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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

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.

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.

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.

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.

$$\lambda = \frac{dP}{dt} = -\frac{1}{N}\frac{dN}{dt}$$

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;

$f_{d,i}$	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);
$f_{s,i}$	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);
$R_{n,E}$	is the net counting rate per second, under the full energy peak corresponding to energy E;
$R_{n,i}$	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$_3$), ρ = 1,42 g/ml.

7.2   Concentrated sulfuric acid (H$_2$SO$_4$), ρ = 1,84 g/ml.

7.3   Silver nitrate solution, ρ = 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, ρ = 1,3 g/l.

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

7.5   Sodium sulfite (Na$_2$SO$_3$).

7.6   Hydrogen peroxide solution (H$_2$O$_2$), ρ = 0,3 g/l.

7.7   Sodium carbonate solution (Na$_2$CO$_3$), 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.