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## **Water quality — Measurement of gross alpha activity in non-saline water — Thick source method**

### **iTeh STANDARD PREVIEW**

*Qualité de l'eau — Mesurage de l'activité alpha globale dans l'eau non saline — Méthode par source concentrée*

ISO 9696:1992

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Reference number  
ISO 9696:1992(E)

## 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 9696 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 alpha activity in non-saline water — Thick source method

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

In all countries strict 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. Specific instructions for the preparation of alpha sources are given in clause 7.

## 1 Scope

### 1.1 Substance determined

This International Standard specifies a method for the determination of gross alpha activity in non-saline waters for alpha-emitting radionuclides which are not volatile at 350 °C. It is possible to determine supported volatile radionuclides measured to an extent determined by half-life, matrix retention (of the volatile species) and the duration of measurement (counting time).

### 1.2 Applicability

The method is applicable to raw and potable waters and can be extended to saline or mineralized waters, but with a reduced sensitivity.

### 1.3 Range of application

The range of application depends on the amount of inorganic material in the water and on the performance characteristics (background count rate and counting efficiency) of the counter.

## 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 stan-

dards 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:—<sup>1)</sup>, *Water quality — Sampling — Part 3: Guidance on the preservation and handling of samples*.

## 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 alpha activity measured by counting in an alpha-particle detector or counting system previously calibrated against an alpha-emitting standard.

## 4 Reagents

All reagents shall be of recognized analytical grade and shall not contain any detectable alpha activity.

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

NOTE 1 A method for preparing reagent blanks to check for endemic radioactivity or contamination is given in 10.1.

#### 4.1 Standard solution, which shall be $^{241}\text{Am}$ .

##### NOTES

2  $^{241}\text{Am}$  is preferred to  $^{239}\text{Pu}$ , because the latter frequently suffers from the presence of  $^{241}\text{Pu}$  which leads to growth of  $^{241}\text{Am}$  in prepared standard solutions of sources, which would therefore need to be continually purified. A uranium compound of known isotopic composition is difficult to obtain and has a sensitivity different from that of  $^{239}\text{Pu}$  (see 9.3).

3 Certified reference materials are available from several sources in most countries. The International Atomic Energy Agency (IAEA) Vienna, Austria is an international supplier. The National Institute of Standards Technology (NIST), USA can also supply to most countries.

4 The choice of alpha standard will depend on a knowledge of the type of radioactive contaminant likely to be present in the waters being tested. In general, this amounts to a choice between naturally occurring and man-made alpha emitters.

5 A uranium compound of certified natural or known isotopic composition has one arguable advantage, in that its specific activity can be calculated from established physical constants and isotopic abundance data which are independent of the calibration procedures of a particular organization.

6 Furthermore, since the energies of the alpha emissions from uranium isotopes are less than those from the artificial transuranic nuclides, the use of a uranium standard tends to give a high result for transuranics. Some authorities prefer to err on the high side in situations where the true composition is unknown.

#### 4.2 Concentrated nitric acid, 50% (V/V).

Dilute 100 ml  $\pm$  5 ml of nitric acid ( $\rho = 1,42$  g/ml) to 200 ml  $\pm$  10 ml with water (4.6).

#### 4.3 Concentrated sulfuric acid, $\rho = 1,84$ g/ml.

4.4 Volatile organic solvents, methanol and acetone.

#### 4.5 Calcium sulfate.

Calcium salts may contain trace amounts of  $^{226}\text{Ra}$  and/or  $^{210}\text{Pb}$  and checks for the presence of these nuclides shall be made (see 7.7 and 10.1).

#### 4.6 Water.

Distilled or deionized water shall be used for all applications.

## 5 Apparatus

Usual laboratory apparatus and

### 5.1 Alpha counter.

Alpha activity shall be counted using either a silver activated zinc sulfide scintillation screen, a silicon surface barrier detector (SSB) or a proportional counter (windowless). Ion-implanted Si detectors and their ( $\leq 100 \mu\text{g}\cdot\text{cm}^{-2}$ ) window-proportional counters may also be used.

If windowless systems are used, carry out checks for possible contamination of the counting system by counting a blank sample between each source counted.

NOTE 7 The particulate nature of the source to be counted may give rise to contamination problems if operated in a vacuum (as in the case of an SSB) or gas flow systems (as used in a proportional counter).

5.2 Planchettes (counting trays), of thickness at least  $2,5 \text{ mg}\cdot\text{mm}^{-2}$  ( $250 \text{ mg}\cdot\text{cm}^{-2}$ ). These shall be lipped and of stainless steel.

##### NOTES

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

9 An evenly spread source is required and some workers find it easier to produce this 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  $350 \text{ }^\circ\text{C} \pm 10 \text{ }^\circ\text{C}$ .

## 6 Sampling

Add 20 ml  $\pm$  1 ml of nitric acid (4.2) 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. Store at a temperature of  $4 \text{ }^\circ\text{C} \pm 2 \text{ }^\circ\text{C}$  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 10 Acidification will minimize the loss of radioactive material from solution by absorption. If carried out before filtration, it will desorb radioactive material already absorbed on the particulate material.

## 7 Procedure

### 7.1 Preliminary

NOTE 11 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 residue, calculate the volume of sample required to produce a mass of solid residue slightly in excess of 0,1*A* mg (where *A* is the area of the planchette (5.2) in square millimetres). Use this as a 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 0,1*A* mg of residue.

NOTE 12 With very soft waters, it is possible that the volume required to produce 0,1*A* mg is impractically large. In these circumstances, the largest practicable volume should be used. (See also note 14.)

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 weighed silica (or glazed porcelain) dish, previously ignited at 350 °C. Wash the beaker carefully with a minimum quantity of water (4.6) and transfer the washings to the dish.

NOTE 13 If the beaker is large, it may be convenient to transfer the washings to a smaller 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 (4.3).

NOTE 14 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 lamp) and continue heating until fumes of sulfuric acid are evolved. Then transfer the dishes 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  $\pm$  10 °C and allow to cool in a desiccator. Note the time and date of removal from the furnace.

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

### 7.5 Source preparation

Weigh 0,1*A* 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<sub>r</sub>* mg.

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

NOTE 15 As alpha-particle counting efficiency is seriously affected by the source thickness, it follows that standard sources of the same mass loading, *m<sub>r</sub>* mg, are required for calibration of the detection system.

Disperse the residue evenly over the planchette by slurring with a few drops of a volatile organic solvent (4.4) and allow to dry. Make a note of the time and date of source preparation. Weigh the planchette and residue again to ensure that no residue has been lost.

NOTE 16 As alpha-particle counting efficiency is seriously affected by source thickness, it is essential to produce evenly spread counting sources. Some workers add vinyl acetate to the solvent to aid in binding the source during evaporation.

### 7.6 Counting stage

Set up the counter (5.1) according to the manufacturer's instructions.

Immediately after drying the source, start measuring the activity on the planchette by counting for an appropriate time. Let the measured count rate be *R<sub>b</sub>* s<sup>-1</sup>. Note the time, duration of count and date.

NOTE 17 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  $R_0 \text{ s}^{-1}$ . Repeated counts will confirm the stability of background.

Check for ingrowth due to decay of radium by repeating the counting procedures in 7.6 and this subclause periodically over a period of 1 month.

NOTE 18 Recounting over a period of one month may reveal ingrowth of daughter radionuclides from radium isotopes. The interpretation of such data can be complicated by the presence of uranium and/or thorium series radionuclides in admixture, either singly or with one predominating. At normal environmental levels, it is rare for these phenomena to be apparent, particularly when the count durations were long. However, over a period of 1 month, sources from raw waters which are naturally high in  $^{226}\text{Ra}$  may show an ingrowth of four times the initial count.

### 7.8 Preparation of counting standard for alpha activity measurement

Accurately weigh approximately 2,5 g of calcium sulfate (4.5) into a 150 ml beaker. Carefully add 10 ml ( $\pm 1\%$ ) of hot nitric acid (4.2), stir and add up to 100 ml of hot water (4.6) to dissolve the residue.

Add an accurately known amount (about 5 Bq to 10 Bq) of standard  $^{241}\text{Am}$ .

Transfer the solution to a 200 ml silica or porcelain dish, weighed to  $\pm 0,001 \text{ g}$ , and heat the solution to dryness using an infrared lamp.

Ignite the dry residue in the muffle furnace (5.3) at  $350 \text{ }^\circ\text{C} \pm 10 \text{ }^\circ\text{C}$  for 1 h.

Calculate the specific activity  $a_s$  of the  $\text{CaSO}_4$ , in becquerels per gram, using the mass of the ignited residue and the amount of activity added as  $^{241}\text{Am}$  (or as  $^{239}\text{Pu}$  or U of natural isotopic composition, if they are used as alternatives).

Crush (and grind with a pestle and mortar if necessary) the solid to produce a fine powder, in a manner similar to that used for the preparation of the sample.

**WARNING** — This procedure requires the preparation of a dry powder spiked with alpha-emitting radionuclides. Accidental ingestion of radioactive particulates must be avoided and the use of a simple closed cabinet glove box is recommended for the preparation of the spiked sources. Alternatively, a laboratory fume cupboard may be used, provided that the extract draught is not excessive and liable to create disturbance or carry fine powder particles into the air.

Prepare planchette sources (0,1A mg on each planchette) in the manner specified for samples (see 7.5).

Measure these standard sources in the alpha detector. Let the measured count rate be  $R_s \text{ s}^{-1}$ .

## 8 Expression of results

### 8.1 Calculation of activity concentration

Calculate the activity concentration  $c$ , in becquerels per litre, of the water sample from the equation

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

NOTE 19 Derivation of equation 1.

In general, the sample activity concentration  $c$ , in becquerels per litre, is calculated as follows:

$$c = R_n \times \frac{1}{\epsilon_s} \times \frac{1}{V_p} \quad \dots (2)$$

where

- $c$  is the alpha activity, in becquerels per litre;
- $R_n$  is the sample count rate per second, corrected for background counts;
- $\epsilon_s$  is the fractional efficiency of counting of the specified radioactive standard;
- $V_p$  is the volume of sample, in litres, equivalent to the mass of solid on the planchette.

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

$$\epsilon_s = \frac{R_s - R_0}{0,1A \times a_s} \times 1\,000$$

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 standard solids, in milligrams, on the planchette (see 7.8);
- $a_s$  is the specific activity of the standard solids, in becquerels per gram (see 7.8),

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 (2) becomes

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

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

As 20 ml of nitric acid (4.2) per litre of sample is added as a stabilizer, it is necessary to correct for this addition. 1 020 ml of acidified sample is equivalent to an initial volume of 1 000 ml.

The final activity equation for  $c$ , in becquerels per litre, (as appropriate standard) then becomes

$$c = \frac{(R_b - R_0)}{(R_s - R_0)} \times \frac{a_s}{1\,000} \times \frac{m}{V} \times 1,02$$

Report the results, together with the dates of sampling, ashing and counting and also the source thickness in milligrams per square millimetre.

**EXAMPLE OF REPORT**

(0,42 ± 0,04) Bq·l<sup>-1</sup> (<sup>241</sup>Am equivalent)

The confidence level (2σ) quoted shall only take counting errors into account.

Sampling date: 10 January 1988

Ashed: 20 January 1988

Counting date: 2 February 1988

Source thickness: 0,1 mg·mm<sup>-2</sup> (10 mg·cm<sup>-2</sup>)

**9 Precision**

**9.1 Standard deviation**

The standard deviation,  $s_c$ , associated with the activity of the sample due to the statistical counting error is calculated as follows:

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

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 alpha 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 alpha activity, for an error probability

$\alpha$  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 will depend on many factors including solids content of water, source size, counting period, background and counter efficiency. The following is a typical value for a specific set of parameters.

Using water with an ignited residue of 0,5 g·l<sup>-1</sup>, a 50 mm diameter source, 60 000 s count duration, a background count rate of 0,001 6 s<sup>-1</sup> and an efficiency fraction of 0,071 (for <sup>239</sup>Pu) the limit of detection is 40 mBq·l<sup>-1</sup> (sulfated). These data have five degrees of freedom.

**9.3 Sensitivity and bias**

These are dependent on the amount of inorganic material in the water, the characteristics of the detector and the radionuclides present.

Typical instrument responses for several radionuclides are given in table 1.

**Table 1**

Radionuclide	Instrument response MeV (approx.)	Counting efficiency fraction
<sup>241</sup> Am	5,4 – 5,5	0,11
<sup>239</sup> Pu	5,1 – 5,15	0,071
U (natural isotopic composition)	<sup>238</sup> U = 4,2	} 0,064
	<sup>234</sup> U = 4,75	
	<sup>235</sup> U = 4,4	
<sup>252</sup> Cf	6,12	0,13

The figures are calculated from data supplied by the laboratory of the government chemist (United Kingdom), using a silver-activated zinc sulfide scintillation screen detector. Fractional efficiencies will vary for different detectors.

**9.4 Optimization of the determination**

As alpha-particles are absorbed by matter, it is necessary to optimize the thickness of the source to enable the maximum amount of sample to be counted with a minimum of absorption. In this method, this shall be 0,1 mg·mm<sup>-2</sup> (10 mg·cm<sup>-2</sup>).

Even when using this constant thickness it is necessary to make the sample and standard source as nearly alike as possible, i.e. in terms of density of material and distribution of radioactivity.

The sensitivity and bias obtained when using different radioactive standards is indicated in A.6, with counting efficiency for a constant size source increasing with alpha-particle energy.

## 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 of nitric acid (4.2), to which 0,14 mg  $\pm$  1 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 0,14 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

#### 10.2.1 Radon isotopes

NOTE 20 Some radionuclides are lost by volatilization when this method is used. Of the radionuclides in the uranium series,  $^{222}\text{Rn}$  would be lost during processing, but with its  $\alpha$ -emitting and  $\beta$ -emitting daughters it would subsequently grow in to the counting source from any  $^{226}\text{Ra}$  present. A similar effect occurs with radionuclides from the  $^{232}\text{Th}$  series.

#### 10.2.2 Polonium

NOTE 21 Some alpha-emitting polonium isotopes which occur naturally as members of the uranium and thorium decay series may comprise a significant proportion of the gross alpha activity of some waters. The element and some of its compounds, particularly the halides which sublime at relatively low temperatures, may be volatilized (for example see [1]). Nitrates ([1] and [2]) and sulfates (for example see [1]) are stable up to temperatures of at least 400 °C to 500 °C, and losses of polonium are therefore not expected from samples which have been acidified with nitric acid and subjected to sulfation.

2) To be published.

### 10.3 Variation of response of the system

NOTE 22 The unavoidable effect of self-absorption will result in a variation of counting efficiency which depends on the composition of the radioactivity in the water. The response of the system to radionuclides which might be encountered should be determined by spiking silica, calcium sulfate or other blank materials with known quantities of standard solutions of these radionuclides. After careful drying and homogenization, sources which are 0,0014 mg·mm<sup>-2</sup> (0,14 mg·cm<sup>-2</sup>) thick can be prepared and counted. The response of the counter, in count rate per unit of activity (counts s<sup>-1</sup>·Bq<sup>-1</sup>), 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 standards and background. Count standard and background planchettes for each batch of samples and prepare suitable quality control graphs (for example [3] and [4]).

Further information can be obtained from ISO/CD 8465:—<sup>2)</sup>, *Guide to control charts*.

NOTE 23 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 an alpha-emitting radionuclide and soluble calcium compound has been added. The quantity of the latter added should be sufficient to ensure that, after ignition, at least 0,14 mg of residue is available to prepare a source for counting.

## 11 Regulations

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

## 12 Test report

The test report shall include the following information:

- a reference to this International Standard;
- all information necessary for complete identification of the sample, including the duration of sampling;
- the standard radionuclides employed;
- the gross alpha-activity content in Bq·l<sup>-1</sup> given to three significant figures,

if the result is lower than the limit of detection (see 9.2), state this fact;



- e) the dates of sampling, ashing and counting;
- f) any noteworthy features observed during the determination;
- g) details of any operations not included in this International Standard;
- h) any conditional steps in the procedure, for example filtration of sample.

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