PD ISO/TS 17307:2016

BSI Standards Publication

Petroleum products — Biodiesel — Determination of total esters content by gas chromatography

bsi.

...making excellence a habit.™

National foreword

This Published Document is the UK implementation of ISO/TS 17307:2016

The UK participation in its preparation was entrusted to Technical Committee PTI/2, Liquid Fuels.

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

This publication does not purport to include all the necessary provisions of a contract. Users are responsible for its correct application.

Published by BSI Standards Limited 2016

ISBN 978 0 580 88915 8

ICS 75.160.20

Compliance with a British Standard cannot confer immunity from legal obligations.

This British Standard was published under the authority of the Standards Policy and Strategy Committee on 29 February 2016.

Amendments/corrigenda issued since publication

Date	Text affected

PD ISO/TS 17307:2016

TECHNICAL SPECIFICATION

ISO/TS 17307

First edition
2016-02-01

Petroleum products — Biodiesel — Determination of total esters content by gas chromatography

Produits pétroliers — Biodiesel — Dosage de la teneur en esters totale par chromatographie en phase gazeuse

Reference number
ISO/TS 17307:2016(E)

COPYRIGHT PROTECTED DOCUMENT

ISO copyright office
Ch. de Blandonnet 8 • CP 401
CH-1214 Vernier, Geneva, Switzerland
Tel. +41 22 749 01 11
Fax +41 22 749 09 47
copyright@iso.org
www.iso.org

Contents

Page

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the WTO principles in the Technical Barriers to Trade (TBT) see the following URL: Foreword - Supplementary information

The committee responsible for this document is ISO/TC 28, *Petroleum products and related products of synthetic or biological origin*, Subcommittee SC 7, *Liquid biofuels*.

Petroleum products — Biodiesel — Determination of total esters content by gas chromatography

WARNING — The use of this Technical Specification might involve the usage of dangerous materials and equipment. It is the responsibility of the user to establish the appropriate security, health and environmental practices, and to determine the applicability of regulatory limitations before their use.

1 Scope

This Technical Specification establishes a method for determining the total methyl ester content in fatty acid methyl ester (FAME) by gas chromatography and using an external standard. The method is suitable for biodiesel which contains esters between C6 and C26. This method allows verifying that the total ester content is greater than 96,5 % (*m/m*).

NOTE 1 The method also allows determination of the total ethyl ester content in FAEE, but precision for this has not been established.

This Technical Specification does not determine the linolenic nor the poly-unsaturated alkyl ester content. Alternative techniques, such as EN 14103[1] and EN 15779[2], respectively, are available for this.

NOTE 2 For the purposes of this Technical Specification, the term "% (*m/m*)" is used to represent the mass fraction, *μ.*

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 3170, *Petroleum liquids — Manual sampling*

ISO 3171, *Petroleum liquids — Automatic pipeline sampling*

ISO 4259, *Petroleum products — Determination and application of precision data in relation to methods of test*

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

3.1
biodiesel
fuel comprised of monoalkyl esters of fatty acids, derived from vegetable oils or animal fat

3.2
total esters
sum of concentration of all esters (C6 – C26)

4 Principle

A sample is analysed by gas chromatography using an external calibration method to quantify the esters present in biodiesel regardless of the raw material used in its production.

The quantification of biodiesel samples with C18 carbon chains is performed using an analytical curve prepared with methyl or ethyl octadecanoate. If there is presence of esters with carbon chain shorter than C_{14}, in addition methyl or ethyl dodecanoate is used for quantifying these esters in the sample.

It is recommended to consult the chromatograms presented in Annex A to facilitate the identification of different matrices of biodiesel.

5 Apparatus

5.1 Gas chromatograph equipped with flame ionization detector (FID), an on-column injector (or equivalent) and oven with temperature programming.

5.2 Data acquisition system, an electronic instrument to obtain and record the peak area in the chromatograms.

5.3 Column, fused silica capillary column, 30 m × 0,32 mm × 0,1 µm, with stationary phase 95 % dimethylpolysiloxane and 5 % phenyl-methylpolysiloxane for high temperature (up to 400 °C).

Any column with better or equivalent efficiency and selectivity may be used. Their usefulness should be observed by comparing the chromatogram obtained with chromatograms presented in Annex A.

NOTE A retention gap of 0,53 mm of internal diameter can be used.

5.4 Automatic sampler.

5.5 Balance, with resolution of 0,1 mg.

5.6 Flask, with the capacity of 50 mL, with lid.

5.7 Micro syringe, with the capacity for 1,0 µl.

5.8 Pasteur pipettes.

5.9 Beaker of 50 ml.

6 Reagents and materials

6.1 *n*-heptane, (CAS[1)] Nº 142-82-5), minimum purity of 99 %.

6.2 Methyl dodecanoate (CAS[1)] Nº 111-82-0) or ethyl dodecanoate (CAS[1)] Nº 106-33-2), minimum purity of 99 %.

6.3 Methyl octadecanoate (CAS[1)] Nº 112-61-8) or ethyl octadecanoate (CAS[1)] Nº 111-61-5), minimum purity of 99 %.

6.4 Carrier gas, hydrogen or helium, minimum purity of 99,999 %, as carrier gas (for detector gas a FID suitable grade is allowed).

6.5 Nitrogen, minimum purity of 99,999 %, grade suitable for FID.

1) Represents the register of chemical substances catalogued in the CAS system. CAS numbers have no chemical meaning, these are numbers designated in sequential order for each substance added to the system.

6.6 Synthetic air, minimum purity of 99,999 %, grade suitable for FID.

7 Sampling

Unless otherwise specified, obtain representative samples for analysis in accordance with the procedures given in ISO 3170, ISO 3171 or an equivalent International Standard.

8 Procedure

8.1 Preparation of the apparatus

8.1.1 Install the column according to the instructions of the manufacturer.

8.1.2 Establish a flow of about 3,0 ml/min of helium (pressure around 180 kPa and average linear velocity around 0,54 m/s and) or hydrogen (pressure around 105 kPa and average linear velocity around 0,70 m/s).

8.1.3 Adjust the following typical operation conditions on the gas chromatograph:

a) programming the oven temperature:

Heating rate °C/min	Temperature °C	Holding time min
—	50	1
15	180	0
7	230	0
20	380	10

b) carrier gas: helium or hydrogen;

c) detector temperature: 380 °C;

d) injector temperature: oven tracking;

e) nitrogen flow for the detector (*make-up gas*): 30 ml/min;

f) hydrogen flow for the detector: 35 ml/min;

g) synthetic air flow for the detector: 350 ml/min;

h) volume to be injected: 0,5 µl;

i) approximate time of analysis: 35 min.

NOTE The detector flows recommended by the manufacturer can also be used.

8.1.4 Evaluate the stability of the baseline running a blank.

8.1.5 After the system stabilizes baseline subtraction or electronic compensation of the signal, following the procedures inside the equipment's manual may be applied to eliminate the deviation of the baseline due to the temperature programming of the oven.

8.2 Preparation of the calibration curve

8.2.1 For biodiesel samples containing mainly fatty acids with C_{16} and C_{18} carbon chains, a calibration curve shall be prepared with methyl or ethyl octadecanoate.

8.2.2 In samples that contain fatty acids with carbon chains less than C_{14}, two calibration curves are required; one using methyl or ethyl dodecanoate to quantify these esters and another using methyl or ethyl octodecanoate to quantify all the others esters.

8.2.3 Prepare a minimum of six standard solutions for any calibration curve, each one corresponding to a point in the curve.

An example of preparation procedure for six points of standard solutions of methyl or ethyl octadecanoate is found in Annex B.

8.2.4 Inject 0,5 µl of the standard solution, at least two times.

Identify the peaks according to the chromatograms in Annex A and obtain the area of each component.

NOTE Depending on the construction of different instruments, there is a risk that the linear range of the FID is exceeded. Check the peak shape to secure that the detector/amplifier has not become overloaded/saturated.

8.2.5 Obtain the calibration curve of each component of the solution by plotting the area in (y) axis versus concentration in mass percentage in (x) axis.

A calibration curve is acceptable if its regression coefficient is >0,999.

8.3 Sample preparation

8.3.1 Add approximately 0,1 g with an accuracy of 0,1 mg of sample to a 50 ml beaker (5.9) and record the mass.

8.3.2 Dilute with 26,8 g of *n*-heptane and determine the total mass of solution.

Homogenize and transfer to the vial of automatic sampler.

8.4 Procedure

8.4.1 Inject 0,5 µl of sample solution (see 8.3) at least two times.

8.4.2 Identify and integrate all the peaks of esters of the sample from C6 up to C26.

For guidance, see the chromatograms of Annex A.

The identification of peaks relating to esters may be done using a standard chromatogram obtained by gas chromatography/mass spectrometry (GC/MS). In that case, GC/MS and GC/FID configurations shall be equivalent.

9 Expression of results

Calculate the total ester content with Formula (1):

$$C = \frac{A - b}{a \times m_a} \times m_t \quad (1)$$

where

C is the mass percentage [% (*m/m*)] of total ester content of the sample;

A is the sum of peak areas of the identified esters of the sample;

a is the slope (angular coefficient) of the calibration curve;

b is the intercept obtained for the calibration curve

m_a is the mass of sample used in 8.3 in grams (g);

m_t is the total mass (mass of sample + mass of *n*-heptane), in grams (g)

Express the results in % (*m/m*) to the nearest 0,1 % (*m/m*).

10 Precision

10.1 General

The precision given in 10.2 and 10.3 was determined by statistical examination of interlaboratory test results in accordance with ISO 4259.

10.2 Repeatability, *r*

The difference between two test results, obtained by the same operator with the same apparatus under constant operating conditions on identical test material, would in the long run, in the normal and correct operation of the test method, exceed the values calculated according to Formula (2) only in one case in twenty.

$$r = -53{,}404 + 0{,}595\,6 \cdot X\ [\%] \quad (2)$$

where

X represents the mean of the two results expressed in % (*m/m*).

10.3 Reproducibility, *R*

The difference between two single and independent test results, obtained by different operators working in different laboratories on identical test material, would in the long run, in the normal and correct operation of the test method, exceed the values calculated according to the Formula (3) only in one case in twenty.

$$R = 17{,}461\,2 + -0{,}128\,9 \cdot X\ [\%] \quad (3)$$

where

X represents the mean of the two results expressed in % (*m/m*).

11 Test report

The test report shall specify the following:

a) the reference to this Technical Specification, i.e. ISO/TS 17307:—;

b) the type and complete identification of the product tested;

c) the used method of sampling;

d) the results of the test (see Clause 9);

e) all operating details not specified in this Technical Specification, or regarded as optional, together with details of any incidents which may have influenced the test result(s);

f) the date of the test.

Annex A
(informative)

Examples of chromatograms

This Annex shows examples of chromatograms that should be used as reference to compare with own chromatograms obtained through the laboratory set-up. All peaks in the chromatograms that are not numbered have not been identified as ester peaks. One should, however, be aware of the possibility that peaks of esters may overlap with other peaks, for instance from glycerides.

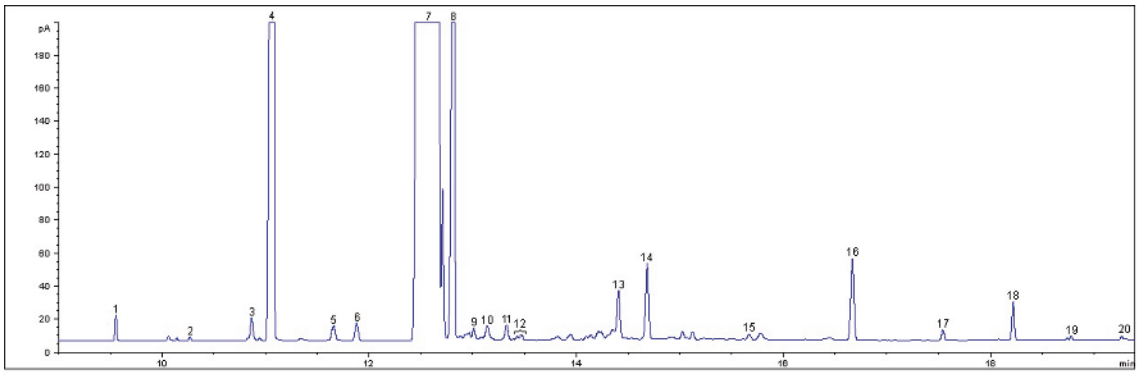


Figure A.1 — Soy biodiesel sample

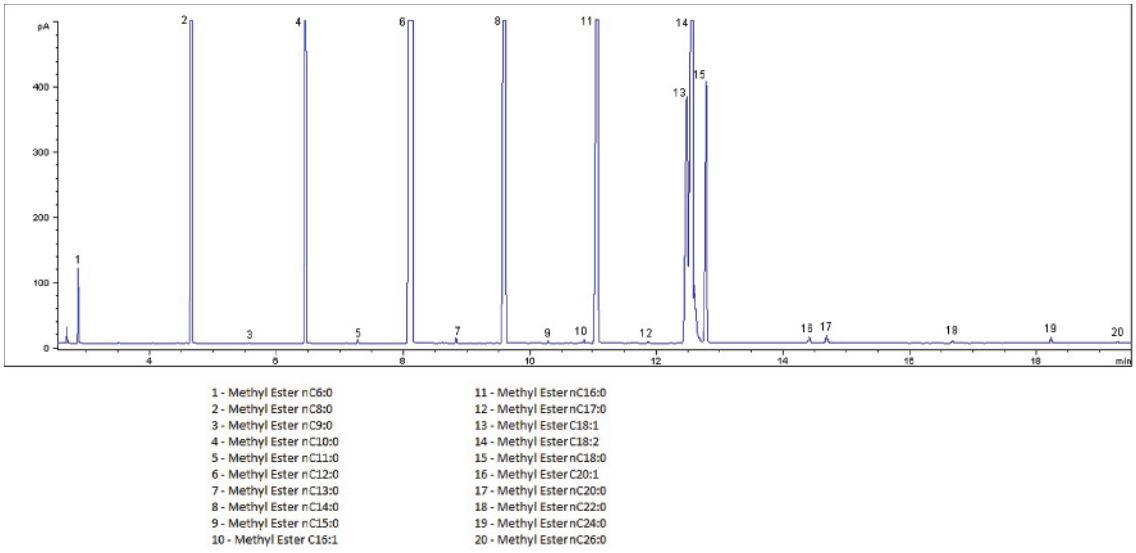
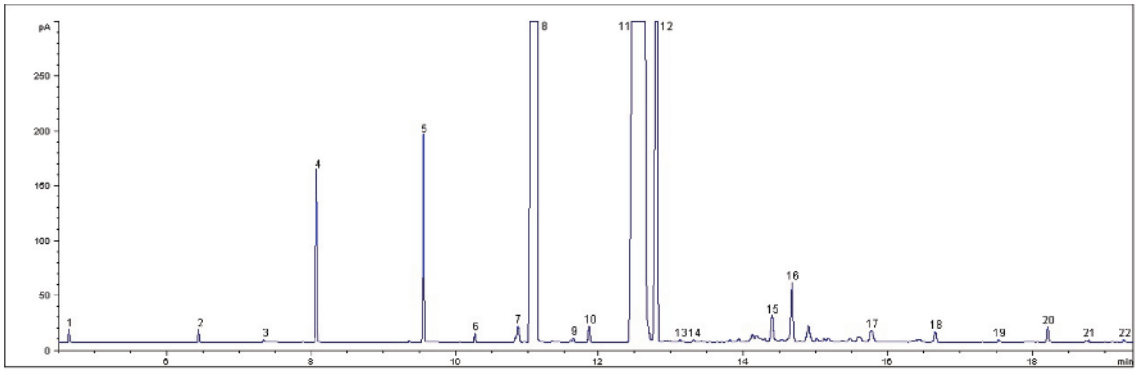
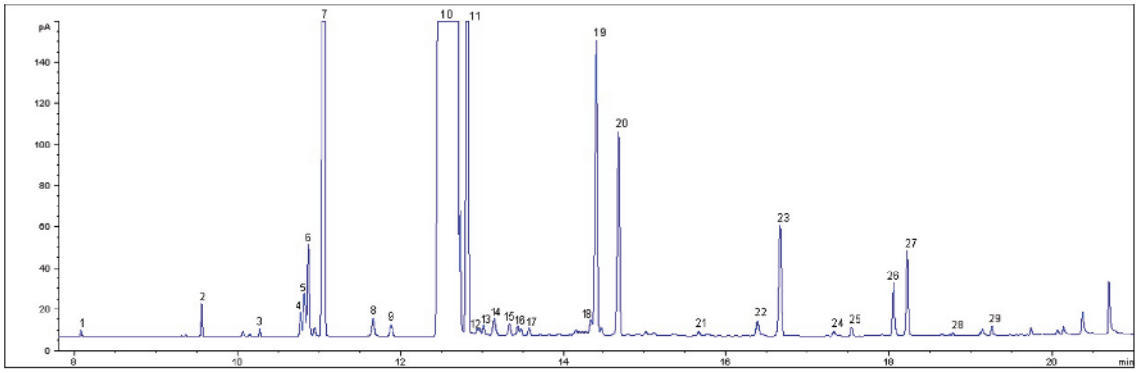


Figure A.2 — Coconut biodiesel sample



1 - Methyl Ester nC8:0
2 - Methyl Ester nC10:0
3 - Methyl Ester nC11:0
4 - Methyl Ester nC12:0
5 - Methyl Ester nC14:0
6 - Methyl Ester nC15:0
7 - Methyl Ester C16:1
8 - Methyl Ester nC16:0
9 - Methyl Ester IC17:1
10 - Methyl Ester nC17:0
11 - Methyl Ester C18:1 e C18:2
12 - Methyl EsternC18:0
13 - Methyl EsterC18:1
14 - Methyl Ester C18:2
15 - Methyl EsterC20:1
16 - Methyl EsternC20:0
17 - Methyl EsternC21:0
18 - Methyl EsternC22:0
19 - Methyl EsternC23:0
20 - Methyl EsternC24:0
21 - Methyl EsternC25:0
22 - Methyl EsternC26:0

Figure A.3 — Palm biodiesel sample



1 - Methyl Ester nC12:0
2 - Methyl Ester nC14:0
3 - Methyl Ester nC15:0
4 - Methyl Ester C16:2
5 - Methyl Ester C16:3
6 - Methyl Ester C16:1
7 - Methyl Ester nC16:0
8 - Methyl Ester C17:1
9 - Methyl Ester nC17:0
10 - Methyl Ester C18:1, C18:2 e C18:3
11 - Methyl EsternC18:0
12 - Methyl EsterC18:2
13 - Methyl EsterC18:3
14 - Methyl EsterC18:3
15 - Methyl EsterC18:2
16 - Methyl EsterC19:2
17 - Methyl EsterC19:1
18 - Methyl EsterC20:2
19 - Methyl EsterC20:1
20 - Methyl EsternC20:0
21 - Methyl EsternC21:0
22 - Methyl Ester C22:1
23 - Methyl Ester nC22:0
24 - Methyl Ester C23:1
25 - Methyl Ester nC23:0
26 - Methyl Ester C24:1
27 - Methyl Ester nC24:0
28 - Methyl Ester nC25:0
29 - Methyl Ester nC26:0

Figure A.4 — Rapeseed biodiesel sample

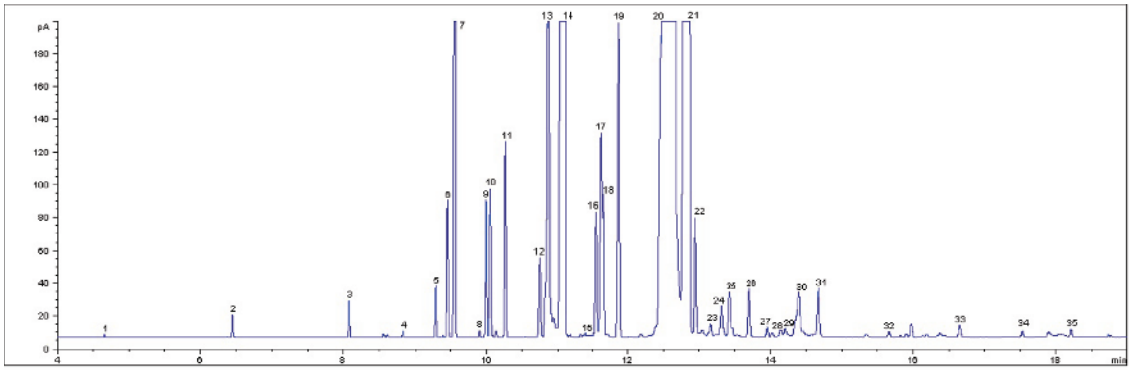


Figure A.5 — Animal fat biodiesel sample

Annex B
(informative)

Preparation of standard solutions

Prepare a standard solution of methyl (or ethyl) octadecanoate in mass corresponding to approximately 40 mL of *n*-heptane according to Table B.1.

This procedure also applies to preparation of solution with methyl (or ethyl) dodecanoate.

Table B.1 — Preparation of standard solutions

Level	Compound mass g	Total mass (compound + *n*-heptane) g	Compound concentration[a] %
1	0,001 0	26,801	0,003 7
2	0,005 0	26,805	0,018 7
3	0,010 0	26,810	0,037 3
4	0,040 0	26,840	0,149 0
5	0,090 0	26,890	0,334 7
6	0,099 0	26,899	0,368 0

[a] Compound concentration (m/m) in sample corresponding to: 1 %, 5 %, 10 %, 40 %, 90 % and 99 %.

Bibliography

[1] EN 14103, *Fat and oil derivatives — Fatty Acid Methyl Esters (FAME) — Determination of ester and linolenic acid methyl ester contents*

[2] EN 15779, *Petroleum products and fat and oil derivates — Fatty acid methyl esters (FAME) for diesel engines — Determination of polyunsaturated (≥4 double bonds) fatty acid methyl esters (PUFA) by gas chromatography*

ICS 75.160.20
Price based on 11 pages

This page deliberately left blank

British Standards Institution (BSI)

BSI is the national body responsible for preparing British Standards and other standards-related publications, information and services.

BSI is incorporated by Royal Charter. British Standards and other standardization products are published by BSI Standards Limited.

About us

We bring together business, industry, government, consumers, innovators and others to shape their combined experience and expertise into standards -based solutions.

The knowledge embodied in our standards has been carefully assembled in a dependable format and refined through our open consultation process. Organizations of all sizes and across all sectors choose standards to help them achieve their goals.

Information on standards

We can provide you with the knowledge that your organization needs to succeed. Find out more about British Standards by visiting our website at bsigroup.com/standards or contacting our Customer Services team or Knowledge Centre.

Buying standards

You can buy and download PDF versions of BSI publications, including British and adopted European and international standards, through our website at bsigroup.com/shop, where hard copies can also be purchased.

If you need international and foreign standards from other Standards Development Organizations, hard copies can be ordered from our Customer Services team.

Subscriptions

Our range of subscription services are designed to make using standards easier for you. For further information on our subscription products go to bsigroup.com/subscriptions.

With **British Standards Online (BSOL)** you'll have instant access to over 55,000 British and adopted European and international standards from your desktop. It's available 24/7 and is refreshed daily so you'll always be up to date.

You can keep in touch with standards developments and receive substantial discounts on the purchase price of standards, both in single copy and subscription format, by becoming a **BSI Subscribing Member**.

PLUS is an updating service exclusive to BSI Subscribing Members. You will automatically receive the latest hard copy of your standards when they're revised or replaced.

To find out more about becoming a BSI Subscribing Member and the benefits of membership, please visit bsigroup.com/shop.

With a **Multi-User Network Licence (MUNL)** you are able to host standards publications on your intranet. Licences can cover as few or as many users as you wish. With updates supplied as soon as they're available, you can be sure your documentation is current. For further information, email bsmusales@bsigroup.com.

BSI Group Headquarters

389 Chiswick High Road London W4 4AL UK

Revisions

Our British Standards and other publications are updated by amendment or revision.

We continually improve the quality of our products and services to benefit your business. If you find an inaccuracy or ambiguity within a British Standard or other BSI publication please inform the Knowledge Centre.

Copyright

Useful Contacts:

Customer Services
Tel: +44 845 086 9001
Email (orders): orders@bsigroup.com
Email (enquiries): cservices@bsigroup.com

Subscriptions
Tel: +44 845 086 9001
Email: subscriptions@bsigroup.com

Knowledge Centre
Tel: +44 20 8996 7004
Email: knowledgecentre@bsigroup.com

Copyright & Licensing
Tel: +44 20 8996 7070
Email: copyright@bsigroup.com

bsi.