BRITISH STANDARD

BS 4341:1968

Methods of test for

Formic acid

Confirmed
January 2011

Co-operating organizations

The Chemicals Industry Standards Committee, under whose supervision the formulation of the United Kingdom point of view in the international work leading to the publication of this British Standard was carried out, consists of representatives from the following Government departments, and scientific and industrial organizations:

Board of Trade
British Steel Industry
Chemical Industries Association*
Fertiliser Manufacturers' Association Ltd.
Gas Council
Institution of Gas Engineers
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Ministry of Health
Ministry of Technology — Laboratory of the Government Chemist*
National Sulphuric Acid Association
Royal Institute of Public Health & Hygiene

This British Standard, having been circulated to the Chemicals Industry Standards Committee and endorsed by the Chairman of the Chemical Divisional Council, was published under the authority of the General Council on 19 September 1968

The following BSI reference relates to the work on this standard:
Committee reference CIC/4/–/2

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Amendments issued since publication

Amd. No.	Date	Comments

Contents

Foreword

This standard makes reference to the following British Standard:

BS 3978, *Water for laboratory use.*

For some years the United Kingdom has participated in the work of preparing methods of test applicable to formic acid for industrial use, carried out by Working Group 4 of Technical Committee 47-Chemistry of the International Organization for Standardization. As international agreement is reached on the methods, it is proposed to publish them as British Standards.

This British Standard is technically identical with ISO Recommendation R731 Formic acid for industrial use — Methods of test.

Summary of pages

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

1 Scope

This British Standard describes methods of test for formic acid for industrial use.

2 Sample

The laboratory sample should be of sufficient size for carrying out all the analyses. It should be preserved in an airtight glass-stoppered bottle of such a size that it is nearly filled by the sample. If it is considered necessary to seal the container, care should be taken to avoid the risk of contaminating the contents in any way.

3 Determination of total acidity

3.1 Principle. Titration of acidity using a standard volumetric solution of sodium hydroxide using phenolphthalein as indicator.

3.2 Reagents. Freshly boiled and cooled distilled water or water of at least equal purity[1] should be used in the test.

3.2.1 *Sodium hydroxide,* N standard volumetric solution.

NOTE If the standard volumetric solution is not of exactly the strength indicated in the list of reagents, a suitable correction factor should be employed in calculating the results.

3.2.2 *Phenolphthalein,* 5 g/l alcoholic solution. Dissolve 0.5 g of phenolphthalein in 100 ml of 95 % (v/v) ethanol and make faintly pink by the addition of dilute sodium hydroxide solution.

3.3 Apparatus. Normal laboratory apparatus together with:

3.3.1 *Thin glass ampoule,* diameter approximately 20 mm (see Figure 1). This is only required for samples believed to contain more than 90 % (m/m) of total acidity.

3.4 Procedure

3.4.1 *For acids believed to contain more than* 90 % (*m*/*m*) *of total acidity, expressed as formic acid.* Weigh the glass ampoule (**3.3.1**) to the nearest 0.5 mg and introduce a test portion of about 1.5 g by partially immersing the ampoule in the bottle containing the laboratory sample. Seal the capillary without loss of glass, using the oxidizing flame of the burner; withdraw the ampoule and invert it. Wipe the end that was immersed in the laboratory sample with a filter paper and seal rapidly. Weigh the ampoule again to the nearest 0.5 mg and determine to the nearest milligramme, by difference between the two weighings, the mass of test portion taken. Place the sealed ampoule in a 250 ml conical flask containing about 50 ml of water. Break up the ampoule with a glass rod, shake, add 0.5 ml of phenolphthalein solution (**3.2.2**) and titrate with the sodium hydroxide solution (**3.2.1**).

3.4.2 *For acids believed to contain less than* 90 % (*m*/*m*) *of total acidity, expressed as formic acid.* Place a test portion of 1.5 g to 2.0 g weighed to the nearest milligramme, into a 250 ml conical flask containing about 50 ml of water. Add 0.5 ml of phenolphthalein solution (**3.2.2**) and titrate with the sodium hydroxide solution (**3.2.1**) to a faint pink end point.

3.5 Expression of results. Total acidity, expressed as formic acid (HCOOH), is given in per cent by mass by the following formula:

$$\frac{V \times A}{E} \times 100$$

where V is the volume, in millilitres, of the N sodium hydroxide solution (**3.2.1**) used for the titration,

A is the mass, in grammes, of formic acid (HCOOH) corresponding to 1 ml of N sodium hydroxide solution (Theoretical value 1 ml = 0.046 03 g of HCOOH; see Note in **3.2.1**.)

and E is the mass, in grammes, of test portion taken.

4 Determination of acids other than formic acid

4.1 Field of application. This method is applicable to formic acid containing between 0.5 % and 6.0 % (m/m) of other acids calculated as acetic acid.

4.2 Principle. Titration with sodium hydroxide solution using a pH meter, of the acids remaining after quantitative oxidation of formic acid with excess mercuric oxide.

4.3 Reagents. Freshly boiled and cooled distilled water, or water of at least equal purity[1] should be used in the test.

4.3.1 *Acetic acid,* approximately 0.5 % (v/v) solution. Dilute 5 ml of glacial acetic acid to 1 000 ml.

4.3.2 *Mercuric oxide* (red).

4.3.3 *Sodium hydroxide,* 0.1 N standard volumetric solution (see Note in **3.2.1**).

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[1] Attention is drawn to BS 3978, "*Water for laboratory use*".

4.4 Apparatus. Normal laboratory apparatus together with:

4.4.1 *Conical flasks,* with ground-glass necks, capacity 250 ml.

4.4.2 *Reflux condenser,* water cooled, with ground-glass joints to fit the flasks.

4.4.3 *pH Meter* with a glass electrode.

4.5 Procedure

4.5.1 ***Test portion***

a) *For content of acids other than formic acid less than* 2 % (*m*/*m*). Weigh 5 g of the laboratory sample (see Section 2) to the nearest 0.01 g.

b) *For content of acids other than formic acid* 2 % (*m*/*m*) *and over.* Weigh 2 g of the laboratory sample (see Section 2) to the nearest 0.005 g.

4.5.2 *Blank test.* At the same time as the analysis, carry out a blank test using the procedure described in **4.5.3** and **4.5.4** and the same quantities of all reagents.

4.5.3 *Preparation of test solution.* Place the test portion (**4.5.1**) in one of the conical flasks (**4.4.1**). Add exactly 5.0 ml of acetic acid solution (**4.3.1**) and an amount of mercuric oxide (**4.3.2**) calculated on the basis of 5.5 g of mercuric oxide per gramme of formic acid present in the test portion. Then add sufficient water to bring the total volume to about 30 ml.

Fit the flask with a condenser (**4.4.2**) and heat gently for 10 min. Fairly strong evolution of carbon dioxide from the solution containing the test portion occurs. Reflux gently for 30 min and rinse the condenser with 20 ml to 25 ml of water. Cool the flask to room temperature and pour the contents without filtering into a 250 ml beaker. Rinse the flask into the beaker with 20 ml to 25 ml of water, and transfer the washings to the beaker.

4.5.4 *Titration.* Stir the solution vigorously, preferably using a magnetic stirrer, and keep stirring during the titration. Titrate the residual acids with the sodium hydroxide solution (**4.3.3**) using the pH meter (**4.4.3**). The end point of the titration is at pH 8.6 for the test and at pH 8.3 for the blank.

Samples requiring more than 10 ml to 15 ml of the Sodium hydroxide solution (**4.3.3**) do not give a very sharp end point and a period of vigorous stirring is necessary in order to obtain a stable final pH.

4.6 Expression of results. The content of acids other than formic acid, expressed as acetic acid (CH_3COOH), is given in per cent by mass by the following formula:

$$\frac{(V_1 - V_2) \times A}{E} \times 100$$

where V_1 is the volume, in millilitres, of the 0.1N sodium hydroxide solution (**4.3.3**) used for the titration of sample solution,

V_2 is the volume, in millilitres, of the 0.1N sodium hydroxide solution (**4.3.3**) used for the titration of the blank,

A is the mass, in grammes, of acetic acid (CH_3COOH) corresponding to 1 ml of 0.1N sodium hydroxide solution, (theoretical value 1 ml = 0.0060 g of CH_3COOH; see Note in **3.2.1**)

and E is the mass, in grammes, of the test portion.

5 Limit test for inorganic chlorides

5.1 Field of application. This method is applicable to samples in which the content of inorganic chloride, expressed as chlorine (Cl), is not greater than 0.5 % (m/m) and not less than 0.0005 % (m/m).

If the inorganic chloride content is above or below that range, the method is applicable by reducing or increasing the mass of sample taken (**5.5.1**).

5.2 Principle. Comparison of the turbidity, obtained by the addition of silver nitrate to a solution prepared from the test sample in presence of nitric acid, with that similarly obtained from a chloride solution of known concentration.

5.3 Reagents. Distilled water, or water of at least equal purity[2] should be used in the test.

All reagents and filter paper should be chloride free.

5.3.1 *Nitric acid,* approximately 5N solution.

5.3.2 *Standard chloride solution* containing 0.1 g/l of Cl^-. Place 28.2 ml of a 0.1N hydrochloric acid solution in a 1 000 ml one-mark volumetric flask. Dilute to the mark and mix thoroughly.

1 ml of this standard solution contains 0.0001 g of Cl^-.

5.3.3 *Silver nitrate,* 50 g/l solution.

5.4 Apparatus. Normal laboratory apparatus.

5.5 Procedure

5.5.1 *Test portion.* Weigh to the nearest 0.5 g, 50 g of the laboratory sample (see Section 2).

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[2] Attention is drawn to BS 3978, "*Water for laboratory use*".

5.5.2 *Preparation of test solution.* Transfer the test portion (**5.5.1**) to a 250 ml one-mark volumetric flask, dilute to the mark and mix thoroughly. If the solution is not clear, pass it through a filter paper. This should remove turbidity due to impurities such as aluminium. If there is turbidity in the filtrate due to contamination with wax, remove it by shaking with a suitable solvent, for example, light petroleum.

5.5.3 *Comparison of chloride content.* Place 1.0 ml of standard chloride solution (**5.3.2**) into a 100 ml Nessler cylinder, dilute to the mark, add 2 ml of the nitric acid solution (**5.3.1**) and mix. For a sample required to contain not more than x % (m/m) of chloride expressed as Cl^-, transfer to a 100 ml Nessler cylinder an aliquot, $0.05/x$ ml[3] of the test solution (**5.5.2**), dilute to the mark, add 2 ml of the nitric acid solution (**5.3.1**), and mix.

Add to each Nessler cylinder 1 ml of silver nitrate solution (**5.3.3**) and mix. Allow the cylinders to stand in the dark for 5 minutes, then compare the turbidities produced by the aliquot of the test solution with that produced by the standard chloride solution (**5.3.2**).

5.6 Expression of results. If the turbidity produced from the test solution is less than that produced from the standard chloride solution, report that the sample contains less than x % of inorganic chloride expressed as Cl^-, otherwise report it as containing not less than x %.

6 Limit test for inorganic sulphates

6.1 Field of application. This method is applicable where the sulphate content, expressed as SO_4, is not greater than 0.1 % and not less than 0.001 % (m/m).

If the sulphate content is above or below that range, the method is applicable by reducing or increasing the mass of the test portion taken (**6.5.1**).

6.2 Principle. Comparison of the turbidity, obtained by the addition of barium chloride to a solution prepared from the laboratory sample in presence of hydrochloric acid, with that similarly obtained from a sulphate solution of known concentration.

6.3 Reagents. Distilled water, or water of at least equal purity[4] should be used in the test.

6.3.1 *Sodium carbonate,* approximately N solution.

6.3.2 *Hydrochloric acid,* approximately N solution.

6.3.3 *Barium chloride,* ($BaCl_2.2H_2O$) 10 g/l solution.

6.3.4 *Standard sulphate solution containing* 0.1 g/l of SO_4. Place 20.8 ml of 0.1N standard volumetric solution of sulphuric acid in a 1 000 ml one-mark volumetric flask. Dilute to the mark and mix thoroughly.

1 ml of this solution contains 0.0001 g of SO_4.

6.4 Apparatus. Normal laboratory apparatus.

6.5 Procedure

6.5.1 *Test portion.* Weigh to the nearest 1 g, 100 ± 1 g of the laboratory sample (see Section 2), into an evaporating basin.

6.5.2 *Preparation of test solution.* To the test portion (**6.5.1**), add 0.2 ml of the sodium carbonate solution (**6.3.1**) and evaporate to dryness on a boiling water bath. Dissolve the residue in water containing 1 ml of hydrochloric acid solution (**6.3.2**), transfer the solution to a 250 ml one-mark volumetric flask, dilute to the mark and mix.

If the solution is not clear, pass it through a filter paper. This should remove turbidity due to impurities such as aluminium. If there is turbidity in the filtrate due to contamination with wax, remove it by shaking with a suitable solvent, for example light petroleum.

6.5.3 *Comparison of sulphate contents.* Place 4.0 ml of the standard sulphate solution (**6.3.4**) into a 100 ml Nessler cylinder, dilute to the mark, add 2 ml of the hydrochloric acid solution (**6.3.2**) and mix. For a sample required to contain not more than x % (m/m) of inorganic sulphate expressed as SO_4, transfer to a 100 ml Nessler cylinder an aliquot $0.1/x$ ml[5] of the test solution (**6.5.2**), dilute to the mark, add 2 ml of the hydrochloric acid solution (**6.3.2**) and mix.

Add to each Nessler cylinder 2 ml of barium chloride solution (**6.3.3**) and mix.

Allow the cylinders to stand for 5 minutes, mix again and compare the turbidities produced by the aliquot of the test solution with that produced by the sulphate solution of known concentration.

6.6 Expression of results. If the turbidity produced from the test solution is less than that produced from the sulphate solution of known concentration (**6.5.3**), report that the sample contains less than x % of inorganic sulphate expressed as SO_4, otherwise report it as containing not less than x %.

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[3] If the mass of the test portion (**5.5.1**) was reduced or increased (see **5.1**), adjust accordingly the numerator of this fraction.

[4] Attention is drawn to BS 3978, "*Water for laboratory use*".

[5] If the mass of the test portion (**6.5.1**) was reduced or increased (see **6.1**), adjust accordingly the numerator of this fraction.

7 Test report

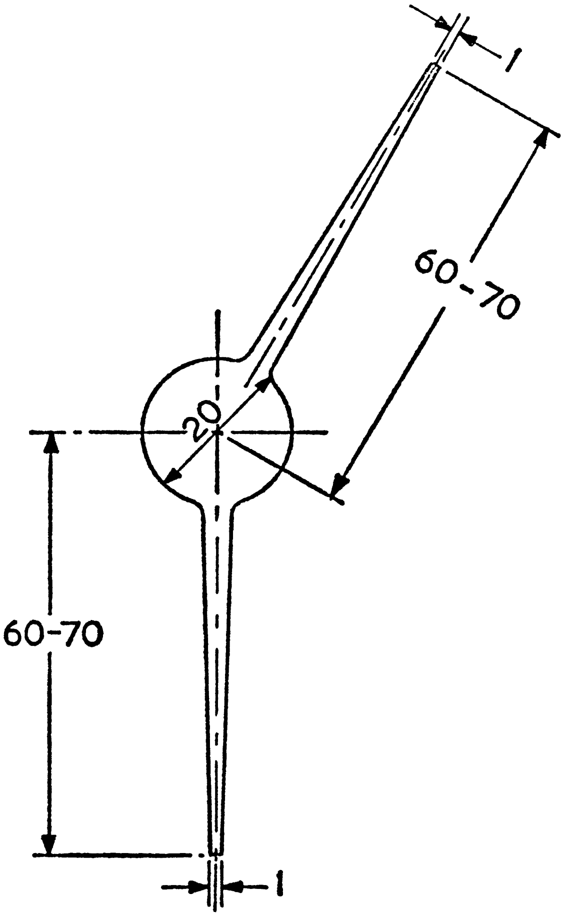
For each test give the following indications:

1) the reference of the method used;

2) the results and the method of expression used;

3) any unusual features noted during the determination;

4) any operation not laid down in this standard or regarded as optional.



All dimensions in millimetres

Figure 1 — Glass ampoule

blank

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