BS EN 16174:2012

BSI Standards Publication

Sludge, treated biowaste and soil — Digestion of aqua regia soluble fractions of elements

bsi.

...making excellence a habit.™

National foreword

This British Standard is the UK implementation of EN 16174:2012.

The UK participation in its preparation was entrusted to Technical Committee H/-/4, Environmental testing programmes.

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 2012

ISBN 978 0 580 56703 2

ICS 13.030.01; 13.080.10

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 30 September 2012.

Amendments issued since publication

Date	Text affected

EUROPEAN STANDARD

NORME EUROPÉENNE

EUROPÄISCHE NORM

EN 16174

August 2012

ICS 13.030.01; 13.080.10

English Version

Sludge, treated biowaste and soil - Digestion of aqua regia soluble fractions of elements

Boues, biodéchets traités et sols - Digestion des éléments solubles dans l'eau régale

Schlamm, behandelter Bioabfall und Boden - Aufschluss von mit Königswasser löslichen Anteilen von Elementen

This European Standard was approved by CEN on 24 May 2012.

EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

Management Centre: Avenue Marnix 17, B-1000 Brussels

Contents

Page

Foreword

This document (EN 16174:2012) has been prepared by Technical Committee CEN/TC 400 “Project Committee - Horizontal standards in the fields of sludge, biowaste and soil”, the secretariat of which is held by DIN.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by February 2013, and conflicting national standards shall be withdrawn at the latest by February 2013.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. CEN [and/or CENELEC] shall not be held responsible for identifying any or all such patent rights.

This document has been prepared under a mandate given to CEN by the European Commission and the European Free Trade Association.

The preparation of this document by CEN is based on a mandate by the European Commission (Mandate M/330), which assigned the development of standards on sampling and analytical methods for hygienic and biological parameters as well as inorganic and organic determinants, aiming to make these standards applicable to sludge, treated biowaste and soil as far as this is technically feasible.

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard: Austria, Belgium, Bulgaria, Croatia, Cyprus, Czech Republic, Denmark, Estonia, Finland, Former Yugoslav Republic of Macedonia, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Romania, Slovakia, Slovenia, Spain, Sweden, Switzerland, Turkey and the United Kingdom.

Introduction

This method is intended to provide a multi-element *aqua regia* digestion of sludge, treated biowaste and soil prior to analysis. It is known that the digestion of environmental samples with *aqua regia* will not necessarily lead to a complete element breakdown, and that the extract from a test sample may not reflect the total concentrations of the target analytes. However, for most environmental applications the result is fit for the purpose.

This European Standard is applicable and validated for several types of matrices as indicated in Table 1 (see also [19] for the results of the validation).

Table 1 — Matrices for which this European Standard is applicable and validated

Matrix	Materials used for validation
Sludge	Municipal sludge Industrial sludge Sludge from electronic industry Ink waste sludge Sewage sludge
Biowaste (Method A)	Compost Composted sludge
Soil	Agricultural soil Sludge amended soils

WARNING — Persons using this European Standard should be familiar with usual laboratory practice. The reagents used in this European Standard are strongly corrosive and partly very toxic. Safety precautions are absolutely necessary, not only due to the strong corrosive reagents, but also to high temperature and high pressure.

The use of laboratory-grade microwave equipment with isolated and corrosion resistant safety devices is required. Domestic (kitchen) type microwave ovens shall not be used, as corrosion by acid vapours may compromise the function of the safety devices and prevent the microwave magnetron from shutting off when the door is open, which could result in operator exposure to microwave energy.

All procedures shall be performed in a fume hood or in closed force-ventilated equipment. By the use of strong oxidising reagents, the formation of explosive organic intermediates is possible, especially when dealing with samples with a high organic content. Do not open pressurized vessels before they have cooled down. Avoid contact with the chemicals and the gaseous reaction products.

IMPORTANT — It is absolutely essential that tests conducted according to this European Standard be carried out by suitably trained staff.

1 Scope

This European Standard specifies two methods for digestion of sludge, treated biowaste and soil by the use of *aqua regia* as digestion solution.

This European Standard is applicable for the following elements:

Aluminium (Al), antimony (Sb), arsenic (As), barium (Ba), beryllium (Be), bismuth (Bi), boron (B), cadmium (Cd), calcium (Ca), cerium (Ce), cesium (Cs), chromium (Cr), cobalt (Co), copper (Cu), dysprosium (Dy), erbium (Er), europium (Eu), gadolinium (Gd), gallium (Ga), germanium (Ge), gold (Au), hafnium (Hf), holmium (Ho), indium (In), iridium (Ir), iron (Fe), lanthanum (La), lead (Pb), lithium (Li), lutetium (Lu), magnesium (Mg), manganese (Mn), mercury (Hg), molybdenum (Mo), neodymium (Nd), nickel (Ni), palladium (Pd), phosphorus (P), platinum (Pt), potassium (K), praseodymium (Pr), rubidium (Rb), rhenium (Re), rhodium (Rh), ruthenium (Ru), samarium (Sm), scandium (Sc), selenium (Se), silicon (Si), silver (Ag), sodium (Na), strontium (Sr), sulphur (S), tellurium (Te), terbium (Tb), thallium (Tl), thorium (Th), thulium (Tm), tin (Sn), titanium (Ti), tungsten (W), uranium (U), vanadium (V), ytterbium (Yb), yttrium (Y), zinc (Zn), and zirconium (Zr).

This European Standard may also be applicable for the digestion of other elements.

Digestion with *aqua regia* will not necessarily accomplish total decomposition of the sample. The extracted analyte concentrations may not necessarily reflect the total content in the sample.

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.

EN 15936, *Sludge, treated biowaste, soil and waste — Determination of total organic carbon (TOC) by dry combustion*

EN 16179, *Sludge, treated biowaste and soil — Guidance for sample pretreatment*

EN ISO 3696, *Water for analytical laboratory use — Specification and test methods (ISO 3696)*

3 Terms and definitions

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

3.1
aqua regia
digestion solution obtained by mixing one volume of concentrated nitric acid and three volumes of concentrated hydrochloric acid

4 Principle

A test portion is digested with *aqua regia* according to one of the following heating procedures:

— Method A: boiling under reflux for 2 h, followed by filtration and adjusting the volume in a volumetric flask;

— Method B: microwave digestion at (175 ± 5) °C for (10 ± 1) min in a closed vessel followed by filtration and adjusting the volume in a volumetric flask.

5 Interferences and sources of errors

Due to the volatility of some compounds care shall be taken, that the sample is not heated before the digestion and that any volatile reaction products formed during the digestion do not escape.

High acid and solute concentrations in the digest may cause interferences at determination.

Contamination shall be avoided. Glass containing e.g. B, Na, K, Al can contaminate samples.

Ensure that all of the test portion is brought into contact with the acid mixture in the digestion vessel.

Some elements of interest can be lost due to precipitation with ions present in the digest solution, e.g. low soluble chlorides, fluorides and sulfates.

6 Reagents

Use only acids and reagents of recognized analytical grade to avoid high blank values for subsequent analytical measurements. Use a test blank solution throughout the procedure applying all steps with the same amount of acids, but without a sample.

6.1 Water, quality 2 according to EN ISO 3696 or better.

6.2 Hydrochloric acid, c(HCl) = 12 mol/l; ρ = 1,18 kg/l.

6.3 Nitric acid, c(HNO_3) = 15 mol/l, ρ = 1,4 kg/l.

6.4 Nitric acid, c(HNO_3) = 0,5 mol/l, ρ = 1,0 kg/l.

Dilute 35 ml nitric acid (6.3) to 1 l with water (6.1).

6.5 Antifoaming agent, e.g. n-dodecane ($C_{12}H_{26}$) or Octanol ($C_8H_{18}O$) are suitable.

7 Apparatus

Usual laboratory apparatus. All glassware and plastics ware shall be adequately cleaned and stored in order to avoid any contamination.

Depending on the concentration of the element of interest, a particular caution to the cleaning of the vessels shall be taken.

7.1 Apparatus used for Method A

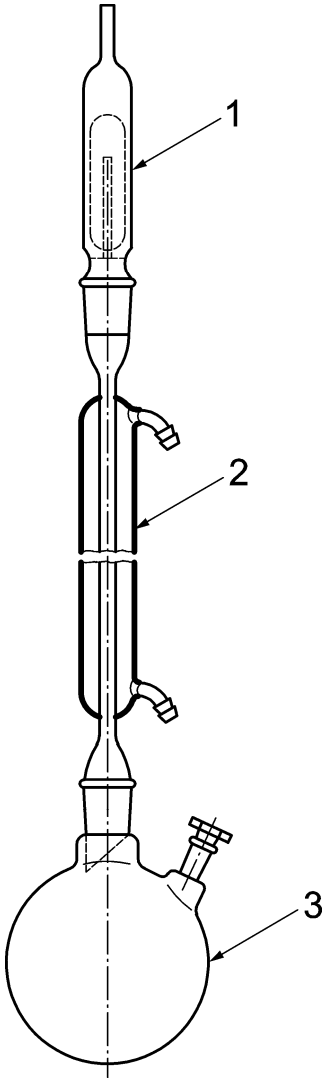
7.1.1 Digestion vessel, see Figure 1, temperature- and pressure-resistant and capable of containing the mixture of sample and digest solution, for example a glass flask of 250 ml. The inner wall of the vessel shall be inert and shall not release substances to the digest in excess of the purity requirements of the subsequent analysis.

NOTE 1 Quartz vessels can be used instead of glass vessels.

NOTE 2 It may be necessary to periodically clean the reaction vessels with a suitable surfactant to remove persistent deposits.

7.1.2 Reflux condenser adaptable to the digestion vessel (7.1.1).

7.1.3 Absorption vessel, volatile species trap, in an open digestion system capable of trapping one or more volatile measurement species, adaptable to the reflux condenser (7.1.2).



Key

1 absorption vessel
2 reflux condenser
3 digestion vessel

Figure 1 — Digestion vessel (7.1.1), reflux condenser (7.1.2) and absorption vessel (7.1.3), assembled

7.1.4 Heating device, for example a heating mantle, thermostatic controlled, or an aluminium block thermostat.

7.2 Apparatus used for Method B

7.2.1 Digestion vessel, for pressurized microwave digestion, preferably of 100 ml volume, reagent-, temperature- and pressure-resistant and capable of containing the mixture of sample and digest solution. The vessel shall be suitable for the safe application in the temperature and pressure range applied, capable of withstanding pressures of at least 3 000 kPa.

Digestion vessels made of perfluoro alkoxyl alkane (PFA), modified polytetrafluoroethene (PTFE) or quartz glass, and equipped with a safety pressure releasing system to avoid explosion of the vessel, shall be used. The inner wall of the vessel shall be inert and shall not release contaminations to the digest solution.

NOTE It may be necessary to periodically clean the reaction vessels with a suitable surfactant to remove persistent deposits.

7.2.2 Microwave digestion system, corrosion resistant and well ventilated. All electronics shall be protected against corrosion for safe operation.

Use a laboratory-grade microwave oven with temperature feedback control mechanisms.

The microwave digestion system should be able to control the temperature with an accuracy of ± 5 °C and automatically adjust the microwave field output power within 2 s of sensing. Temperature sensors shall be accurate to ± 2 °C, including the final reaction temperature of (175 ± 5) °C. Temperature feedback control provides the primary performance mechanism for the method. Due to the variability in sample matrix types and microwave digestion equipment (i.e. different vessel types and microwave designs), control of the temperature during digestion is important for reproducible microwave heating and comparable data.

The accuracy of the temperature measurement system should be periodically controlled at an elevated temperature according to the manufactures instructions. If the temperature deviates by more than 2 °C from the temperature measured by an external, calibrated temperature measurement system, the microwave temperature measurement system should be calibrated.

7.2.3 Rotating turntable, with a minimum speed of 3 min^{-1}.

7.3 Sample containers, plastics and glass containers are both suitable.

All containers shall be adequately acid cleaned and stored in order to avoid any contamination.

7.4 Filter paper, resistant to *aqua regia*.

7.5 Volumetric flasks, usually of nominal capacity of 50 ml or 100 ml.

7.6 Analytical balance, with an accuracy of 0,1 mg or better.

7.7 Boiling aids, anti-bumping granules or glass beads, diameter 2 mm to 3 mm, acid washed.

8 Procedure

8.1 General

Pretreat the test sample according to EN 16179, if not otherwise specified.

8.2 Blank test

Carry out a reagent blank test digestion in parallel with the determination, using the same procedure and the same quantities of all the reagents as in the determination, but omitting the test portion.

NOTE The measurement of a blank is introduced to determine the contribution of the extracting solution, glassware and filter paper used to the measured value.

8.3 Method A: Thermal heating under reflux conditions

Weigh approximately 3 g, to the nearest 0,01 g, of the test sample and transfer to the 250 ml digestion vessel (7.1.1).

In case of dry samples moisten the test portion with about 0,5 ml to 1,0 ml of water (6.1) and add, dropwise, if necessary, to reduce foaming, with mixing, (21 ± 0,1) ml of hydrochloric acid (6.2) followed by (7 ± 0,1) ml of nitric acid (6.3). Connect the reflux condenser (7.1.2) to the digestion vessel (7.1.1). Fill the absorption vessel (7.1.3) with approximately 15 ml nitric acid (6.4). Connect the absorption vessel to the reflux condenser, and let stand at room temperature until any effervescence almost ceases to allow for slow oxidation of the organic matter in the sample.

NOTE The time of standing at room temperature may have an influence on the digestion rate of *aqua regia*. For comparison reasons of the method it is recommended to start heating as soon as possible after the first strong reaction has ceased.

30 ml of *aqua regia* is only sufficient for the oxidation of about 0,5 g organic carbon. If there is any doubt of the amount of carbon present, estimate the amount of carbon in the sample or carry out a determination of TOC according to EN 15936. If there is more than 0,5 g of organic carbon in the test portion, proceed as follows.

Allow first reaction with the *aqua regia* to subside. Then add an extra 1 ml of nitric acid (6.3) only to every 0,1 g of organic carbon above 0,5 g. Do not add more than 10 ml of nitric acid at any given time, and allow any reaction to subside before proceeding further.

Connect the digestion vessel (7.1.1) to the heating device (7.1.4) and raise the temperature of the reaction mixture to reflux conditions and maintain for 2 h ensuring that the condensation zone is lower than 1/3 of the height of the reflux condenser, then allow to cool. Add the content of the absorption vessel to the reaction vessel via the reflux condenser, rinsing both the absorption vessel and condenser with further 10 ml of diluted nitric acid (6.4).

Add about 20 ml of water, filter the sample through an acid resistant membrane or filter paper (7.4) into a 100 ml volumetric flask, and wash the filter residue with diluted nitric acid (6.4), and fill up to volume with water.

Alternatively another procedure can be applied, such that the adjustment to volume with the solid residue still present shall be carried out immediately after extraction, followed by filtration or centrifugation of a sample solution aliquot for final measurement.

The measurement solution is now ready for analysis for elements of interest using appropriate elemental analysis techniques.

If the measurement solution contains particles due to precipitation which may clog nebulizers or interfere with an injection of the sample into the instrument, the sample may be centrifuged, allowed to settle, or filtered.

8.4 Method B: Microwave heating with temperature control at (175 ± 5) °C

Weigh an amount of not more than 2 g of the test portion (typically 0,5 g to 1 g of dry sample) containing not more than 0,5 g of organic carbon with an accuracy of 0,001 g and transfer it into the digestion vessel (7.2.1).

Referring to the manufacturer’s instructions, the upper limits of mass of the test portion shall be taken into account.

Moisten the test portion with a few drops of water (6.1). Add separately (6 ± 0,1) ml of hydrochloric acid (6.2) and (2 ± 0,1) ml of nitric acid (6.3) and mix well.

If a vigorous reaction occurs, allow the reaction cease before capping the vessel. If excessive foaming occurs, add a drop of anti-foaming agent (6.5).

Cap the digestion vessel according to the manufacturer's instructions. Weigh the digestion vessel before digestion. Place in all positions of the microwave carrousel (usually 6, 12, 16 or 40 positions) sample vessels. If a lower number of samples are available compared to the vessel positions, place vessels filled with same amount of *aqua regia* without sample. This is to ascertain same microwave energy absorption during each digestion procedure. This method is an operationally defined method, designed to achieve consistent digestion of samples by specific reaction conditions. The temperature of the digestion mixture in each vessel shall be raised with a heating rate of approximately 10 °C/min to 15 °C/min to (175 ± 5) °C and remain at (175 ± 5) °C for (10 ± 1) min. Cool down to room temperature.

WARNING — Too high a temperature increase may cause a vigorous, exothermic reaction in digestion solution with high pressure increase and blow off of security valve. Losses of analytes are possible.

At the end of the microwave programme, allow the vessels to cool according to the manufacturer's instructions before removing them from the microwave system. Cooling of the vessels may be accelerated by internal or external cooling devices.

After reaching room temperature, check if the microwave vessels maintained their seal throughout the digestion. Due to the wide variety of vessel designs, a single procedure is not appropriate. Weigh the vessels after digestion to evaluate seal integrity. If the weight loss of the sample exceeds 10 % of the weight of the added test portion and reagents before the start of digestion, the respective sample is considered compromised.

Carefully uncap and vent each vessel in a well-ventilated fume hood according to the manufacturer's instructions. Add about 20 ml of water, filter the sample through an acid resistant membrane or filter paper (7.4) into a volumetric flask, and wash the residue with diluted nitric acid (6.4), and fill up to volume with water (typically 50 ml or 100 ml).

Alternatively another procedure can be applied, such that the adjustment to volume with the solid residue still present shall be carried out immediately after extraction, followed by filtration or centrifugation of a sample solution aliquot for final measurement.

The measurement solution is now ready for analysis for elements of interest using appropriate elemental analysis techniques.

If the measurement solution contains particles due to precipitation which may clog nebulizers or interfere with an injection of the sample into the instrument, the sample may be centrifuged, allowed to settle, or filtered.

9 Test report

The test report shall contain at least the following information:

a) a reference to this European Standard (EN 16174);

b) all information necessary for identification of the sample;

c) information about the pretreatment and method of digestion of the sample;

d) any details not specified in this European Standard or which are optional, as well as any factor which may have affected the results.

Annex A
(informative)

Repeatability and reproducibility data

A.1 Materials used in the interlaboratory comparison study

The interlaboratory comparison of digestion of *aqua regia* soluble fractions of trace elements in sludge, treated biowaste and soil was carried out with 20 to 23 European laboratories on five materials. Detailed information can be found in the final report on the interlaboratory comparison study mentioned in [19].

Table A.1 lists the types of materials tested.

Table A.1 — Materials tested and parameters analysed in the interlaboratory comparison of the digestion for the extraction of *aqua regia* soluble fractions of trace elements in sludge, treated biowaste and soil

Grain size	Sample	Material	Parameters
Sludge (< 0,5 mm)	Sludge 1	Mix 1 of municipal waste water treatment plant sludges from North Rhine Westphalia, Germany	As, Cd, Cr, Cu, Fe, Mn, Ni, P, Pb, Zn
	Sludge 2	Mix 2 of municipal waste water treatment plant sludges from North Rhine Westphalia, Germany	As, Cd, Cr, Cu, Fe, Mn, Ni, P, Pb, Zn
Fine grained (< 2,0 mm)	Compost 2	Compost from Germany	As, Cd, Cr, Cu, Fe, Mn, Ni, P, Pb, Zn
	Soil 1	A sludge amended soil from Pavia, Italy	As, Cd, Cr, Cu, Fe, Mn, Ni, P, Pb, Zn
	Soil 2	A sludge amended soil from Düsseldorf, Germany	As, Cd, Cr, Cu, Fe, Mn, Ni, P, Pb, Zn

Bibliography

[1] EN 1233, *Water quality — Determination of chromium — Atomic absorption spectrometric methods*

[2] EN 1483, *Water quality — Determination of mercury — Method using atomic absorption spectrometry*

[3] EN 13346, *Characterization of sludges — Determination of trace elements and phosphorus — Aqua regia extraction methods*

[4] EN 13650, *Soil improvers and growing media — Extraction of aqua regia soluble elements*

[5] EN 13657, *Characterization of waste — Digestion for subsequent determination of aqua regia soluble portion of elements*

[6] EN 45001, *General criteria for the operation of testing laboratories*

[7] EN ISO 5961, *Water quality — Determination of cadmium by atomic absorption spectrometry (ISO 5961)*

[8] EN ISO 11885, *Water quality — Determination of selected elements by inductively coupled plasma optical emission spectrometry (ICP-OES) (ISO 11885)*

[9] EN ISO 11969, *Water quality — Determination of arsenic — Atomic absorption spectrometry method (hydride technique) (ISO 11969)*

[10] ISO 8288, *Water quality — Determination of cobalt, nickel, copper, zinc, cadmium and lead — Flame atomic absorption spectrometric methods*

[11] ISO 11074, *Soil quality — Vocabulary*

[12] ISO 11464, *Soil quality — Pretreatment of samples for physico-chemical analysis*

[13] ISO 11466:1995, *Soil quality — Extraction of trace elements soluble in aqua regia*

[14] EPA Method 3051A:1998, *Microwave assisted acid digestion of sediments, sludges, soils and oils*

[15] EPA Method 3052:1995, Microwave assisted acid digestion of siliceous and organically based materials

[16] EPA Method 3051:1994, *Microwave assisted acid digestion of sediments, sludges, soils and oils*

[17] EPA Method 3015:1990, *Microwave assisted acid digestion of aqueous samples and extracts*

[18] Explanatory note PARTICIPANTS IN VALIDATION OF HORIZONTAL STANDARDS http://horizontal.ecn.nl/

[19] JRC Scientific and Technical Reports, Project HORIZONTAL Validation Report on aqua regia digestion

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.

...making excellence a habit.™