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Water quality — Measurement of gross beta activity in non-saline water

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Foreword

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International Standard ISO 9697 was prepared by Technical Committee ISO/TC 147, *Water quality*, Sub-Committee SC 3, *Radiological methods*.

Annex A forms an integral part of this International Standard. Annex B is for information only.

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Water quality — Measurement of gross beta activity in non-saline water

WARNING — Manufacturer's instructions should be consulted with regard to the safe operating of high voltages used in counting equipment.

In all countries regulations are issued to cover the use of radioactive materials in laboratories. These regulations are enforceable and the regulatory body should be contacted by prospective users.

1 Scope

1.1 Substance determined

This International Standard specifies a method for the determination of gross beta activity in non-saline waters. The method covers non-volatile β -active radionuclides with β -max energies > 0.3 MeV. Very low energy β -emitters including ^3H , ^{14}C , ^{35}S and ^{241}Pu are not included in the determination.

1.2 Applicability

The method is applicable to the analysis of raw and potable waters, but is not directly applicable to saline or mineralized waters without adaptation.

1.3 Range of application

The sample size is limited by the inorganic components of the water and the size of planchette that can be accepted by the counting equipment in use.

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 in-

dicated 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:—¹⁾, *Water quality — Sampling — Part 3: Guidance on the preservation and handling of samples*.

ISO 9964-1:—²⁾, *Water quality — Determination of sodium and potassium — Part 1: Determination of sodium by atomic absorption spectrometry*.

3 Principle

The sample is acidified to stabilize it, evaporated almost to dryness, converted to the sulfate form and then ignited at 350 °C. A portion of the residue is transferred to a planchette and the beta-activity measured by counting in a Geiger counting assembly previously calibrated against a potassium standard.

4 Reagents

Reagents shall be of recognized analytical grade and shall contain minimum background radioactivity.

1) To be published. (Revision of ISO 5667-3:1985)

2) To be published.

NOTE 1 A method for checking is given in 10.1.

4.1 Water.

Distilled or deionized water shall be used for all applications.

NOTES

2 The distilled (or deionized) water used for blank determinations in the method itself, and in the preparation of other reagents, should have a radioactive content which is low compared with that of the smallest amount encountered in the samples.

3 The specification for some ion-exchange resins indicates that ^{90}Sr may be present in the resin (and can be eluted). If deionized water is used, all new supplies should be checked before use.

4.2 **Standard reference source**, potassium chloride, dried to constant mass at 105 °C.

4.3 **Concentrated nitric acid**, 50 % (V/V).

Dilute 100 ml \pm 5 ml of nitric acid ($\rho = 1,42$ g/ml) to 200 ml \pm 5 ml with water (4.1).

4.4 **Concentrated sulfuric acid**, $\rho = 1,84$ g/ml.

4.5 **Volatile organic solvents**, methanol and acetone.

5 Apparatus

Usual laboratory apparatus and

5.1 Low-background Geiger counter or other counting assembly

The distance of the source from the detector shall not exceed 10 mm (10 mm of air = 0,01 mg/mm² thickness). The detector system shall be capable of presenting an external absorber thickness of 0,07 mg·mm⁻² \pm 0,02 mg·mm⁻² (7 mg·cm⁻² \pm 2 mg·cm⁻²) to the source. This can be achieved by the use of either the detector end-window alone or a thinner end-window with an added absorber of appropriate thickness. In addition, any coincidence/anticoincidence arrangements for background reduction shall not alter the efficiency of the system to different emission energies.

NOTE 4 A background count of less than 1 count per minute (cpm) is desirable, but one of 5 cpm will suffice in most cases (see 9.2).

5.2 **Planchettes** (counting trays), of thickness at least 2,5 mg·mm⁻² (250 mg·cm⁻²). These shall be lipped and of stainless steel. This ensures that saturation backscatter is achieved for energies up to 3,6 MeV.

NOTES

5 The diameter of the planchette to be used is determined by the counter requirements, i.e. the detector diameter and source holder dimensions.

6 ^{60}Co may be encountered as a contaminant in stainless steel and may therefore affect the background count but not necessarily the sample or blank, as the activity will be absorbed by the residue.

7 An evenly spread source is required and some workers find it easier to produce on a polished metal surface, whereas others prefer to use an etched or roughened planchette (sand blasting and chemical etching have been applied for this purpose).

5.3 **Muffle furnace**, capable of maintaining a temperature of 350 °C \pm 10 °C.

6 Sampling

Add 20 ml \pm 1 ml of nitric acid (4.3) per litre of sample to be collected to a clean polythene bottle, and then collect the sample in accordance with ISO 5667-1, ISO 5667-2 and ISO 5667-3. The acidification minimizes the absorption of radioactivity onto the walls of the bottles. Store at a temperature of 4 °C \pm 2 °C and analyse the sample as soon as possible after collection.

Carry out filtration immediately on collection and before acidification, if it is desired to measure the activity of the filtered sample of water.

NOTE 8 The activity will be distributed between aqueous solution and absorption on particulate matter. Therefore filtration, if performed, should be carried out before acidification which may upset this distribution.

7 Procedure

7.1 Preliminary

NOTE 9 The analysis should be carried out in an area where radio-tracers are not used.

Determine the total solids content of the water according to annex A. Making due allowance for changes in composition due to ignition at 350 °C and sulfation of the residues, calculate the volume of sample required to produce a mass of solid residue slightly in excess of 0,1A mg (where A is the area of the planchette (5.2) in square millimetres). Use this as guide to the volume of sample required for the concentration stage which follows.

7.2 Concentration stage

Transfer to a beaker a measured volume V, in litres, (\pm 1 %) of the sample (see clause 6) chosen such that after ignition there is at least 0,1A mg of residue.

NOTE 10 With very soft waters, it is possible that the volume required to produce 0,1A mg is impractically large. In these circumstances, the largest practicable volume should be used. (See also note 12.)

Evaporate carefully on a hot-plate until the volume is reduced to about 50 ml and allow to cool.

Transfer the concentrated solution to a tared silica (or glazed porcelain) dish, previously ignited at 350 °C. Wash the beaker carefully with a minimum quantity of water (4.1) and transfer the washings to the dish.

NOTE 11 If the beaker is large, it may be convenient to transfer the washings to a smaller (e.g. 500 ml) beaker. The washings can then be concentrated to a low bulk to facilitate transfer to the silica dish.

7.3 Sulfation stage

Ensure that the washings in the dish are cool and add 1 ml ($\pm 20\%$) of sulfuric acid (4.4).

NOTE 12 Some water may, on drying and ignition, produce a residue which is unsuitable for the measurement of radioactivity, because it is hygroscopic or difficult to disperse. This sulfation process is a suitable treatment for many such samples. The volume of sulfuric acid chosen is capable of sulfating about 1,8 g of calcium carbonate. To allow for an excess of acid, the initial volume of sample should be chosen such that the total solids content does not exceed 1 g. (Experience with some waters may show this step to be unnecessary.)

Carefully evaporate the contents of the dish to dryness.

To avoid spitting, expose the dish to heat from above (from an infrared or similar lamp) and continue heating until fumes of sulfuric acid are evolved. Then transfer the dish to a hot-plate and continue heating until no further fumes are evolved.

7.4 Ignition stage

Transfer the dish and contents to the muffle furnace (5.3), ignite for 1 h at a temperature of 350 °C ± 10 °C and allow to cool in a desiccator.

Weigh the dish and residue and obtain by difference the mass m , in milligrams of the ignited residue.

7.5 Source preparation

Weigh 0,1A mg ($\pm 1\%$) of the ash onto a planchette (5.2). If the ash is not fine, grind it in a pestle and mortar. Let this mass be m_r mg.

If the volume (V) used in 7.2 has produced less than 0,1A mg of residue, transfer as much as possible of the residue to the planchette.

Disperse the residue evenly over the planchette by slurring with a few drops of a volatile organic solvent (4.5) and allow to dry.

NOTE 13 The sample may be covered by a thin mylar film.

7.6 Counting stage

Set up the Geiger counter or other beta-counting assembly (5.1) according to the manufacturers instructions.

Measure the activity on the planchette by counting in the assembly for an appropriate length of time. Let the measured count rate be R_b s⁻¹.

NOTE 14 The duration of counting depends on the sample and background count rates and also on the precision required (see clause 9).

7.7 Background determination

Measure the background activity using an identical clean planchette (5.2). Let the measured count rate be R_0 s⁻¹. Repeated counts will confirm the stability of background.

7.8 Reference source measurement

Using potassium chloride (4.2) instead of sample ash, carry out the steps described in 7.5 and 7.6. Let the measured count rate be R_s s⁻¹.

8 Expression of results

8.1 Calculation of activity concentration

Calculate the activity concentration c , in becquerels per litre, of the solution from the equation

$$c = R_n \times \frac{1}{\epsilon_s} \times \frac{1}{V_p} \quad \dots (1)$$

where

c is the beta activity, in becquerels per litre;

R_n is the sample count rate per second, corrected for background counts;

ϵ_s is the fractional efficiency of counting of the ⁴⁰K standard;

V_p is the volume of sample, in litres, equivalent to the mass of solid on the planchette.

Thus

$$R_n = R_b - R_0$$

where

R_b is the observed sample count rate, in pulses per second (see 7.6);

R_0 is the background planchette count rate, in pulses per second (see 7.7);

and

$$\varepsilon_s = \frac{(R_s - R_0)}{0,1A \times 14,4} \times 1\,000$$

where

R_s is the observed standard count rate, in pulses per second (see 7.8);

A is the area of the planchette, in square millimetres;

$0,1A$ is the mass of potassium chloride solid or ash, in milligrams, on the planchette (see 7.8).

NOTE 15 The β -activity of ^{40}K in natural potassium is $27,4 \text{ Bq}\cdot\text{g}^{-1}$ (see [4]) and hence in potassium chloride it is $14,4/1\,000 \text{ Bq}\cdot\text{mg}^{-1}$. One becquerel is one disintegration per second.

and

$$V_p = \frac{V}{m} \times 0,1A$$

where

V is the volume of sample, in litres (see 7.2);

m is the mass, in milligrams, of ignited residue from volume V , (see 7.4).

Thus the general equation (1) becomes

$$c = \frac{(R_b - R_0) \times 0,1A \times 14,4 \times m}{(R_s - R_0) \times 1\,000V \times 0,1A}$$

$$= \frac{(R_b - R_0) \times 14,4 \times m}{(R_s - R_0) \times 1\,000 \times V}$$

The final activity equation for c , in becquerels per litre, then becomes

$$c = \frac{(R_b - R_0) \times 14,4 \times m \times 1,02}{(R_s - R_0) \times 1\,000 \times V} \quad \dots (2)$$

NOTE 16 It is important that the factor 1,02 be included in the final equation, to correct for the 20 ml of nitric acid added per litre as a stabilizer (see clause 6).

If it is necessary to express the radioactivity of the sample while excluding that of ^{40}K , assess its contribution by measuring the potassium content of the

original sample in accordance with ISO 9964-1. From the result, calculate the activity using the information in note 15 and subtract this from the value obtained for c .

9 Precision

9.1 Standard deviation

The standard deviation s_c associated with the activity of the sample corrected for background is calculated as follows:

$$s_c = \sqrt{\frac{R_b}{t_b} + \frac{R_0}{t_0}} \times \frac{14,4 \times m \times 1,02}{(R_s - R_0) \times 1\,000 \times V} \quad \dots (3)$$

where t_b and t_0 are the respective durations of the counts of the sample and background.

The standard deviation associated with the counting of the standard potassium chloride source is insignificant compared with that of counting the sample, and therefore the result shall be indicated with a standard deviation "due to counting errors alone".

9.2 Limit of detection

The limit of detection achievable in the determination of gross beta activity, for an error probability α or a confidence coefficient k , shall be calculated to a good approximation using the relation:

$$c_{\min} = k \times \frac{a_s \times m \times 1,02}{(R_s - R_0) \times 1\,000 \times V} \times \sqrt{\frac{R_0}{t_b} \left(1 + \frac{t_b}{t_0}\right)}$$

where a_s is the specific activity of the standard, in becquerels per gram.

The limit of detection depends on the inorganic components of the water, the radionuclides present, the equipment used and the length of counting time.

The results given in table 1 were obtained with a ^{137}Cs test sample ($723 \text{ mBq}\cdot\text{l}^{-1}$).

Source area counting time, background count rate and degrees of freedom are given in table 2.

9.3 Sensitivity

Counting efficiency varies from approximately 0,05 to 0,5 depending on the energy of the beta particles. Using ^{40}K as a standard leads to an overestimate of radionuclides with $\beta_{\max} > 1,32 \text{ MeV}$ and an underestimate of the radionuclides with a lower β_{\max} .

Table 1

Laboratory	Residue		Limit of detection mBq l ⁻¹
	m/V	$s \pm m/V^{(1)}$	
AERE	522	1,4	40
LGC	578	2,8	70
WRC	535	2,5	114

AERE: Atomic Energy Research Establishment (Harwell)
LGC: Laboratory of the Government Chemist (London)
WRC: Water Research Centre (Stevenage)

1) See clause 7 for the definitions of m and V .

10 Interference control

10.1 Contamination

Check the contamination of reagents by evaporating the volumes of the reagents used in the procedures onto separate planchettes. Ensure that the activities are negligible compared with that of the sample. Check the contamination of the whole system by

processing 1 litre \pm 10 ml of distilled water acidified with 20 ml \pm 1 ml of nitric acid (4.3), to which 0,1A mg of chromatographic reagent grade silica gel has been added, and measure the activity. This can be compared with the activity of a direct slurry of 0,1A mg of the silica gel on a counting tray.

Again, ensure that the activity is negligible compared with that of the sample. If the activity is not negligible, select reagents with lower radioactivity, or include a blank determination in the main procedure using the procedure for checking the contamination of the whole system given in the first paragraph of this subclause instead of that described in 7.7.

10.2 Losses of activity

It is obvious that some radionuclides will be lost during the determination or not be able to be measured using this method. For example, ³H, ¹⁴C and some ³⁵S will be lost on evaporation and ignition.

Beta-emitters of low energy would not be measured (or would be measured with very low efficiency) with 0,1 mg·mm² (10 mg·cm⁻²) self absorption and 0,07 mg·mm⁻² (7 mg·cm⁻²) external absorption. Of the radionuclides in the uranium series, ²²²Rn would be lost during processing but, with its β -emitting daughters ²¹⁴Pb and ²¹⁴Bi and ²²⁶Ra present.

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Table 2

Laboratory	Source area cm ²	Counting time s	Background count rate c·s ⁻¹	Counting efficiency to ⁴⁰ K (counts per disintegration)	Degrees of freedom ($n - 1$)	Activity found	
						mBq l ⁻¹	% s
AERE	19,6	$1,2 \times 10^4$	0,014	0,29	5	370	6,9
LGC	20,3	6×10^4	0,116	0,29	5	401	3,7
WRC	19,6	6×10^4	0,153	0,30	5	409	16,9

AERE: Atomic Energy Research Establishment (Harwell)
LGC: Laboratory of the Government Chemist (London)
WRC: Water Research Centre (Stevenage)

10.3 Variations of response of the system

NOTE 17 The unavoidable effect of self-absorption will result in a variation of counting efficiency which depends on the composition of the water. The response of the system to radionuclides which might be encountered should be determined by spiking silica or other blank materials with known quantities of standard solutions of these radionuclides. After careful drying and homogenization, sources $0,001A \text{ mg}\cdot\text{mm}^{-2}$ ($0,1A \text{ mg}\cdot\text{cm}^{-2}$) thick can be prepared and counted. The response of the counter, in count rate per unit of activity (counts $\text{s}^{-1}\cdot\text{Bq}^{-1}$), can then be calculated.

10.4 Quality control

Follow the manufacturer's suggestions for instrumental quality control and also prepare quality assurance graphs for the potassium chloride standards (see 7.8) and background planchettes (see 7.7) which have been counted with each batch of samples.

Further information can be obtained from ISO/CD 8465:—³⁾, *Guide to control charts*.

NOTE 18 An operator's performance can be checked by the production of at least six counting sources prepared from 1 litre portions of distilled water, to each of which a known amount of potassium chloride has been added. The quantity added should be sufficient to ensure that, after ignition, at least 0,1A mg of residue is available to prepare a source for counting.

11 Regulations

Ensure that all national and international regulations governing the use of radioactive materials and the disposal of radioactive wastes in the country of application are applied.

12 Test report

The test report shall include the following information:

- a) a reference to this International Standard;
- b) all information necessary for complete identification of the sample, including the duration of sampling;
- c) the gross beta-activity content, in becquerels per litre, given to three significant figures,
if the result is lower than the limit of detection (see 9.2), state this fact;
- d) actual time and date of counting and sampling time;
- e) any noteworthy features observed during the determination;
- f) details of any operations not included in this International Standard;
- g) any conditional steps in the procedure, for example filtration of sample.

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3) To be published.

Annex A (normative)

Total dissolved solids (TDS) dried at 180 °C

A.1 Performance characteristics of the method

A.1.1 Substance determined

Non-volatile organic and/or inorganic matter which is not removed from water by filtration through a membrane filter with 0,45 µm pore size.

A.1.2 Type of sample

Natural and polluted waters and certain effluents, but not sea water or waters high in both magnesium and chloride (however, see A.10).

A.1.3 Basis of the method

Filtration through a membrane filter. The mass of dissolved matter in the filtrate is determined by evaporation, drying at 180 °C and weighing. (See A.10 also.)

A.1.4 Range of application

The lower limit is dependent on the sensitivity of the balance available. There is no real upper limit.

A.1.5 Standard deviation (see table A.1)

Table A.1

Total dissolved solids obtained by drying at 180 °C mg/l	Standard deviation (within batch) mg/l	Degrees of freedom
569	5,32	9
343	5,54	9
202	2,89	9

NOTE — Data provided by Mid-Kent Water Company.

A.1.6 Limit of detection

As written, about 10 mg/l, but it depends on the balance used.

A.1.7 Sensitivity

For a 100 ml aliquot, each 10 mg/l of total dissolved solids will correspond to a change in mass of 1 mg.

A.1.8 Bias

The bias is undetermined, but from a consideration of the method it is likely to be slightly negative and to depend on the sample. However, it may be slightly positive if the sample contains salts which are hygroscopic. Some organic compounds may char, some compounds (e.g. ammonium salts) may volatilize.

A.1.9 Interferences

No specific tests have been made, but waters containing hydrogen carbonate may require prolonged drying at 180 °C to ensure complete conversion of hydrogen carbonate to carbonate.

A.1.10 Time required for analysis

Depends on the type of sample and is usually within one day.

A.2 Scope

A.2.1 Object

The method determines non-volatile organic and/or inorganic matter which is not removed from water by filtration through a membrane filter with 0,45 µm pore size.

A.2.2 Applicability

The method is applicable to natural and polluted waters and some effluents.

A.2.3 Determination of total dissolved solids

The filtrate from the determination of suspended matter (membrane filtration method) may be used for the determination of total dissolved solids (see A.8.1, note 20).