

**Methods of test for
petroleum and its
products —
BS 2000-272:
Determination of
mercaptan sulfur and
hydrogen sulfide
content of liquefied
petroleum gases
(LPG) — Electrometric
titration method**

(Identical with IP 272:2000)

ICS 75.160.30

Confirmed
January 2010

National foreword

This British Standard reproduces verbatim IP 272/2000. It supersedes BS 2000-272:1993 which is withdrawn.

The UK participation in its preparation was entrusted to Technical Committee PTI/13, Petroleum testing and terminology, which has the responsibility to:

- aid enquirers to understand the text;
- present to the responsible international/European committee any enquiries on the interpretation, or proposals for change, and keep the UK interests informed;
- monitor related international and European developments and promulgate them in the UK.

A list of organizations represented on this committee can be obtained on request to its secretary.

The Institute of Petroleum publishes and sells all Parts of BS 2000, and all BS EN petroleum test methods that would be Part of BS 2000, both in its annual publication “Standard methods for analysis and testing of petroleum and related products and British Standard 2000 Parts” and individually.

Further information is available from:

**The Institute of Petroleum, 61 New Cavendish Street,
London W1G 7AR.**

Tel: 020 7467 7100. FAX: 020 7255 1472.

Cross-references

The British Standards which implement international or European publications referred to in this document may be found in the BSI Standards Catalogue under the section entitled “International Standards Correspondence Index”, or by using the “Find” facility of the BSI Standards Electronic Catalogue.

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 1 to 8, an inside back cover and a back cover

The BSI copyright date displayed in this document indicates when the document was last issued.

Amendments issued since publication

Amd. No.	Date	Comments

This British Standard, having been prepared under the direction of the Materials and Chemicals Sector Policy and Strategy Committee, was published under the authority of the Standards Policy and Strategy Committee on 18 June 2002

© Institute of Petroleum and BSI 18 June 2002

Determination of mercaptan sulfur and hydrogen sulfide content of liquefied petroleum gases (LPG) — Electrometric titration method

This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

1 Scope

This method describes a procedure for the determination of mercaptan sulfur in liquefied petroleum gases. Hydrogen sulfide if present may also be determined. With a 12 l gas sample the method gives a minimum detection level of 14 mg/m³ (as sulfur) for mercaptans and 7 mg/m³ (as sulfur) for hydrogen sulfide. The method is applicable in the presence of acetylenes but cyanides may interfere.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this standard. At the time of publication the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this standard are encouraged to investigate the possibility of applying the most recent editions of the standards listed below.

ASTM D1265 — 92, Standard Practice for Sampling Liquefied Petroleum (LP) Gases (Manual Method).

ISO 4260:1987, Petroleum products and hydrocarbons — Determination of sulfur content — Wickbold combustion method.

ISO 3696:1987, Water for analytical laboratory use — Specification and test methods.

3 Definition

For the purposes of this standard, the following definition applies.

3.1

Liquefied petroleum gases (LPG)

hydrocarbon gases that can be stored and/or handled in liquid phase under moderate conditions of pressure and at ambient temperatures. They consist essentially of C₃ and C₄ alkanes and alkenes, or mixtures of these, and contain generally less than 5% by liquid volume of material of higher carbon number, and have a vapour pressure not exceeding approximately 1600 kPa at 40 °C.

4 Principle

A measured amount of liquefied petroleum gas is vaporised and bubbled through an alkaline solution. Mercaptans and hydrogen sulfide are absorbed. The solution is titrated electrometrically using silver nitrate solution with a glass/silver sulfide electrode system to indicate the end point.

5 Reagents and materials

Use only reagents of recognised analytical grade and only water of at least grade 3 purity as specified in ISO 3696.

5.1 Absorbent, 30% (m/m) sodium hydroxide in water.

WARNING Sodium hydroxide is corrosive and can cause severe burns. In the preparation of solution heat is generated which can cause the solution to boil violently with splashing. To avoid this, small portions of solid sodium hydroxide should be dissolved at any one time until the required concentration is reached. Cooling of the beaker should be applied as required.

5.2 Titrant, 0,01 M silver nitrate in water, prepared by exact dilution of standard 0,1 M solution.

NOTE 1 If required, 0,01 M silver nitrate in alcohol may be used. This should be prepared daily by exact dilution of standard 0,1 M silver nitrate with propan-2-ol which has previously been passed through a column of activated alumina in order to remove peroxides.

5.3 Ammonium Hydroxide, 32 % – 35 % NH_3 in water.

5.4 Sodium sulfide, 10 g/l solution.

Dissolve 10 g of sodium sulfide anhydrous (Na_2S) or 30,8 g sodium sulfide hydrated ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$) in water and dilute to 1 litre with water. Prepare a fresh solution as needed.

5.5 Potassium Iodide, 0,1 mol/l standard solution.

Dissolve approximately 17 g of potassium iodide (KI), weighed to the nearest 0,01 g, in 100 ml water and dilute to 1 litre in a volumetric flask with water. Calculate molarity using the following formula:

$$\frac{W}{166.01}$$

where

W is the weight of the potassium iodide.

5.6 Silver nitrate, standard solution, $c(\text{AgNO}_3) = 0,1 \text{ mol/l}$. Use commercially prepared solution, or prepare in accordance with 5.6.1 and standardise in accordance with 5.6.2.

5.6.1 Preparation. Dissolve 17,0 g of silver nitrate (AgNO_3) in 100 ml of water and dilute to 1 litre with water, store in a dark bottle and standardise weekly.

5.6.2 Standardisation. To standardise, add 6 drops of concentrated nitric acid (HNO_3) (density = 1,42 g/ml) to 100 ml water in a 300 ml tall-form beaker and remove the oxides of nitrogen by boiling for 5 min. Cool to ambient temperature. Pipette 5 ml of potassium iodide solution (5.5) into the beaker, and titrate with the silver nitrate solution prepared in 5.6.1, taking the end point at the inflection of the titration curve.

5.6.3 Nitrogen, special purity grade 99,999% and oxygen content less than $5 \mu\text{l/l}$.

6 Apparatus

6.1 Sample container, as described in ASTM D1265.

6.2 Sample measuring and control system, consisting of a stainless-steel 3 mm bore needle valve and gas meter (wet type), capacity about 3 litres per revolution, cumulative 300 l, fitted with thermometer and water manometer.

6.3 Absorption system, high-speed absorbers of any suitable design. If sintered glass diffusers are used they should be very coarse. Suggested designs are shown in Annex A. Cover the absorbers with black paper or suitable alternative material to exclude light.

6.4 Titration system

6.4.1 Meter, a continuous electronic voltmeter or potentiometer having an accuracy of $\pm 0,005$ volt over a range of at least 0,5 volt, a sensitivity of 0,002 volt and designed to operate on an input current of less than 5 picoampere.

The meter should be shielded and the shield earthed. The compensation device for asymmetry-potential of the glass electrode should cover a range of at least 0,100 volt. For mains operated pH meters and titrimeters the influence from voltage and frequency variations of about 10% in the mains supply should be less than 0,005 volt.

An automatic titrimer may be used, providing that it meets the above specification.

6.4.2 Titration stand, provided with supports for the electrodes and the electric stirrer, all earthed. No permanent change in the meter readings should be noticeable on connecting or disconnecting the stirrer motor.

6.4.3 Microburette, 10 ml capacity.

6.4.4 Glass electrode, pencil-type, made of chemically resistant glass and having a resistance of 100 to 1000 megohms at 25°C . The entire electrical connection from the electrode to the meter terminal must be surrounded by an earthed shield to prevent electrostatic interference.

6.5 Abrasive cloth or paper, having an average particle size of $18 \mu\text{m}$.

NOTE 2 The absorbing stage should be carried out under a fume hood.

7 Sampling

7.1 Because of the inherent instability of sulfur compounds, particularly in the presence of moisture and alkalinity, it is recommended that, whenever possible, the LPG to be tested should be passed directly into the absorption train from the production unit or bulk storage container. When this is not possible, use a sample container as described in 7.2.

7.2 Sample container, a stainless-steel sample pressure vessel of suitable size (usually 200, 500 or 1000 ml) is used to obtain a sample in the liquid phase from the source, following the procedure described in ASTM D1265. The gas is taken directly from this through a heated control valve to the absorbers and the amount of sample measured by connecting a gas meter to the outlet of the absorbers. Alternatively the weight of vaporised sample may be determined by weighing the pressure vessel before and after the absorption stage.

CAUTION Due consideration must be given, in both sampling and handling, to the potential hazards of pressure build-up and fire risk. Suitable precautions are detailed in ASTM D1265.

8 Apparatus preparation

8.1 Silver/silver sulfide electrode, burnish the silver electrode with an abrasive cloth or paper (6.5) until a clean, polished silver surface shows.

Place the electrode in position on the titrimer, immersing in a beaker containing 20 ml of sodium hydroxide solution (5.1), 8 ml of sodium sulfide solution (5.4), 1 ml of ammonium hydroxide solution (5.3) and 70 ml of water. Add from a burette, with stirring, 10 ml of 0.1 M silver nitrate, over a period of 10 to 15 min. Remove the electrode, wash it with distilled water, and wipe it with a clean tissue. The electrode is now ready for use. When not in use the electrode should be stored in a solution containing 1,36 g of sodium acetate ($\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$), 2,5 ml distilled water and 95,5 ml propan-2-ol to which has been added 0,5 ml of the 0,1 M silver nitrate (5.6).

8.2 Glass electrode. Glass electrodes should be sensitised according to the manufacturer's directions. When not in use they should be stored in distilled water.

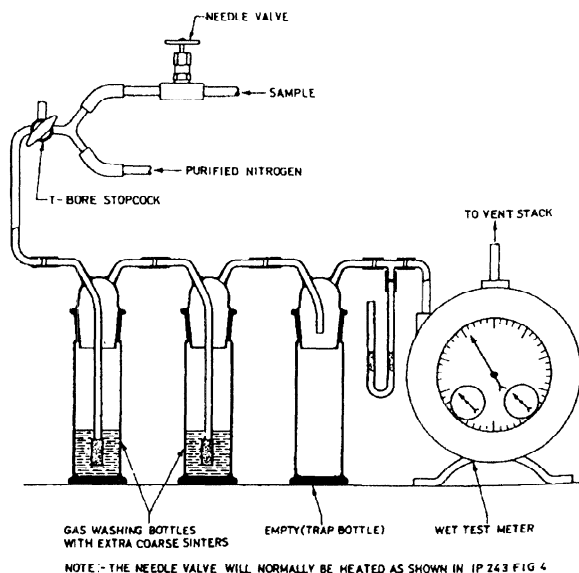


Figure 1 — Apparatus assembly

9 Procedure

9.1 Assemble the absorbers in series, (Figure 1) and connect the outlet tube of the empty trap bottle to the gas meter. A water manometer should be fitted to the meter inlet to indicate and relieve pressure build-up. Connect the inlet tube of the first absorber via a suitable T-bore stopcock or vent system to the flow control valve on the sample line and to the nitrogen supply in such a way that either sample or nitrogen may be passed through the absorbers without disconnecting from the system. Make all connections as short as possible, using glass tubing joined by means of butt joints with short lengths of non-reactive tubing, e.g. PVC, polythene, or silicone rubber.

NOTE 3 A suitable alternative vent system to the use of a T-bore stopcock is obtained by placing a 'T'-piece between the sample/nitrogen inlet and the first absorber, with the free end sealed with non-reactive tubing pinched with a screw clip. This enables the gas to be vented rapidly in the event of a pressure build-up.

CAUTION Since the absorbent solution is 30% sodium hydroxide, it is recommended that a shield is placed around the absorber in order to confine the liquid in the event of a blow-out. Special care should be taken throughout the method in handling the 30% m/m sodium hydroxide solution as this is very corrosive and can cause severe burns.

Place 30 ml of the absorbent (5.1) in each absorber, and purge the assembly with nitrogen (5.6) for 10 min at a rate of 1 to 2 l/min. Alkaline sulfide and mercaptide solutions oxidise easily. Oxygen must also be rigidly excluded during the transfer and titration.

9.2 Record the initial gas meter reading and the temperature of the gas at the meter.

Pass a volume of gas (vaporised from the liquid phase according to directions given in ISO 4260 section 8.6.3) through the absorbers at a rate of 1 to 2 l/min, such that a final titration of between 0,5 ml and 10 ml of 0,01 M silver nitrate is obtained. Not less than 3 l of gas should be used, due to limitations in the accuracy of the gas meter. During absorption the pressure on the meter should not exceed 20 mm of water.

Stop the gas flow, and record the meter reading, the temperature of the gas at the meter and the barometric pressure. Purge the system with nitrogen (5.1) for 10 min at a rate of 1 to 2 l/min.

NOTE 4 Carry out the following transfer and titration stages with minimum delay to reduce oxidation effects.

9.3 Decant the contents of both absorbers into a tall-form beaker, washing each absorber with 25 ml de-aerated distilled water in a nitrogen (5.1) atmosphere. Add the washings to the titration beaker and add 1 ml ammonium hydroxide (5.3).

CAUTION Ammonium hydroxide must not be added after the titration has commenced because of possible formation of explosive silver compounds.

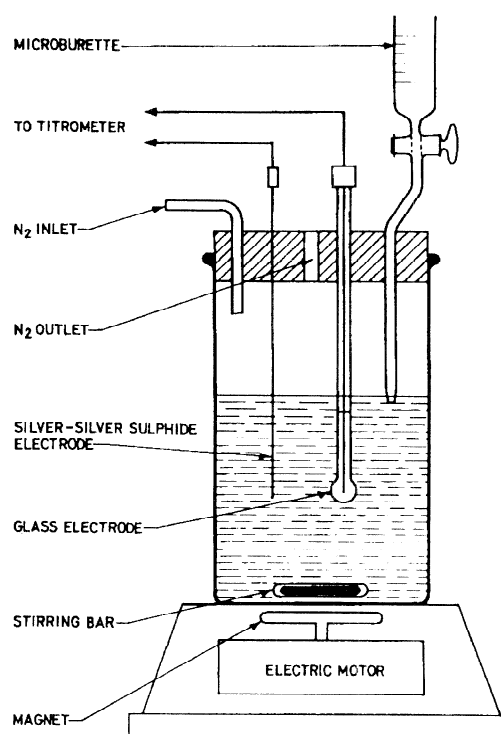


Figure 2 – Titration cell assembly

Assemble the titration vessel (Figure 2). Place the beaker on the titration stand and adjust its position so that the electrodes are half immersed in the liquid. Start a nitrogen purge on to the liquid surface and continue this during the titration. Start the stirrer and adjust to give vigorous stirring without splashing. Fill the burette with 0,01 M silver nitrate (5.2) and immerse the tip just below the surface of the solution. Record the initial emf. Add suitable portions of silver nitrate.

NOTE 5 It is recommended that initially 0,5 ml increments should be added reducing to 0,1 ml or less as the end point is approached. If black silver sulfide or yellow silver mercaptide is precipitated, tap the silver electrode to dislodge precipitate otherwise equilibrium may not be reached between titration additions. Erratic readings with freshly prepared electrodes may be caused by electrodes that have not been properly conditioned. The difficulty usually disappears with succeeding titrations; otherwise reconditioning may be necessary.

Allow time after each addition for the cell potential to reach equilibrium, then record the potential and burette reading. 5 to 10 min may elapse before an unchanging potential is attained. The potential may be considered constant if it changes by less than 6 mV/min. Continue the titration until the rate of change of potential is less than 2 mV/0.1 ml of titrant. If hydrogen sulfide and mercaptan are present the potential change should cover approximately 800 mV.

9.4 Plot a graph of emf against volume (ml) of titre, the end point being the most positive value of the steepest portion of curve (Figure 3).

If the solution contains only mercaptan, the potential change will be only about 500 mV. The potentials may vary with different makes of instrument. Typical curves are shown in Annex B.

10 Calculation

10.1 Calculate the volume of the gaseous sample in litres of dry gas at 0 °C and standard atmospheric pressure using the formula:

$$V \times \frac{273}{(273 + T)} \times \frac{(P_1 - P_2)}{A}$$

where

V	is the observed volume of gas in litres
P_1	is the barometric pressure in kPa
P_2	is the vapour pressure of water at the temperature T °C (see Annex C)
A	is standard atmospheric pressure i.e. 101,325 kPa
T	is the recorded gas temperature in °C

10.2 Calculate the mercaptan content as sulfur in mg/m³, using the formula:

$$\frac{(B - A) \times M \times 32\,066}{V}$$

where

A	is the volume in ml of silver nitrate solution used in titrating to the first (hydrogen sulfide) end point
-----	--

B	is the volume in ml of silver nitrate used in titrating to the second (mercaptan) end point
M	is the molarity of the silver nitrate solution
V	is the volume in litres of dry gas

NOTE 6 To express results for mercaptan content (as sulfur) as mg/kg substitute m for V in the above equation, where m is the mass of the sample in grams.

10.3 If volume A in the titration is measurable, thus indicating the presence of hydrogen sulfide, calculate its concentration in mg S/m³, using the following formula

$$\frac{A \times M \times 16\,033}{V}$$

where

A	is the volume in ml of the silver nitrate used in titrating to the first (hydrogen sulfide) end point
M	is the molarity of the silver nitrate
V	is the volume in litres of dry gas

NOTE 7 To express results for hydrogen sulfide content (as sulfur) as mg/kg substitute m for V in the above equation, where M is the mass of the sample in grams.

11 Expression of results

Report the results, as mg sulfur/m³ as mercaptans and sulfur as hydrogen sulfide, to the nearest mg.

12 Precision

The instability of sulfur compounds under sample pressure vessel conditions has so far rendered a correlation programme impracticable. It is therefore not yet possible to quote confident repeatability and reproducibility levels. However, tests carried out within individual laboratories demonstrate that this method reliably meets the terms of reference given in Section 1.

Annex A (normative)

Gas absorption vessel

A.1 Suggested designs for the gas absorption vessel

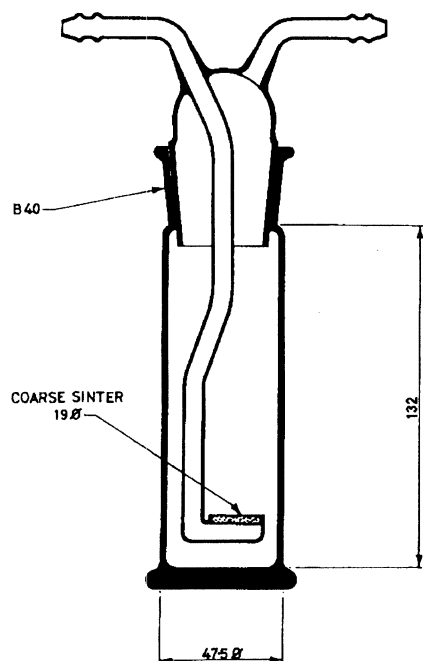


Figure 3 — Gas absorption vessel

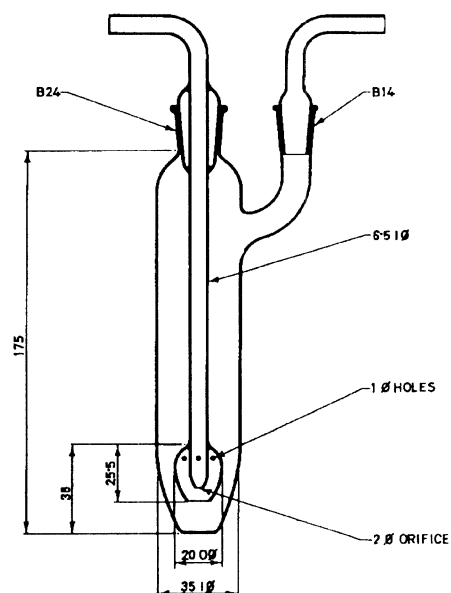


Figure 4 — Gas absorption vessel

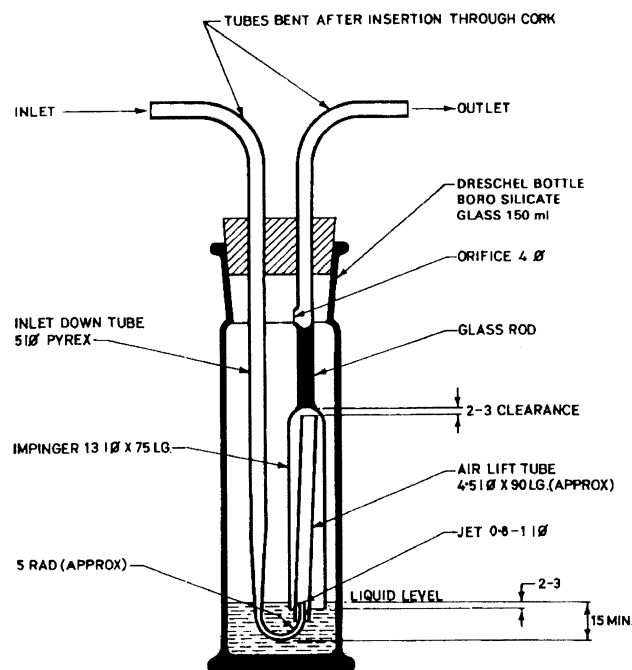
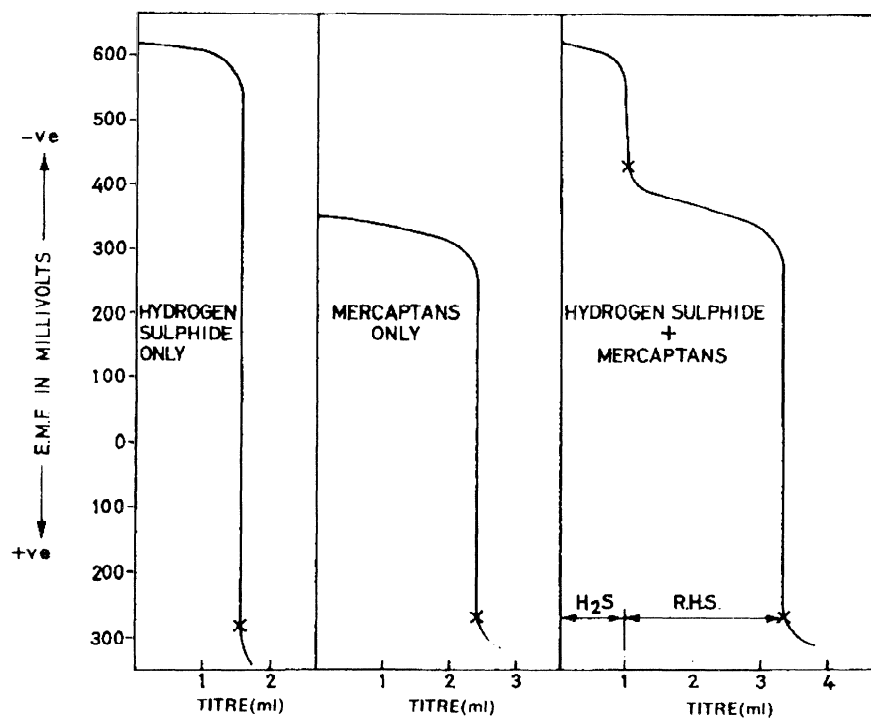


Figure 5 — High speed air lift impinger absorber

Annex B (normative)

Titration curves

B.1 Typical titration curves



NOTE:- THE E.M.F RANGE MAY VARY ACCORDING TO THE MAKE OF INSTRUMENT USED

Figure 6 — Typical titration curves

NOTE The EMF range may vary according to the make of instrument used.

Annex C (normative)

Vapour pressure

C.1 Water vapour pressure at various temperatures

Temp. °C	Vapour pressure/kPa	Temp. °C	Vapour pressure/kPa
16	1,81	28	3,77
18	2,06	30	4,24
20	2,33	32	4,74
22	2,64	34	5,32
24	2,98	36	5,95
26	3,36	38	6,63

The Institute of Petroleum

61. New Cavendish Street
London
W1G 7AR

Tel: +44 (0)20 7467 7100
Fax: +44 (0)20 7255 1472
www.petroleum.co.uk

Buying Parts of BS 2000

Orders for BS 2000 publications should be addressed to:

The Library at the Institute of Petroleum

British Standards Institution — Customer services
389 Chiswick High Road
London
W4 4AL

Tel: +44 (0)20 8996 9001
Fax: +44 (0)20 8996 7001
www.bsi-global.com

Order hard copy standards securely via:
www.bsi-global.com/bsonline

Copyright

Copyright subsists in all BS 2000 publications. No part of this publication may be reproduced in any form without the prior permission in writing of BSI and the IP. Enquiries about copyright should be made to the Secretary of PTI/13 at the IP.



THE INSTITUTE
OF PETROLEUM

PTI/13