BRITISH STANDARD

BS 506-2:
1984

Incorporating
Amendment No. 1

Methanol for industrial use —

Part 2: Methods of test

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Committees responsible for this British Standard

The preparation of this British Standard was entrusted by the Chemicals Standards Committee (CIC/-) to Technical Committee CIC/4 upon which the following bodies were represented:

Chemical Industries Association
Ministry of Defence
Oil and Colour Chemists' Association
Royal Society of Chemistry
Society of Chemical Industry

The following bodies were also represented in the drafting of the standard, through subcommittees and panels:

British Pharmacopoeia Commission
British Society of Perfumers
Cosmetic, Toiletry and Perfumers Association Limited
Department of Industry (Laboratory of the Government Chemist)

This British Standard, having been prepared under the direction of the Chemicals Standards Committee, was published under the authority of the Board of BSI and comes into effect on 30 March 1984

The following BSI references relate to the work on this standard:
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Contents

Foreword

This Part of this British Standard has been prepared under the direction of the Chemicals Standards Committee and provides a comprehensive series of test methods for methanol for industrial use. Although applicable to the material in general, it includes all the test methods required to assess compliance with BS 506-1.

This Part of this standard is based on ISO 1387:1982 "*Methanol for industrial use — Methods of test*". ISO 1387, which constitutes the revision of ISO Recommendation R 1387, has been prepared with the active participation of the UK by Technical Committee 47, Chemistry, of the International Organization for Standardization (ISO).

With the following exceptions the technical content of this Part of this standard agrees with ISO 1387.

a) The method for the determination of methyl ketones has been omitted as a consequence of its disapproval by the UK on technical grounds.

b) References in the text to International Standards have been replaced by references to the corresponding British Standards.

c) Hazard warnings have been included in respect of methanol and 2,4-dinitrophenylhydrazine.

d) To conform with UK practice, additional ways have been given in **11.6** and **12.6** for expressing the carbonyl compounds content as a percentage by mass of acetone.

e) A method for determination of sulphur compounds is included in this Part of this standard but not in ISO 1387.

ISO 1387 records UK disapproval of the method for determination of permanganate time. It is, however, now acceptable to the UK as a consequence of alterations made to the published text and has therefore been included in this Part of this standard.

For ease of production, it has been found convenient to reproduce the text of ISO 1387, which has been amended to incorporate the differences outlined above. Some terminology and certain conventions are not identical with those used in British Standards; attention is drawn especially to the following.

The comma has been used as a decimal marker. In British Standards it is current practice to use a full point on the baseline as the decimal marker.

In British Standards it is current practice to use the symbol "L" for litre (and in its submultiples), rather than "l".

NOTE 1 It is not permissible to use duty-free ethanol, received under the provisions of The Alcoholic Liquors Duties Act 1979, Section 10, for purposes for which industrial methylated spirits is an acceptable alternative to ethanol. In such circumstances the ethanol used as a reagent in a determination may be replaced for this purpose by industrial methylated spirits, 95 % (*V*/*V*), complying with BS 3591. It should be noted that the use of industrial methylated spirits is governed by The Methylated Spirits Regulations 1983 (S.I. 1983, No. 252).

NOTE 2 Unless otherwise stated, water complying with the requirements of these determinations is specified in BS 3978 "*Water for laboratory use*".

This Part of this standard specifies methods of test only and should not be used as a specification defining limits of purity. Reference to this Part of this standard should indicate that the methods of test used are in accordance with the appropriate clause(s) of BS 506-2.

Summary of pages

This document comprises a front cover, an inside front cover, pages i to iv, pages 1 to 10, 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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WARNING. Methanol is toxic and can have poisonous effects if drunk, inhaled or absorbed through the skin. Strict precautions should always be observed and, in particular, any pipettes used should be of the safety bulb type.

1 Scope and field of application

This British Standard gives general instructions and describes methods of test for the analysis of methanol for industrial use.

The methods of test relating to methanol for industrial use are the following:

— Determination of density at 20 °C
— Determination of residue on evaporation on a water bath
— Measurement of colour
— Determination of distillation range
— Determination of water content
— Detection of the alkalinity or determination of the acidity to phenolphthalein
— Estimation of content of carbonyl compounds present in small amounts — Spectrometric method
— Estimation of content of carbonyl compounds present in moderate amounts — Titrimetric method
— Test for miscibility with water
— Determination of permanganate time
— Determination of sulphur compounds

2 References

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

General instructions

3 Sampling[1]

Place the laboratory sample in the dark, in a clean, dry and airtight, ground glass stoppered bottle or a screw-capped bottle fitted with a polyethylene cone insert of such capacity that it is almost filled by the sample. If it is necessary to seal the bottle, care shall be taken to avoid contaminating the contents in any way.

NOTE 1 Sufficient ullage should be left in the bottle to avoid excessive pressure changes that could arise from temperature variations during storage and handling. About 10 % ullage is recommended.

NOTE 2 A sample of not less than 1 000 ml is necessary for performing all the tests described in this standard.

4 Test report

The test report, for each determination, shall contain the following particulars:

a) an identification of the sample;

b) the reference of the method used;

c) the results and the method of expression used;

d) any unusual features noted during the determination;

e) any operation not included in this British Standard or in the British Standards to which reference is made, or regarded as optional.

Methods of test

5 Determination of density at 20 °C

Use the method specified in BS 4522.

6 Determination of residue on evaporation on a water bath

Use the method specified in BS 4524.

7 Measurement of colour

Use the method specified in BS 5339.

8 Determination of the distillation range

Use the method specified in BS 4591:1971 with the following modifications appropriate to methanol.

8.1 Thermometer (see BS 4591, clause 3.2)

Use a thermometer complying with the requirements of BS 4591 suitable for measuring temperatures in the range 24 to 78 °C.

8.2 Corrections to be applied to temperatures

If the corrected barometric pressure deviates from 1 013 mbar[2], apply a correction to the observed temperature by subtracting 0,025 °C for every millibar above, or adding 0,025 °C for every millibar below, 1 013 mbar.

9 Determination of water content

Use one of the methods specified in BS 2511.

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[1] Additional guidance on sampling is given in BS 5309-1 and BS 5309-3.

[2] 1 bar = 10^5 Pa

10 Detection of alkalinity or determination of acidity to phenolphthalein

10.1 Applicability

The method is applicable to products having acidities, expressed as formic acid (HCOOH), greater than or equal to 0,000 8 % (*m*/*m*).

10.2 Principle

Dilution of a test portion with carbon dioxide-free water.

Checking whether the test solution is alkaline or acid to phenolphthalein, and, if appropriate, determination of the acidity by titration with standard volumetric sodium hydroxide solution.

10.3 Reagents

During the analysis, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity, carbon dioxide-free, recently prepared.

10.3.1 *Water*, carbon dioxide-free.

Boil distilled water and allow it to cool in a flask fitted with a stopper carrying a soda-lime guard-tube.

10.3.2 *Sodium hydroxide*, standard volumetric solution, $c(\mathrm{NaOH}) = 0{,}1$ mol/l.

10.3.3 *Phenolphthalein*, 5 g/l ethanolic solution.

Dissolve 0,5 g of phenolphthalein in 100 ml of 95 % (*V*/*V*) ethanol and add the sodium hydroxide solution (**10.3.2**) until a pale pink coloration is obtained.

10.4 Apparatus

Ordinary laboratory apparatus, and

10.4.1 *Conical flask*, of borosilicate glass, of capacity 500 ml, fitted with a ground glass stopper carrying a soda-lime guard-tube.

10.4.2 *Burette*, of capacity 10 ml, graduated in 0,02 ml.

10.5 Procedure

10.5.1 *Test portion*

Take 100 ± 0,1 ml of the laboratory sample (see clause **3**).

10.5.2 *Determination*

Place 100 ml of the water (**10.3.1**) in the conical flask (**10.4.1**), add 0,5 ml of the phenolphthalein solution (**10.3.3**) and restore the pale pink coloration by the addition of 1 or 2 drops of the sodium hydroxide solution (**10.3.2**). Add the test portion (**10.5.1**) and a further 0,5 ml of the phenolphthalein solution (**10.3.3**) and note whether the solution is alkaline; if acid, titrate the test solution with the sodium hydroxide solution (**10.3.2**), stoppering the flask and swirling its contents after each addition, until a pink coloration, persisting for about 15 s, is obtained. Shake the contents of the flask, with the stopper in position, after each addition of sodium hydroxide solution.

10.6 Expression of results

10.6.1 *Alkaline products*

Indicate whether the product is alkaline to phenolphthalein.

10.6.2 *Acidic products*

The acidity, expressed as a percentage by mass of formic acid (HCOOH), is given by the formula

$$\frac{0{,}004\,6 \times V}{\varrho}$$

where

V is the volume, in millilitres, of the sodium hydroxide solution (**10.3.2**) used for the determination;

ϱ is the density, in grams per millilitre, of the sample at 20 °C (see clause **5**);

0,004 6 is the mass, in grams, of formic acid corresponding to 1,00 ml of sodium hydroxide solution, $c(\mathrm{NaOH}) = 0{,}100$ mol/l.

NOTE If the concentration of the standard volumetric solution used is not exactly as specified in the list of reagents, an appropriate correction should be made.

11 Estimation of content of carbonyl compounds present in small amounts — Spectrometric method

11.1 Applicability

The method is applicable to products having carbonyl compounds contents, expressed as formaldehyde, between 0,000 2 and 0,01 % (*m*/*m*).

NOTE This method, which is used commercially, allows determination of only those carbonyl compounds which react under the specified conditions.

11.2 Principle

Reaction in acid medium of the carbonyl compounds in a test portion with 2,4-dinitrophenylhydrazine. Formation of the corresponding 2,4-dinitrophenylhydrazones, which, after making the solution alkaline, take on a yellowish-red coloration.

Spectrometric measurement of this red coloration at a wavelength of about 445 nm.

11.3 Reagents

During the analysis, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

11.3.1 *Methanol*, free from carbonyl compounds, purified as follows.

Boil under reflux 1 000 ml of methanol with 10 g of 2,4-dinitrophenylhydrazine and 10 drops of the hydrochloric acid solution (**11.3.3**), for 2 to 3 h. Distil the methanol slowly using a Widmer distillation column, about 300 mm long and about 25 mm in diameter, or any other suitable column. Reject the first 75 ml of distillate and collect the next 850 ml, rejecting the remainder. If the distillate is coloured, redistil it.

11.3.2 *2,4-Dinitrophenylhydrazine*, saturated solution in the methanol (**11.3.1**) at ambient temperature [about 0,06 % (*m*/*m*) solution].

WARNING. 2,4-dinitrophenylhydrazine specified in 11.3.1 and 11.3.2 is harmful if inhaled, if in contact with skin or eyes, or if swallowed and carries the risk of explosion by shock, friction, heat or by other sources of ignition, particularly when dry. Inhalation of dust and contact with skin and eyes should be avoided. Particular care should be taken when using the dry material.

11.3.3 *Hydrochloric acid*, ϱ approximately 1,19 g/ml, about 38 % (*m*/*m*) solution.

11.3.4 *Potassium hydroxide*, 100 g/l solution in a 70 % (*V*/*V*) solution of the methanol (**11.3.1**).

11.3.5 *Carbonyl compounds*, standard solution corresponding to 0,030 g of carbonyl compounds, expressed as formaldehyde, per litre.

Weigh, to the nearest 0,000 1 g, 1,200 g of acetophenone, and dissolve it in a little of the methanol (**11.3.1**). Transfer quantitatively to a 100 ml one-mark volumetric flask, dilute to the mark with the methanol and mix. Take 5,0 ml of this solution, transfer it to a 500 ml one-mark volumetric flask, dilute to the mark with the methanol (**11.3.1**) and mix.

1 ml of this standard solution contains 30 µg of carbonyl compounds, expressed as formaldehyde.

11.4 Apparatus

Ordinary laboratory apparatus, and

11.4.1 *Water bath*, capable of being controlled at 50 ± 2 °C.

11.4.2 *Test tubes*, fitted with ground glass stoppers.

11.4.3 *Spectrometer with a radiation selector for continuous variation*, fitted with cells of optical path length 1 cm, or

11.4.4 *Spectrometer with a radiation selector for discontinuous variation*, fitted with filters providing maximum transmission at a wavelength of about 445 nm.

11.5 Procedure

11.5.1 *Test portion*

Take 1,0 ml of the laboratory sample (see clause **3**) and place it in one of the test tubes (**11.4.2**).

11.5.2 *Blank test*

Carry out a blank test at the same time as the determination, following the same procedure and using the same quantities of all the reagents used for the determination, but replacing the test portion by 1,0 ml of the methanol (**11.3.1**).

11.5.3 *Preparation of the calibration graph*

11.5.3.1 Preparation of dilute standard solutions, with a view to preparation of standard colorimetric solutions

Into a series of seven 25 ml one-mark volumetric flasks, introduce the volumes of the standard carbonyl compounds solution (**11.3.5**) indicated in the following table and dilute to the mark with the methanol (**11.3.1**).

Standard carbonyl compounds solution (11.3.5)	Corresponding mass of carbonyl compounds, expressed as HCHO	Mass of carbonyl compounds in 1 ml of dilute standard solution
ml	µg	µg
0[a]	0	0
1,5	45,0	1,8
2,5	75,0	3,0
5,0	150,0	6,0
7,5	225,0	9,0
10,0	300,0	12,0
12,5	375,0	15,0

[a] Compensation solution.

11.5.3.2 Preparation of standard colorimetric solutions, for spectrometric measurements carried out in cells of optical path length 1 cm

Into a series of seven of the test tubes (**11.4.2**), place 1,0 ml of each of the dilute standard solutions (**11.5.3.1**) and treat the contents of each tube according to the procedure specified in **11.5.3.3**.

11.5.3.3 *Colour development*

Add 1,0 ml of the 2,4-dinitrophenylhydrazine solution (**11.3.2**) and one drop of the hydrochloric acid solution (**11.3.3**). Stopper the tubes and heat for 30 min using the water bath (**11.4.1**), controlled at 50 ± 2 °C. Allow to cool, add 5,0 ml of the potassium hydroxide solution (**11.3.4**), mix, and allow to stand for 5 min.

11.5.3.4 *Spectrometric measurements*

Immediately carry out the spectrometric measurements on each of the standard colorimetric solutions, using either the spectrometer (**11.4.3**), set at a wavelength of about 445 nm, or the spectrometer (**11.4.4**) fitted with appropriate filters, after having first adjusted the instrument to zero absorbance against the methanol (**11.3.1**).

11.5.3.5 *Plotting the graph*

Deduct the absorbance of the compensation solution from those of the standard colorimetric solutions (**11.5.3.3**). Plot a graph having, for example, the masses, in micrograms, of carbonyl compounds, expressed as HCHO, in 1 ml of each dilute standard solution (**11.5.3.1**) as abscissae, and the corresponding corrected values of absorbance as ordinates.

11.5.4 ***Determination***

11.5.4.1 *Colour development*

Treat the test portion (**11.5.1**) in the test tube, following the procedure specified in **11.5.3.3**.

11.5.4.2 *Spectrometric measurements*

Immediately carry out the spectrometric measurements on the coloured test solution and the blank test solution following the procedures specified in **11.5.3.4**, after having adjusted the instrument to zero absorbance against the methanol (**11.3.1**).

NOTE If the absorbance exceeds the maximum of the calibration graph, repeat the determination (**11.5.4**) using as the test portion 1,0 ml of a test solution prepared by diluting 1,0 ml of the laboratory sample with an appropriate volume (not more than 4,0 ml) of the methanol (**11.3.1**).

11.6 Expression of results

By means of the calibration graph (**11.5.3.5**), determine the masses of carbonyl compounds corresponding to the values of the spectrometric measurements.

The carbonyl compounds content, expressed as a percentage by mass of formaldehyde (HCHO), is given by the formula

$$\frac{(m_1 - m_0) \times 100}{1{,}0 \times \varrho \times 10^6} \times r_D$$

$$= \frac{m_1 - m_0}{\varrho \times 10^4} \times r_D$$

where

m_0 is the mass, in micrograms, of carbonyl compounds found in the blank test solution (**11.5.2**);

m_1 is the mass, in micrograms, of carbonyl compounds found in the test solution;

ϱ is the density, in grams per millilitre, of the sample at 20 °C (see clause **5**);

r_D is the ratio of the volume of the diluted test solution (see the note to **11.5.4.2**) to the volume of the aliquot portion taken for the determination (if the test portion was not diluted, r_D is equal to 1);

1,0 s the volume, in millilitres, of the test portion (**11.5.1**).

The results can also be expressed as a percentage by mass of acetone [$(CH_3)_2CO$] by multiplying the above results by 1,93.

12 Estimation of content of carbonyl compounds present in moderate amounts — Titrimetric method

12.1 Applicability

The method is applicable to products having carbonyl compounds contents, expressed as formaldehyde, greater than or equal to 0,01 % (*m*/*m*).

NOTE This method, which is used commercially, allows determination of only those carbonyl compounds which react under the specified conditions.

12.2 Principle

Reaction of hydroxylammonium chloride with the carbonyl compounds present in a test portion and titration of the hydrochloric acid formed with a standard volumetric sodium hydroxide solution in the presence of bromophenol blue as indicator.

12.3 Reagents

During the analysis, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

12.3.1 *Hydroxylammonium chloride reagent*

WARNING — Corrosive and irritating. Avoid contact with eyes and skin.

Dissolve 4 g of hydroxylammonium chloride in 20 ml of water and dilute to 200 ml with 95 % (*V*/*V*) ethanol. Heat under reflux for 30 min on a boiling water bath, cool to ambient temperature, add 5 ml of the bromophenol blue solution (**12.3.4**) and just sufficient of the sodium hydroxide solution (**12.3.2**) to produce a dichroic green coloration.

12.3.2 *Sodium hydroxide*, standard volumetric solution, $c(\mathrm{NaOH}) = 0{,}1$ mol/l.

12.3.3 *Hydrochloric acid*, approximately 4 g/l solution.

12.3.4 *Bromophenol blue*, 2 g/l ethanolic solution.

Dissolve 0,2 g of bromophenol blue in 1,5 ml of the sodium hydroxide solution (**12.3.2**) and dilute to 100 ml with 95 % (*V*/*V*) ethanol.

12.4 Apparatus

Ordinary laboratory apparatus and

12.4.1 *Conical flasks*, of capacity 250 ml, fitted with ground glass stoppers.

12.5 Procedure

12.5.1 *Test portion*

Take 50 ± 0,1 ml of the laboratory sample (see clause **3**) by means of a safety pipette and place it into one of the conical flasks (**12.4.1**).

12.5.2 *Determination*

Place 50 ml of the hydroxylammonium chloride reagent (**12.3.1**) in a second conical flask (**12.4.1**), to be used as the colour standard.

Add 1,25 ml of the bromophenol blue solution (**12.3.4**) to the flask containing the test portion (**12.5.1**) and add, drop by drop, either the sodium hydroxide solution (**12.3.2**) or the hydrochloric acid solution (**12.3.3**) until the colour matches that of the colour standard. Then add, to each of the flasks, 25 ml of the hydroxylammonium chloride reagent (**12.3.1**) and stopper the flask containing the colour standard.

Loosely stopper the flask containing the test solution and heat it for 10 min on a boiling water bath. Remove the flask from the water bath, cool to ambient temperature and titrate the solution with the sodium hydroxide solution (**12.3.2**) until the colour matches as closely as possible that of the colour standard.

12.6 Expression of results

The carbonyl compound content, expressed as a percentage by mass of formaldehyde (HCHO), is given by the formula

$$\frac{0{,}003\,0 \times V \times 100}{50 \times \varrho}$$

$$= \frac{0{,}006\,0\,V}{\varrho}$$

where

V is the volume, in millilitres, of the sodium hydroxide solution (**3.2**) used for the determination;

ϱ is the density, in grams per millilitre, of the sample at 20 °C (see clause **5**);

0,003 0 is the mass, in grams, of carbonyl compounds, expressed as formaldehyde, corresponding to 1,00 ml of sodium hydroxide solution, $c(\mathrm{NaOH}) = 0{,}100$ mol/l sodium hydroxide solution;

50 is the volume, in millilitres, of the test portion (**12.5.1**).

The results can also be expressed as a percentage by mass of acetone [$(\mathrm{CH_3})_2\mathrm{CO}$] by multiplying the above results by 1,93.

NOTE If the concentration of the standard volumetric solution used is not exactly as specified in the list of reagents, an appropriate correction should be made.

13 Test for miscibility with water

13.1 Principle

Addition of water to a test portion, under specified conditions, and examination for opalescence.

13.2 Reagent

During the analysis, use only distilled water or water of equivalent purity.

13.3 Apparatus

Ordinary laboratory apparatus, and

13.3.1 *Two matched Nessler cylinders,* of capacity 100 ml.

13.4 Procedure

13.4.1 *Test portion*

Take 5 ml of the laboratory sample (see clause **3**) or a different volume agreed between the interested parties.

13.4.2 ***Test***

Place the test portion (**13.4.1**) in one of the Nessler cylinders (**13.3.1**), and dilute with water to the 100 ml mark. Mix and adjust the temperature to about 20 °C. Place 100 ml of water in the other Nessler cylinder.

Examine the cylinder containing the test solution vertically for opalescence, against a black background with side illumination, using the second Nessler cylinder containing water as the standard.

13.5 Expression of results

Report the dilution-ratio of the test portion and the presence or absence of opalescence.

14 Determination of permanganate time

14.1 Definition

permanganate time
the number of minutes required, after adding 2 ml of 0,2 g/l potassium permanganate solution to 50 ml of the sample, for the colour to match that of a colour standard

14.2 Principle

Addition to a test portion, under specified conditions, of potassium permanganate solution. Determination of the time taken for the colour of this test solution to match that of a cobalt(II) chloride and uranyl nitrate colour standard.

14.3 Reagents

During the analysis, unless otherwise stated, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

14.3.1 *Potassium permanganate,* 0,2 g/l solution.

Use water previously boiled for 30 min with sufficient dilute potassium permanganate solution to give a stable faint pink coloration. Cool the water to ambient temperature before preparation of the solution.

Prepare this solution immediately before use and protect it from light.

14.3.2 *Cobalt(II) chloride and uranyl nitrate,* colour standard.

To 5 ml of a 50 g/l solution of cobalt(II) chloride hexahydrate ($CoCl_2.6H_2O$), add 7 ml of a 40 g/l solution of uranyl nitrate hexahydrate [$UO_2(NO_3)_2.6H_2O$], and dilute with water to 50 ml.

Prepare this solution on the day of use.

14.4 Apparatus

NOTE Thoroughly clean the glassware used so as to avoid any risk of contamination.

Ordinary laboratory apparatus, and

14.4.1 *Water bath,* capable of being controlled at 15 ± 0,2 °C.

14.4.2 *Two matched cylinders,* of capacity 100 ml, of transparent and colourless glass, graduated at 50 ml and fitted with ground glass stoppers.

14.4.3 *Burette,* of capacity 10 ml, graduated in 0,05 ml divisions.

NOTE Grease should not be used for lubricating the tap. Use of a PTFE tap is recommended.

14.5 Procedure

14.5.1 ***Test portion***

Carry out the test as soon as possible after receipt of the sample. (Instructions for the storage of the sample are specified in clause **3**.)

Rinse one of the cylinders (**14.4.2**), first with 15 to 20 ml of hydrochloric acid, ϱ approximately 1,19 g/ml, about 38 % (*m*/*m*) solution, then six times with tap water, twice with distilled water and finally with some of the laboratory sample.

Immediately fill the cylinder to the mark with more of the laboratory sample at a temperature of about 15 °C.

14.5.2 ***Determination***

Fill the second cylinder (**14.4.2**) to the mark with the colour standard (**14.3.2**).

Place the cylinder containing the test portion (**14.5.1**) in the water bath (**14.4.1**), controlled at 15 ± 0,2 °C, so that the water level in the bath is approximately 25 mm below the neck of the cylinder. After 15 min, remove the cylinder from the water bath and, using the burette (**14.4.3**), add 2,0 ml of the potassium permanganate solution (**14.3.1**). Note the time. Immediately stopper the cylinder, shake, and replace it in the water bath.

Remove the cylinder from the water bath, at intervals of 1 min, and compare the colour, viewing vertically downwards against a white background, with the colour of the colour standard. Avoid exposing the test solution to strong daylight.

Note the time at which the colour of the test solution matches that of the colour standard.

14.6 Expression of results

Report the time, in minutes, from the addition of the potassium permanganate solution, for the colour of the test solution to match that of the colour standard.

15 Determination of sulphur compounds

15.1 Applicability

The method determines all sulphur compounds normally encountered in methanol for industrial use. It does not determine alkyl sulphones and other oxygen-bonded sulphur compounds.

15.2 Principle

Reaction with Raney nickel of the sulphur compounds in a test portion to form nickel sulphide which is then decomposed with hydrochloric acid; the hydrogen sulphide evolved is absorbed in sodium hydroxide solution before being titrated with standardized mercury(II) acetate solution in the presence of dithizone as indicator.

15.3 Apparatus

Ordinary laboratory apparatus, and

15.3.1 *Reduction apparatus,* as shown in Figure 1.

15.3.2 *Burette,* of capacity 10 ml, graduated in 0,02 ml.

15.4 Reagents

During the analysis, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

15.4.1 *Nitrogen, gas*, free from carbon dioxide.

15.4.2 *Acetone*

15.4.3 *Raney nickel*

WARNING — Raney nickel is spontaneously flammable in air. After use, it is essential to dispose of it immediately by dissolving in dilute hydrochloric acid.

Treat 10 g of 50/50 nickel/aluminium alloy with 100 ml of 100 g/l sodium hydroxide solution, cooling with ice while the reaction proceeds. Wash the Raney nickel three times with water, remove the water by decantation and store the Raney nickel under 100 ml of propan-2-ol. Raney nickel prepared in this way retains its activity for about 3 days.

5 ml of this suspension will reduce quantitatively 1,0 to 1,5 mg of organic sulphur to hydrogen sulphide.

A stabilized form of Raney nickel is available commercially in pellet form.

15.4.4 *Sodium hydroxide,* approximately 40 g/l solution.

15.4.5 *Hydrochloric acid solution*

Dilute 3 volumes of concentrated hydrochloric acid, ρ approximately 1,19 g/ml, with 2 volumes of water.

15.4.6 *Mercury(II) acetate solution*

WARNING — Mercury compounds are very toxic. It is essential that adequate precautions are taken including avoidance of inhalation of mercury oxide dust. The disposal of mercury compounds may be subject to local restrictions.

Dissolve 0,200 g of mercury(II) oxide in 25 ml of water containing 1 ml of glacial acetic acid, and dilute to 1 000 ml with water.

15.4.7 *Methanol,* sulphur-free.

Into a 2 litre round bottom flask with two necks, measure 10 ml of the Raney nickel suspension; alternatively, measure 20 ml of acetone into the flask, add 0,5 g (1 pellet) of Raney nickel, warm until the pellet has disintegrated and decant the acetone. Add 1 500 ml of methanol, place the flask into a heating mantle and fit with a reflux condenser. Insert the nitrogen lead into the second neck and pass in gas at the rate of two bubbles per second.

Heat until slight effervescence is observed on the methanol surface and continue for 30 min. Turn off the gas flow and the heating, and allow the nickel to settle. Decant the methanol into a flask, and distil. Reject the first 250 ml and collect the next 1 000 ml, rejecting the remainder.

15.4.8 *Dithizone,* 1 g/l solution in acetone.

15.5 Procedure

Transfer 5 ml of the Raney nickel suspension to the flask of the reduction apparatus (**15.3.1**); alternatively, measure 10 ml of the acetone (**15.4.2**) into the flask, add 0,25 g (½ pellet) of Raney nickel and warm until the pellet has disintegrated and decant the acetone. Add 100 ml of the sample, place the flask into a heating mantle and pass the nitrogen (**15.4.1**) through at the rate of about 3 l/h. Adjust the temperature of the heating mantle until slight effervescence appears on the surface (just below boiling point). Continue for 30 min, swirling the flask at intervals.

Transfer 10 ml of the sodium hydroxide solution (**15.4.4**) and 10 ml of the acetone (**15.4.2**) to the absorber. Add two drops of the dithizone solution (**15.4.8**) and, by means of the burette (**15.3.2**), one drop of the mercury(II) acetate solution (**15.4.6**) to the absorber.

NOTE The colour change should be from yellow to pink. Liberation of hydrogen sulphide will reverse this colour change.

Transfer 15 ml of the hydrochloric acid solution (**15.4.5**) to the dropping funnel, switch off the heating mantle, and attach a second nitrogen lead to the glass tube in the top of the dropping funnel so as to apply a slight gas pressure. Admit the acid, a few millilitres at a time, to the flask and begin titrating the contents of the absorber with the mercury(II) acetate solution (**15.4.6**), as necessary to restore the pink colour. When all the acid has been added disconnect the nitrogen supply to the top of the dropping funnel, increase the nitrogen flowrate to about 12 l/h, switch on the heating mantle again and continue heating for a further 20 min. When all the hydrogen sulphide has apparently been titrated, switch off the heating mantle, divert the flow of nitrogen momentarily, cool the flask by blowing on it, allow the absorbent to travel up the delivery tube in the absorber (to recover any hydrogen sulphide which may be absorbed on its surface) and complete the titration.

Carry out a blank test by following the same procedure and using the same quantities of reagents as in the determination but using 100 ml of the sulphur-free methanol (**15.4.7**) in place of the test portion.

15.6 Standardization of the mercury(II) acetate solution

Add a known amount of an aliphatic sulphur compound (e.g. di-isoamyl sulphide), equivalent to 0,65 mg to 0,85 mg of sulphur, to 500 ml of the sulphur-free methanol (**15.4.7**). Carry out a determination by the method described in **15.5**, using 100 ml of this solution. From the volume of the mercury(II) acetate solution required in the titration, calculate the mass, in micrograms, of sulphur equivalent to 1 ml of the mercury(II) acetate solution.

15.7 Expression of results

The sulphur compounds content, expressed as a percentage by mass of sulphur (S), is given by the formula

$$\frac{m \times (T_1 - T_2) \times 100}{10^6 \times 100 \times \rho}$$

i.e.

$$\frac{m \times (T_1 - T_2)}{10^6 \times \rho}$$

where

m is the mass, in micrograms, of sulphur equivalent to 1 ml of the mercury(II) acetate solution (determined as in **15.6**);

T_1 is the volume, in millilitres, of the mercury(II) acetate solution required in the test determination;

T_2 is the volume, in millilitres, of the mercury(II) acetate solution required in the blank test;

ρ is the density, in grams per millilitre, of the sample at 20 °C (see clause **5**).

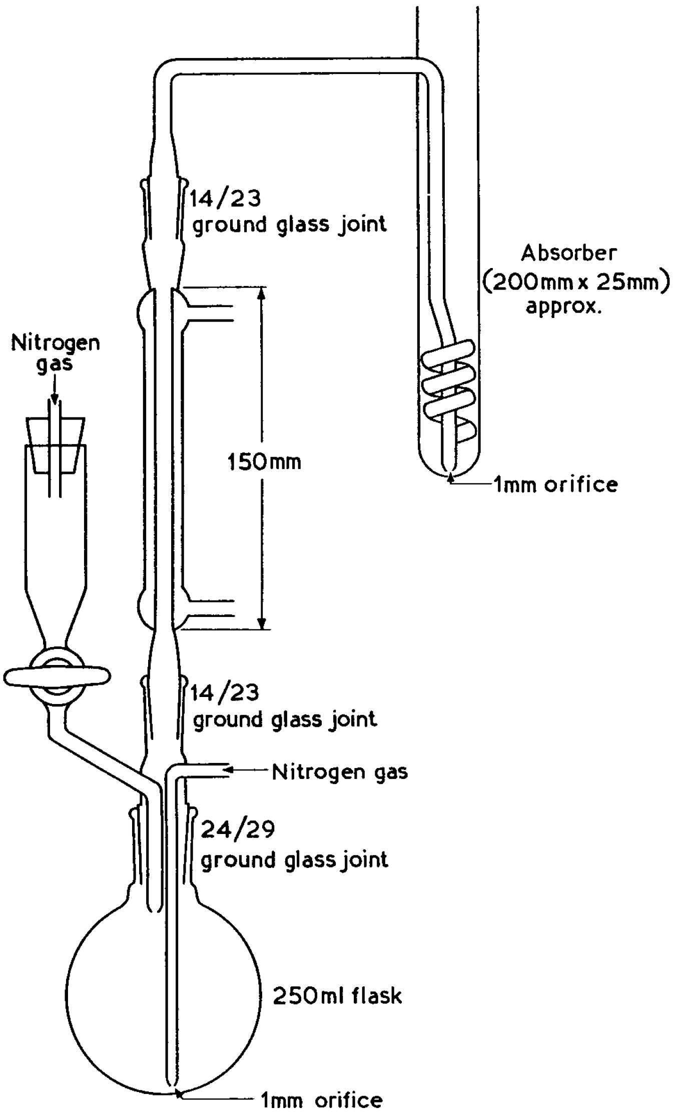

Figure 1 — Reduction apparatus for the determination of sulphur compounds

blank

Publications referred to

BS 506, *Methanol for industrial use.*
BS 506-1, *Specification*[3].
BS 2511, *Methods for the determination of water (Karl Fischer method).*
BS 3591, *Industrial methylated spirits*[3].
BS 3978, *Water for laboratory use*[3].
BS 4522, *Method for the determination of density of liquids at 20 °C.*
BS 4524, *Method for the determination of residue on evaporation on a water bath.*
BS 4591, *Method for the determination of distillation characteristics.*
BS 5309, *Methods for sampling chemical products.*
BS 5309-1, *Introduction and general principles.*
BS 5309-3, *Sampling of liquids.*
BS 5339, *Method of measurement of colour in Hazen units (platinum-cobalt scale) of liquid chemical products.*
ISO 1387, *Methanol for industrial use — Methods of test*[3].

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[3] Referred to in the foreword only.

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