BRITISH STANDARD

BS 6068-2.37:
1990
ISO 9297:1989

Water quality —

Part 2: Physical, chemical and biochemical methods —

Section 2.37 Method for the determination of chloride via a silver nitrate titration with chromate indicator (Mohr's method)

Committees responsible for this British Standard

The preparation of this British Standard was entrusted by the Environment and Pollution Standards Policy Committee (EPC/-) to Technical Committee EPC/44, upon which the following bodies were represented:

Association of Consulting Scientists
British Association for Chemical Specialities
British Gas plc
Chemical Industries Association
Department of the Environment for Northern Ireland
Department of the Environment (Water Directorate)
Department of Trade and Industry (Laboratory of the Government Chemist)
Electricity Supply Industry in England and Wales
Industrial Water Society
Institute of Petroleum
Institution of Gas Engineers
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

This British Standard, having been prepared under the direction of the Environment and Pollution Standards Policy Committee, was published under the authority of the Board of BSI and comes into effect on 30 September 1990

The following BSI references relate to the work on this standard:
Committee reference EPC/44
Draft for comment 88/50947 DC

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Amendments issued since publication

Amd. No.	Date	Comments

Contents

National foreword

This Section of BS 6068, which has been prepared under the direction of the Environment and Pollution Standards Policy Committee, is identical with ISO 9297:1989 "*Water quality — Determination of chloride — Silver nitrate titration with chromate indicator (Mohr's method)*".

The International Standard was prepared by subcommittee 2, Physical, chemical and biochemical methods, of Technical Committee 147, Water quality, of the International Organization for Standardization (ISO) with the active participation and approval of the UK.

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

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.*

Cross-references

International standard	Corresponding British Standard
	BS 6068 Water quality
ISO 5667-1:1980	Section 6.1:1981 Guidance on the design of sampling programmes (Identical)
ISO 5667-2:1982	Section 6.2:1983 Guidance on sampling techniques (Identical)
ISO 5667-3:1985	Section 6.3:1986 Guidance on the preservation and handling of samples (Identical)
ISO 5725:1986	BS 5497 Precision of test methods Part 1:1987 Guide for the determination of repeatability and reproducibility for a standard test method by interlaboratory tests (Identical)

The Technical Committee has reviewed the provisions of ISO 385-1, which is referred to in the text, and has decided that they are acceptable for use in conjunction with this standard.

A related British Standard to ISO 385-1 is BS 846 "*Specification for burettes*".

A British Standard does not purport to include all the necessary provisions of a contract. Users of British Standards are responsible for their correct application.

Compliance with a British Standard does not of itself confer immunity from legal obligations.

Summary of pages

This document comprises a front cover, an inside front cover, pages i to iv, pages 1 to 4, 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.

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1 Scope

1.1 Application range

This International Standard specifies a titration method for the determination of dissolved chloride in water. The method is applicable to the direct determination of dissolved chloride in concentrations between 5 mg/l and 150 mg/l. The working range may be extended to 400 mg/l by using a burette of larger capacity or by sample dilution. Due to many interferences the method is not applicable to heavily polluted waters of low chloride content.

1.2 Interferences

Normal concentrations of common constituents of ground water, surface water and potable water do not interfere with the determination.

The following substances interfere with the method

— Substances forming insoluble silver compounds, such as bromides, iodides, sulfides, cyanides, hexacyanoferrates(II) and hexacyanoferrates(III). If necessary, bromide and iodide ions shall be determined separately, and the result of the chloride determination corrected accordingly.

— Compounds forming complexes with silver ions, such as ammonium and thiosulfate ions.

— Compounds which will reduce chromate ions, including iron(II) and sulfite ions.

The interferences mentioned above will lead to high chloride values.

Highly coloured or turbid solutions may obscure the end point, for example hydrated iron oxide.

Table 1 — Interferences

Substance	Amount interfering mg/l
Br^-	3
I^-	5
S^{2-}	0,8
CN^-	1
$Fe(CN)_6^{4-}$	2
$Fe(CN)_6^{3-}$	2
NH_4^+	100
$S_2O_3^{2-}$	200
SO_3^{2-}	70
SCN^-	3
CrO_4^{2-}	1 000
PO_4^{3-}	25

Table 1 gives a summary of the concentrations of interfering compounds, in milligrams per litre, that give an increase of approximately 2 % in the result when in the presence of 70 mg/l of chloride.

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 385-1:1984, *Laboratory glassware — Burettes — Part 1: General requirements.*

ISO 5667-1:1980, *Water quality — Sampling — Part 1: Guidance on the design of sampling programmes.*

ISO 5667-2:1982, *Water quality — Sampling — Part 2: Guidance on sampling techniques.*

ISO 5667-3:1985, *Water quality — Sampling — Part 3: Guidance on the preservation and handling of samples.*

ISO 5725:1986, *Precision of test methods — Determination of repeatability and reproducibility for a standard test method by inter-laboratory tests.*

3 Principle

Reaction of chloride with added silver ions to form insoluble silver chloride which precipitates quantitatively. Addition of a small excess of silver ions to form a red brown silver chromate with chromate ions that have been added as an indicator. This reaction is used for indicating the end-point. The pH is maintained in the range of 5 to 9,5 throughout the titration in order to allow precipitation.

4 Reagents

NOTE 1 All silver compounds and solutions are sensitive to light. Silver salts temporarily stain the skin brown.

Use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

4.1 *Silver nitrate,* standard volumetric solution, $c(AgNO_3) \approx 0{,}02$ mol/l.

Dissolve 3,3974 g of silver nitrate ($AgNO_3$), previously dried at 105 °C in water and dilute to 1000 ml in a one-mark volumetric flask.

If stored in the dark in a brown glass bottle with glass stoppers, the solution is stable for several months. The solution is standardized against 10 ml sodium chloride standard reference solution (diluted to 100 ml) using the procedure given in **6.1**, however, there is no need for pH adjustment.

4.2 *Potassium chromate,* indicator, 100 g/l solution. Dissolve 10 g of potassium chromate (K_2CrO_4) in water and dilute to 100 ml.

4.3 *Sodium chloride,* standard reference solution, c(NaCl) = 0,02 mol/l. Dissolve 1,168 8 g of sodium chloride (NaCl), previously dried at 105 °C, in water and dilute to 1 000 ml in a one-mark volumetric flask.

4.4 *Nitric acid,* $c(HNO_3) \approx 0{,}1$ mol/l.

Stored in a glass bottle, the solution is stable indefinitely.

4.5 *Sodium hydroxide,* solution, $c(NaOH) \approx 0{,}1$ mol/l.

4.6 *Reagent,* for improvement of the buffer capacity.

Calcium carbonate ($CaCO_3$) or sodium hydrogen carbonate ($NaHCO_3$) in powder form.

5 Apparatus

Ordinary laboratory equipment and

5.1 *Burette,* of capacity 25 ml, complying with ISO 385-1.

6 Procedure

For sampling and preservation of samples refer to ISO 5667-1, ISO 5667-2 and ISO 5667-3.

6.1 Titration

Pipette a test portion of 100 ml, or a smaller volume of the sample diluted to 100 ml (volume V_a), into either a white porcelain basin, or a conical flask or a beaker held against a white background.

If the pH of the sample is outside the range of 5 to 9,5, adjust the pH using nitric acid (**4.4**) or sodium hydroxide (**4.5**) as appropriate, and note the volume required.

If ammonium ions are present in the sample in concentrations exceeding 10 mg/l, adjust the pH to between 6,5 and 7.

Adjust the pH in one aliquot, then take another and, this time without measuring the pH, add the same amounts of acid/hydroxide solution.

NOTE 2 If the pH is less than 5, pH-adjustment with calcium carbonate or sodium hydrogen carbonate (**4.6**) is preferable. This will also improve the buffer capacity. The amount added should be chosen so that a carbonate residue is left in the sample even after titration.

Add 1 ml of potassium chromate indicator solution (**4.2**). Titrate the solution by dropwise addition of silver nitrate solution until the colour of the solution just changes to a reddish brown (volume V_s).

After addition of one drop of sodium chloride solution (**4.3**), the colour should disappear.

Use the titrated sample treated with sodium chloride solution for comparison with the next titrations.

Where the titrant volume exceeds 25 ml, repeat the determination using a larger capacity burette or a smaller test portion volume.

6.2 Blank test

Titrate a blank solution as described in **6.1**, using 100 ml of water instead of the test sample.

The blank value should not exceed 0,2 ml of **4.1**. Otherwise check the purity of the water.

7 Expression of results

7.1 Calculation

The chloride content ρ_{Cl}, in milligrams per litre, is given by the formula

$$\rho_{Cl} = \frac{(V_s - V_b) \cdot c \cdot f}{V_a}$$

where

ρ_{Cl} is the concentration, in milligrams per litre, of chloride;

V_a is the volume, in millilitres, of the test sample (maximum 100 ml; dilutions must be taken into account);

V_b is the volume, in millilitres, of the silver nitrate solution used for the titration of the blank;

V_s is the volume, in millilitres, of the silver nitrate solution (**4.1**) used for the titration of the sample;

c is the actual concentration, expressed in moles of $AgNO_3$ per litre, of the silver nitrate solution;

f is the conversion factor, f – 35 453 mg/mol.

Report the result to the nearest 1 mg/l, giving three significant figures only.

7.2 Precision

The precision of the method is given in Table 2.[1)]

[1)] Values taken from an interlaboratory trial carried out in Germany, F.R., in 1983 in accordance with ISO 5725, except that the method to reject outliers was different.

8 Test report

The test report shall include the following information:

a) a reference to this International Standard;

b) all information necessary for a complete identification of the sample;

c) the results and the method of expression a used;

d) details of any operations not included in this International Standard or regarded as optional, together with any circumstances that may have affected the results.

Table 2 — Precision data

Sample	L	N	x mg/l	$\bar{x}$ mg/l	σ_r mg/l	CV_r %	σ_R mg/l	CV_R %
Drinking water	11	44	12,57	12,75	0,213	1,7	0,572	4,5
Drinking water, with chloride ions added	9	36	63,79	64,20	0,372	0,6	0,787	1,2
Municipal waste water	10	39	106,4	106,6	0,676	0,6	1,287	1,2

where

L is the number of laboratories;

x is the true value;

ρ is the reproducibility standard deviation;

σ_r is the repeatability standard deviation;

N is the number of values;

$\bar{x}$ is the mean value;

CV_R is the reproducibility variation coefficient;

CV_r is the repeatability variation, coefficient.

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Publication(s) referred to

See national foreword.

BSI — British Standards Institution

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Revisions

British Standards are updated by amendment or revision. Users of British Standards should make sure that they possess the latest amendments or editions.

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