BRITISH STANDARD

BS 4105:1990

Specification for

Liquid carbon dioxide, industrial

Confirmed
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Committees responsible for this British Standard

The preparation of this British Standard was entrusted by the Chemicals Standards Policy Committee (CIC/-) to Technical Committee CIC/19, upon which the following bodies were represented:

British Compressed Gases Association
British Fire Services' Association
British Soft Drinks Association Ltd.
Chemical Industries Association
Institute of Brewing
STC Water Regulations and Fittings Scheme

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Contents

Foreword

This British Standard has been prepared under the direction of the Chemicals Standards Policy Committee to provide specifications suitable for the requirements of industry, Government and other users. It supersedes BS 4105:1967, which is withdrawn. It is not intended to apply to carbon dioxide for medical use, for welding or for fire extinguishing.

The principal differences between this British Standard and the previous edition are as follows:

a) omission from the scope of fire-fighting and welding applications;

b) reduction in the level of impurities specified;

c) introduction of a requirement for the content of nitric oxide and nitrogen dioxide for type 2 carbon dioxide;

d) improvement in methodology in line with modern practice.

A British Standard does not purport to include all the necessary provisions of a contract. Users of British Standards are responsible for their correct application.

Compliance with a British Standard does not of itself confer immunity from legal obligations.

Summary of pages

This document comprises a front cover, an inside front cover, pages i and ii, pages 1 to 20, 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

Warning. Care should be exercised when using carbon dioxide in a confined space because it can displace air and form a suffocating layer.

NOTE Attention is drawn to the following two HSE Guidance Notes.
CS9 "Bulk storage and use of liquid carbon dioxide"; and EH 40 "Occupational exposure limits".

1 Scope

This British Standard specifies two types of carbon dioxide for industrial use. Type 1 is suitable for industrial non-food applications, e.g. purging, inerting, life raft inflation. Type 2 is a higher quality grade which is also suitable for industrial food applications, e.g. beverages, gas packaging, food freezing and chilling.

NOTE 1 Type 2 carbon dioxide is covered by the specific and general criteria of purity laid down in The Miscellaneous Additives in Food Regulations 1980 (SI 1980 No. 1834) in which carbon dioxide is referred to as E290.

This standard does not apply to carbon dioxide for:

a) medical use, for which a specification is included in the British Pharmacopoeia;

b) fire fighting, for which BS 6535-1 applies;

c) welding.

NOTE 2 Throughout this standard, concentrations expressed by mass or volume are at a temperature of 20 °C and 101.3 kPa[1] pressure.

NOTE 3 The titles of the publications referred to in this standard are listed on the inside back cover.

2 Definition

For the purposes of this British Standard the following definition applies.

carbon dioxide

a high pressure liquefiable gas expressed by the chemical formula CO_2

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[1] 10^2 kPa = 10^5 N/m^2 = 1 bar.

Section 2. Carbon dioxide, type 1

3 Description

The product shall consist essentially of carbon dioxide, CO_2, in liquid form.

4 Sampling

The product shall be sampled from the liquid phase by the method specified in the appropriate method of test and as described in Appendix A. Care shall be taken to purge the valve and connecting line before taking a sample.

NOTE Attention is drawn to the provisions of BS 341-1.

5 Residual gases content

The product shall comply with either of the following:

a) the product, if delivered otherwise than in cylinders, shall not contain more than 0.025 % (*V*/*V*) of total residual gases when completely vaporized at 20 °C and 101.3 kPa pressure and determined in accordance with Appendix B;

b) the product, if delivered in cylinders filled to their rated capacity, shall not contain more than 0.2 % (*V*/*V*) of total residual gases when completely vaporized at 20 °C and 101.3 kPa pressure and determined in accordance with Appendix B.

6 Water content

The product shall comply with either of the following:

a) the product, if delivered otherwise than in cylinders, shall not contain more than 50 mg/kg of water when determined in accordance with Appendix C;

b) the product, if delivered in cylinders filled to their rated capacity, shall not contain more than 150 mg/kg of water for cylinders fitted with syphon tubes, and 500 mg/kg of water for cylinders without syphon tubes, when determined in accordance with Appendix C.

NOTE If the carbon dioxide is removed from a cylinder as gas, the water content of the residual carbon dioxide will increase.

7 Packaging and identification

The liquid product shall be supplied in containers designed and manufactured in accordance with BS 5045 or BS 5500. The valves fitted to cylinders shall be designed and manufactured in accordance with BS 341-1. Cylinders shall be identified in accordance with BS 349.

NOTE Attention is drawn to the provisions of The Classification Packaging and Labelling of Dangerous Substances Regulations 1984 (SI 1984 No. 1244).

Section 3. Carbon dioxide, type 2

8 Description

The product shall consist essentially of carbon dioxide, CO_2, in liquid form.

A carbonated solution of the product in tasteless water, with a headspace vapour pressure of 300 kPa at 20 °C, shall be free from any objectionable taste or odour.

9 Sampling

The product shall be sampled from the liquid phase by the method specified in the appropriate method of test and as described in Appendix A. Care shall be taken to purge the valve and connecting line before taking a sample.

NOTE Attention is drawn to the provisions of BS 341-1.

10 Residual gases content

The product shall comply with either of the following:

a) the product, if delivered otherwise than in cylinders, shall not contain more than 0.025 % (*V*/*V*) of total residual gases when completely vaporized at 20 °C and 101.3 kPa pressure and determined in accordance with Appendix B;

b) the product, if delivered in cylinders filled to their rated capacity, shall not contain more than 0.2 % (*V*/*V*) of total residual gases when completely vaporized at 20 °C and 101.3 kPa pressure and determined in accordance with Appendix B.

11 Water content

The product shall comply with either of the following:

a) the product, if delivered otherwise than in cylinders, shall not contain more than 50 mg/kg of water when determined in accordance with Appendix C;

b) the product, if delivered in cylinders filled to their rated capacity, shall contain not more than 150 mg/kg of water for cylinders fitted with syphon tubes, and 500 mg/kg of water for cylinders without syphon tubes, when determined in accordance with Appendix C.

NOTE If the carbon dioxide is removed from a cylinder as gas, the water content of the residual carbon dioxide will increase.

12 Oil content

The product shall comply with either of the following:

a) the liquid product, if delivered otherwise than in cylinders, shall not contain more than 2 mg/kg of oil when determined in accordance with Appendix D;

b) the liquid product, if delivered by cylinders with or without syphon tubes and filled to their rated capacity, shall not contain more than 5 mg/kg of oil when determined in accordance with Appendix D.

13 Content of sulphur compounds

The liquid product shall not contain more than 0.5 mg/kg of sulphur compounds, calculated as sulphur, when determined in accordance with Appendix E.

14 Content of nitric oxide (NO) and nitrogen dioxide (NO_2)

The liquid product shall not contain more than 1 mg/kg of nitric oxide and nitrogen dioxide when determined in accordance with Appendix F.

15 Packaging and identification

The liquid product shall be supplied in containers designed and manufactured in accordance with BS 5045 or BS 5500. The valves fitted to cylinders shall be designed and manufactured in accordance with BS 341-1. Cylinders shall be identified in accordance with BS 349.

NOTE Attention is drawn to the provisions of The Classification Packaging and Labelling of Dangerous Substances Regulations 1984 (SI 1984 No. 1244) which, for containers intended for use in the food industry, are extended by The Miscellaneous Additives in Food Regulations 1980 (SI 1980 No. 1834).

Appendix A Methods for sampling

A.1 General

Samples of carbon dioxide needed to perform all the tests required by this British Standard shall be taken from the same manufacturing lot, using identical sampling procedures. Rigid metal connections or flexible reinforced nylon hose shall be used throughout the sampling equipment and shall be kept as short as possible. All components shall have a design pressure of not less than 2×10^4 kPa.

A.2 Principle of sampling methods

Two methods are given as follows:

a) direct sampling, in which the sample is passed to an evaporator and then directly to the analytical apparatus;

b) sampling in a cylinder in which case the sample is transferred in a cylinder to a laboratory.

A.3 Direct sampling

Connect the sample valve (see **A.1**) to an evaporating device and then via a control valve to the analytical apparatus. Thoroughly purge the connections, valves and the evaporating device with the sample.

A.4 Sampling in a cylinder

A.4.1 *Requirements for the cylinder*

The cylinder, of water capacity 1.4 kg or 2.0 kg, shall comply with BS 5045-1, and be fitted with a valve at each end complying with BS 341-1. An internal copper syphon tube of at least 5 mm diameter, and a length equal to one third of the length of the cylinder shall be brazed to the base of one valve. This valve shall be clearly identified. The cylinder shall be coated internally with tin (containing 1 % (m/m) lead) applied by hot dipping the cylinder after the walls have been descaled. Alternatively, stainless steel cylinders designed for the purpose may be used. The stainless steel cylinders shall have a valve fitted at each end. An internal stainless steel syphon tube of at least 5 mm diameter, and of length equal to one third of the length of the cylinder, shall be fitted to the base of one valve and this valve shall be clearly identified.

A.4.2 *Procedure*

Flush both cylinder valves with liquid carbon dioxide and thoroughly purge the sample point with the liquid carbon dioxide to be sampled. Connect the non-syphon valve to the sample point using suitable connections (see **A.1**). Hold the cylinder vertically with the syphon valve uppermost and open the non-syphon valve to pressurize the cylinder. Slowly open the syphon valve and fill the cylinder with liquid carbon dioxide by blowing off first gas and then carbon dioxide snow. Disconnect the cylinder and blow off approximately one fifth of the carbon dioxide from the gas phase through the non-syphoned valve in the uppermost position. Shake the cylinder and blow off the remaining carbon dioxide through the non-syphoned valve in the lower position.

Reconnect the sample cylinder to the sample point and, holding the cylinder vertically with the syphoned valve uppermost, open the non-syphon valve to pressurize the cylinder. Slowly open the syphon valve and fill the cylinder with liquid carbon dioxide by blowing off first gas and then carbon dioxide snow. Continue blowing snow from the syphoned valve for about 1 min and then isolate the sample by turning off first the syphoned valve and then the non-syphoned valve. Hold the cylinder vertically and, with the syphoned valve uppermost, open the syphoned valve several times until only carbon dioxide gas is discharged from it. The free end of the syphon tube will then be just above the liquid carbon dioxide level in the cylinder.

Allow the sample to equilibrate to room temperature prior to analysis. Analyse the sample as soon as is practicable after this thermal equilibrium is attained.

To withdraw the sample for analysis support the sampling cylinder vertically with the syphoned valve uppermost. Connect the non-syphoned valve of the sampling cylinder (liquid carbon dioxide) to an evaporating device and then via a control valve to the analytical apparatus. Thoroughly purge the connections, valves, and the evaporating device before starting the analysis.

NOTE For the determination of oil content (see Appendix D) the liquid carbon dioxide is solidified by isenthalpic expansion.

Appendix B Method for determination of residual gases content

B.1 Principle

A known volume of sample is isolated in a gas burette, at atmospheric pressure, and absorbed in potassium hydroxide solution. The bubble of unabsorbed residual gas is manipulated into the measuring section of the burette and its volume is measured.

B.2 Apparatus

B.2.1 *Ordinary laboratory apparatus*, and the gas burettes, specified for two ranges of estimated residual gas content (**B.2.2** and **B.2.3**).

B.2.2 *Gas burette*, for determination of 0 % (*V/V*) to 0.0300 % (*V/V*) residual gases content (see Figure 1), consisting of a gas burette of capacity 100 ± 0.5 mL, determined in accordance with **B.2.4** to within a tolerance of 0.2 mL, fitted with a two-way, gas-tight stopcock at each end; a precision bore capillary tube to bore 0.8 ± 0.01 mm, calibrated in accordance with **B.2.4**, is fitted between the upper stopcock and the burette body. Stopcock A connects the burette either to the potassium hydroxide reservoir or to atmosphere. Stopcock B connects the burette either to the mercury reservoir or to atmosphere.

B.2.3 *Gas burette*, for determination of 0.03 % (*V/V*) to 1.0 % (*V/V*) residual gases content (see Figure 2), consisting of a gas burette of capacity approximately 100 mL, determined to within a tolerance of 0.2 mL, fitted at the upper end with a single-way, gas-tight stopcock (C) and at the lower end with a two-way gas-tight stopcock (D). Stopcock C connects the burette to atmosphere. Stopcock D connects the burette either to the water reservoir or to the potassium hydroxide reservoir. A measuring section of volume 1.0 mL, in 0.01 mL divisions, calibrated to within 0.1 mL, is fitted between stopcock C and the burette body.

NOTE 1 Determination of the internal volume should be carried out in accordance with **B.2.4.1**, but substituting water for mercury.

NOTE 2 It is acceptable to calibrate the measuring section with water and weighing, to the nearest 0.1 g, the drop-wise elution from the upper scribed mark.

B.2.4 *Calibration of the burette*

CAUTION. It is strongly recommended to have a layer of water on top of the mercury in the reservoir to depress the escape of mercury vapour and to have the whole apparatus standing in an instrument tray containing a layer of water in case of spillage. Since the apparatus uses mercury as the isolating liquid, it is essential that care be taken in its manipulation to avoid over-pressurization. Also, the CO_2 delivery line shall not be gas permeable and silicone rubber shall not be used. Thick wall tubing made of polyvinylchloride or polytetrafluoroethylene are recommended.

B.2.4.1 *Determination of internal volume*

Fill the burette to the base of the upper stopcock with clean, dry mercury and determine the mass of mercury in the burette, to the nearest 0.1 g, by running the mercury into a previously weighed beaker and reweighing. Ensure that only the mercury between the stopcocks is run into the beaker. Manipulate the stopcocks in such a way that prevents mercury in the bore of the stopcocks being included. Record the temperature of the mercury to the nearest 1 °C and calculate, to the nearest 0.1 mL, the internal volume of the burette at this temperature using mercury density tables.

B.2.4.2 *Calibration of the measuring section*

B.2.4.2.1 The measuring section of the burette requires checking for uniformity of bore and determination of actual bore. Conduct both calibration checks in accordance with **B.2.4.2.2** to **B.2.4.2.10**.

B.2.4.2.2 Mark the mid-point of the capillary section with a felt-tipped pen. Measure 30 mm either side of the mark and scribe a thin line, into the wall of the capillary, at both points. Erase the felt-tipped pen mark. The section of capillary between these upper and lower marks is to be the measuring section of the burette.

NOTE The measuring section is restricted in this procedure to avoid use of any part of its length which may have distorted in the production of the burette.

B.2.4.2.3 Completely fill the burette, including stopcocks, with water, ensuring that all air bubbles are excluded and that the potassium hydroxide reservoir is approximately half full of water. Close both stopcocks.

B.2.4.2.4 Add a few drops of clean, dry mercury to a weighing pipette (Lunge-Rey or similar). Weigh, to the nearest 0.0001 g, the pipette and mercury. Transfer one drop of mercury from the pipette to the potassium hydroxide reservoir. Tap the pipette and reweigh to the nearest 0.0001 g.

B.2.4.2.5 Slowly open the upper stopcock (stopcock A, see Figure 1) to the reservoir and manipulate the mercury bead into the capillary so that the top of the bead is level with the upper scribed mark. This bead should be approximately 20 mm long but, if not, weigh a little more mercury into the apparatus, as described in **B.2.4.2.4**.

B.2.4.2.6 Measure the length of the bead.

B.2.4.2.7 By manipulating the stopcocks, lower the mercury bead and measure its length again at the mid-point of the measuring section and again when the bottom of the bead is level with the lower mark.

B.2.4.2.8 If there is a variation of greater than 0.5 mm between the measurements of bead length then reject the burette on the grounds of non-uniformity.

B.2.4.2.9 Calculate the actual bore of the burette, b_1 (in mm), using the density tables for mercury, from the following equation:

$$b_1 = \sqrt{\left(\frac{4000m}{d\pi l_1}\right)} \qquad (1)$$

where

m is the mass of mercury taken (in g);

d is the density of mercury (in g/mL);

l_1 is the length of the mercury bead (in mm).

B.2.4.2.10 Calculate the volume, v_1(in mL) of a 1 mm length of the capillary from the following equation:

$$v_1 = \frac{b_1^2 \pi}{4000} \qquad (2)$$

where

b_1 is the bore of the burette (see **B.2.4.2.9**).

B.3 Reagents

B.3.1 *General*. Use only reagents of a recognized analytical grade and water complying with grade 3 of BS 3978.

B.3.2 *Potassium hydroxide solution*, approximately 600 g/L.

B.3.3 *Mercury*, clean, dry and free from grease.

B.4 *Test sample*

Take a test sample of about 300 mL for each determination in accordance with Appendix A.

B.5 *Procedure for 0 % (V/V) to 0.0300 % (V/V) residual gases content*

B.5.1 *Determination*

Clean and dry the burette (**B.2.2**) and grease the stopcocks. Fill the reservoir with mercury (**B.3.3**) through stopcock B with stopcock A open. Allow a few millilitres of mercury to enter the potassium hydroxide reservoir. Close stopcock A.

Pour about 10 mL of the potassium hydroxide solution (**B.3.2**) into the potassium hydroxide reservoir. Open stopcock A and adjust the mercury level so that no mercury is left in the potassium hydroxide reservoir or in the stopcock. The bore of stopcock A should be full of potassium hydroxide solution. Reverse stopcock A.

Raise the mercury reservoir and completely fill the glass delivery line with mercury. Close stopcock A.

Connect a short length of gas impermeable, e.g. polyvinyl chloride, flexible tubing to the exit of the evaporating device. Purge this flexible tubing with the carbon dioxide test sample (see **B.4**). Connect the flexible tubing to the glass delivery line of the burette and, by lowering the mercury reservoir with stopcock A open, introduce carbon dioxide through stopcock A into the gas burette.

When only a few millilitres of mercury remain in the gas burette, turn stopcock B so that this small quantity of mercury in the stopcock is discarded through the carbon dioxide purge line.

Continue purging the carbon dioxide (see **B.4**) through the apparatus for about 2 min.

NOTE The purge line should be led directly into a beaker, half full of water, using flexible tubing. This covers the discharged mercury with water and gives a visual indication of the purging rate.

Close stopcock A and disconnect the sample delivery line. Quickly close stopcock B.

Adjust the level of the mercury reservoir, with stopcock B open, to give a slight negative pressure in the burette and then open stopcock A to the potassium hydroxide reservoir. Allow about 5 mL of the potassium hydroxide solution (**B.3.2**) to enter the burette. Close stopcock A.

Raise the mercury reservoir during the absorption of the carbon dioxide to maintain a slight positive pressure on the burette. Make small additions of potassium hydroxide solution towards the end of the absorption by suitable manipulation of the mercury reservoir and stopcock A.

Ease the remaining bubble of residual gas into the capillary measuring section of the burette by manipulation of the mercury reservoir and stopcock A.

Level off the mercury columns and then measure the length of the bubble of residual gas (in mm).

B.5.2 ***Calculation***

Calculate the content of residual gases r [expressed in % (V/V)], using the following equation:

$$r = \frac{lv_2}{v_1} \times 100 \qquad (3)$$

where

l is the length of the bubble of residual gas (see **B.5.1**) (in mm);

v_2 is the internal volume of the burette (**B.2.2**) (in mL);

v_1 is the volume of 1 mm length of capillary (see **B.2.4.2.10**) (in mL).

NOTE The value of v_1 is calculated from the equation:

$$v_1 = (b_2{}^2\pi)/4000$$

where

b_2 is the bore of the capillary (in mm).

B.6 Procedure for 0.03 % (V/V) to 1.00 % (V/V) residual gases content

B.6.1 ***Determination***

Clean and dry the burette (**B.2.3**) and grease the stopcocks. Fill one reservoir with the potassium hydroxide solution (**B.3.2**) and fill the other reservoir with water. Raise the water reservoir and open stopcock D to connect the water reservoir to the burette. Open stopcock C and allow water to fill the burette completely. Close stopcock C.

Connect a short length of gas impermeable, e.g. polyvinyl chloride, flexible tubing to the exit of the evaporating device. Purge this tubing with the carbon dioxide test sample (see **B.4**), connect to stopcock C and allow the sample to displace all the water from the burette. When all the water has been displaced allow the test sample (see **B.4**) to bubble through the water reservoir for 15 s to 30 s. Close stopcock C and disconnect the flexible tubing. The burette will now be under a slight positive pressure from the water reservoir. Carefully open stopcock C to atmosphere until the water in the tubing, connecting the water reservoir to the burette, reaches stopcock D. Close stopcock C and stopcock D. Open stopcock D to connect the potassium hydroxide reservoir to the burette. Allow the potassium hydroxide solution to flow into the burette. Use gentle agitation to assist the absorption of the carbon dioxide. Manipulate the bubble of residual gases into the measuring section of the burette. Level off the potassium hydroxide solution in the reservoir with the bottom edge of the bubble and read off the volume of residual gases (in mL).

B.6.2 ***Calculation***

Calculate the content of residual gases r [expressed in % (V/V)], using the following equation:

$$r = (v_3/v_4) \times 100 \qquad (4)$$

where

v_3 is the volume of residual gases determined (see **B.6.1**) (in mL);

v_4 is the internal volume of the burette (**B.2.3**) (in mL).

Appendix C Method for determination of water content

C.1 Principle

The water content of the sample is determined by passing the gas through a direct reading hygrometer.

C.2 Apparatus

A direct reading hygrometer of one of the following types shall be used:

a) cooled mirror frost point measurement;

b) electrolytic;

c) capacitance;

d) piezoelectric.

C.3 Test sample

Take the sample in accordance with **A.3** or **A.4**.

NOTE Direct sampling in accordance with **A.3** is the preferred method.

C.4 Procedure

Operate the direct reading hygrometer in accordance with the manufacturer's instructions. Keep all sample lines as short as practicable and, together with all ancillary equipment, ensure that they have only polytetrafluoroethylene or stainless steel wetted parts. Record the reading.

C.5 Calculation

Calculate water content w (expressed in mg/kg) using the following equation:

$$w = c\,q \qquad (5)$$

where

c is the concentration (in μL/L) determined from either:

a) the direct instrument reading; or

b) the frost point data, by reference to the partial pressure tables for carbon dioxide.

q is the ratio of the relative molecular mass of water to that of carbon dioxide and is equal to 0.409.

Appendix D Method for determination of oil content

D.1 Principle

The liquid sample is converted to solid and allowed to sublime in a beaker. The residue in the beaker is dissolved in 1,1,2-trichlorotrifluoroethane and the content of oil in this solvent is determined by infra-red spectrometry at the wavelength of maximum absorbance.

D.2 Apparatus

D.2.1 *Ordinary laboratory apparatus*. Clean all glassware with 1,1,2-trichlorotrifluoroethane (**D.3.1**) and dry.

D.2.2 *Beaker*, of capacity 600 mL, squat form.

D.2.3 *Infra-red spectrometer*, and accessories.

D.2.4 *Pressure gauge*, capable of measuring pressure within the range 0 kPa to 7×10^3 kPa.

D.2.5 *Solid carbon dioxide preparation apparatus.*

D.2.6 *Pipettes*, of capacity 5 mL, complying with class A of BS 1583.

D.2.7 *Fourteen one-mark volumetric flasks*, of capacity 5 mL, complying with BS 1792.

D.3 Reagents

D.3.1 *Solvent*, 1,1,2-trichlorotrifluoroethane of analytical reagent grade.

D.3.2 *Standard oil solution*, dissolve 0.200 g of liquid paraffin BP in 100 mL of the solvent (**D.3.1**). Take 10 mL of this solution and dilute to 100 mL with the solvent.

NOTE A volume of 1 mL of this solution contains 200 µg of oil.

D.4 Test sample

Take a test sample of about 500 g for each determination in accordance with **A.4**.

D.5 Procedure

D.5.1 *Determination*

Thoroughly clean the beaker (**D.2.2**) by rinsing with the solvent (**D.3.1**). Check the final rinsings on the spectrometer against a reference of the fresh solvent. If any absorbance is noted in the rinsings, continue cleaning the beaker until the rinsings show no absorbance. Place a clean watch glass over the beaker. Ensure that the beaker is kept covered as much as possible throughout the test. Weigh the beaker and watch glass to the nearest 0.1 g. Cool the solid carbon dioxide preparation apparatus (**D.2.5**) with carbon dioxide. Record the equilibrium pressure of the liquid carbon dioxide test sample (see **D.4**) and then make a block of solid carbon dioxide of approximately 100 g in mass in the cold apparatus (**D.2.5**) by isenthalpic expansion. Transfer the block carefully to the clean beaker and cover with the clean watch glass. Immediately weigh the beaker plus watch glass and block to the nearest 0.1 g. Allow the solid carbon dioxide to sublime. After complete sublimation has been confirmed visually, add, using the pipette (**D.2.6**), 5 mL of the solvent (**D.3.1**) to the beaker and swirl to dissolve the oil residue. Following the manufacturer's instructions for the operation of the particular instrument used, measure the absorbance of the contents of the beaker against a reference blank of the fresh solvent (**D.3.1**) at the wavelength of maximum absorbance (about 3 417 nm). Record the result.

D.5.2 *Calibration*

Prepare, using the one-mark volumetric flasks (**D.2.7**) and pipettes (**D.2.6**), a series of 5 mL calibration solutions containing portions 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 2.0, 3.0, 4.0 and 5.0 mL of the standard oil solution (**D.3.2**), diluting to the mark each flask with the fresh solvent (**D.3.1**). Measure the absorbance of these solutions in accordance with **D.5.1**. Prepare a calibration graph by plotting the masses of oil contained in each calibration solution (in μg) against the corresponding absorbances.

D.6 Calculation

Using the absorbance value obtained (see **D.5.1**), read the corresponding mass of oil, m_1, from the calibration graph (see **D.5.2**). The oil content o (expressed in mg/kg) is given by the following equation:

$$o = \frac{m_1 f}{m_2} \qquad (6)$$

where

m_1 is the mass of oil determined (in μg);

m_2 is the mass of the solid carbon dioxide block (see **D.5.1**) (in g);

f is the fractional conversion of liquid to solid determined from Figure 3.

Appendix E Method for determination of content of sulphur compounds

E.1 Principle

Sulphur compounds present are reduced by mixing the sample with twice its volume of hydrogen and passing the mixture through a silica tube at 1000 °C. The hydrogen sulphide produced is subsequently absorbed in an alkali/zinc acetate mixture. The sulphide content in this mixture is determined spectrometrically.

E.2 Apparatus

E.2.1 Ordinary laboratory apparatus.

E.2.2 *Sulphur compounds determination assembly*, (see Figure 4), comprising the following:

a) *flowmeter*, float type, capable of measuring a hydrogen flow of 200 mL/min to 2 000 mL/min;

b) *flowmeter*, float type, capable of measuring a carbon dioxide flow of 100 mL/min to 1 000 mL/min;

c) *furnace tube*, Grötte-Krekler pattern, of transparent silica 50 cm long with an internal diameter of 16 mm;

d) *furnace and control*, consisting of a tube furnace about 46 cm long, capable of operating at 1 000 ± 15 °C and fitted with an indicating temperature controller;

e) *soda-lime tower*, or absorption tube;

f) *dreschel pattern gas inlet head;*

g) *high speed bubbler*, as shown in Figure 5;

h) *connections*, of flexible polyvinyl chloride tubing.

NOTE Rubber tubing is not to be used due to its reactivity with sulphides.

E.2.3 *Spectrometer*, equipped to measure absorbance at 580 nm.

E.2.4 *Pipette*, of capacity 25 mL, complying with class A of BS 1583.

E.2.5 *Three pipettes*, of capacity 1 mL, complying with class A of BS 1583.

E.2.6 *Measuring cylinder*, of capacity 10 mL, complying with BS 604.

E.2.7 *Eight one-mark volumetric flasks*, of capacity 50 mL, complying with class A of BS 1792.

E.2.8 *One-mark volumetric flask*, of capacity 1 000 mL, complying with class A of BS 1792.

E.2.9 *Two burettes*, of capacity 50 mL, complying with class A of BS 846.

E.2.10 *Two conical flasks*, of capacity 250 mL, complying with BS 2734.

E.3 Reagents

E.3.1 *General*. Use only reagents of recognized analytical grade and water complying with grade 3 of BS 3978.

E.3.2 *Hydrogen gas.*

E.3.3 *Zinc acetate solution*, $c\ [Zn(CH_3COO)_2] = 40$ g/L.

E.3.4 *p-phenylenediamine hydrochloride solution.* Dissolve 1 g of *p*-phenylenediamine hydrochloride in 100 mL of the hydrochloric acid solution (**E.3.7**). Discard this reagent after 3 days and the solid *p*-phenylenediamine hydrochloride after 3 months.

E.3.5 *Iron(III) chloride solution.* Dissolve 1 g of iron(III) chloride in 100 mL of the hydrochloric acid solution (**E.3.7**).

E.3.6 *Sodium hydroxide solution*, $c(NaOH) = 1$ mol/L.

E.3.7 *Hydrochloric acid solution*, $c(HCl) = 2$ mol/L. Dilute 160 mL of concentrated hydrochloric acid ($\rho = 1.18$) to 1 L with water. Do not use concentrated volumetric solutions of hydrochloric acid as these may include stabilizers that interfere in the determination.

E.3.8 *Soda-lime*, fresh, in lumps.

WARNING. The soda-lime shall not have been used in other determinations where pure oxygen has been present as explosions may occur.

E.3.9 *Sodium sulphide*, ($Na_2S\ xH_2O$), crystals.

E.3.10 *Sodium thiosulphate standard volumetric solution,* $c(Na_2S_2O_3) = 0.01$ mol/L.

E.3.11 *Soluble starch solution*, 10 g/L approximately.

E.3.12 *Iodine solution,* $c(I_2) = 0.05$ mol/L.

E.3.13 *Nitrogen gas*, oxygen-free.

E.3.14 *Oxygen-free water*. Boil 2 L of water in a large conical flask for 10 min. Blow nitrogen (**E.3.13**) over the surface of the liquid and plug the neck of the flask with clean cotton wool. Cool the flask.

E.4 Test sample

Take a test sample of 50 g for each determination in accordance with **A.4**. Connect the outlet of the evaporating device to the assembly shown in Figure 4. Ensure that all connections are as short as possible.

E.5 Procedure

E.5.1 *Determination*

Set and maintain the furnace temperature at 1 000 ± 15 °C. Disconnect the hydrogen soda-lime tower (see Figure 4) from the Drechsel head inlet to the Grötte-Krekler tube and purge the air out of the soda-lime tower and the flowmeter with the hydrogen gas (**E.3.2**). Purge the air out of the rest of the assembly (**E.3.1**) with the test sample (see **E.4**). Reconnect the hydrogen soda-lime tower to the Drechsel head inlet and set the hydrogen flow rate to approximately 1 000 mL/min with the carbon dioxide flow rate set to approximately 500 mL/min. Add to the high speed bubbler (see Figure 5), by pipette, 25 mL of the zinc acetate solution (**E.3.3**) and 1 mL of the sodium hydroxide solution (**E.3.6**). Attach the high speed bubbler to the exit of the Grötte-Krekler tube and continue to pass the carbon dioxide test sample and hydrogen gas at the same flow rates for 30 ± 1 min. Record the actual carbon dioxide flow rate and the times of commencement and termination of the determination.

Disconnect the high speed bubbler and allow to cool. Shut off the supplies of hydrogen and carbon dioxide. Measure 10 mL of the hydrochloric acid (**E.3.7**) into the measuring cylinder (**E.2.6**) and add, by pipette, 1 mL of the *p*-phenylenediamine hydrochloride solution (**E.3.4**) to the measuring cylinder and mix. Pour this mixture into the high speed bubbler and quickly add, by pipette (**E.2.5**), 1 mL of the iron (III) chloride solution (**E.3.5**). Mix, by swirling the high speed bubbler and record the time. Prepare a reagent blank in a 50 mL volumetric flask (**E.2.7**) by adding 25 mL of the zinc acetate solution (**E.3.3**) and 1 mL of the sodium hydroxide solution (**E.3.6**) followed by 10 mL of the hydrochloric acid solution (**E.3.7**), 1 mL of the *p*-phenylenediamine hydrochloride solution (**E.3.4**) and 1 mL of the iron (III) chloride solution (**E.3.5**). After 10 min have elapsed from mixing the reagents in the high speed bubbler, transfer the contents of the high speed bubbler to a 50 mL volumetric flask (**E.2.7**) and dilute to the mark with water. Dilute to the mark the contents of the reagent blank with water. After a total of 30 min have elapsed from mixing the reagents in the high speed bubbler, measure the absorbance of the test solution against the reagent blank using cells of optical path length 1 cm in the spectrometer (**E.2.3**) set at 580 nm. From the absorbance, deduce the mass of sulphur in the test solution using the calibration graph prepared in accordance with **E.5.2**.

E.5.2 *Calibration*

NOTE The calibration involves using a dilute solution of sodium sulphide and the precaution of using oxygen-free water is necessary to prevent oxidation in solution.

Take a crystal of the sodium sulphide (**E.3.9**) on a filter paper and wash with a little water. Take part of the crystal estimated to weigh approximately 0.1 g and dissolve in 1 L of the oxygen-free water (**E.3.14**) in the 1 000 mL volumetric flask (**E.2.8**) to give the calibration solution. Fill a 50 mL burette (**E.2.9**) with the sodium thiosulphate solution (**E.3.10**). Add to each of the two conical flasks (**E.2.10**) 20 mL of the oxygen-free water (**E.3.14**) and, by pipette (**E.2.5**), 1 mL of the iodine solution (**E.3.12**). To each of five 50 mL volumetric flasks (**E.2.7**) add, by pipette (**E.2.4**), 25 mL of the oxygen-free water (**E.3.14**), 10 mL of the hydrochloric acid solution (**E.3.7**) from the measuring cylinder (**E.2.6**) and, by pipette (**E.2.5**), 1 mL of the *p*-phenylenediamine hydrochloride solution (**E.3.4**). Fill a 50 mL burette (**E.2.9**) with the sodium sulphide solution so prepared and add, respectively, 0, 1, 2, 3 and 4 mL of the sodium sulphide solution, from the burette to the five volumetric flasks followed by 1 mL portions, by pipette (**E.2.5**), of the iron (III) chloride solution (**E.3.5**). When all the additions have been made, add 40 mL of the sodium sulphide calibration solution to one of the conical flasks containing iodine. Mix, and titrate with the sodium thiosulpate solution (**E.3.10**) using the soluble starch solution (**E.3.11**) as indicator and record the titre value, T (in mL). Likewise titrate the contents of the other conical flask and record the titre value, B (in mL).

After 10 min have elapsed from addition of the sodium sulphide solution to the volumetric flasks dilute to the mark the contents of each flask with oxygen-free water. After a further 20 min period measure the absorbance of each solution in accordance with **E.5.1**.

Calculate the concentration of the sodium sulphide solution c_1 (in μg/mL) from the iodine titrations using the following equation:

$$c_1 = 400c_2\,(B - T)$$

where

c_2 is the concentration of the sodium thiosulphate solution = 0.01 mol/L;

B is the blank titre (in mL);

T is the sample titre (in mL).

Prepare a calibration graph by plotting the masses of sulphide sulphur (in μg) against the corresponding absorbance.

E.6 Calculation

Calculate the content of sulphur compounds, s, expressed as sulphur (in mg/kg) from the following equation:

$$s = \frac{m_3}{at\ \ 0.00184}$$

where

m_3 is the mass of sulphur determined (see **E.5.1**) (in μg);

a is the flow rate, at 20 °C and 101.3 kPa, of the test sample (see **E.5.1**) (in mL/min);

t is the duration of flow of the test portion (see **E.5.1**) (in min).

Appendix F Method for determination of content of nitric oxide and nitrogen dioxide

F.1 Principle

The sample is passed through an oxidant of chromium (VI) oxide, then through an absorbing mixture of acetic acid and sulphanilic acid in which a stable colour is produced by a diazotization reaction. The intensity of the colour, which is proportional to the amount of nitrogen dioxide thus prepared and absorbed by the solution, is measured spectrometrically.

F.2 Apparatus

F.2.1 *Ordinary laboratory apparatus.*

F.2.2 *Microdetermination assembly* (see Figure 6),comprising the following:

a) *flowmeter*, float type, capable of measuring carbon dioxide flow of 100 mL/min to 500 mL/min;

b) *measuring cylinder*, of capacity 10 mL, complying with BS 604;

c) *midget fritted bubbler*, fitted with quartz wool plugs moistened with water (**E.3.1**) (see Figure 7);

d) *U tube*, 125 mm × 15 mm.

F.2.3 *Nine one-mark volumetric flasks*, of capacity 25 mL, complying with class A of BS 1792.

F.2.4 *Two one-mark volumetric flasks*, of capacity 1 000 mL, complying with class A of BS 1792.

F.2.5 *Pipette*, of capacity 10 mL, complying with class A of BS 1583.

F.2.6 *Spectrometer*, equipped to measure absorbance at 550 nm.

F.3 Reagents

F.3.1 *General.* Use only reagents of recognized analytical grade and water complying with grade 3 of BS 3978.

F.3.2 *Absorbing solution.* Dissolve 1.25 g of sulphanilic acid in 200 mL of water and 35 mL of glacial acetic acid. Add 5 mL of *N*-(1-naphthyl) ethylenediamine dihydrochloride solution, 1.0 g/L, and dilute the mixture to 250 mL with water.

F.3.3 *Chromium (VI) oxide.*

F.3.4 *Sodium nitrite.*

F.4 Test sample

Take a test sample of about 50 g for each determination in accordance with **A.4**. Connect the outlet of the evaporating device to the assembly shown in Figure 6. Ensure that all connections are as short as possible.

F.5 Procedure

F.5.1 *Determination*

Assemble the apparatus as shown in Figure 6. Ensure that the retaining plugs in the bubbler remain moist. Add, from a measuring cylinder, 10 mL of the absorbing solution (**F.3.2**) to the midget fritted bubbler. Purge the evaporating device and the sample lines with the test sample (**F.4**). Connect the outlet of the evaporating device to the midget fritted bubbler and set the carbon dioxide sample flow rate so that the maximum possible foam is obtained in the midget fritted bubbler.

NOTE The flow rate should be within the range of 350 mL/min to 400 mL/min of carbon dioxide.

Record the time of commencement of the determination and the carbon dioxide flow rate.

Continue to pass the test sample until a discernible pink coloration is evident. Discontinue the flow and record the time of termination to the nearest minute. Add this pink solution to a one-mark volumetric flask (**F.2.3**) and dilute to the mark with fresh absorbing solution. Measure the absorbance of this solution after a period of 15 min in the spectrometer (**F.2.6**) set at 550 nm using cells of optical path length 1 cm, using fresh absorbing solution as the blank. From the absorbance deduce the mass (in g) of nitrogen dioxide absorbed using the calibration graph prepared in accordance with **F.5.2**.

F.5.2 *Calibration*

Dissolve approximately 0.5 g of the sodium nitrite (**F.3.4**), weighed to the nearest 0.001 g, in water and dilute to the mark in a volumetric flask (**F.2.4**). This is solution A. Transfer 10 mL of solution A into a volumetric flask (**F.2.4**) and dilute to the mark. This is solution B. Add, respectively, by pipette (**F.2.5**), to seven volumetric flasks (**F.2.3**) 0, 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 mL of solution B and dilute to the mark with the absorbing solution (**F.3.2**). Leave the flasks for 15 min to allow full colour development and then measure the absorbance of each solution is accordance with **F.5.1**.

Calculate the mass of nitrite, m_5, expressed as nitrogen dioxide (in g) in each volumetric flask from the following equation:

$$m_5 = 10 m_4 \times \frac{46}{69 \times 0.72}$$

where

m_4 is the mass of sodium nitrite dissolved (in g);

0.72 is a correction factor: under the conditions of the experiment 0.72 moles of sodium nitrite produces the same colour as 1 mole of nitrogen dioxide.

Prepare a calibration graph by plotting the masses of nitrogen dioxide (in μg) against the corresponding absorbance.

F.6 Calculation

Calculate the content of nitric oxide and nitrogen dioxide, n, expressed as nitrogen dioxide, NO_2 (in mg/kg) from the following equation:

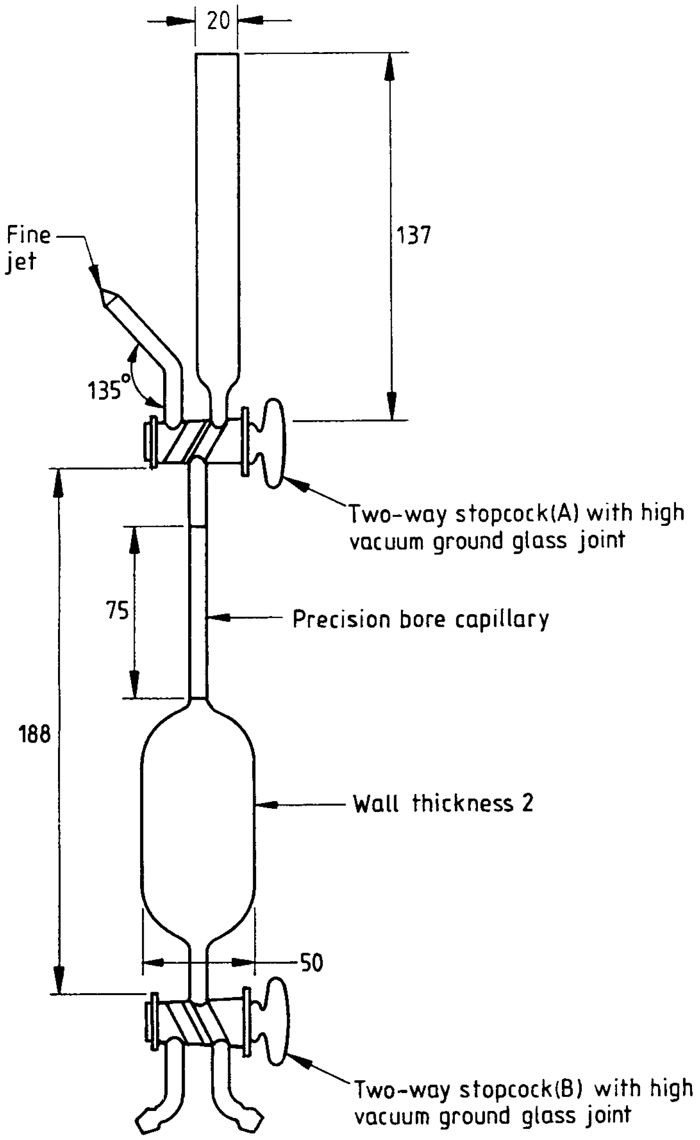
$$n = \frac{m_5}{a\,t \times 0.00184}$$

where

m_5 is the mass of nitrogen dioxide determined (see **F.5.1**) (in μg);

a is the flow rate, at 20 °C and 101.3 kPa, of the test sample (see **F.5.1**) (in mL/min);

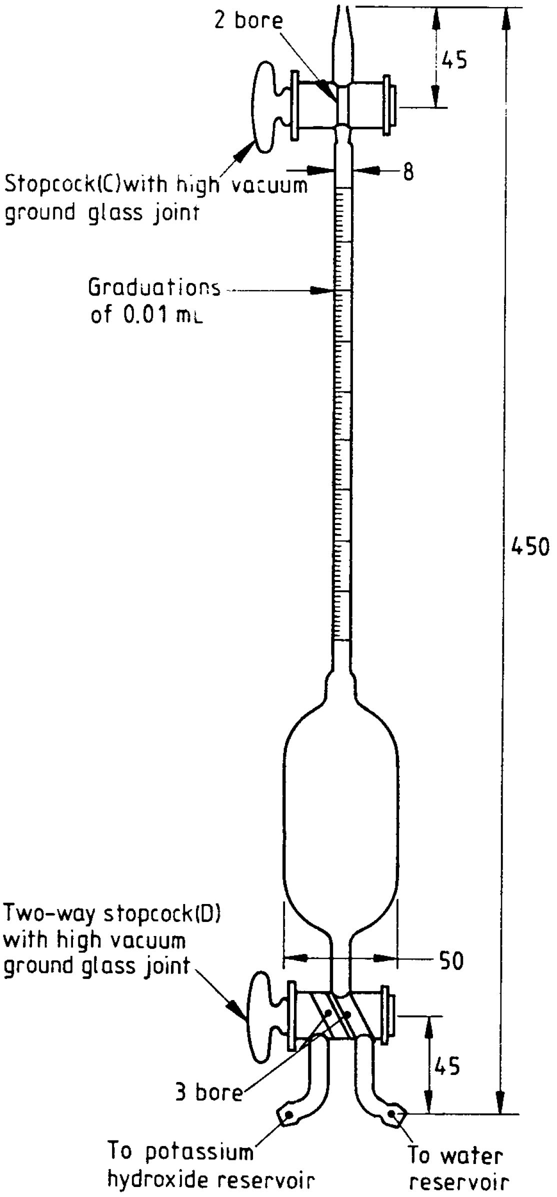
t is the duration of flow of the test portion (in min).



All linear dimensions are in millimetres.

NOTE The dimensions are typical values.

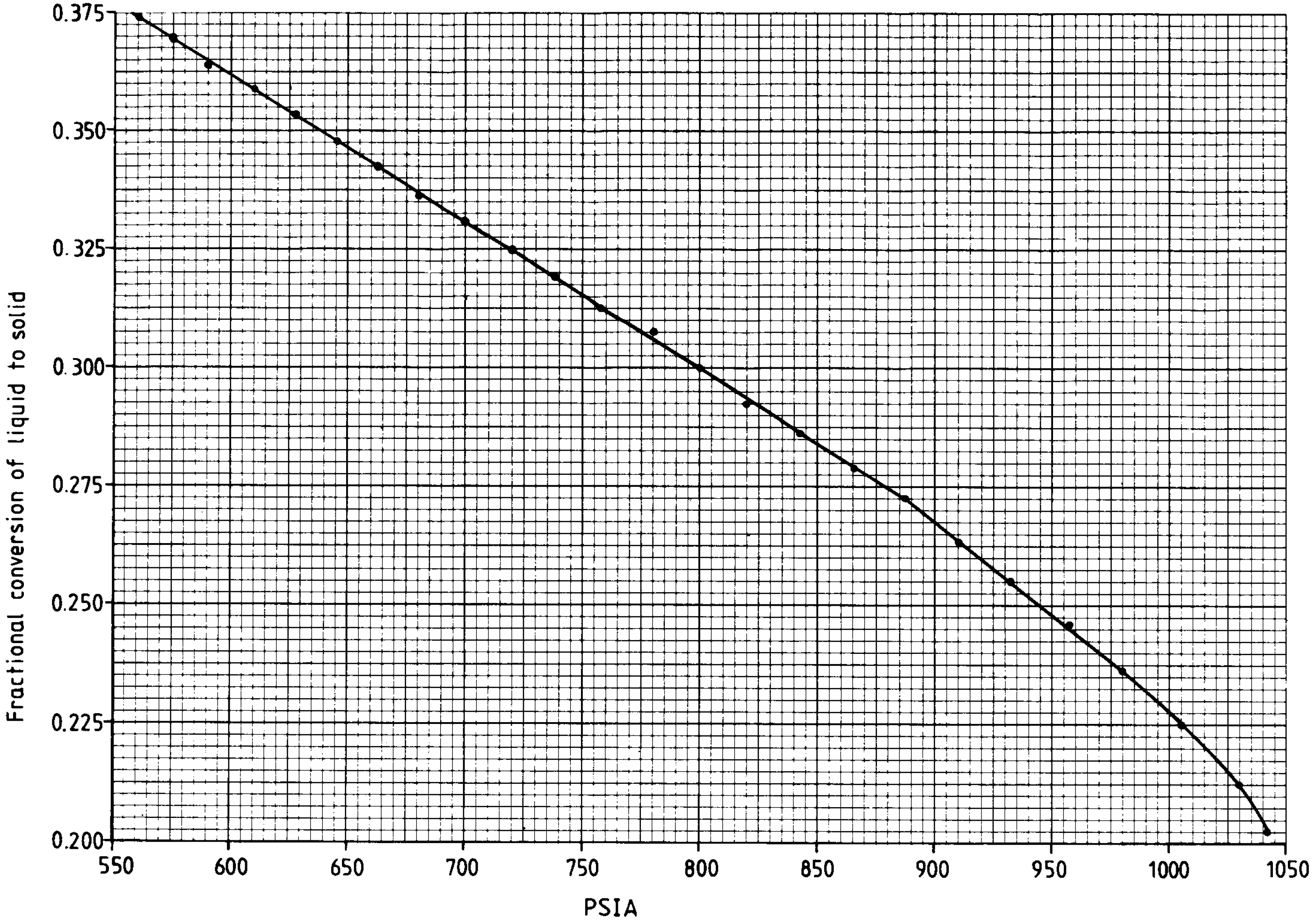
Figure 1 — Burette for determination of residual gases content (see **B.2.2**)



All linear dimensions are in millimetres.

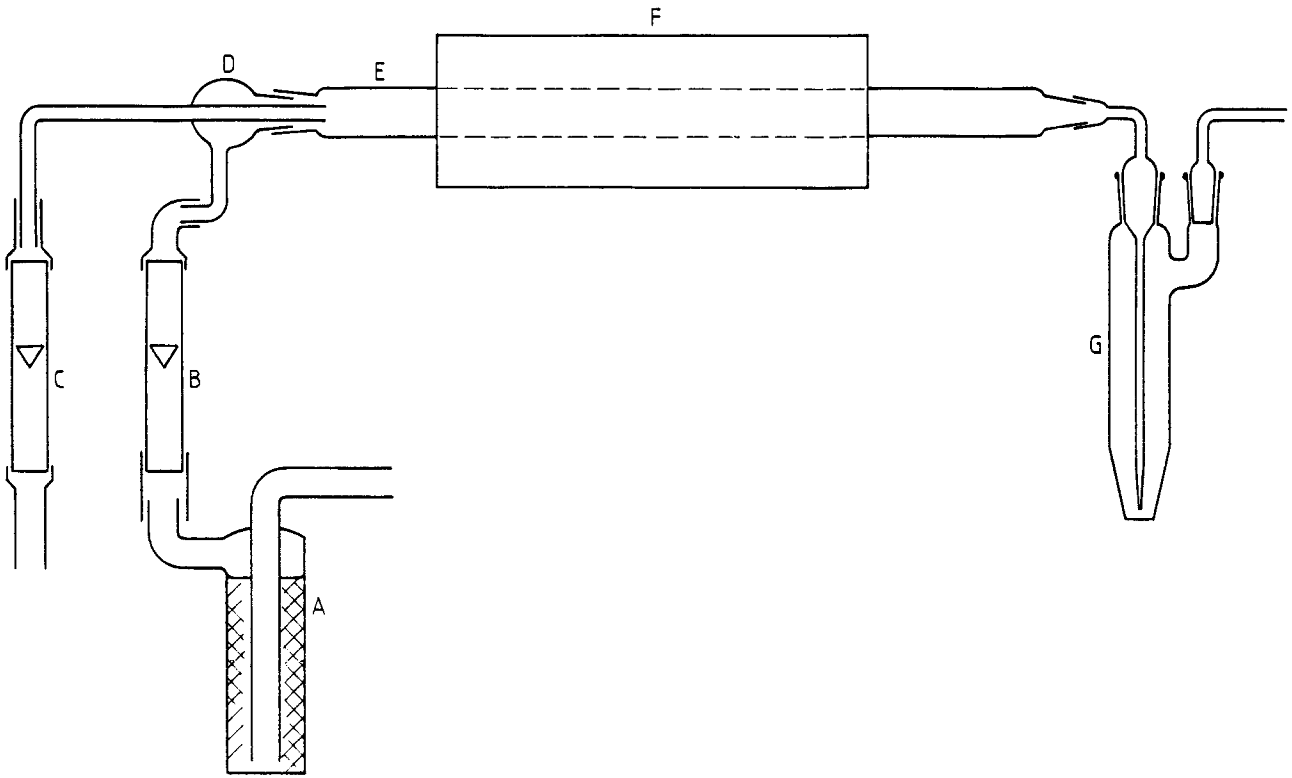
NOTE The linear dimensions are typical values.

Figure 2 — Burette for determination of residual gases content (see **B.2.3**)



NOTE PSIA = bar absolute × 14.7 and 1 bar = 10^2 kPa = 10^5 N/m^2.

Figure 3 — Fractional conversion of CO_2 liquid to solid at various starting pressures (isenthalpic expansion assumed)



Key

A Soda-lime tower for hydrogen

B Hydrogen flowmeter

C Carbon dioxide flowmeter

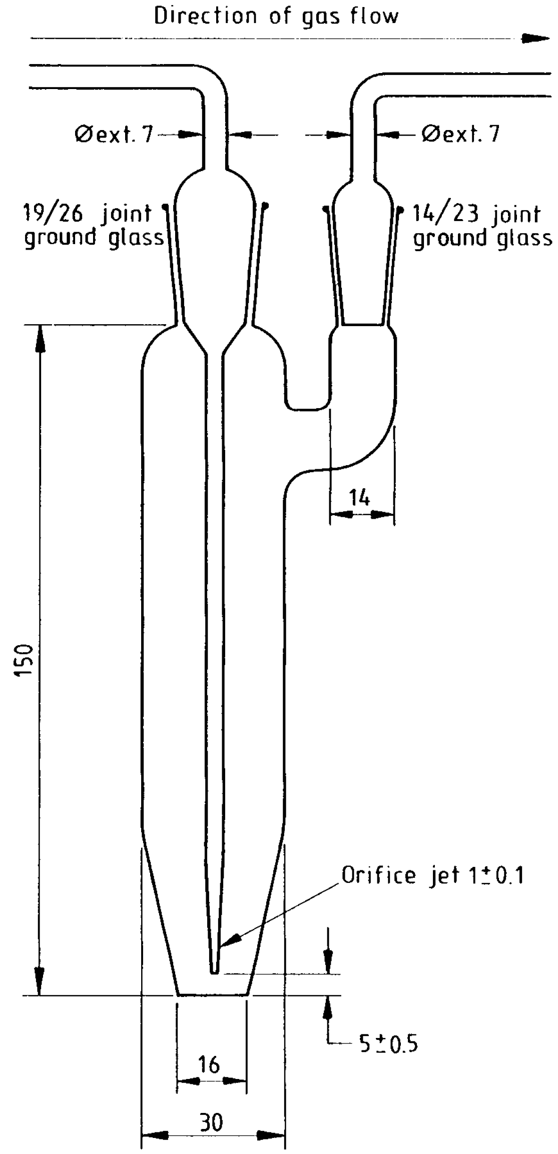
D Dreschel bottle insert

E Grötte-Krekler tube fitted with ground glass sockets

F Electrically heated furnace capable of heating the Grötte-Krekler tube to 1000 ± 15 °C

G High speed bubbler (see figure 5)

Figure 4 — Sulphur compounds determination assembly

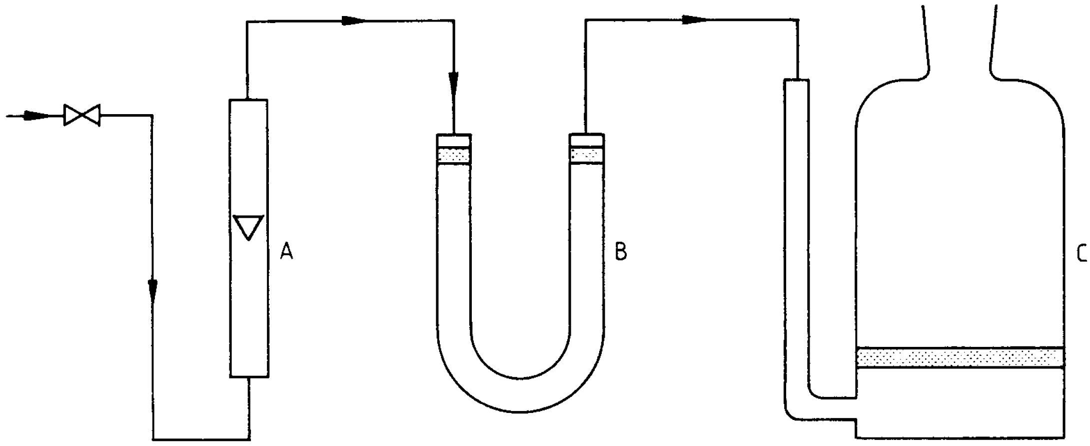


All dimensions are in millimetres.

NOTE 1 These are typical dimensions unless tolerances are given.

NOTE 2 See Figure 4.

Figure 5 — High speed bubbler



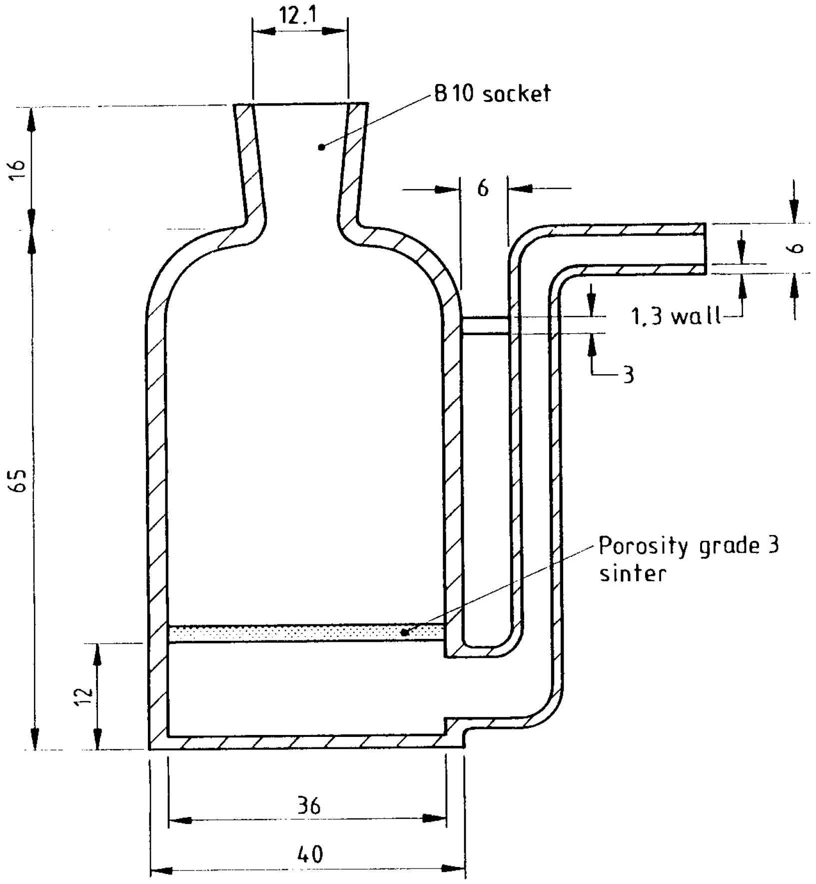
Key

A Flowmeter

B U-tube filled with chromium(VI) oxide

C Midget fritted bubbler (see figure 7)

Figure 6 — Assembly for the microdetermination of nitric oxide and nitrogen dioxide



All dimensions are in millimetres.

NOTE The dimensions are typical values.

Figure 7 — Midget fritted bubbler

blank

Publications referred to

BS 341, *Specification for valve fittings for compressed gas cylinders.*

BS 341-1, *Valves with taper stems (excluding valves used for breathing and medical purposes).*

BS 349, *Specification for identification of the contents of industrial gas containers.*

BS 604, *Specification for graduated glass measuring cylinders.*

BS 846, *Specification for burettes.*

BS 1583, *Specification for one-mark pipettes.*

BS 1792, *Specification for one-mark volumetric flasks.*

BS 2734, *Specification for boiling flasks (narrow-necked), conical, flat bottom and round bottom.*

BS 3978, *Specification for water for laboratory use.*

BS 5045, *Transportable gas containers.*

BS 5045-1, *Specification for seamless steel gas containers above 0.5 litre water capacity.*

BS 5045-2, *Steel containers up to 130 litres water capacity with welded seams.*

BS 5045-3, *Specification for seamless aluminium alloy gas containers above 0.5 litre water capacity and up to 300 bar charged pressure at 15 °C.*

BS 5045-5, *Specification for aluminium alloy containers above 0.5 litre up to 130 litres water capacity with welded seams.*

BS 5045-6, *Specification for seamless containers of less than 0.5 litre water capacity.*

BS 5500, *Specification for unfired fusion welded pressure vessels.*

BS 6535, *Fire extinguishing media.*

BS 6535-1, *Specification for carbon dioxide.*

HSE, *Guidance Note CS9 Bulk storage and use of liquid carbon dioxide*2).

HSE, *Guidance Note EH40 Occupational exposure limits*2).

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2) Available from HMSO Publications Centre, PO Box 276, London SW8 5DT.

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