

METHODS OF TESTING WATER USED IN INDUSTRY

Part 6. Chloride and sulphate

BS 2690: Part 6: 1968

THIS BRITISH STANDARD, having been endorsed by the Chairman of the Chemical Divisional Council, was published under the authority of the General Council on 29th March, 1968.

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The Institution desires to call attention to the fact that this British Standard does not purport to include all the necessary provisions of a contract.

In order to keep abreast of progress in the industries concerned, British Standards are subject to periodical review. Suggestions for improvements will be recorded and in due course brought to the notice of the committees charged with the revision of the standards to which they refer.

A complete list of British Standards, numbering over 4000, fully indexed and with a note of the contents of each, will be found in the British Standards Yearbook. The BS Yearbook may be consulted in many public libraries and similar institutions.

This standard makes reference to the following British Standards:

- BS 1328. Methods of sampling water used in industry.
- BS 2690. Methods of testing water used in industry.
Part 2. Dissolved oxygen, hydrazine and sulphite.

British Standards are revised, when necessary, by the issue either of amendment slips or of revised editions. It is important that users of British Standards should ascertain that they are in possession of the latest amendments or editions.

The following BSI references relate to the work on this standard:
Committee references C/37, C/37/1, C/37/1/1
Draft for comment 67/19183

CO-OPERATING ORGANIZATIONS

The Technical Committee which has been working under the supervision of the Chemical Divisional Council, and which is responsible for the preparation of this British Standard, consists of representatives from the following Government departments and scientific and industrial organizations:

- Association of Shell Boiler Makers
- British Launderers' Research Association
- *Chemical Industries Association
- *Electricity Council, the Central Electricity Generating Board
and the Area Boards in England and Wales
- Greater London Council
- Institute of Fuel
- Institute of Marine Engineers
- Institution of Chemical Engineers
- *Institution of Gas Engineers
- Institution of Mechanical Engineers
- Institution of Municipal Engineers
- *Ministry of Defence, Navy Department
- Ministry of Labour (H.M. Factory Inspectorate)
- *Ministry of Technology—Lab. of the Government Chemist
- National Coal Board
- Royal Institute of Chemistry
- Society of Laundry Engineers and Allied Trades Ltd.
- *The Steel Industry

The Government departments and scientific and industrial organizations marked with an asterisk in the above list, together with the following, were directly represented on the committee entrusted with the preparation of this British Standard:

- Gas Council
- Institute of Petroleum
- London Transport Board
- Society for Water Treatment and Examination
- Water-tube Boilermakers' Association

BRITISH STANDARD METHODS OF TESTING WATER USED IN INDUSTRY

Part 6. Chloride and sulphate

FOREWORD

This British Standard has been prepared under the authority of the Chemical Divisional Council.

Since the original publication of BS 2690 in 1956 an addendum was published in 1960 extending the methods to cover the testing of very pure waters. Since that time various further advances have been made in the development of methods of analysing water and a revision of the standard has commenced.

For each substance to be determined, where more than one method is given, the first is the simplest and the last is the most sensitive. An intermediate method will be intermediate in some respects such as sensitivity or accuracy in the presence of interferences.

The standard is being published in separate parts so that it will in the future be simpler to revise these parts and also in order that new methods may be made available as soon as possible. The methods given in this part supersede those in the 1956 edition.

The following have already been published:

Part 1. Copper and iron.

Part 2. Dissolved oxygen, hydrazine and sulphite.

Part 3. Silica and phosphate.

Part 4. Aluminium, calcium, magnesium and fluoride.

Part 5. Alkalinity, acidity, pH value and carbon dioxide.

NOTE. The coherent system of units adopted by the ISO, known as the SI system, has been used in this part of the revision. In particular the siemens is the name given to the unit formerly called the 'mho' (reciprocal ohm), and conductivities are accordingly expressed in terms of microsiemens per metre ($\mu\text{S/m}$) where

$$1 \text{ micromho/cm} = 100 \mu\text{S/m}.$$

Also, wavelengths are expressed in terms of nanometres (nm) rather than $\text{m}\mu$; these units are equivalent.

METHODS OF TEST

1. GENERAL

1.1 REAGENTS

All reagents shall be of a recognized analytical reagent quality unless otherwise specified.

1.2 WATER

Subject to the special requirements of certain methods, pure water having a conductivity of less than $50 \mu\text{S/m}$ at 20°C when freshly prepared and measured out of contact with air is to be used whenever water is required. This can be achieved by treating water with the correct grades of ion exchange resins.

1.3 RANGES

Where the range of amounts of the substance being determined is stated at the beginning of a test it is usually given in either microgrammes (μg) or milligrammes (mg); occasionally the range is given in p.p.m., i.e. mg/litre . The procedures described for the various tests cover the stated ranges, but may in certain cases be modified by taking a smaller volume of the sample and diluting with water or by taking a larger volume of the sample and evaporating. The test portion shall then be adjusted to the appropriate volume before proceeding with the determination.

1.4 SAMPLING

It is important to obtain a representative sample. Appropriate methods of sampling are described in BS 1328*.

1.5 INTERFERENCES

It must always be realized that although the methods given will be applicable in almost all cases, occasionally some substance may be present which will render the method unsuitable.

1.6 COLORIMETRIC METHODS

It is recommended that the spectrophotometer for colorimetric determinations should have a band width not exceeding 1% of the wavelength at which the measurement is carried out.

2. CHLORIDE

2.1 METHOD 1. ELECTROMETRIC TITRATION

2.1.1 Range. The range of determination is as follows:

0.2 mg Cl^- and above.

1.3 p.p.m. Cl^- and above.

2.1.2 Maximum size of sample. The maximum size of sample is 150 ml.

* BS 1328, 'Methods of sampling water used in industry'.

2.1.3 Introduction. The chloride is titrated with 0.01N silver nitrate using a reference half cell which consists of a length of silver wire dipping into a solution of similar silver concentration to that which will obtain in the sample solution at its end point; the sample solution with a second silver electrode forms the other half cell. During titration the difference in the opposing potentials is indicated by a sensitive galvanometer and the end point is reached when the galvanometer spot is at its zero position.

2.1.4 Interferences. Bromide and iodide will titrate as chloride. The following are known not to interfere when present in the sample solution up to the amounts stated:

Sulphite (SO_3^{2-})	15 000 μg
Sulphate (SO_4^{2-})	15 000 μg
Orthophosphate (as PO_4^{3-})	10 000 μg
Glassy sodium phosphate*	10 000 μg
Copper (Cu^{2+})	5 000 μg
Oil	750 μg
Iron (Fe^{3+})	75 μg

2.1.5 Apparatus. The following apparatus is required:

(1) *A high resistance spot galvanometer* with centre zero and a sensitivity of about 100–200 mm/ μA .

(2) *Reference half cell.* This is constructed from the outer glass sheath of a ground-sleeve type reference electrode. A length of silver wire 1.6 mm in diameter passes through a vented rubber stopper and into the reference solution. A second length of the silver wire is wrapped around the outside of the half cell as shown in Fig. 1.

Clean the silver electrodes by immersing them for a few seconds in dilute nitric acid (1:1) until brisk effervescence begins, remove from the solution and wash thoroughly with water. Do not touch the electrodes with the fingers after cleaning. Charge the half cell with the reference solution daily and check that the ground glass sleeve allows a slight seepage of the electrolyte.

- (3) *Tapping key* (A).
- (4) *Shorting plug* (B).
- (5) *1 M Ω resistance* (C).
- (6) *10 k Ω resistance* (D).
- (7) *Mechanical stirrer.*
- (8) *25 ml burette with bent delivery jet.*

The apparatus is assembled as shown in Fig. 1.

* Glassy sodium phosphate is the preferred name for the polymeric sodium metaphosphate widely used as a water treatment chemical.

- A = Tapping key
 B = Shorting plug
 C = $1\text{ M } \Omega$ resistance
 D = $10\text{ k } \Omega$ resistance

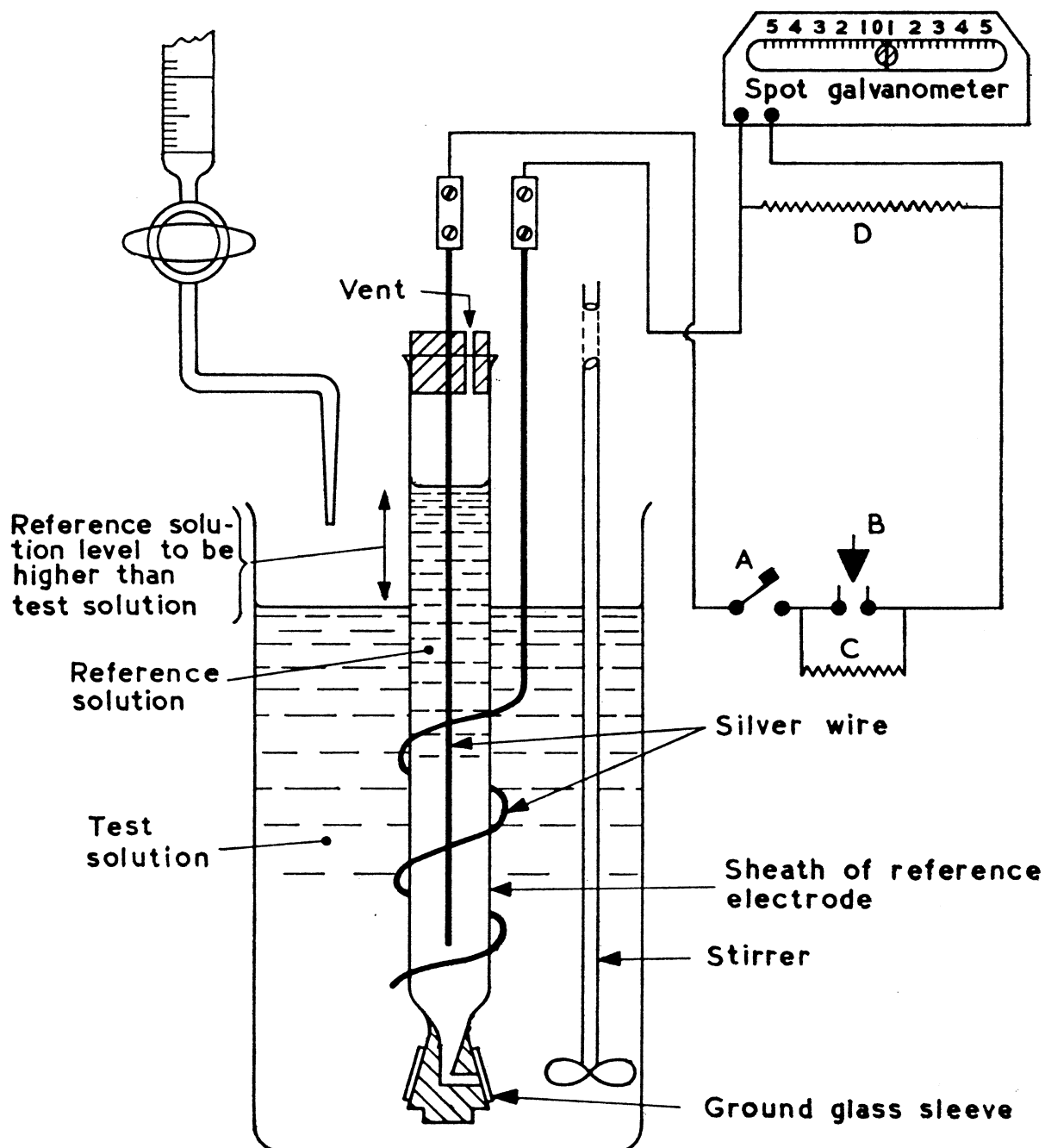


Fig. 1. Apparatus for electrometric titration of chloride

2.1.6 Reagents. The following reagents are required:

- (1) *Dilute nitric acid*, 1:1 by volume.
- (2) *Nitric acid*, N.
- (3) *Sodium chloride*, 0.01N.
- (4) *Silver nitrate*, 0.01N.
- (5) *Bromophenol blue indicator solution*. Warm 0.1 g of bromophenol blue with 3.0 ml of 0.05N sodium hydroxide solution and 5 ml of 95% (v/v) ethanol; after solution is effected add 50 ml of water and 200 ml of 95% (v/v) ethanol. Mix well.
- (6) *Solution for reference half cell*, prepared from the following:
 - 2.0 ml N nitric acid.
 - 25.00 ml 0.01N sodium chloride solution.
 - 25.05 ml 0.01N silver nitrate solution.

Make up to 200 ml with water and mix. Store in an amber bottle away from sunlight and check by filling the reference half cell and carrying out the titration as described in 2.1.7 using 150 ml of water in place of the sample. A titration figure of 0.08–0.10 ml of 0.01N silver nitrate solution indicates that the reference solution is satisfactory. If necessary the silver nitrate content of the reference solution may be adjusted to bring the titration figure within the recommended limits.

2.1.7 Procedure. Measure 150 ml of the sample, or a smaller quantity diluted to 150 ml, into a beaker, neutralize with N nitric acid using bromophenol blue indicator and add a further 1.5 ml of N nitric acid.

Suspend the reference half cell in the sample beaker so that the level of the reference solution in the cell is higher than the level of the sample solution. Connect up the apparatus as shown in Fig. 1, start the stirrer and titrate with 0.01N silver nitrate solution. Leave the shorting plug B out in the early part of the titration to reduce the sensitivity of the galvanometer deflection and assist in avoiding polarization of the cell. Depress the tapping key A momentarily at intervals during the titration and note the galvanometer deflection. When the galvanometer spot approaches the zero mark, insert the shorting plug B and continue the titration to the end point which is reached when the galvanometer spot is on the zero mark.

Carry out a blank determination on 145 ml of water to which has been added 5.00 ml of 0.01N sodium chloride solution.

2.1.8 Calculation

Blank = ml of 0.01N silver nitrate solution — 5.00

Chloride (expressed as Cl^-) =

$$\frac{(\text{ml of 0.01N silver nitrate solution} - \text{blank}) \times 355}{\text{ml of sample}} \text{ p.p.m.}$$