

Methods of test for

Sulphuric acid, oleum and liquid sulphur trioxide

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- Chemical Industries Association*
- Chemical Society — Analytical Division
- Department of Health and Social Security
- Department of Industry
- Department of Industry — Laboratory of the Government Chemist
- Fertilizer Manufacturers' Association Ltd
- Ministry of Agriculture, Fisheries and Food
- National Sulphuric Acid Association*
- Royal Institute of Public Health and Hygiene
- Soap and Detergent Industry Association*
- Society for Analytical Chemistry

The 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:

British Textile Employers' Association

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Foreword

This British Standard has been prepared under the authority of the Chemical Standards Committee and includes methods of test for sulphuric acid, oleums and liquid sulphur trioxide of commercial quality and intended for general industrial purposes.

The standard, first published in 1965, has been revised in the light of current requirements. Where possible, methods adopted by the International Organization for Standardization (ISO) have been used and the situation in this respect is summarized as tabulated opposite.

This revision also differs from the 1965 publication in the following respects.

- a) Methods for the determination of density and temperature rise are omitted following the decision that only the titrimetric method for the determination of sulphuric acid content should be used for referee purposes.
- b) The methods for the determination of copper and aluminium contents, which are seldom used, are omitted.
- c) In accordance with current practice, alternative methods for the determination of iron and lead contents by atomic absorption spectrophotometry are included. The original methods in the 1965 publication are, however, retained and have undergone no significant change in the course of the revision.

WARNING. Concentrated sulphuric acid, oleum and sulphur trioxide are extremely corrosive and poisonous and should be used with all necessary precautions. Protective clothing, including goggles and gloves, should be worn at all times when handling these materials.

Determination	Relationship to ISO method of test
Residue on heating	Heating temperature is identical with that used in ISO/R 913
Sulphur dioxide content	Conforms to the method specified in ISO 3423 amended to incorporate comments made by the United Kingdom during its development
Arsenic content	Conforms to the method specified in ISO 2590
Ammoniacal nitrogen content	Conforms to the method specified in ISO 2899
Nitrogen oxides content	Conforms to the method specified in ISO 2363
Chloride content	Conforms to the method specified in ISO 2877
Iron content (spectrophotometric method)	Is similar in principle to the method specified in ISO/R 915
Lead content (spectrophotometric method)	Conforms to the method specified in ISO 2717

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Summary of pages

This document comprises a front cover, an inside front cover, pages i and ii, pages 1 to 24, 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.

Section 1. General

1 Scope

This British Standard specifies methods of test for commercial sulphuric acid, oleum and liquid sulphur trioxide. Section 2 covers tests for acids containing up to 100 % of H_2SO_4 . Section 3 describes methods of test for oleums and liquid sulphur trioxide and includes a method for their dilution prior to analysis by the methods specified in section 2, clauses 5 to 9.

2 References

The titles of the publications referred to in this standard are listed on the inside back cover.

Section 2. Methods of test for acids containing up to 100 % of H_2SO_4

3 Determination of sulphuric acid content

NOTE This method differs from that specified in ISO/R 910 which was disapproved for technical reasons by the United Kingdom.

3.1 Principle. A weighed quantity of the sample is diluted with water and titrated directly with standard volumetric sodium hydroxide solution using screened methyl orange as indicator.

3.2 Reagents. The reagents used shall be of a recognized analytical quality. Water complying with the requirements of BS 3978 shall be used throughout.

3.2.1 Sodium hydroxide, N standard volumetric solution.

3.2.2 Screened methyl orange indicator solution, 1 g/l, prepared as described in BS 4123.

3.3 Apparatus. Ordinary laboratory apparatus and the following are required.

3.3.1 Lunge-Rey pipette, complying with the requirements of BS 2058.

3.3.2 Bulb burette, 105 ml nominal capacity, complying with the requirements of BS 846, having a bulb capacity of 80 ml and a scale range from 80 ml to 105 ml with 0.05 ml subdivisions.

3.4 Procedure. By means of the Lunge-Rey pipette (3.3.1), transfer a quantity of sample equivalent to 4.5 g to 5 g of 100 % sulphuric acid, weighed to the nearest 1 mg, to a 400 ml conical beaker already containing 50 ml of water. Add a few drops of the screened methyl orange indicator solution (3.2.2) and titrate with the N sodium hydroxide solution (3.2.1), contained in the bulb burette (3.3.2), until the first appearance of a green tint.

3.5 Expression of results. Sulphuric acid content, expressed as a percentage by mass of H_2SO_4 , is given by the formula:

$$\frac{4.904 \times V}{M}$$

where

V is the volume of N sodium hydroxide solution used (in ml)

M is the mass of the test portion (in g)

4 Determination of residue on heating

NOTE This method uses the heating temperature specified in ISO/R 913.

4.1 Field of application. The method is applicable to samples in which the residue on heating is equal to or greater than 5 mg/kg.

4.2 Principle. The sample is evaporated and the residue is heated at $800 \pm 50^\circ\text{C}$.

4.3 Apparatus. Ordinary laboratory apparatus and the following are required.

4.3.1 Platinum basin, flat bottom, capacity about 100 ml.

4.3.2 Muffle furnace, capable of being controlled at $800 \pm 50^\circ\text{C}$.

4.3.3 Desiccator

4.4 Procedure. Heat the platinum basin (4.3.1) in the muffle furnace (4.3.2) controlled at 800 ± 50 °C. Cool in the desiccator (4.3.3) and weigh to the nearest 0.1 mg. Transfer to the basin approximately 50 g of sample weighed to the nearest 0.01 g.

Evaporate the acid carefully on a sand bath inside a fume cupboard and heat the basin containing the residue to dryness. Transfer the basin containing the residue to the muffle furnace controlled at 800 ± 50 °C and heat for about 15 min. Remove the basin from the furnace, place in a desiccator, cool and weigh to the nearest 0.1 mg. Repeat the operations of heating, cooling and weighing until the difference between successive weighings does not exceed 0.5 mg.

4.5 Expression of results. The residue on heating, expressed as milligrams per kilogram, is given by the formula:

$$\frac{M_1 \times 10^6}{M_2}$$

where

M_1 is the mass of the residue (in g)

M_2 is the mass of the test portion (in g)

5 Determination of sulphur dioxide content

NOTE This method conforms to that specified in ISO 3423 as amended to incorporate the comments made by the United Kingdom during its development.

5.1 Field of application. The method is applicable to products with sulphur dioxide content equal to or greater than 2 mg/kg.

5.2 Principle. Sulphur dioxide is removed from the sample by means of a current of nitrogen and absorbed into a known volume of iodine solution. The excess iodine is titrated against standard volumetric sodium thiosulphate solution.

5.3 Reagents. The reagents used shall be of a recognized analytical quality. Water complying with the requirements of BS 3978 shall be used throughout.

5.3.1 Hydrazinium sulphate

5.3.2 Iodine, approximately 0.1N, 0.05N or 0.01N solution, as required (see 5.5.3). Prepare this solution at the time of use.

5.3.3 Sodium thiosulphate, 0.1N, 0.05N or 0.01N standard volumetric solution, as required (see 5.5.4). Prepare this solution at the time of use.

5.3.4 Starch, 5 g/l solution.

5.3.5 Nitrogen, pure, containing less than 0.001 % of oxygen.

It is recommended that the reduction valve from the nitrogen cylinder be connected to a gas-washing bottle containing a 150 g/l solution of titanium (III) chloride.

5.3.6 Crushed ice, prepared from water complying with the requirements of BS 3978.

5.4 Apparatus. Ordinary laboratory apparatus and the following are required.

5.4.1 Glass apparatus, with ground glass joints, as shown in Figure 1, comprising the following:

- 3-necked flask (A), 500 ml or 250 ml capacity;
- cylindrical dropping funnel (B) fitting into one of the two side-necks of the flask;
- tube, fitted with a stopcock (C), fitting into the central neck of the flask and terminating in a fritted disc at a level of about 10 mm above the bottom of the flask;
- three gas-washing bottles (D_1), (D_2), (D_3), Dreschel type, 100 ml or 125 ml capacity, with the inlet tubes terminating in fritted discs complying with the requirements of BS 1752 (grade no. 4, pore diameter $5 \mu\text{m}$ to $15 \mu\text{m}$) to disperse the gas.

NOTE The corresponding ISO method uses fritted discs of grade P16, pore diameter $4 \mu\text{m}$ to $16 \mu\text{m}$.

5.4.2 Glass flask, with a ground glass stopper.

5.4.3 Flowmeter or bubble-counter, for use in the range 5 l/h to 50 l/h.

5.5 Procedure

5.5.1 Test portion. Fill the flask (5.4.2) with the test sample and take, weighing by difference to the nearest 0.05 g, a test portion of approximately 200 g.

If the density of the sample exceeds 1.70 g/ml, slowly pour the test portion, cooling so that the temperature remains below 10 °C, onto sufficient of the crushed ice (5.3.6) to give a solution of density approximately 1.70 g/ml.

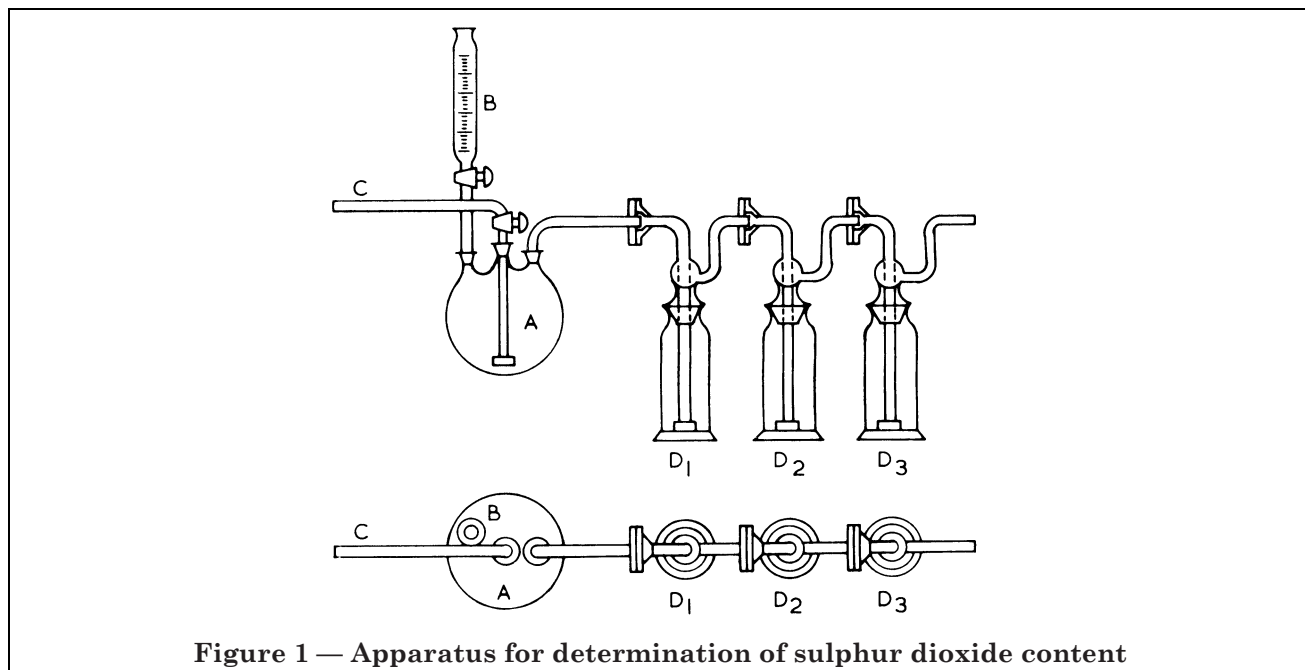


Figure 1 — Apparatus for determination of sulphur dioxide content

5.5.2 Blank test. At the same time as the determination, carry out a blank test following the same procedure and using the same quantities of all reagents as used in the determination.

5.5.3 Preparation of the apparatus. Place 50 ml of the appropriate iodine solution (5.3.2) in the first gas-washing bottle (D_1). Divide 25 ml of the corresponding standard volumetric sodium thiosulphate solution (5.3.3) between the second and third gas-washing bottles (D_2 , D_3), if necessary adding a little water to ensure sufficient scrubbing of the gas.

Expected sulphur dioxide content	Strength of iodine solution
mg/kg	N (approximate)
2 to 30	0.01
30 to 150	0.05
> 150	0.1

NOTE The two bottles (D_2) and (D_3) are intended to retain any entrained iodine.

Place the bottle (D_1) in a cooling bath and ensure that during all subsequent operations the temperature of its contents does not rise above 10 °C and that the bottle is not exposed to a bright light.

If the sample contains nitrite or nitrate ions, place an excess of the hydrazinium sulphate solution (5.3.1) in the flask (A) in relation to the nitrite and nitrate contents in the test portion. Connect up the apparatus (5.4.1) and displace the air by means of a rapid current of the nitrogen (5.3.5).

5.5.4 Determination. Run the test portion (5.5.1) into the flask (A) through the dropping funnel (B) and pass a current of the nitrogen (5.3.5) at a rate, measured by the flowmeter or bubble-counter (5.4.3), of about 20 l/h for 3 h. At the end of this time there should still be an excess of iodine in the gas-washing bottle (D_1).

Disconnect the three gas-washing bottles (D_1), (D_2) and (D_3) and transfer their contents quantitatively into a beaker. Rinse the bottles with a few millilitres of water, collecting the washings in the beaker. Titrate the excess of iodine with the appropriate standard volumetric sodium thiosulphate solution (5.3.3) in the presence of the starch solution (5.3.4).

5.6 Expression of results. The sulphur dioxide content, expressed as milligrams of sulphur dioxide (SO_2) per kilogram, is given by the formula:

$$\frac{32 \times T \times 1000}{M} [(50.00 - 25.00 - V_1) - (50.00 - 25.00 - V_0)] = \frac{32\,000 \times T(V_0 - V_1)}{M}$$

where

V_0 is the volume of the standard volumetric sodium thiosulphate solution (5.3.3) used for the blank test (in ml)

V_1 is the volume of the standard volumetric sodium thiosulphate solution (5.3.3) used for the determination (in ml)

M is the mass of the test portion (in g)

T is the exact normality of the sodium thiosulphate solution used (5.3.3)

32 5.6.1 is the mass of sulphur dioxide (SO_2) corresponding to 1 ml of exactly 1N standard volumetric sodium thiosulphate solution (in mg)

6 Determination of arsenic content

NOTE This method conforms to that specified in ISO 2590, which corresponds to BS 4404.

6.1 Field of application. The method is applicable to the determination of arsenic in the range 1 mg to 10 mg of arsenic per kilogram.

6.2 Principle. The arsenic in the sample is reduced with zinc, the arsine evolved is absorbed in a solution of silver diethyldithiocarbamate in pyridine and the absorbance of the complex is measured spectrophotometrically. A test solution is prepared and tested by the method described in BS 4404.

6.3 Reagents and apparatus. As described in BS 4404.

6.4 Procedure

6.4.1 Preparation of test solution. Transfer 7 ml of the concentrated hydrochloric acid [5.2(1) of BS 4404] into a 50 ml graduated cylinder and add 25 ml of water. Add from a Lunge-Rey pipette (see BS 2058) a volume of sample equivalent to 1 ± 0.1 g of 100 % sulphuric acid and dilute to 50 ml with water.

6.4.2 Arsine evolution. Transfer the contents of the graduated cylinder to the 100 ml conical flask [4.1(1) of BS 4404]. To the contents of the conical flask add the potassium iodide and stannous chloride solutions as described in 6.1.1 of BS 4404 and proceed as for that method.

6.4.3 Blank test. At the same time as the determination, carry out a blank test following the same procedure as 6.4.1 but add 1 g of the sulphuric acid [5.2(2) of BS 4404:1968] instead of the test portion.

6.5 Expression of results. Obtain the corrected arsenic content M_1 from the calibration graph (6.1 of BS 4404:1968). The arsenic content of the sample, expressed as milligrams of arsenic per kilogram of sample, is given by the following formula:

$$\frac{M_1}{M_2}$$

where

M_1 is the mass of arsenic found in the sample (in μg)

M_2 is the mass of the test portion (in g)

7 Determination of ammoniacal nitrogen content

NOTE This method conforms to that specified in ISO 2899.

7.1 Field of application. The method is applicable to the determination of ammoniacal nitrogen content in the range 1 mg to 5 mg of nitrogen per kilogram.

7.2 Principle. The ammonia present in the sample is distilled in the presence of an excess of sodium hydroxide and the distillate is collected in excess acid. The excess acid is neutralized and a coloured complex is formed by treatment with sodium hydroxide, phenol and sodium hypochlorite in the presence of acetone. The indophenol obtained is determined spectrophotometrically at a wavelength of approximately 630 nm.

7.3 Reagents. The reagents used shall be of a recognized analytical quality. Water complying with the requirements of BS 3978, and of which the ammoniacal nitrogen content is negligible, shall be used throughout.

7.3.1 Ammonia-free ice, prepared from water (7.3).

7.3.2 Sodium hydroxide, 350 g/l solution, previously boiled for 20 min to remove traces of ammoniacal nitrogen. Make up to original volume.

7.3.3 Sulphuric acid, 0.1N standard volumetric solution.

7.3.4 Sodium hydroxide, N standard volumetric solution.

7.3.5 Sodium hydroxide, 0.1N standard volumetric solution.

7.3.6 Acetone

7.3.7 Sodium phenoxide reagent solution. Dissolve 62.5 g of phenol in 18.5 ml of the acetone (7.3.6), dilute to 100 ml with 95 % (v/v) ethanol¹⁾ and mix.

Store this solution in the dark, preferably in a refrigerator.

Dissolve 27 g of sodium hydroxide in 100 ml of water.

When required, prepare the reagent by mixing 20 ml of each solution and diluting to 100 ml with water.

7.3.8 Sodium hypochlorite reagent solution, 10 g/l available chlorine. Dilute with water a stock sodium hypochlorite solution containing preferably 100 g/l to 140 g/l of available chlorine (do not use a sodium hypochlorite solution containing less than 80 g/l of available chlorine). Standardize this solution weekly by the method specified in BS 4426.

Keep this solution in a cool place away from direct sunlight. The solution remains usable for about four weeks.

7.3.9 Ammonium chloride stock solution, corresponding to 1 g of ammoniacal nitrogen per litre. Dissolve in a little water 3.819 g of ammonium chloride, previously dried at 100 °C and cooled in a desiccator, transfer to a 1 000 ml one-mark volumetric flask and dilute to the mark with water.

1 ml of this solution contains 1 mg of ammoniacal nitrogen. Replace the solution at least once a month.

¹⁾ Ethanol may be replaced for this purpose by industrial methylated spirits, 66 degrees O.P., complying with the requirements of BS 3591. It should be noted that the use of industrial methylated spirits is governed by The Methylated Spirits Regulations, 1952 (S.I. 1952, No. 2230). It is not permissible to use duty-free ethanol, received under the provisions of the Customs and Excise Act 1952, Section 111, for purposes for which industrial methylated spirits is an acceptable alternative to ethanol.