

METHODS OF TESTING WATER USED IN INDUSTRY

Part 1. Copper and Iron

B.S. 2690 : Part 1 : 1964

THIS BRITISH STANDARD, having been endorsed by the Chairman of the Chemical Divisional Council, was published under the authority of the General Council on 6th August, 1964.

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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 5000, indexed and cross-indexed for reference, together with an abstract of each standard, will be found in the Institution's Yearbook.

This standard makes reference to the following British Standard:

B.S. 1328. Methods of sampling water used in industry.

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 B.S.I. references relate to the work on this standard:
Committee reference C/37, C/37/1, C/37/1/1
Draft for comment D63/7245

CO-OPERATING ORGANIZATIONS

The Technical Committee appointed by the Chemical Divisional Council, under whose supervision this British Standard was prepared, consists of representatives from the following Government departments and scientific and industrial organizations:

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Association of Shell Boiler Makers
British Iron & Steel Federation
British Launderers Research Association
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Water Research Association
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BRITISH STANDARD

METHODS OF TESTING WATER
USED IN INDUSTRY

Part 1. Copper and Iron

FOREWORD

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

Since the original publication of B.S. 2690 in 1950 an addendum was published in 1961 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 document has commenced.

The document will be in suitable 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.

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 respect such as sensitivity or accuracy in the presence of interference.

GENERAL

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

Water. Subject to the special requirements of certain methods. Pure water having a conductivity of less than 0.5 micromho/cm 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 resin.

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. 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.

Sampling. It is important to obtain a representative sample. Appropriate methods of sampling are described in B.S. 1328, 'Methods of sampling water used in industry'.

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.

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

Methylated spirits. Industrial methylated spirits is specified in some tests. It is pointed out that the use of this material is governed by the Industrial Methylated Spirits Regulation 1952 (S.I. 1952 No. 2230)*.

COPPER

METHOD 1

Range: 5 to 100 μg Cu.

Maximum size of sample: 100 ml.

Introduction. Biscyclohexanone oxalyldihydrazone with cupric and cuprous ions forms a water soluble blue complex in a solution at pH between 7 and 10. The blue coloured complex is not formed in acid solution, while in strongly alkaline media the colour fades rapidly.

In this method the sample to be tested is acidified with hydrochloric acid and treated with bromine to destroy, if possible, any inherent colour of the sample. Excess of bromine is removed by boiling and after cooling the blue copper complex is produced in a buffered solution.

Ammonium citrate, present in the buffer solution, also prevents precipitation of the hydroxides of certain metals which may be present.

The sample should be collected in a borosilicate glass or polythene vessel containing sufficient hydrochloric acid for the final acid concentration to be $0.1 \pm 0.01\text{N}$.

Interferences. Under the conditions described in the method the presence of 1000 μg of iron, aluminium, zinc, nickel, chromium, calcium, magnesium, manganese, phosphate (PO_4 as orthophosphate) and phosphate (PO_4 as metaphosphate) either individually or collectively, causes no significant interference.

Reagents.

Hydrochloric acid ($d = 1.18$).

Hydrochloric acid ($0.1 \pm 0.01\text{N}$). Made with the water to be used in the test.

Sodium hydroxide, 5 per cent w/v solution.

Bromine water, saturated.

Methyl orange indicator, 0.04 per cent w/v solution.

* Ethanol may be substituted for industrial methylated spirits if desired.

Ammonia-ammonium citrate buffer solution. Dissolve 50 g of citric acid monohydrate in about 300 ml of water. Add 130 ml of ammonia ($d = 0.91$) and dilute with water to 500 ml.

Biscyclohexanone oxalyldihydrazone, 0.25 per cent w/v solution. Dissolve 0.250 g of biscyclohexanone oxalyldihydrazone in 100 ml of a warm solution of equal volumes of ethanol and water. Cool.

Copper standard solution. Dissolve 0.393 g of copper sulphate $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ in water, add 10 ml of hydrochloric acid ($d = 1.18$) and dilute to 1 litre.

Copper working solution. Dilute 10 ml of the copper standard solution to 100 ml.

$$1 \text{ ml} \equiv 10 \mu\text{g Cu}$$

Preparation of calibration graph. Measure accurately volumes of the copper working solution containing 0, 10, 20, 40, 60, 80 and 100 μg copper into a series of 100 ml one-mark volumetric flasks. Add 1 ml of hydrochloric acid to each solution and then dilute to about 70 ml. Now add 10 ml of the ammonia-ammonium citrate buffer, mix and add 5.0 ml of the biscyclohexanone oxalyldihydrazone solution. Dilute to 100 ml, mix and allow to stand for 15 minutes. Measure the optical densities of the solutions at a known temperature between 20 and 25°C in a spectrophotometer at the wavelength corresponding to maximum absorption (approximately 595 m μ but the exact wavelength shall be checked for each spectrophotometer) using a 4 cm cell. Use water in the compensating cell. Correct the readings for the blank with no added copper and from the net optical densities obtained and the known copper contents of the solutions plot the calibration graph.

Procedure. Measure a suitable volume of the sample into a 250 ml beaker and if less than 100 ml dilute to 100 ml with water. Place an equal volume of 0.1N hydrochloric acid into a second 250 ml beaker to serve as a blank and dilute to 100 ml with water if necessary. To each add 1 drop of methyl orange and neutralize with sodium hydroxide solution. Now add 1 ml of hydrochloric acid ($d = 1.18$) to the sample and the blank. Continue with the procedure treating the sample and blank similarly.

Add 5 ml of bromine water and boil until the volume is reduced to about 50 ml.

Cool the solution and proceed as directed under *a* or *b*.

a. If the solution is clear transfer it to a 100 ml one-mark volumetric flask and dilute to about 70 ml.

b. If the solution is not clear filter it through a 9 cm diameter copper-free filter paper*. Wash the filter a few times with small volumes of water. Collect

* Whatman No. 541 or Barcham Green Hydruo 81F is suitable.