = 3{,}2$ g/l.

Dissolve 3,2 g of silver nitrate in water acidified with 0,1 ml of nitric acid and dilute to a total volume of 1 l with water.

7.4 **Potassium iodide solution**, $c(KI) = 1{,}3$ g/l.

Dissolve 1,3 g of potassium iodide in 1 l of water.

7.5 **Sodium sulfite**, Na_2SO_3.

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

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

8 Gamma spectrometry equipment

Basically the measuring apparatus consists of two parts, the detector and the device which handles, stores and analyses the signals from the detectors. The output of the detector is fed into a multichannel analyser and buffers (MCA and MCB) and all handling, display, storage and analysis of data is carried out by a microprocessor with software and peripheral hardware.

For electronic parts, digital components (DSP) are more and more commonly used.

The apparatus shall consist of the parts described in 8.1 to 8.8.

8.1 High purity germanium detector

The performance of the detector shall be tested as specified in IEC 60973.

NOTE The detectors are commercially available mainly in three different shapes, each having its own advantage depending on the circumstances : planar, coaxial and well-type detectors. 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 the Bibliography.

8.2 High voltage power supply

WARNING – Take necessary safety precautions in accordance with the manufacturer's instructions.

8.3 Preamplifier

The preamplifier 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 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 or electric cooler**, to keep 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).

The HPGe detector can 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 may consist of three successive layers of cadmium, copper and for instance 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 close to the detector if at all possible;
- ventilation, air filtration, other materials of the system and the construction of the system 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, should have pulse-shaping capacities and shall be equipped with a pole-zero network and a DC-restorer. The conformity of the actual characteristics parameters with the manufacturer's specifications shall be tested as specified in IEC 61151.

NOTE When high counting rates ($> 5\,000\ \mathrm{s}^{-1}$), are to be expected, a pulse pile-up rejection circuit can be useful.

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

The optimum number of channels depends on the energy resolution and the studied energy range. For good resolution in the energy range of 100 keV to 2 000 keV, 4 096-8 192 channels are required (see Reference [11]).

8.8 Computer, including peripherical devices and software

The computer, in combination with the available hardware and software (see References [1] and [2]), 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 (energy calibration), by making use of the appropriate reference source;
- determine the energy-dependent efficiency over the entire energy range to be studied (efficiency calibration), by making use of the appropriate reference source;
- detect peaks, to 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 to determine the uncertainty of this number;
- identify the radionuclides responsible for the observed full energy peaks by making use of radionuclide references, for instance see References [4] to [7];
- calculate the activity concentration 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, for instance see References [4] to [7];
- calculate the standard uncertainty of the activity concentration of the identified radionuclides;

- calculate the detection limit and the decision threshold of radionuclides to be measured but not found in the sample.

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.

NOTE Whenever necessary, calculations and identification can be performed manually.

9 Sampling

The sample shall be collected and preserved as specified in ISO 5667-1, ISO 5667-3 and ISO 5667-14. 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 heterogeneity, this shall be removed by filtration, and the residue shall be measured separately if necessary;
- for the sampling, polyethylene bottles should be used, cleaned with 1 mol/l hydrochloric acid, followed by leaching with dilute nitric acid solution and rinsing with distilled or deionized water;
- depending on the time duration between the sampling and the measurement (if storage is more than several days) as well as the radionuclide to measure, the sample should be acidified to pH < 2 with nitric acid; if particulate matter is removed by filtration or centrifugation, this shall be carried out before acidification;
- between acidification and measurement, the sample should be transported and/or stored in the absence of light and at a temperature of $1\ °C < t < 5\ °C$.

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

NOTE In some cases, it can be desirable to add a carrier solution to the sample. For example, 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 in the test report.

The choice of method depends on the limit of detection required. However, if radionuclides of iodine have to be determined, the choice can be made between 10.1.1 and 10.1.3, depending on the limit of detection required.

10.1.1 Direct measurement without preparation

Direct measurement can be used to get the results rapidly, for example in situations such as emission monitoring or accident control. The sample is measured directly, preferably in a Marinelli beaker type.

When the water sample is filtrated, 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 1 Homogenization of the suspended matter in the sample can be made by adding a gelling agent.

NOTE 2 A partial evaporation of the sample can be performed to reduce the volume and concentrate the activity before the direct measurement.

10.1.2 Evaporation without iodine retention

Evaporate the water to dryness. If necessary, determine the mass of the residue and measure the activity of the quantity corresponding to the mass of the standard geometry. In the test report, the method shall be referred to as "evaporation without iodine retention".

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 sulphuric acid (7.2) per litre of unfiltered water sample. After stirring for 5 min, add 10 ml of silver nitrate solution (7.6) 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 in accordance with 10.1.2. In the test report, the method shall be referred to as "evaporation with iodine retention".

10.2 Calibration

Calibration shall follow the requirements of IEC 61452.

10.2.1 Energy calibration

Place the reference source in the spectrometer. 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 system, the relationship 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 function which expresses this relationship with an accuracy of 0,1 keV or better.

Generally, this task is carried out using appropriate software to deal with the standard spectra, record the useful information to be used for future analyses and automatically convert the channel scale of the converter into a photon energy scale. Using the energy calibration spectra, the full-width at half maximum of the full-energy peaks can be determined as a function of the gamma energy. This information is usually required by the evaluation software.

10.2.2 Efficiency calibration

The counting efficiency is affected by the following factors:

- the detector and the settings of the electronics used;
- the geometry of the sample with respect to the detector (solid angle);
- the density of the sample and the sample container characteristics.

Taking these factors into account, the counting efficiency shall be determined under the same measuring conditions as the sample source. 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 calibration sources. Depending on the purpose of the measurement (single radionuclide or multi-radionuclide determination), the 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 has to be used when the energy region 40 keV $< E <$ 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. It might also be necessary when random summing corrections become important, i.e. in well-type detectors.

10.2.2.1 Procedure

Prepare a calibration source from the reference source with the same physical and chemical properties as the source sample. It can, for example, be produced by spiking a volume of water and preparing the calibration source like the sample source to be measured.

Place the calibration source in the spectrometer 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. 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.

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.

10.2.2.2 Counting efficiency as a function of energy

Determine the counting efficiency at energy E for all the peaks to be used from Equation (1):

The efficiency for energy E shall be calculated by:

$$\varepsilon_E = \frac{n_{N\mathrm{s},E} / t_\mathrm{s}}{A \cdot P_E} \tag{1}$$

For an undisturbed peak at an energy E, the number of counts $n_{Ns,E}$ in the net-peak area of a γ-spectrum is calculated using Equation (2):

$$n_{N\mathrm{s},E} = n_{\mathrm{gs},E} - n_{\mathrm{bs},E} \tag{2}$$

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.

When using calibration sources of a radionuclide with different emission lines, summation effects or coincidence losses should be taken into account.

Repeat the procedure described in 10.2 regularly as a check and for each different measuring geometry.

10.2.2.3 Radionuclide-specific counting efficiency

The efficiency for each specific radionuclide i, at energy E, is determined using Equation (3):

$$\varepsilon_{i,E} = \frac{n_{N\mathrm{s},E} / t_\mathrm{s}}{A_i \cdot P_E} \tag{3}$$

NOTE 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.

10.3 Recording a spectrum of the sample

Place the sample in the measuring apparatus, reset the MCA 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.

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 blank sample. Only non-contaminated containers should be re-used. When 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.

10.4 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 under 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.

It is highly preferable to check visually the agreement between the peaks that have been detected by the software program and the measured spectrum as small, wide and double peaks can be incorrectly detected and/or quantified.

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

Detailed information see Reference [11].

11 Expression of results

11.1 Calculation of the activity concentration

The activity concentration, c_A, of each radionuclide present in the sample is obtained from the net count $n_{N,E}$ from the peak of an individual γ-line without any interference using Equation (4):

$$c_A = \frac{n_{N,E} / t_\mathrm{g}}{P_E \cdot \varepsilon_E \cdot V \cdot f_E} \tag{4}$$

where

f_E is the correction factor considering all necessary corrections according to Equation (5):

$$f_E = f_\mathrm{d} \cdot f_{\mathrm{cl},E} \cdot f_{\mathrm{su},E} \tag{5}$$

where

f_d is the factor to correct for decay for a reference date;

$f_{cl,E}$ is the factor to correct for coincidence losses (summing-out);

$f_{\mathrm{su},E}$ is the factor to correct summing-in effects by coincidences.

For an undisturbed peak at an energy E, the count $n_{N,E}$ in the net-peak area of a γ-spectrum is calculated using Equation (6):

$$n_{N,E} = n_{\mathrm{g},E} - n_{\mathrm{b},E} \tag{6}$$

Thus, Equation (4) might be expressed as:

$$c_A = \frac{n_{N,E} / t_\mathrm{g}}{P_E \cdot \varepsilon_E \cdot V \cdot f_E} = \frac{n_{\mathrm{g},E} - n_{\mathrm{b},E}}{P_E \cdot \varepsilon_E \cdot V \cdot f_E \cdot t_\mathrm{g}} = (n_{\mathrm{g},E} - n_{\mathrm{b},E}) \cdot w / t_g \quad \text{with} \quad w = \frac{1}{P_E \cdot \varepsilon_E \cdot V \cdot f_E} \tag{7}$$

11.1.1 Decay corrections

Depending on the half-life of the radionuclide to be measured, the specific activity must be corrected by f_d. To take into account the radioactive decay during the counting time and during the time between the reference instant ($t = 0$) and the measuring instant ($t = t_i$), f_d must be calculated by

$$f_\mathrm{d}^{-1} = e^{\lambda \cdot t_i} \cdot \left[\frac{\lambda \cdot t_\mathrm{g}}{1 - e^{-\lambda \cdot t_\mathrm{g}}} \right] \tag{8}$$

11.1.2 Summation effects or coincidence losses corrections

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

These corrections are important for point sources samples measured very close to detector surface, and are specific for each radionuclide, each detector, measuring geometry and sample to detector distance.

Most of the theoretical methods to calculate summation are related with the use of transport theory and Monte-Carlo techniques (see References [15] to [18]). Given the difficulties to model the detectors, some experimental procedures can be applied for each specific situation.

Some of these experimental procedures use data from the specialized literature, but given the wide range of detector possibilities and measuring conditions, direct measurement as given below can be made:

a) Prepare a source containing the multi-line photon emitting radionuclide whose correction factor at energy E must be calculated along with another radionuclide emitting at a similar energy, E', which has negligible summing corrections. The geometry must be the same as that used for the sample source.

b) Measure this source at a long distance from the detector. Calculate the relationship between the net peak counts at energies E and E'.

c) Measure the sample in the normal measuring position. The relationship between the net peak counts at energies E and E' will be similar to that calculated above and the theoretical net peak counts, $n_{N,E}^T$, at energy E, can be estimated.

The relationship between theoretical, $n_{N,E}^T$, and measured, $n_{N,E}$, net peak counts is the summing correction factor for energy E of the multi-line photon emitting radionuclide that must be applied to the analysis of the calibration and source sample spectrum.

Further information is given in References [8] and [12].

11.2 Standard uncertainty

According to the GUM, the standard uncertainty of c_A is calculated by:

$$u(c_A) = \sqrt{(w / t_\mathrm{g})^2 \cdot [u^2(n_{\mathrm{g},E}) + u^2(n_{\mathrm{b},E})] + c_A^2 \cdot u_\mathrm{rel}^2(w)} \tag{9}$$

Where the standard uncertainty of the counting time is neglected and the relative standard uncertainty of w is calculated by

$$u_\mathrm{rel}^2(w) = u_\mathrm{rel}^2(P_E) + u_\mathrm{rel}^2(V) + u_\mathrm{rel}^2(\varepsilon_E) + u_\mathrm{rel}^2(f_E) \tag{10}$$

Taking into acount Equation (1) the relative standard uncertainty of ε_E is calculated by

$$u_{\text{rel}}^2(\varepsilon_E) = u_{\text{rel}}^2(n_{N\text{s},E}) + u_{\text{rel}}^2(A) + u_{\text{rel}}^2(P_E) = u_{\text{rel}}^2(n_{\text{gs},E} - n_{\text{bs},E}) + u_{\text{rel}}^2(A) + u_{\text{rel}}^2(P_E) \tag{11}$$

where $u_{\text{rel}}(A)$ includes all the uncertainties related to the calibration source: calibration certificate of the standard solution and preparation of the calibration source and the addition of this calibration source.

For the calculation of the characteristic limits (see ISO 11929), one needs $\tilde{u}(\tilde{c}_A)$, i.e. the combined standard uncertainty of c_A as a function of its true value. For a true value, $\tilde{c}_A$, one expects $n_{\text{g},E}/t_\text{g} = \tilde{c}_A/w + n_{\text{b},E}/t_\text{g}$ and with $u^2(n_\text{g}) = n_\text{g}$, one obtains:

$$\tilde{u}(\tilde{c}_A) = \sqrt{w^2 \cdot [(\tilde{c}_A/w + n_{\text{b},E}/t_\text{g})/t_\text{g} + u^2(n_{\text{b},E})/t_\text{g}^2] + \tilde{c}_A^2 \cdot u_{\text{rel}}^2(w)} \tag{12}$$

Note The uncertainties $u(n_N)$, $u(n_\text{g})$, and $u(n_\text{b})$ are calculated according to the GUM, taking into account that the individual counts n_i in a channel i of a multi-channel spectrum are the result of a Poisson process and hence $u^2(n_i) = n_i$ holds. The values of n_N, n_g, and n_b and their associated standard uncertainties $u(n_N)$, $u(n_\text{g})$, and $u(n_\text{b})$ may be calculated with a computer code. Since there are various methods of subtracting the background below a peak in order to derive the number of counts in the net peak area, no generally applicable formulas can be given. An example of the simple case of linear background subtraction is given in Annex B. For calculating the decision threshold and the detection limit at least n_N and n_b and $u(n_N)$ and $u(n_\text{b})$ must be known.

11.3 Decision threshold

The decision threshold, c_A^*, is obtained from Equation (12) for $\tilde{c}_A = 0$ (see ISO 11929) .This yields:

$$c_A^* = k_{1-\alpha} \cdot \tilde{u}(0) = k_{1-\alpha} \cdot \left(w/t_\text{g}\right) \cdot \sqrt{n_{\text{b},E} + u^2\left(n_{\text{b},E}\right)} \tag{13}$$

$\alpha = 0{,}05$ and then, $k_{1-\alpha} = 1{,}65$ is often chosen by default.

11.4 Detection limit

The detection limit, $c_A^\#$, is calculated using the implicit Equation (14) (see ISO 11929):

$$c_A^\# = c_A^* + k_{1-\beta} \cdot \tilde{u}(c_A^*) = c_A^* + k_{1-\beta} \cdot \sqrt{w^2 \cdot [(c_A^\#/w + n_{\text{b},E}/t_\text{g})/t_\text{g} + u^2(n_{\text{b},E})/t_\text{g}^2] + c_A^{\#2} \cdot u_{\text{rel}}^2(w)} \tag{14}$$

$\beta = 0{,}05$ and then, $k_{1-\beta} = 1{,}65$ is often chosen by default.

The detection limit can be calculated by solving Equation (14) for $c_A^\#$ or, more simply, by iteration with a starting approximation $c_A^\# = 2 \cdot c_A^*$.

When taking $k_{1-\alpha} = k_{1-\beta} = k$, the solution of Equation (14) is given by Equation (15):

$$c_A^\# = \frac{2 \cdot c_A^* + \left(k^2 \cdot w\right)/t_\text{g}}{1 - k^2 \cdot u_{\text{rel}}^2\left(w\right)} \tag{15}$$

11.5 Confidence limits

The lower, $c_A^\triangleleft$, and upper, $c_A^\triangleright$, confidence limits are calculated using Equations (16) and (17) (see ISO 11929):

$$c_A^\triangleleft = c_A - k_p \cdot u\left(c_A\right)\ ;\ p = \omega \cdot (1 - \gamma/2) \tag{16}$$

$$c_A^{\triangleright} = c_A + k_q \cdot u(c_A) \; ; \; q = 1 - \omega \cdot \gamma/2 \tag{17}$$

where

$\omega = \Phi\left[y/u(y)\right]$, Φ being the distribution function of the standardized normal distribution;

$1-\gamma$ is the probability for the confidence interval of the measurand;

$\omega = 1$ may be set if $c_A \geqslant 4 \cdot u(c_A)$. In this case:

$$c_A^{\triangleleft}, c_A^{\triangleright} = c_A \pm k_{1-\gamma/2} \cdot u(c_A) \tag{18}$$

$\gamma = 0{,}05$ and then, $k_{1-\gamma/2} = 1{,}96$ is often chosen by default.

11.6 Corrections for contributions from other radionuclides and background

In gamma spectrometry, two types of contribution frequently have to be corrected for.

d) The gamma line of the radionuclide to be determined contains contributions from gamma radiation of another radionuclide in the sample. The contributing radionuclide has another gamma line from which the contribution to the line in question can be estimated taking into account the emission probabilities of the gamma lines.

e) The gamma line of the radionuclide to be determined occurs also in the background of the spectrometer. By measuring a background spectrum with a blank sample for a counting time t_0, this contribution can be corrected for, taking into account the different counting times of the two spectra.

For both cases, the specific activity can be calculated using a model according to Equation (19):

$$c_{A,\mathrm{c}} = (n_{N,E}/t_\mathrm{g} - x \cdot n_{N0,E}/t_0) \cdot w \tag{19}$$

where x is a factor whose expression depends on the type of correction. For both contribution cases, this model gives the necessary correction.

11.6.1 Contribution from other radionuclides

The gamma line to be corrected at the energy E_1 has the net peak area $n_{N,E1}$. The contribution of the radionuclide is calculated using the ratio of the contributing radionuclide for gamma energy E_1. Equation (19) gives the necessary correction with $x = P_{E_1} \cdot \varepsilon_1 / P_{E_2} \cdot \varepsilon_2$ and $t_0 = t_\mathrm{g}$. This yields

$$c_{A,\mathrm{c}} = (n_{N,E_1} - x \cdot n_{N,E_2}) \cdot w / t_\mathrm{g} \tag{20}$$

Neglecting the standard uncertainty of x, the standard uncertainty of $c_{A,\mathrm{c}}$ is calculated by

$$u^2(c_{A,\mathrm{c}}) = (w/t_\mathrm{g})^2 \left\{ n_{\mathrm{g},E_1} + u^2(n_{\mathrm{b},E_1}) + x^2 \left[n_{\mathrm{g},E_2} + u^2(n_{\mathrm{b},E_2}) \right] \right\} + c_{A,\mathrm{c}}^2 \cdot u_\mathrm{rel}^2(w) \tag{21}$$

and with a true value $\tilde{c}_{A,\mathrm{c}}$ instead of $c_{A,\mathrm{c}}$:

$$\tilde{u}_c{}^2(\tilde{c}_{A,\mathrm{c}}) = (w/t_\mathrm{g})^2 \left\{ \tilde{c}_{A,\mathrm{c}}\, t_\mathrm{g}/w + n_{\mathrm{b},E_1} + u^2(n_{\mathrm{b},E_1}) + x\,(n_{\mathrm{g},E_2} - n_{\mathrm{b},E_2}) + x^2 \left[n_{\mathrm{g},E_2} + u^2(n_{\mathrm{b},E_2}) \right] \right\} + \ldots$$
$$\ldots + \tilde{c}_{A,\mathrm{c}}{}^2 \cdot u_\mathrm{rel}^2(w) \tag{22}$$

Then, the decision threshold $c_{A,\mathrm{c}}^*$ is given by

$$c_{A,\mathrm{c}}^* = k_{1-\alpha} \cdot (w/t_\mathrm{g}) \cdot \sqrt{n_{\mathrm{b},E_1} + u^2(n_{\mathrm{b},E_1}) + x(n_{\mathrm{g},E_2} - n_{\mathrm{b},E_2}) + x^2 \left[n_{\mathrm{g},E_2} + u^2(n_{\mathrm{b},E_2}) \right]} \tag{23}$$

and the detection limit , $c^{\#}_{A,\mathrm{c}}$, by

$$c^{\#}_{A,\mathrm{c}} = c^{*}_{A,\mathrm{c}} + k_{1-\beta} \times \ldots$$
$$\ldots \times \sqrt{\left(w/t_{\mathrm{g}}\right)^{2}\left\{c^{\#}_{A,\mathrm{c}}t_{\mathrm{g}}/w + n_{b,E_1} + u^{2}\left(n_{b,E_1}\right) + x\left(n_{\mathrm{g},E_2} - n_{\mathrm{b},E_2}\right) + x^{2}\left[n_{\mathrm{g},E_2} + u^{2}\left(n_{\mathrm{b},E_2}\right)\right]\right\} + c^{\#}_{A,\mathrm{c}}{}^{2}u^{2}_{\mathrm{rel}}\left(w\right)} \tag{24}$$

The detection limit can be calculated by solving Equation (24) for $c^{\#}_{A,\mathrm{c}}$ or, more simply, by iteration with a starting approximation $c^{\#}_{A,\mathrm{c}} = 2 \cdot c^{*}_{A,\mathrm{c}}$.

When taking $k_{1-\alpha} = k_{1-\beta} = k$ the solution of Equation (24) is given by Equation (25):

$$c^{\#}_{A,\mathrm{c}} = \frac{2 \cdot c^{*}_{A,\mathrm{c}} + \left(k^{2} \cdot w\right)/t_{\mathrm{g}}}{1 - k^{2} \cdot u^{2}_{\mathrm{rel}}\left(w\right)} \tag{25}$$

11.6.2 Contribution from background

In this case, Equation (19) is used for the correction with $x = 1$ and $u(x) = 0$. $n_{N0,E}$ is the net peak area of the gamma line in the background spectrum and t_0 the counting time of the background spectrum. This yields

$$c_{A,\mathrm{c}} = (n_{N,E}/t_{\mathrm{g}} - n_{N0,E}/t_0) \cdot w \tag{26}$$

The standard uncertainty of $c_{A,\mathrm{c}}$ is calculated by

$$u^{2}(c_{A,\mathrm{c}}) = w^{2}(n_{\mathrm{g},E}/t_{\mathrm{g}}^{2} + n_{\mathrm{g0},E}/t_{0}^{2} + u^{2}(n_{\mathrm{b},E})/t_{\mathrm{g}}^{2} + u^{2}(n_{\mathrm{b0},E})/t_{0}^{2}) + c_{A,\mathrm{c}}^{2} \cdot u_{\mathrm{rel}}^{2}(w) \tag{27}$$

and with a true value $\tilde{c}_{A,\mathrm{c}}$ of $c_{A,\mathrm{c}}$.

$$\tilde{u}_{c}^{2}\left(\tilde{c}_{A,\mathrm{c}}\right) = w^{2}\left\{\tilde{c}_{A,\mathrm{c}}/t_{\mathrm{g}}w + \left[n_{\mathrm{b},E} + u^{2}\left(n_{\mathrm{b},E}\right)\right]/t_{\mathrm{g}}^{2} + \left[n_{\mathrm{g0},E} + u^{2}\left(n_{\mathrm{b0},E}\right)\right]/t_{0}^{2} + \left(n_{\mathrm{g0},E} - n_{\mathrm{b0},E}\right)/t_{0}t_{\mathrm{g}}\right\} + \ldots$$
$$\ldots + \tilde{c}_{A,\mathrm{c}}^{2}u_{\mathrm{rel}}^{2}\left(w\right) \tag{28}$$

Then, the decision threshold $c^{*}_{A,\mathrm{c}}$ is given by

$$c^{*}_{A,\mathrm{c}} = k_{1-\alpha} \cdot w \cdot \sqrt{[n_{\mathrm{b},E} + u^{2}(n_{\mathrm{b},E})]/t_{\mathrm{g}}^{2} + [n_{\mathrm{g0},E} + u^{2}(n_{\mathrm{b0},E})]/t_{0}^{2} + (n_{\mathrm{g0},E} - n_{\mathrm{b0},E})/t_{0}t_{\mathrm{g}}} \tag{29}$$

and the detection limit $c^{\#}_{A,\mathrm{c}}$ by

$$c^{\#}_{A,\mathrm{c}} = c^{*}_{A,\mathrm{c}} + k_{1-\beta} \times \ldots$$
$$\ldots \times \sqrt{w^{2}\left\{\frac{c^{\#}_{A,\mathrm{c}}}{t_{\mathrm{g}}w} + \left[n_{\mathrm{b},E} + u^{2}(n_{\mathrm{b},E})\right]/t_{\mathrm{g}}^{2} + \left[n_{\mathrm{g0},E} + u^{2}(n_{\mathrm{b0},E})\right]/t_{0}^{2} + (n_{\mathrm{g0},E} - n_{\mathrm{b0},E})/t_{0}t_{g}\right\} + c^{\#}_{A,\mathrm{c}}{}^{2}u_{\mathrm{rel}}^{2}(w)} \tag{30}$$

The detection limit can be calculated by solving Equation (30) for $c^{\#}_{A,\mathrm{c}}$ or, more simply, by iteration with a starting approximation $c^{\#}_{A,\mathrm{c}} = 2 \cdot c^{*}_{A,\mathrm{c}}$.

When taking $k_{1-\alpha} = k_{1-\beta} = k$, the solution of Equation (30) is given by Equation (31):

$$c_{A,\mathrm{c}}^{\#} = \frac{2 \cdot c_{A,\mathrm{c}}^{*} + \left(k^2 \cdot w\right) / t_\mathrm{g}}{1 - k^2 \cdot u_\mathrm{rel}^2 (w)} \tag{31}$$

The limits of the confidence interval are calculated according to Equations (16) and (17).

12 Test report

The test report shall conform to ISO/IEC 17025 requirements. It shall contain the following information:

a) reference to this International Standard (ISO 10703:2007);

b) identification of the sample;

c) units in which the results are expressed ;

d) test result, $c_A \pm u_c(c_A)$ or $c_A \pm U$, with the associated k value.

Complementary information can be provided such as:

e) probabilities α, β and $(1 - \gamma)$;

f) decision threshold and the detection limit;

g) depending on the customer request there are different ways to present the result:

   1) when the activity concentration, c_A, is compared with the decision threshold (see ISO 11929), the result of the measurement should be expressed as $\leqslant c_A^*$ when the result is below the decision threshold;

   2) when the activity concentration, c_A, is compared with the detection limit, the result of the measurement can be expressed as $\leqslant c_A^{\#}$ when the result is below the detection limit. If the detection limit exceeds the guideline value, it shall be documented that the method is not suitable for the measurement purpose;

h) mention of any relevant information likely to affect the results.