BS 6200 : Subsection 3.10.2 : 1989
EN 10 188 : 1989

UDC 669.1 : 620.1 : 546.76 : 543.422

British Standard

Sampling and analysis of iron, steel and other ferrous metals

Part 3. Methods of analysis
Section 3.10 Determination of chromium

Subsection 3.10.2 Steel and cast iron: flame atomic absorption spectrometric method

Echantillonnage et analyse du fer, de l'acier et d'autres métaux ferreux
Partie 3. Méthodes d'analyse
Section 3.10 Dosage du chrome
Sous-section 3.10.1 Aciers et fontes: méthode par spectrométrie d'absorption atomique dans la flamme

Probenahme und Analyse von Eisen, Stahl und anderen Eisenmetallen
Teil 3. Analysenverfahren
Abschnitt 3.10 Chrombestimmung
Unterabschnitt 3.10.1 Stahl und Gußeisen : flammenaromabsorptionsspektrometrisches Verfahren

Contents

National foreword

This subsection of BS 6200 has been prepared under the direction of the Iron and Steel Standards Policy Committee. It is the English language version of EN 10 188 : 1989 'Chemical analysis of ferrous materials. Determination of chromium in steels and irons. Flame atomic absorption spectrometric method', published by the European Committee for Standardization (CEN).

There is no corresponding British Standard for Euronorm 18. Appropriate procedures from Euronorm 18 will be incorporated in BS 6200 : Part 2 'Methods of sampling and sample preparation', which will be published in due course.

Information Circular No 8 and Information Circular No 9 have been published under the auspices of the European Coal and Steel Community. The texts of both documents are being adopted unchanged in, respectively, BS 6200 : Section 6.1 'Recommendations for the drafting of standard methods for the chemical analysis of iron and steel by flame atomic absorption spectrometry' and BS 6200 : Section 6.2 'Recommendations for the application of flame atomic absorption spectrometry in standard methods for the chemical analysis of iron and steel'.

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

This European Standard EN 10 188 has the status of a British Standard.

British Standards Institution

EN 10 188

EUROPEAN STANDARD
NORME EUROPÉENNE
EUROPÄISCHE NORM

May 1989

UDC 669.1 : 620.1 : 546.76 : 543.422

Key words: Iron and steel products, steels, cast irons, chemical analysis, chromium, atomic absorption spectrometry, flame photometry

English version

Chemical analysis of ferrous materials. Determination of chromium in steels and irons. Flame atomic absorption spectrometric method

Analyse chimique des matériaux sidérurgiques. Dosage du chrome dans les aciers et les fontes. Méthode par spectrométrie d'absorption atomique dans la flamme

Chemische Analyse von Eisenwerkstoffen. Bestimmung von Chrom in Stahl und Eisen. Flammenatomabsorptionsspektrometrisches Verfahren

This European Standard was accepted by CEN on 15 May 1989. CEN members are bound to comply with the requirements of the CEN/CENELEC Common Rules which stipulate the conditions for giving this European Standard the status of a national standard without any alteration.

Up-to-date lists and bibliographical references concerning such national standards may be obtained on application to the CEN Central Secretariat or to any CEN member.

This European Standard exists in three official versions (English, French, German). A version in any other language made by translation under the responsibility of a CEN member into its own language and notified to CEN Central Secretariat has the same status as the official versions.

CEN members are the national standards organizations of Austria, Belgium, Denmark, Finland, France, Germany, Greece, Iceland, Ireland, Italy, Luxemburg, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland and United Kingdom.

CEN

European Committee for Standardization
Comité Européen de Normalisation
Europäisches Komitee für Normung

Central Secretariat: rue Bréderode 2, B-1000 Brussels

Brief history

This European Standard takes over the contents of EURONORM 188-87 'Chemical analysis of ferrous materials – Determination of chromium in steels and irons – Flame atomic absorption spectrometric method' prepared by ECISS/TC 20, Methods of chemical analysis, the secretariat of which is allocated to the Dansk Standardiseringsraad (DS).

It was submitted to the CEN Formal Vote following the decision of the Coordinating Commission (COCOR) of the European Committee for Iron and Steel Standardization on 24/25 November 1987.

According to the Common CEN/CENELEC Rules, the following countries are bound to implement this European Standard:

Austria, Belgium, Denmark, Finland, France, Germany, Greece, Iceland, Ireland, Italy, Luxemburg, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland and United Kingdom.

Chemical analysis of ferrous materials
Determination of chromium in steels and irons
Flame atomic absorption spectrometric method

CONTENTS

1 SCOPE AND FIELD OF APPLICATION

This European Standard specifies a method for the determination of chromium in steels and irons by means of flame atomic absorption spectrometry.

The method is applicable to non-alloy and low-alloy steels and irons with chromium contents of 0.002 to 2.0 % (m/m) (see Annex).

2 REFERENCES

Euronorm 18 – Selection and preparation of samples and test pieces for steel and iron and steel products.

Information Circular No 8 – Recommendations for the drafting of standard methods of analysis employing flame atomic absorption spectrometry for the chemical analysis of iron and steel.

Information Circular No 9 – Operational guidelines for the application of flame atomic absorption spectrometry in standard methods for the chemical analysis of iron and steel.

3 PRINCIPLE

Dissolution of a test portion with hydrochloric acid followed by oxidation with nitric acid. Filtration and ignition of the acid insoluble residue. Removal of silica with hydrofluoric acid. Fusion of the residue with potassium hydrogen sulphate, extraction of the melt in acid and addition of the extract to the reserved filtrate.

Determination of the chromium by means of the spectrometric measurement of the atomic absorption of the 357.87 nm line emitted by a chromium hollow cathode lamp when the solution is nebulized into a nitrous oxide acetylene flame.

4 REAGENTS

During the analysis, use only reagents of recognized analytical reagent quality and having a very low chromium content, and only distilled water or water of equivalent purity.

4.1 Iron, of high purity, with a chromium content < 1 µg/g.

4.2 Potassium hydrogen sulphate ($KHSO_4$).

4.3 Hydrochloric acid, ρ 1.19 g/ml approximately, (12 mol/l approximately).

4.4 Nitric acid, ρ 1.40 g/ml approximately, (14 mol/l approximately).

4.5 Sulphuric acid, ρ 1.84 g/ml approximately, (18 mol/l approximately).

4.6 Hydrofluoric acid, ρ 1.15 g/ml approximately, (20 mol/l approximately).

4.7 Sulphuric acid, ρ 1.84 g/ml approximately, diluted 1+3 (V/V), (4.5 mol/l approximately).

4.8 Background solution

Weigh 10 g of iron (4.1) into a 1 litre beaker. Add 10 g of potassium hydrogen sulphate (4.2) and 150 ml of hydrochloric acid (4.3). Heat gently until dissolved, then oxidize with 30 ml of nitric acid (4.4), added in small portions. Allow to cool, transfer to a 250 ml volumetric flask, dilute to the mark with water and mix.

4.9 Chromium reference solution, corresponding to 1 mg of chromium per ml.

Weigh 1.000 g of high purity chromium metal ($\geqslant$ 99.7% (m/m) pure). Transfer to a 250 ml beaker and dissolve in 40 ml of hydrochloric acid (4.3). Cool, transfer to a 1 000 ml volumetric flask, dilute to the mark with water and mix.

Note: ρ equals the density.

5 APPARATUS

Ordinary laboratory equipment and

5.1 Atomic absorption spectrometer; a chromium hollow cathode lamp; supplies of nitrous oxide and acetylene sufficiently pure to give a steady, clear fuel-lean flame, free from water and oil and free from chromium.

The atomic absorption spectrometer used will be satisfactory if after optimization according to 7.3.4, the limit of detection and characteristic concentration are in reasonable agreement with the values given by the manufacturer and it meets the following performance requirements.

5.1.1 Minimum precision

The standard deviation of 10 measurements of the absorbance of the most concentrated calibration solution shall not exceed 1.5 % of the mean absorbance.

The standard deviation of 10 measurements of the absorbance of the least concentrated calibration solution (excluding the zero calibration solution) shall not exceed 0.5 % of the mean absorbance of the most concentrated calibration solution.

For example, if the top and bottom calibration solutions represent 0.10 % and 0.02 % chromium in the sample, the precision called for (as two standard deviations) would be 0.003 % and 0.001 % chromium respectively, assuming curve linearity.

5.1.2 Additional performance requirements

It is also desirable that the instrument should conform to the following additional performance requirements (see Information Circular No 8, Section 2):

(a) Characteristic concentration – The characteristic concentration for chromium in a matrix similar to the final sample test solution shall be better than 0.25 µg/ml.

(b) Limit of detection – The limit of detection of chromium in a matrix similar to the final sample test solution shall be better than 0.05 µg/ml.

(c) Curve linearity – The slope of the calibration curve covering the top 20 % concentration range (expressed as a change in absorbance) shall not be less than 0.7 of the value of slope for the bottom 20 % concentration range determined in the same way.

For instruments with automatic standardization using only two calibration solutions, one being twice the concentration of the other, the acceptable curve linearity is limited to such an extent that the absorption of the lower calibration solution does not exceed 0.55 of the absorption of the higher calibration solution.

5.2 Ancillary equipment

A strip chart recorder and/or digital readout device is recommended to evaluate the criteria in 5.1 and for all subsequent measurements.

6 SAMPLING

Sampling shall be carried out in accordance with Euronorm 18.

7 PROCEDURE

7.1 Test portion

Weigh the mass (m) indicated below to the nearest 0.001 g:

$$m = 1\ g \pm 1\ \%$$

7.2 Blank test

With each analytical run, carry out an analysis on a reagent blank in parallel with the test portion analysis, using identical reagents, conditions, analytical procedures and dilutions throughout.

7.3 Determination

7.3.1 Preparation of the test solution

Place the test portion (7.1) in a 250 ml beaker. Add 15 ml of hydrochloric acid (4.3), cover the beaker and heat gently until solvent action ceases. Oxidize with 3 ml of nitric acid (4.4) added dropwise and boil for 1 minute to remove oxides of nitrogen. Cool, dilute with about 15 ml of water and filter through a pulp pad prepared from macerated filter paper, collecting the filtrate in a 100 ml volumetric flask. Wash the filter with water, collecting the washings in the same 100 ml volumetric flask, but taking care to leave sufficient room for the fusion extract of the acid insoluble residue, about 20 ml, to be added later. Reserve the filtrate. Transfer the filter and residue to a small platinum capsule or crucible, dry and ignite at as low a temperature as possible until all carbonaceous matter is removed and finally at about 800 °C for at least 15 minutes. Cool, add 2 drops of sulphuric acid solution (4.7) and about 2 ml of hydrofluoric acid (4.6). Evaporate to dryness, heat to about 800 °C and cool. Add 1 g of potassium hydrogen sulphate (4.2) and fuse carefully until a clear melt is obtained.

Note: For residues which contain chromium carbide, prolonged heating may be necessary for complete fusion. The potassium hydrogen sulphate can be regenerated by allowing the melt to cool, adding 2 drops of sulphuric acid solution (4.5) and repeating the fusion until the residue has dissolved.

Cool and transfer the crucible and solidified melt to a small beaker. Add 10 ml of water and 2 ml of hydrochloric acid (4.3) and heat gently until the solid has dissolved. Cool, add the extract to the reserved filtrate in the 100 ml volumetric flask, dilute to the mark with water and mix. This is the sample solution S.

Set up the instrument as described in 7.3.3. Test the solution S at various approximate dilutions to obtain the dilution factor D, that brings the solution near the midway of the optimum working range of the instrument, e.g. 0.25 to 0.45 absorbance units. Accurately dilute the sample solution S with water by the dilution factor D to obtain the test solution N. Dilute the blank test solution (7.2) in the same way.

Note: Volumes of sample solution S less than 5 ml shall not be taken for dilution.

7.3.2 Preparation of the calibration solution

If the test solution N gives an absorbance above 0.25, accurately dilute the standard chromium solution (4.9) to give a stock solution approximately 600 times the characteristic concentration (5.1.2). Using a burette, transfer 0, 5, 10, 15, 20 ml of the above chromium stock solution to 100 ml volumetric flasks. Add $25 \times {}^{1}/_{D}$ ml of background solution (4.8) to each and dilute to the mark with water (D is the dilution of the sample solution).

If the test solution N gives an absorbance below 0.25, prepare two solutions each containing 25 ml of background solution (4.8) per 100 ml, one containing 5 µg/ml of chromium, the other no added chromium. Using these, a rough estimate of the chromium in the test solution can be made. Accurately dilute the standard chromium solution (4.9) to give a stock solution of concentration 10 times the chromium level in the test solution, as estimated above. Using a burette, transfer 0, 5, 10, 15, 20 ml of the chromium stock solution to 100 ml volumetric flasks. Add 25 ml of background solution (4.8) to each and dilute to the mark with water.

The top standard shall contain at least sufficient chromium to give full scale deflection when using maximum scale expansion.

7.3.3 Adjustment of atomic absorption spectrophotometer (5.1)

Type of lamp:	chromium hollow cathode,
Wavelength:	357.87 nm,
Flame:	nitrous oxide/acetylene,
Lamp current:	follow manufacturer's recommendations,
Slit width:	follow manufacturer's recommendations.

Note – The manufacturer's recommendations should be closely followed and particular attention is drawn to the following safety points:

(a) the explosive nature of acetylene, and regulations concerning its use;

(b) the need to shield the eyes of the operator from UV radiation by means of tinted glass;

(c) the need to keep the burner head clear of deposits. A badly clogged burner may cause a flash back;

(d) the need to ensure that the liquid trap is filled with water.

See also Information Circular No 9 – Appendix C.

7.3.4 Optimization of the atomic absorption spectrometer settings

Follow the manufacturer's instructions for preparing the instrument for use. (See also Information Circular No 9 – Appendix A).

When the current to the lamp, the wavelength and the flow of gas have been adjusted and the burner lit, spray water until the indication has stabilized. Set the absorbance value to zero. Choose a damping setting or integration time to give a signal steady enough to fulfil the precision requirements (5.1.1).

Adjust the flame to be fuel-lean and the burner height to about 1 cm below the light path. Spraying, alternately, the high and zero calibration solutions, adjust the gas flow and burner position (horizontally, vertically and rotationally) until the difference in absorbance between the calibration solutions is at a maximum. Check that the spectrometer is set on the required wavelength.

Evaluate the criteria of 5.1.1 to ensure that the instrument is suitable for the determination.

7.3.5 Atomic absorption measurements

Set the scale expansion so that the top calibration solution gives nearly full scale deflection. Aspirate the calibration solutions in ascending order repetitively until each gives the specified precision (5.1.1) thus showing that the instrument has achieved stability. Select two calibration solutions, one having an absorbance just lower than the test portion solution and one just higher. Aspirate these first in ascending order, then in descending order, with the test solution as the middle solution in each case, measuring the absorbance in relation to water. Aspirate the complete range of calibration solutions again.

It is recognized that these procedures cannot be followed with automatic instruments which accept two calibration solutions only. In this case, it is suggested that the two 'sandwiching' solutions should not be used for the primary calibration but should be analysed alternately with the test solution.

Spray a calibration solution at frequent intervals during the measurement of a batch of determinations. Clean the burner if the results show loss of precision caused by clogging.

Obtain the net mean absorbance of each calibration solution by subtracting the mean absorbance of the zero calibration solution.

Obtain the mean absorbance of the test solution and the mean absorbance of the reagent blank solution.

Convert the mean absorbances of the test solution and of the reagent blank solution to micrograms of chromium per millilitre by means of the calibration graph (7.4).

7.4 Establishment of the calibration graph

It is necessary to draw up a new calibration graph for each series of determinations, and for the range of chromium contents expected.

If pure metals and reagents have been used, the blank test and zero calibration standard should give equal and negligibly small absorbances. In this case, prepare a calibration graph by plotting the mean absorbance values of the calibration solutions against micrograms of chromium per millilitre. Refer the mean test solution absorbances and the absorbances of the two adjacent calibration solutions to the graph.

If, however, the zero calibration solution has a significant absorbance, a more complicated procedure is required. (See Information Circular No 8, Section 5.) In this case, the concentration of chromium in the zero calibration solution can be calculated using the formula:

$$C_z = C_1 \times \frac{A_z}{A_1 - A_z}$$

where

C_z is the concentration of chromium in the zero calibration solution,

C_1 is the concentration of chromium added to the first calibration solution,

A_z is the absorbance of the zero calibration solution,

A_1 is the absorbance of the first calibration solution.

The derived value C_z is then added to each of the nominal calibration concentrations in order to obtain a mean calibration curve passing through the origin. Refer the absorbances of the reagent blank, the test solution and the two adjacent calibration solutions to this graph. Subtract the concentration of the reagent blank from the other concentrations.

If the results of the two calibration readings do not deviate from the graph by more than the permitted precision criteria then the test solution readings are acceptable.

8 EXPRESSION OF RESULTS

The percentage by mass of chromium (Cr) is given by the expression

$$\text{Cr}\ \%\ (m/m) = \frac{(b - c) \times D \times 100}{10^6} \times \frac{100}{m} = \frac{(b - c) \times D}{100\ m}$$

where

b is the concentration of chromium in the test solution expressed in µg/ml,

c is the concentration of chromium in the reagent blank solution expressed in µg/ml,

D is the dilution factor applied in 7.3.1,

m is the mass, in g, of the test portion.

9 TEST REPORT

The test report shall contain the following particulars:

(a) the method of analysis used by reference to this European Standard;

(b) the results obtained, as well as the form in which they are expressed;

(c) any particular details which may have been noted during the determination;

(d) any optional not specified in this European Standard or any optional operations which could have had an influence on the result;

(e) all indications necessary for the identification of the sample;

(f) the laboratory and the date of analysis.

ANNEX

Precision data

Planned trials of this method were carried out in 12 laboratories from six countries. With the following exceptions, each analyst carried out five determinations on each of five samples. The exceptions were that one laboratory supplied four results per sample and four laboratories were unable to analyse the test sample of lowest chromium content because they had no other iron available sufficiently low in chromium for use in the calibration solutions. Three further results were excluded from the statistical analysis because they had been reported as less than a given figure. From the remaining 273 results, the means (M_m) and standard deviations (S_m) of laboratory means have been calculated. Also the repeatabilities (r) and the reproducibilities (R) have been calculated following, as far as possible, the procedures of ISO 5725. These statistical data and also within laboratory standard deviations (S_w) and between laboratory standard deviations (S_b) are shown in the Table below. Also included is a sub-table of predicted values for r and R at chosen chromium concentrations, these being the best available predictions based on the 273 results submitted. Figure 1 shows the relationship between chromium content and repeatability (r) and reproducibility (R) plotted on a log – log scale.

Alloy type	Certified value Cr % (m/m)	M_m %	s_m %	r %	R %	S_w %	S_b %
High purity iron	0.002	0.0020	0.0002	0.0007	0.0008	0.0002	0.0001
Carbon steel	0.067	0.0682	0.0023	0.0024	0.0065	0.0008	0.0023
Alloy iron	0.56	0.5684	0.0090	0.0176	0.0299	0.0062	0.0086
Ni-Cr-Mo steel	1.08	1.087	0.0140	0.0335	0.0495	0.0119	0.0130
Low alloy steel	2.10	2.100	0.0297	0.0636	0.1011	0.0225	0.0279

Logarithmic regression equations:	Correlation coefficient:
log r = 0.6550 × log Cr % - 1.5538	0.973
log R = 0.6788 × log Cr % - 1.3176	0.996

Predicted values for r and R from the above equations:

Cr % (m/m)	(0.001)	0.002	0.005	0.010	0.020	0.050
r	(0.0003)	0.0005	0.0009	0.0014	0.0022	0.0039
R	(0.0004)	0.0007	0.0013	0.0021	0.0034	0.0063

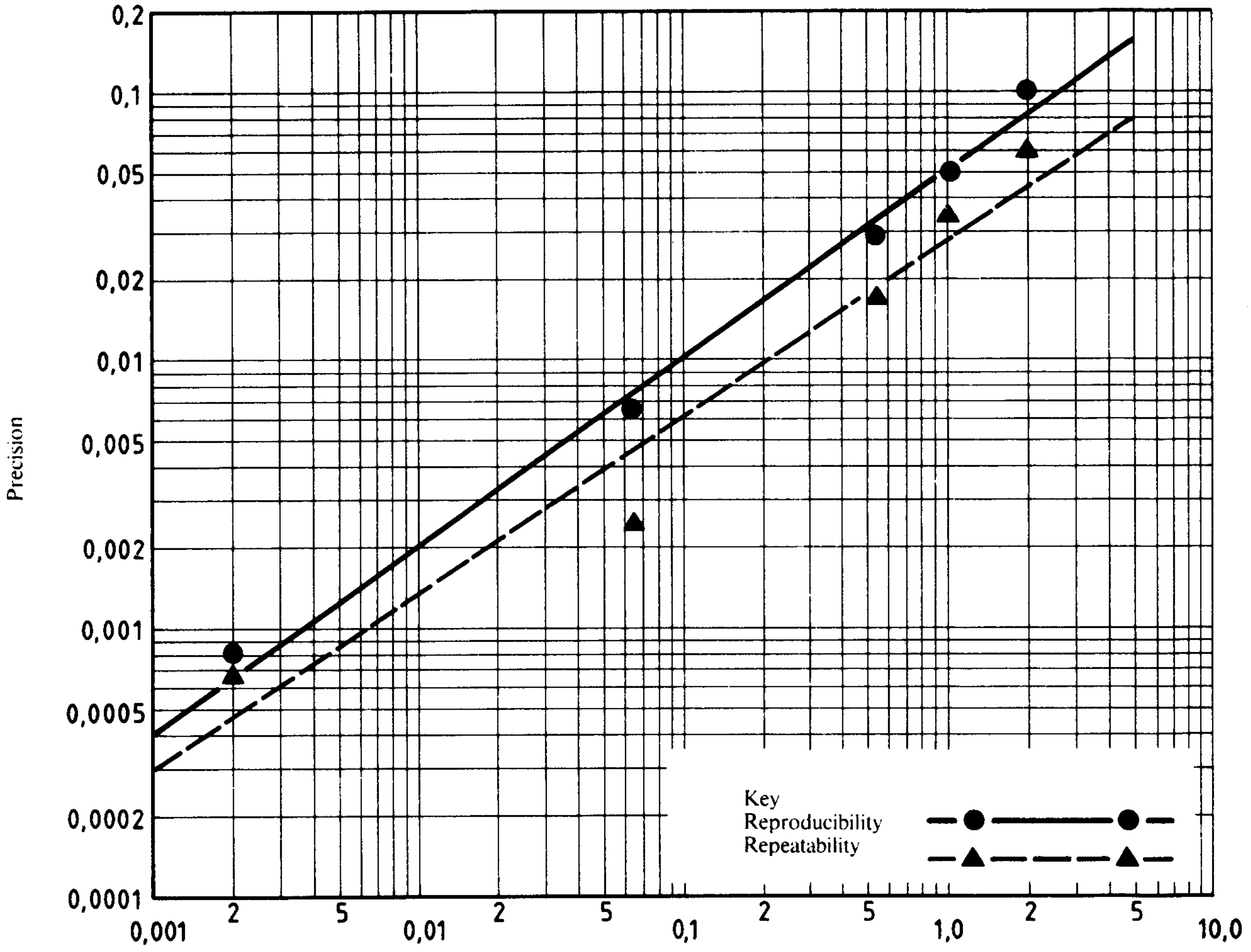
Cr % (m/m)	0.10	0.20	0.50	1.00	2.00	(5.00)
r	0.0062	0.0097	0.0177	0.0279	0.0440	(0.080)
R	0.0101	0.0161	0.0301	0.0481	0.0771	(0.144)

Repeatability, r

The difference between two single results found on identical material by one analyst using the same apparatus within a short time interval will exceed the repeatability, r, on average not more than once in 20 cases in the normal and correct operation of the method.

Reproducibility, R

The difference between two single and independent results found by two operators working in different laboratories on identical material will exceed the reproducibility, R, on average not more than once in 20 cases in the normal and correct operation of the method.



Chromium content % (m/m)
Atomic absorption spectrometry at 357.87 nm

Figure 1: Relationship between the precision and the chromium content

Publications referred to

See national foreword.

BS 6200 : Subsection 3.10.2 : 1989
EN 10 188 : 1989

This British Standard was published under the authority of the Board of BSI and comes into effect on 30 March 1990

ISBN 0 580 17824 2

The following BSI references relate to the work on this standard:
Committee reference ISM/18 Draft for comment 86/35721 DC

Cooperating organizations

The European Committee for Standardization, under whose supervision this European Standard was prepared, comprises the national standards organizations of the following Western European countries.

Austria	Oesterreichisches Normungsinstitut
Belgium	Institut belge de normalisation
Denmark	Dansk Standardiseringsraad
Finland	Suomen Standardisoimisliito, r.y.
France	Association française de normalisation
Germany	Deutsches Institut für Normung e.V.
Greece	Hellenic Organization for Standardization
Iceland	Icelandic Council for Standardization
Ireland	National Standards Authority of Ireland
Italy	Ente Nazionale Italiano di Unificazione
Luxemburg	Inspection des travails et des mines
Netherlands	Nederlands Normalisatie-instituut
Norway	Norges Standardiseringsforbund
Portugal	Instituto Português da Qualidade
Spain	Instituto Español de Normalización
Sweden	Standardiseringskommissionen i Sverige
Switzerland	Association suisse de normalisation
United Kingdom	British Standards Institution

BS 6200 : Subsection 3.10.2 : 1989
EN 10 188 : 1989

Amendments issued since publication

Amd. No.	Date of issue	Text affected

British Standards Institution · 2 Park Street London W1A 2BS · Telephone 01-629 9000 · Telex 266933