BRITISH STANDARD

BS 6068-2.48:
1995
ISO 10359-2:
1994

Water quality —

Part 2: Physical, chemical and biochemical methods —

Section 2.48 Determination of inorganically bound total fluoride after digestion and distillation

Committees responsible for this British Standard

The preparation of this British Standard was entrusted to Technical Committee EPC/44, Water quality, upon which the following bodies were represented:

Association of Consulting Scientists
British Association for Chemical Specialists
British Gas plc
Chemical Industries Association
Convention of Scottish Local Authorities
Department of the Environment (Water Directorate)
Department of the Environment for Northern Ireland
Department of Trade and Industry (Laboratory of the Government Chemist)
Electricity Association
Industrial Water Society
Institute of Gas Engineers
Institution of Water Officers
Institution of Water and Environmental Management
National Rivers Authority
Royal Institute of Public Health and Hygiene
Royal Society of Chemistry
Scottish Association of Directors of Water and Sewerage Services
Soap and Detergent Industry Association
Water Companies Association
Water Research Centre
Water Services Association of England and Wales

The following bodies were also represented in the drafting of the standard, through subcommittees and panels:

The Association of the Laboratory Supply Industry
British Agrochemicals Association Ltd.
British Ceramic Research
British Soft Drinks Association Ltd.
GAMBICA (BEAMA) Ltd.
Society of Chemical Industry
Swimming Pool and Allied Trades Association Ltd.

This British Standard, having been prepared under the direction of the Health and Environment Sector Board, was published under the authority of the Standards Board and comes into effect on 15 April 1995

The following BSI references relate to the work on this standard:
Committee reference EPC/44
Draft for comment 92/58404 DC

ISBN 0 580 23959 4

Amendments issued since publication

Amd. No.	Date	Comments

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National foreword

This Section of BS 6068 has been prepared by Technical Committee EPC/44, and is identical with ISO 10359-2:1994 *Water quality — Determination of fluoride — Part 2: Determination of inorganically bound total fluoride after digestion and distillation.*

The international standard was prepared by Technical Committee 147, Water quality, of the International Organization for Standardization (ISO) with the active participation and approval of the UK.

BS 6068 is being published in a series of Parts subdivided into Sections that will generally correspond to particular international standards. Sections are being, or will be, published in Parts 1 to 7, which, together with Part 0, are listed below.

— *Part 0: Introduction;*

— *Part 1: Glossary;*

— *Part 2: Physical, chemical and biochemical methods;*

— *Part 3: Radiological methods;*

— *Part 4: Microbiological methods;*

— *Part 5: Biological methods;*

— *Part 6: Sampling;*

— *Part 7: Precision and accuracy;*

NOTE The tests described in this Section of BS 6068 should only be carried out by suitably qualified persons with an appropriate level of biological expertise. Standard chemical procedures should be followed throughout.

Cross-reference

International standard	**Corresponding British Standard**
ISO 5667-3:1994	BS 6068 *Water quality* Section 6.3:1986 *Guidance on the preservation and handling of samples*[a]

[a] In preparation. The 1986 edition was identical with ISO 5667-3:1985.

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Summary of pages

This document comprises a front cover, an inside front cover, pages i and ii, pages 1 to 6, an inside back cover and a back cover.

This standard has been updated (see copyright date) and may have had amendments incorporated. This will be indicated in the amendment table on the inside front cover.

Introduction

Fluoride ions occur in almost all ground and surface waters. Their concentration depends primarily on the hydrogeological conditions and is generally below 1 mg/l. Certain industrial waste waters may also contain fluoride ions in higher concentrations.

The fluoride concentration is also dependant on the type and concentration of cations present at the same time in water, such as Ca^{2+}, Mg^{2+}, Al^{3+} or Fe^{3+}, which may form sparingly soluble compounds with fluoride ions or complexes of low dissociation grade. In addition, stable boron-fluoride complexes exist. Several different methods are available for determining fluoride and the choice of method depends on the type of problem posed as follows.

a) Direct measurement using fluoride ion selective electrodes. This method is suitable for the determination of fluoride in drinking and surface water. It is included in ISO 10359-1.

b) Determination of inorganically bound total fluoride using decomposition, distillation and potentiometric measurement. This method is included in this part of ISO 10359.

1 Scope

1.1 Field of application

This part of ISO 10359 specifies a method for the determination of inorganically bound total fluoride. The method is applicable to waste waters which are highly contaminated inorganically, with a fluoride ion concentration of more than 0,2 mg/l.

1.2 Interferences

Interferences caused by certain cations (see introduction) or boron, which may occur in the determination of fluoride, need to be eliminated by distillation.

2 Normative reference

The following standard contains provisions which, through reference in this text, constitute provisions of this part of ISO 10359. At the time of publication, the edition indicated was valid. All standards are subject to revision, and parties to agreements based on this part of ISO 10359 are encouraged to investigate the possibility of applying the most recent edition of the standard indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

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

3 Principle

Evaporation of the water sample to dryness in an alkaline medium. Fusing of the residue with sodium hydroxide. Separation of the fluoride by steam distillation in the presence of a phosphoric acid/sulfuric acid mixture. Determination of the fluoride concentration in the distillate by means of a fluoride ionselective electrode (see ISO 10359-1).

4 Reagents

During the analysis, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

4.1 *Hydrochloric acid* (HCl), $\rho = 1{,}12$ g/ml.

4.2 *Phosphoric acid* (H_3PO_4), $\rho = 1{,}71$ g/ml.

4.3 *Sulfuric acid* (H_2SO_4), $\rho = 1{,}64$ g/ml; 72,5 % (*V*/*V*).

4.4 *Sodium hydroxide* (NaOH), solid.

4.5 *Sodium hydroxide solution* c(NaOH) = 5 mol/l.

Dissolve cautiously 100 g ± 0,5 g of sodium hydroxide in water, cool and dilute to 500 ml.

4.6 *Methyl red solution*

Dissolve 0,2 g of the sodium salt of methyl red ($C_{15}H_{14}N_3NaO_2$) in 100 ml of ethanol.

4.7 *Total ionic strength adjustment buffer* (TISAB).

Add 58 g of sodium chloride (NaCl) and 57 ml of glacial acetic acid [$\rho(CH_3COOH) = 1{,}05$ g/ml] to 500 ml of water in a 1 litre beaker. Stir until dissolved. Add 150 ml of the sodium hydroxide solution (**4.5**) and 4 g of CDTA (*trans*-1,2-diaminocyclohexane-*N,N,N',N'*-tetraacetic acid). Continue stirring until all the solids have dissolved and adjust the solution to pH 5,2 with sodium hydroxide solution using a pH-meter. Transfer to a 1 000 ml one-mark volumetric flask, make up to the mark with water and mix.

The solution is stable for about 6 months, but do not use it if a precipitate forms.

NOTE 1 This solution is commercially available.

4.8 *Fluoride,* stock solution, $\rho = 1\,000$ mg/l.

Dry a portion of sodium fluoride (NaF) at 150 °C for 4 h and cool in a desiccator.

Dissolve 2,210 g ± 0,001 g of the dried material in water contained in a 1 000 ml one-mark volumetric flask. Make up to the mark with water and mix.

Store the solution in a screw-capped polyethylene container.

4.8.1 *Fluoride,* working standard solution I, $\rho = 10$ mg/l.

Pipette 10 ml of the fluoride stock solution (**4.8**) into a 1 000 ml one-mark volumetric flask. Make up to the mark with water and mix.

4.8.2 *Fluoride,* working standard solution II, $\rho = 5$ mg/l.

Pipette 5 ml of the stock solution (**4.8**) into a 1 000 ml one-mark volumetric flask and make up to the mark with water.

4.8.3 *Fluoride,* working standard solution III, $\rho = 1$ mg/l.

Pipette 100 ml of the working standard solution I (**4.8.1**) into a 1 000 ml one-mark volumetric flask and make up to the mark with water.

4.8.4 *Fluoride,* working standard solution IV, $\rho = 0{,}5$ mg/l.

Pipette 100 ml of the working standard solution II (**4.8.2**) into a 1 000 ml one-mark volumetric flask and make up to the mark with water.

4.8.5 *Fluoride,* working standard solution V, $\rho = 0{,}2$ mg/l.

Pipette 20 ml of the working standard solution I (**4.8.1**) into a 1 000 ml one-mark volumetric flask and make up to the mark with water.

All standard solutions are stored in plastics bottles and are usable for 1 month.

5 Apparatus

Usual laboratory apparatus and

5.1 *Meter,* a millivoltmeter with an impedance of not less than 10^{12} Ω, capable of resolving potential differences of 0,1 mV or better.

5.2 *Fluoride ion-selective electrode,* which shall give stable readings. The e.m.f. response, using standard solutions, shall not be less than 55 mV per decade change in fluoride concentration at 25 °C.

5.3 *Reference electrode,* either a calomel electrode, filled with saturated potassium chloride (KCl) solution, or a silver/silver chloride electrode shall be used.

NOTE 2 Single junction, sleeve type electrodes which reduce the liquid-liquid junction potential are preferable.

5.4 *Measuring cells,* of capacity 100 ml, made of polypropylene and fitted with a thermostatted jacket.

5.5 *Water bath,* capable of supplying water to the jacket of the measuring cell (**5.4**) at a temperature of 25 °C ± 0,2 °C.

5.6 *Magnetic stirrer,* with a PTFE-coated stirring bar (PTFE = polytetrafluoroethylene).

5.7 *Polyethylene beaker,* of capacity 100 ml.

5.8 *Nickel dishes,* of a suitable size up to a capacity of 700 ml.

5.9 *Crucibles,* of 60 ml nominal capacity, made of glazed porcelain or nickel.

5.10 *Distillation apparatus,* (for example as shown in Figure 1) made of borosilicate glass, suitable for steam distillation, consisting of a steam generating device, a 250 ml distillation flask, provided with a thermometer pocket with a 14/23 standard joint accomodating a distillation head provided with a splash head and dropping funnel and a coiled coolant tube condenser (with a jacket length of at least 30 cm). The thermometer has a 14/23 standard joint and shall be suitable for a temperature range up to 200 °C.

5.11 *Heating device for the distillation flask,* preferably an appropriately dimensioned heating jacket.

5.12 *Round-bottomed flasks,* of capacities 500 ml and 1 000 ml.

5.13 *Volumetric flasks,* of capacities 100 ml, 250 ml and 500 ml.

5.14 *One-mark bulb pipettes,* of capacities 10 ml, 20 ml, 25 ml and 50 ml.

5.15 *Pipettes*

5.16 *Narrow-mouthed reagent bottles,* of capacity 500 ml, made of brown glass.

6 Sampling and samples

Samples shall be taken in polyethylene bottles which have been washed thoroughly and rinsed with fluoride-free water. No preservative is normally necessary but perform the analysis as soon as possible, preferably within 3 days. For further information on sample preservation see ISO 5667-3.

7 Procedure

7.1 Evaporation and decomposition

Transfer 500 ml of the water sample, which has been homogenized by shaking to a nickel dish (**5.8**). The fluoride concentration shall be between 0,2 mg/l and 2 000 mg/l. For higher fluoride concentrations, take a suitably smaller volume.

Adjust the pH of the water sample to 11 to 12 by adding sodium hydroxide solution (**4.5**) and concentrate by evaporation to a volume of approximately 30 ml. Transfer to a crucible (**5.9**) and carefully evaporate to dryness, avoiding overheating or splashing.

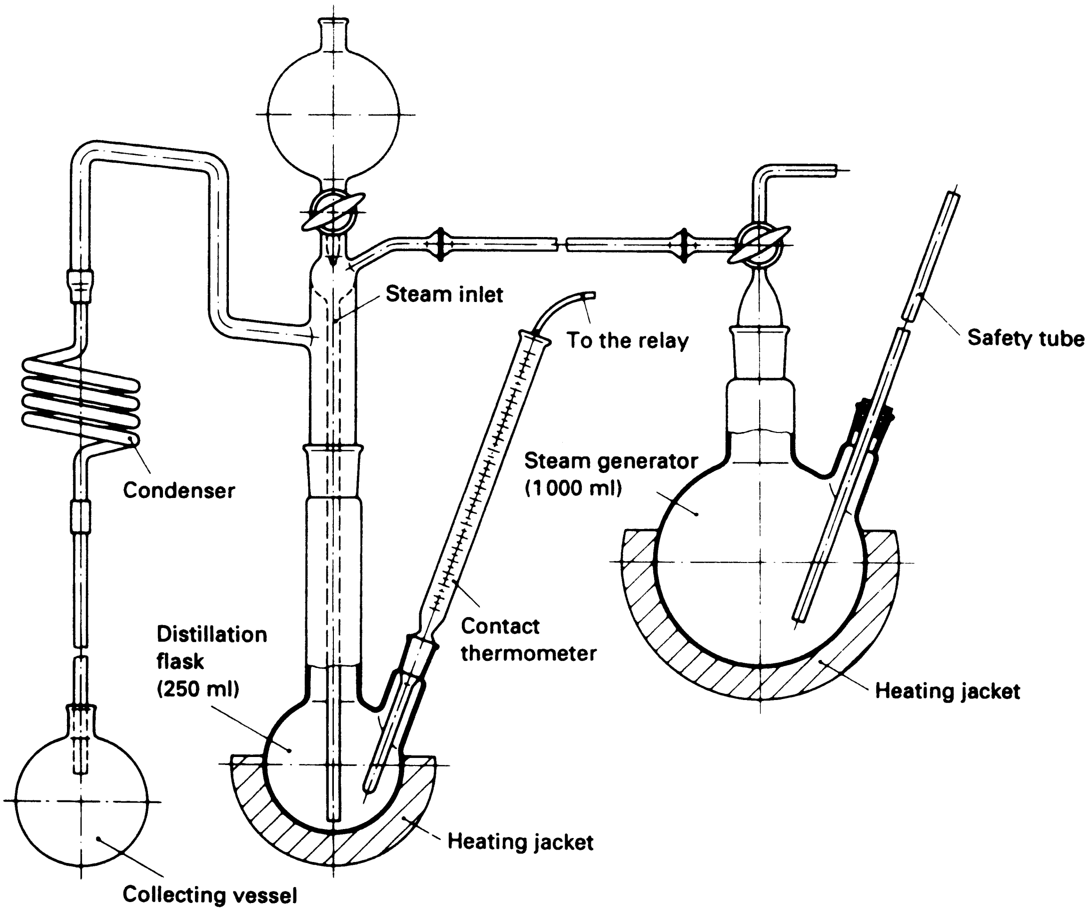

Figure 1 — Example of a distillation apparatus

Cover the residue with 2 g of sodium hydroxide (**4.4**).

Heat the contents of the crucible to 400 °C to 500 °C (dull red heat) and wait for 10 min.

Cool and dissolve the melt in a small volume of water.

7.2 Distillation

Transfer the dissolved melt (see **7.1**) to a distillation flask (see **5.10**), ensuring that the total volume does not exceed 50 ml.

Connect the flask to the rest of the distillation apparatus (**5.10**).

Using the dropping funnel, carefully add 60 ml of sulfuric acid (**4.3**) and then 10 ml of phosphoric acid (**4.2**).

Place a 500 ml volumetric flask containing 20 ml of sodium hydroxide solution (**4.5**) under the condenser outlet. Submerge the outlet tube of the condenser in the solution.

Switch on the steam generator and the heating jacket (**5.11**) for the distillation flask.

When the contents of the flask begin to boil, introduce steam.

Continue heating until the contents of the distillation flask reach a temperature of 155 °C.

Regulate the heating to keep this temperature approximately constant.

Adjust the steam supply for a distillation rate of approximately 10 ml/min.

NOTE 3 For larger series of analyses, it is advisable to replace the thermometer by a contact thermometer and to control the heating using a relay.

Stop the distillation when the amount of distillate is approximately 450 ml.

Rinse the condenser outlet tube inside and outside with a small volume of water.

Neutralize the contents of the volumetric flask against methyl red (**4.6**) and make up to the mark with water.

NOTE 4 Any interference caused by the distillation apparatus, which could lead to excessive fluoride concentrations after the distillation, can be eliminated by a blank distillation before carrying out the next determination.

7.3 Preparation for measurement

Since the electrode characteristics of a fluoride ionselective electrode (**5.2**) generally vary in the course of time, check the calibration curve on the day of use (see **7.4**).

To improve the electrode response, condition the electrode prior to measurement in the following way.

Prior to measurement, immerse the electrode for 1 h in the cell (**5.4**) which contains the reference solution **5** (see Table 1).

After rinsing with the first solution to be measured, the electrode is ready for use.

7.4 Calibration

Establish a calibration function using the five reference solutions in the corresponding concentration range.

For the range 0,2 mg/l to 10 mg/l, proceed as follows:

- — pipette 25,0 ml of the buffer solution (**4.7**) into each of five measuring cells;
- — pipette the respective volumes of the working standard fluoride solutions as specified in Table 1 into the measuring flasks.

For the establishment of the calibration function, proceed step by step from the most dilute solution to the most concentrated solution, rinsing after each measurement with the solution of the next highest concentration.

After the above measurements have been completed, recondition the electrode for 5 min to 10 min, using the reference solution **5** (see Table 1) in order to eliminate memory effects.

Use the following order of measurement (the numbers refer to the reference solutions in Table 1):

5 — rinse — 4 — rinse — 3 — rinse — 2 — rinse — 1 — rinse with 5 — recondition — repeat measuring run.

If the individual values of the parallel series vary from the first series by more than ± 0,5 mV, repeat the measuring run.

Regular checking of the calibration graph is essential. Ensure that the slope is not less than 55 mV, otherwise check the equipment and establish a new calibration graph.

7.5 Calibration after distillation

For regular checking of the calibration curve (e.g. after every 20 runs), also carry out a calibration including the digestion and distillation procedure.

7.6 Measurement

Pipette 25 ml of the buffer solution (**4.7**), followed by 25 ml of the distillate (see **7.2**), into a dry measuring cell (**5.4**).

Ensure that the pH is 5,2 ± 0,2; if necessary, adjust the pH with hydrochloric acid or sodium hydroxide solution, using volumes as small as possible.

For a series of determinations, start the measurement with the lowest concentration and finish with the highest, following the anticipated concentration of the samples.

After measuring the high concentrations, recondition the electrode before measuring the concentrations (see **7.3**).

Measure all the solutions according to the following procedure.

Wait until a constant temperature (e.g. 25 °C ± 0,5 °C) is reached and carry out all the measurements at this temperature.

Table 1 — Preparation of reference solutions (see 7.4)

Reference solution	Buffer solution	Working standard solution		Fluoride concentration[a]
No.	ml	No.[b]	ml	mg/l
1	25	I	25	10
2	25	II	25	5
3	25	II	25	1
4	25	IV	25	0,5
5	25	V	25	0,2

[a] The term “concentration” refers principally to the concentration of the Working standard solutions and the sample solutions, but not to the concentration of the measuring solution after addition of the buffer.

[b] See **4.8.1** to **4.8.5**.

Put a stirring bar into the measuring cell (**5.4**) and place it on the magnetic stirrer (**5.6**).

Insert the electrodes (**5.2**) into the solution and fix them in place.

Adjust the stirring rate to about 180 min^{-1} to 200 min^{-1}.

When the cell potential does not change by more than 0,5 mV in 5 min, switch off the stirrer. After at least 15 s, record the value obtained.

Rinse the stirring bar and the electrodes with the next solution to be measured, before starting the next measurement.

NOTE 5 Any dilution of the distillate needs to be taken into account during calculation of the results.

7.7 Determination of blank value

For each set of samples, carry out a blank determination following the complete procedure described in **7.1** to **7.5**, but replacing the sample by water.

8 Calculation

Plot the calibration values obtained as described in **7.4** on semi-logarithmic paper, with the fluoride concentrations, in milligrams per litre, on the abscissa and the cell potential, in millivolts, on the ordinate and establish the regression line.

Read the value for the distillate from the regression line and express the mass concentration of fluoride in milligrams per litre.

NOTE 6 The evaluation may also be calculated using the Nernst equation (see for example [1] in Annex A).

Calculate the mass concentration of fluoride ρ_F in the water sample using the equation

$$\rho_F = \frac{V_D(\rho_{F,D} - \rho_{F,0})}{V}$$

where

ρ_F is the mass concentration, in milligrams per litre, of fluoride ions in the water sample;

$\rho_{F,D}$ is the mass concentration, in milligrams per litre, of fluoride ions in the distillate of the water sample;

$\rho_{F,0}$ is the mass concentration, in milligrams per litre, of fluoride ions in the distillate of the blank;

V is the volume, in millilitres, of the water sample;

V_D is the volume, in millilitres, of the distillate.

9 Precision

An interlaboratory trial, carried out in April 1983, gave the results shown in Table 2.

The samples used were spiked industrial waste waters.

Table 2 — Precision data

No.	l	n	Outlier %	ρ mg/l	$\bar{x}$ mg/l	WFR	σ_r mg/l	VCr %	σ_R mg/l	VC_R %
1	13	48	12,7	0,60	0,667	111,2	0,152	22,7	0,026	3,90
2	12	48	14,3	6,00	5,63	93,8	0,316	5,6	0,233	4,13
3	13	50	9,1	60,0	55,5	92,5	3,806	6,9	1,757	3,17

l Number of laboratories, with outliers rejected

n Number of values, with outliers rejected

ρ Mass concentration of fluoride

$\bar{x}$ Total mean

σ_r Repeatability standard deviation

VC_r Repeatability variation coefficient

σ_R Reproducibility standard deviation

VC_R Reproducibility variation coefficient

WFR Recovery rate

10 Test report

The test report shall include the following information:

a) a reference to this part of ISO 10359;

b) the date and place of testing;

c) a precise identification of the sample;

d) a description of the electrode pair used;

e) the results and the method of expression used;

f) any deviation from the procedure specified or any other circumstances that may have affected the results.

Annex A (informative) Bibliography

[1] BAILEY, P.L., *Analysis with Ion-selective Electrodes,* Heyden, London, New York (1976).

List of references

See national foreword.

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