BRITISH STANDARD

BS EN 15199-1:2006
BS 2000-480: 2006

Petroleum products — Determination of boiling range distribution by gas chromatography method —

Part 1: Middle distillates and lubricating base oils

The European Standard EN 15199-1:2006 has the status of a British Standard

ICS 75.080

NO COPYING WITHOUT BSI PERMISSION EXCEPT AS PERMITTED BY COPYRIGHT LAW

British Standards

Licensed copy: Lee Shau Kee Library, HKUST, Version correct as of 03/01/2015, (c) The British Standards Institution 2013

Licensed copy: Lee Shau Kee Library, HKUST, Version correct as of 03/01/2015, (c) The British Standards Institution 2013

National foreword

This British Standard was published by BSI. It is the UK implementation of EN 15199-1:2006.

The UK participation in its preparation was entrusted to Technical Committee PTI/13, Petroleum testing and terminology.

A list of organizations represented on PTI/13 can be obtained on request to its secretary.

Energy Institute, under the brand of IP, 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:
Energy Institute, 61 New Cavendish Street, London W1G 7AR.
Tel: 020 7467 7100. Fax: 020 7255 1472.

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

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 31 January 2007

© BSI and Energy Institute 2007

ISBN 978 0 580 50180 7

Amendments issued since publication

Amd. No.	Date	Comments

EUROPEAN STANDARD

NORME EUROPÉENNE

EUROPÄISCHE NORM

EN 15199-1

October 2006

ICS 75.080

English Version

Petroleum products - Determination of boiling range distribution by gas chromatography method - Part 1: Middle distillates and lubricating base oils

Produits pétroliers - Détermination de la répartition dans l'intervalle de distillation par méthode par chromatographie en phase gazeuse - Partie 1: Distillats moyens et huiles lubrifiantes

Mineralölerzeugnisse - Gaschromatographische Bestimmung des Siedeverlaufes - Teil 1: Mitteldestillate und Grundöle

This European Standard was approved by CEN on 28 August 2006.

CEN members are bound to comply with the CEN/CENELEC Internal Regulations 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 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 the Central Secretariat has the same status as the official versions.

CEN members are the national standards bodies of Austria, Belgium, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Romania, Slovakia, Slovenia, Spain, Sweden, Switzerland and United Kingdom.

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

Management Centre: rue de Stassart, 36 B-1050 Brussels

© 2006 CEN All rights of exploitation in any form and by any means reserved worldwide for CEN national Members.

Ref. No. EN 15199-1:2006: E

Licensed copy: Lee Shau Kee Library, HKUST, Version correct as of 03/01/2015, (c) The British Standards Institution 2013

Licensed copy: Lee Shau Kee Library, HKUST, Version correct as of 03/01/2015, (c) The British Standards Institution 2013

Contents

Page

Foreword 3

1 Scope 4

2 Normative references 4

3 Terms and definitions 4

4 Principle 6

5 Reagents and materials 6

6 Apparatus 9

7 Sampling 10

8 Preparation of the apparatus 11
8.1 Gas chromatograph preparation 11
8.2 System performance check 11

9 Sample preparation 11

10 Calibration 11

11 Procedure 13

12 Visual inspection of the chromatograms 13

13 Calculation 14

14 Expression of results 14

15 Precision 14
15.1 General 14
15.2 Repeatability 15
15.3 Reproducibility 15

16 Test report 15

Annex A (normative) Calculation procedure 16

Annex B (normative) System performance check 20

Annex C (informative) Boiling points of normal alkanes 22

Bibliography 23

Licensed copy: Lee Shau Kee Library, HKUST, Version correct as of 03/01/2015, (c) The British Standards Institution 2013

Foreword

This document (EN 15199-1:2006) has been prepared by Technical Committee CEN/TC 19 “Gaseous and liquid fuels, lubricants and related products of petroleum, synthetic and biological origin”, the secretariat of which is held by NEN.

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 April 2007, and conflicting national standards shall be withdrawn at the latest by April 2007..

EN 15199 consists of the following parts, under the general title *Petroleum products — Determination of boiling range distribution by gas chromatography method:*

— *Part 1: Middle distillates and lubricating base oils*

— *Part 2: Heavy distillates and residual fuels*

— *Part 3: Crude oil*

This part of the standard describes the determination of boiling range distribution of materials with initial boiling points (IBP) above 100 °C and final boiling points (FBP) below 750 °C. For testing materials with initial boiling points (IBP) above 100 °C and final boiling point (FBP) above 750 °C, part 2 of the standard may be used. For testing materials with initial boiling points (IBP) below 100 °C and final boiling points (FBP) above 750 °C, such as crude oils, part 3 may be used.

This part of the standard is a joint development between the EI [1], ASTM [2] and CEN.

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

Licensed copy: Lee Shau Kee Library, HKUST, Version correct as of 03/01/2015, (c) The British Standards Institution 2013

1 Scope

This European Standard specifies a method for the determination of the boiling range distribution of petroleum products by capillary gas chromatography using flame ionisation detection. The standard is applicable to materials having a vapour pressure low enough to permit sampling at ambient temperature and a boiling range of at least 100 °C. The standard is applicable to distillates with initial boiling points (IBP) above 100 °C and final boiling points (FBP) below 750 °C, for example, middle distillates and lubricating base stocks.

The test method is not applicable for the analysis of petroleum or petroleum products containing low molecular weight components (for example naphthas, reformates, gasolines, diesel). Components containing hetero atoms (for example alcohols, ethers, acids, or esters) or residue are not to be analyzed by this test method.

NOTE For the purposes of this European Standard, the terms "% (*m/m*)" and "% (*V/V*)" are used to represent respectively the mass fraction and the volume fraction.

WARNING — The use of this European Standard may involve hazardous materials, operations and equipment. This European 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 to determine the applicability of regulatory limitations prior to use.

2 Normative references

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

EN ISO 3170, *Petroleum liquids — Manual sampling (ISO 3170:2004)*

EN ISO 3171, *Petroleum liquids — Automatic pipeline sampling (ISO 3171:1988)*

3 Terms and definitions

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

NOTE Explanation of some of the terms is given in Figure 1.

3.1
initial boiling point
IBP
temperature corresponding to the retention time at which a net area count equal to 0,5 % of the total sample area under the chromatogram is obtained

3.2
final boiling point
FBP
temperature corresponding to the retention time at which a net area count equal to 99,5 % of the total sample area under the chromatogram is obtained

3.3
area slice
area resulting from the integration of the chromatographic detector signal within a specified retention time interval

NOTE In area slice mode peak detection parameters are bypassed and the detector signal integral is recorded as area slices of consecutive, fixed duration time interval.

Licensed copy: Lee Shau Kee Library, HKUST, Version correct as of 03/01/2015, (c) The British Standards Institution 2013

3.4
corrected area slice
area slice corrected for baseline offset by subtraction of the exactly corresponding area slice in a previously recorded blank (non-sample) analysis

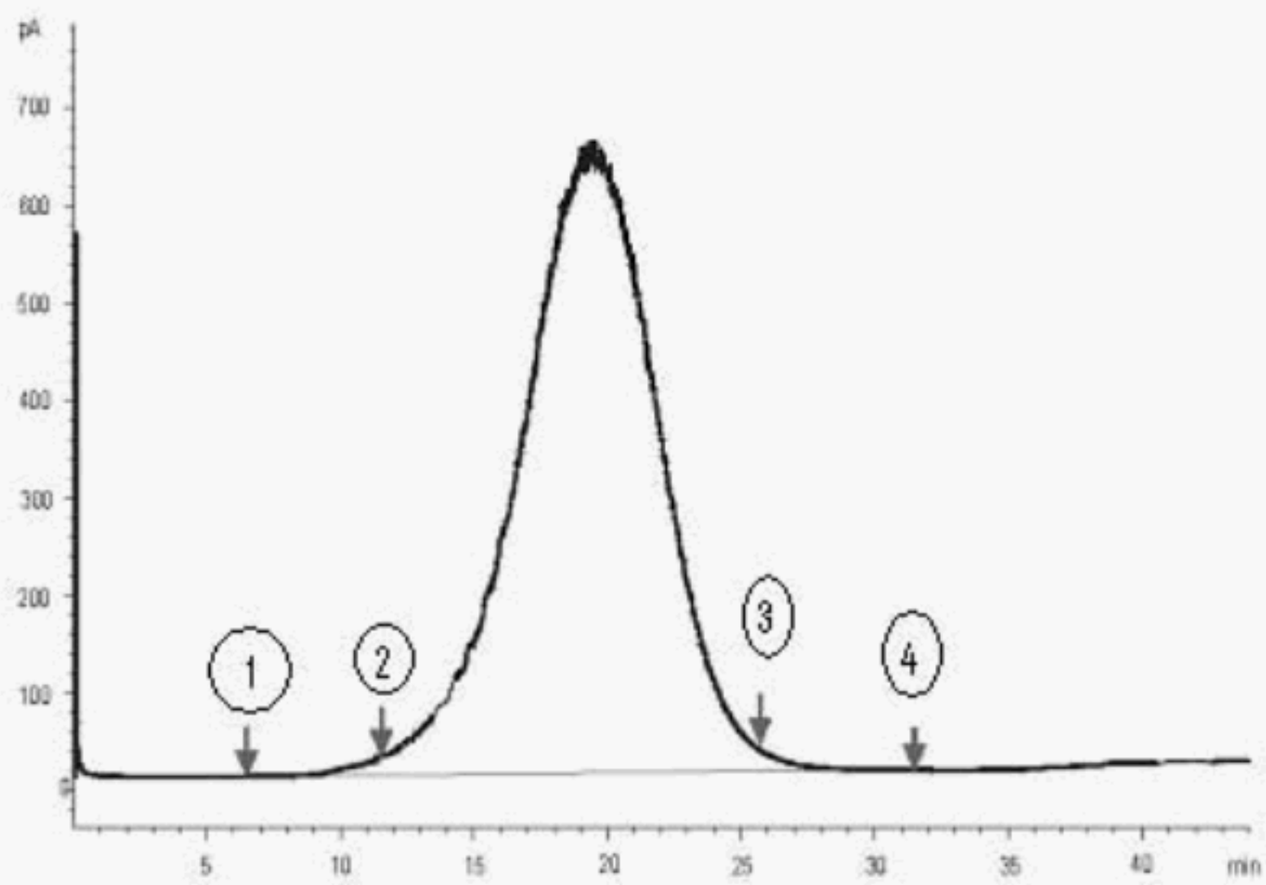
3.5
cumulative corrected area
accumulated sum of corrected area slices from the beginning of the analysis through a given retention time, ignoring any non-sample area for example of solvent

3.6
slice rate
time interval used to integrate the continuous (analogue) chromatographic detector response during an analysis

NOTE The slice rate is expressed in Hz (for example integrations per second or slices per second).

3.7
slice time
analysis time associated with each area slice throughout the chromatographic analysis

NOTE The slice time is the time at the end of each contiguous area slice.



Key:

1 start of elution
2 initial boiling point (IBP)
3 final boiling point (FBP)
4 end of elution

Figure 1 — Typical chromatogram

3.8
total sample area
cumulative corrected area, from the initial area point to the final area point, where the chromatographic signal has returned to baseline after complete sample elution

3.9
net area
cumulative area counts for the sample minus the cumulative area count for the blank

Licensed copy: Lee Shau Kee Library, HKUST, Version corrected as of 03/01/2015, (c) The British Standards Institution 2013

3.10
recovery
ratio of the cumulative area count of the sample to that of the reference material (external standard) corrected for dilution and material weights combined with the percentage of light ends, if applicable

4 Principle

A test portion is introduced into a gas chromatographic column, which separates hydrocarbons in the order of increasing boiling point. The column temperature is raised at a linear reproducible rate and the area under the chromatogram is recorded throughout the analysis. Boiling points are assigned to the time-axis from a calibration curve obtained by running a mixture of known normal alkanes, covering the sample boiling range, under the same conditions. From these data, the boiling range distribution is obtained.

5 Reagents and materials

Unless otherwise stated, only chemicals of recognized analytical quality shall be used.

5.1 Liquid stationary phase, a methyl silicone stationary phase for the column.

5.2 Carrier gases, helium, nitrogen or hydrogen, of at least 99,999 % (*V/V*) purity. Any oxygen present is removed by a chemical resin filter.

WARNING — Follow the safety instructions from the filter supplier.

5.3 Hydrogen, grade suitable for flame ionisation detectors

5.4 Compressed air, regulated for flame ionisation detectors.

5.5 Alkanes, normal alkanes of at least 98 % (*m/m*) purity from C_5 to C_{10}, C_{12}, C_{14}, C_{16}, C_{18}, C_{20}, C_{24} and C_{28} to be used with Polywax (5.6).

NOTE The calibration mixture from ISO 3924 [3] is also suitable.

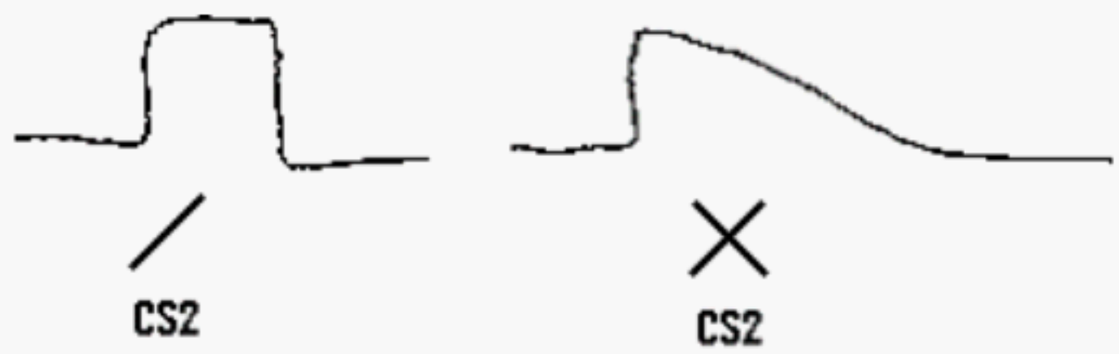
5.6 Polywax 655 or 1000

5.7 Carbon disulfide, purity 99,7 % (*V/V*) minimum.

WARNING — Extremely flammable and toxic by inhalation.

NOTE To confirm the suitability of the carbon disulfide as a solvent, it is recommended to check elution profiles (see Figure 2).

Licensed copy: Lee Shau Kee Library, HKUST, Version correct as of 03/01/2015, (c) The British Standards Institution 2013



Key:

/ good
X bad

Figure 2 — Solvent peak shape

5.8 Calibration mixture

The mixture shall contain at least one normal alkane with a boiling point lower than the IBP of the sample, and at least one normal alkane with a boiling point higher than the FBP of the sample.

Dissolve 0,1 g of Polywax (5.6) in 7 ml carbon disulfide (5.7), warming gently if necessary. Prepare an equal volume mixture of alkanes (5.5) and add 10 µl to the Polywax solution.

NOTE 1 Commercially available alkane standards are suitable for column performance checks.

NOTE 2 The calibration mix is used to determine the column resolution, skewness of the C_{20} peak, and retention time versus boiling point calibration curve.

5.9 Reference materials (RM)

5.9.1 A reference material has two functions:

— External Standard: to determine the recovery of samples by comparing the total sample area (3.8) of the reference material with the total sample area of the unknown sample;

— Boiling Point Distribution Standard: to check the proper functioning of the system by comparing the results with a known boiling point distribution on a routine basis. A typical example is given in (5.9.2).

5.9.2 Reference Material 5010, a reference sample that has been analyzed by laboratories participating in the test method cooperative study. Consensus values for the boiling range distribution of this sample are given in Table 1.

5.9.3 Cyclohexane. (C_6H_{12})—(99+ % pure) may be used in place of CS_2 for the preparation of the calibration mixture.

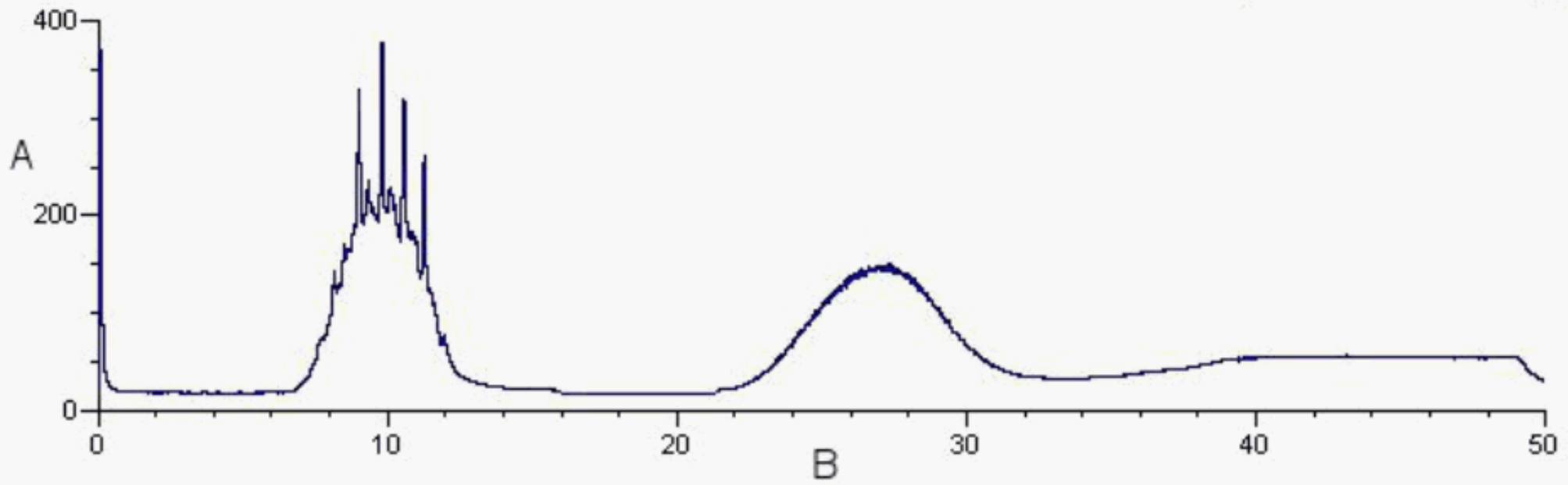
5.9.4 Binary gravimetric blend, a binary distillate mixture with boiling points ranges that gives a baseline at the start, a baseline between the two peaks and an end time that is as close to the end of the chromatogram as possible (see Figure 3 and B.3). This mixture is used to check the relative response of the two distillates and to check the baselines at the start, middle and end of the chromatogram.

Licensed copy: Lee Shau Kee Library, HKUST, Version correct as of 03/01/2015, (c) The British Standards Institution 2013

Table 1 — Reference Material 5010

% recovered	Reference temperature °C	Maximum allowable range 95,5 % CI °C
IBP	428	9
5	477	3
10	493	3
15	502	3
20	510	3
25	518	4
30	524	4
35	531	4
40	537	4
45	543	4
50	548	5
55	554	4
60	560	4
65	566	4
70	572	4
75	578	5
80	585	4
85	593	4
90	602	4
95	616	4
FBP	655	18

Licensed copy: Lee Shau Kee Library, HKUST, Version correct as of 03/01/2015, (c) The British Standards Institution 2013



Key:

A response
B retention time (min)

Figure 3 — Typical chromatogram of binary gravimetric blend distillate

6 Apparatus

6.1 Gas chromatograph, with the following performance characteristics.

6.1.1 Flame ionisation detector, connected to the column so as to avoid any cold spots. The detector shall be capable of operating at a temperature at least equivalent to the maximum column temperature employed in the method.

NOTE The capillary column should sit just below the flame tip and it is recommended that the orifice of the jet should be 0,6 mm minimum to prevent frequent blocking with silicones.

6.1.2 Column temperature programmer, capable of linear programmed temperature operation over a range of 10 °C above ambient to 450 °C.

6.1.3 Sample inlet system, consisting of a programmable temperature vaporizer (PTV) or cold on-column (COC) injection port. The maximum temperature of the injection device shall be equal to, or higher than, the final oven temperature. The minimum temperature shall be low enough to prevent sample or solvent flashback, but high enough to allow sample focusing at the front of the column. Table 2 contains the typical operating conditions.

6.2 Column

Use a metal column with 0,53 mm internal diameter and coated with methyl silicone (5.1). Commercially available columns with film thickness (d_f) = 0,09 µm (for analysis up to C_{120}) and (d_f) = 0,17 µm (for analysis up to C_{100}) have been found to be satisfactory.

NOTE 1 It is recommended that the column resolution, R, is at least 2 and not more than 4 (see B.2).

Use some form of column bleed compensation to obtain a stable baseline.

NOTE 2 This may be carried out by subtraction of a column bleed profile previously obtained using exactly the same conditions as used for the sample analysis, by injecting the same volume, using solvent for the blank run and sample dilution from one batch taken at the same time, to avoid differences due to contamination.

Licensed copy: Lee Shau Kee Library, HKUST, Version correct as of 03/01/2015, (c) The British Standards Institution 2013

8 Preparation of the apparatus

8.1 Gas chromatograph preparation

8.1.1 Set up and operate the gas chromatograph in accordance with the manufacturer's instructions.

Typical operating conditions are shown in Table 2.

8.1.2 Deposits may form on the jet from combustion of decomposition products from the liquid stationary phase. These will affect the characteristics of the detector and should be removed.

NOTE The following parameters are affected by deposits on the jet: increase in inlet pressure; FID difficult to light; increase in the CS_2 response and an off specification reference material. To clean the jet, it is recommended that it is put in an ultrasonic cleaner with a suitable solvent, and a cleaning wire used.

8.2 System performance check

Check the system performance at the intervals given and by the procedures specified in Annex B.

9 Sample preparation

Make a 2g/100ml to 3g/100ml solution of the sample in carbon disulfide. Transfer to an autosampler vial and immediately cap.

CAUTION — It is recommended that all work with carbon disulfide is carried out in an explosion protected fume cupboard.

10 Calibration

10.1 Carry out the steps given in 10.2 to 10.4 each day before sample analysis. The first run of the day shall not be a blank, a reference material or a sample, due to the possible elution of extraneous components, which have built up in the injector, but it may be the calibration mixture (5.8).

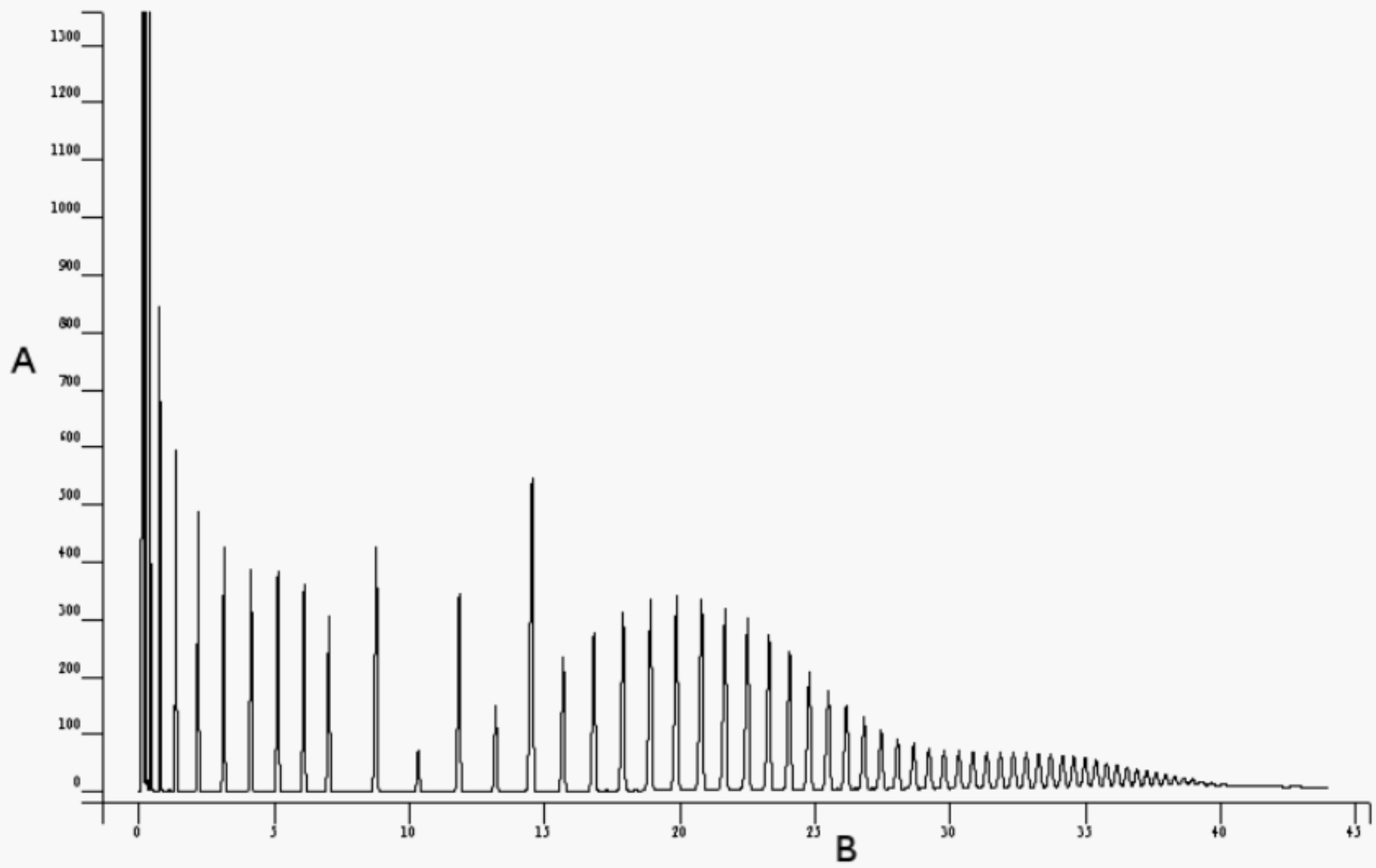
10.2 Run the calibration mixture (5.8) using the specified procedure described in Clause 11.

NOTE Take care to ensure the test portion volume chosen does not allow any peak to exceed the linear range of the detector, or overload the column. A skew of > 3 indicates the sample is too concentrated and a skew of < 1 indicates an old column or dirty liner. As a guide, 1 µl of the calibration mixture (5.8) has been found to be suitable for columns with film thickness less than 0,17 µm.

10.3 Record the retention time of each component and plot the retention time versus the atmospheric boiling point for each component to obtain the calibration curve.

NOTE The atmospheric boiling points of the alkanes are given in Annex C.

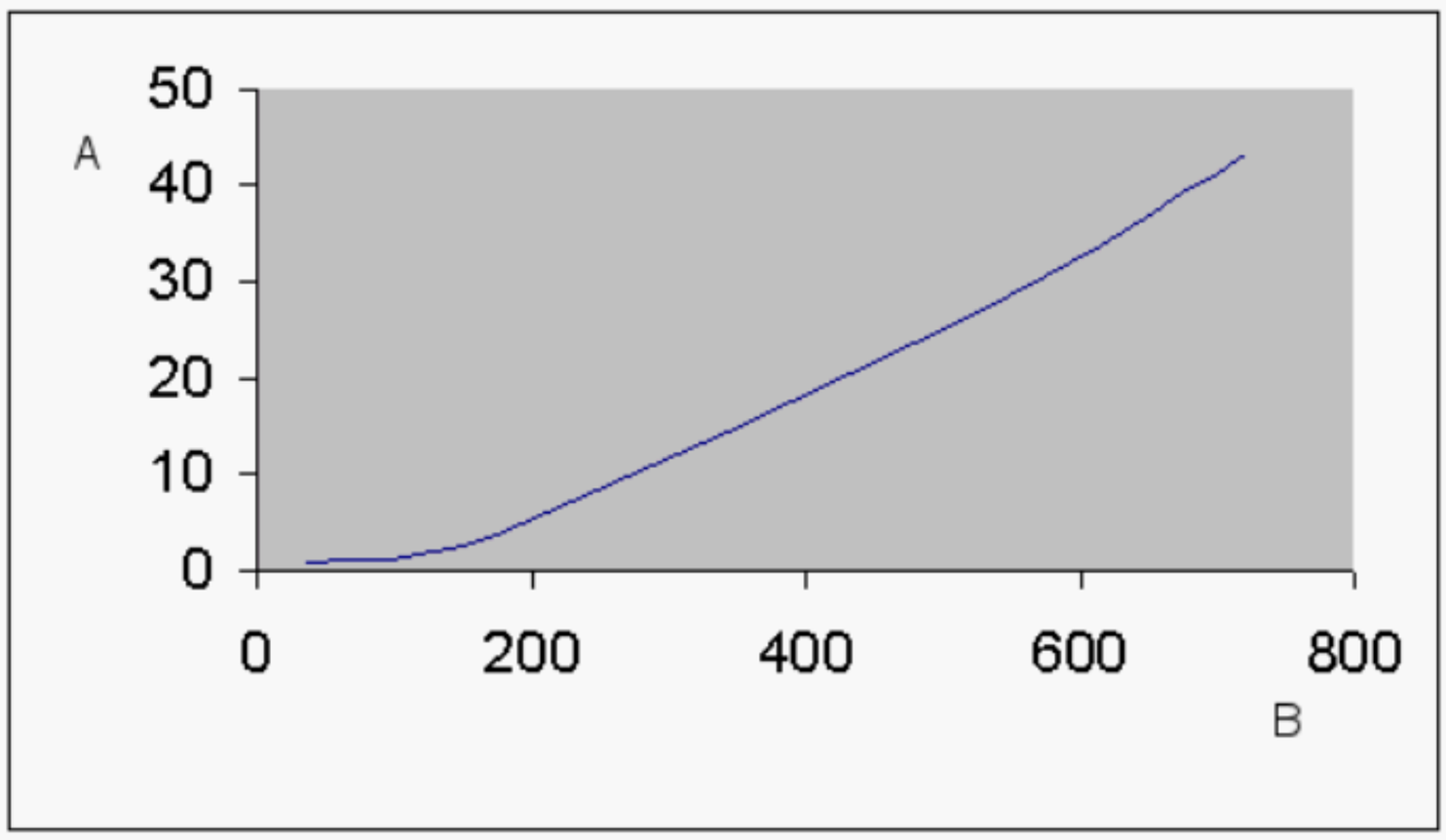
A typical chromatogram of the calibration mixture (5.8) is given in Figure 4 and a typical calibration curve is given in Figure 5.



Key:

A response
B retention time

Figure 4 — Typical chromatogram of calibration mixture



Key

A retention time
B temperature °C

Figure 5 — Typical calibration curve

Licensed copy: Lee Shau Kee Library, HKUST, Version correct as of 03/01/2015, (c) The British Standards Institution 2013

Licensed copy: Lee Shau Kee Library, HKUST, Version correct as of 03/01/2015, (c) The British Standards Institution 2013

10.4 Run the Reference Material 5010 (5.9.2) using the specified procedure in Clause 11. Calculate the boiling range distribution of the reference material by the procedures specified in Annex A and compare this with the consensus values for the reference material used. If the results are not within the specified range, it is advised to carefully follow the manufacturer's instructions regarding chromatographic problem solving and related diagnostics.

11 Procedure

11.1 Run a solvent (blank) baseline analysis before the first sample analysis, and then after every five samples. Subtract blank baselines from subsequent analyses (see Figure 6).

Figure 6 — Baselines

The identification of a constant baseline at the end of the run is critical to the analysis. Constant attention shall be given to all factors that influence baseline stability, e.g. column substrate bleed, septum bleed, detector temperature control, constancy of carrier gas flow, leaks and instrument drift. The baseline at the end of each analysis shall merge with the baseline of the blank run associated with it. Both signals shall merge to confirm integrity; if they do not, the analysis shall be repeated.

NOTE Users are encouraged to use in addition blank validation or rejection criteria proposed by simulated distillation software.

11.2 Cool the column to the starting temperature, and inject the selected sample volume.

11.3 Immediately start programming the column temperature (and PTV if used) upward at a rate so that the chromatogram conforms to the system checks given in Annex B.

11.4 Continue the run until the time for the highest component used for calibration has been exceeded.

12 Visual inspection of the chromatograms

Using the data system, expand the chromatogram of the reference or sample, by 5 times. Merge the blank baseline and observe the following points:

The start of the area of interest is taken at a point on the baseline where the blank and the sample baselines are merged. This is taken before the start of the sample and after the end of the solvent.

Licensed copy: Lee Shau Kee Library, HKUST, Version correct as of 03/01/2015, (c) The British Standards Institution 2013

The end of the area of interest is taken at a point on the baseline where the blank and the sample baselines are merged. This is taken after the end of the sample and at or before the end of run.

The start of the sample is determined as given in A.5.

The end of the sample is determined as given in A.6.

13 Calculation

Use the calculation protocol given in Annex A for the production of results.

14 Expression of results

Report the tabulated results as follows:

a) report all temperatures to the nearest 1 °C;

b) report all percentages to the nearest 1 % (*m/m)*;

c) report the 0,5 % (*m/m*) point as the initial boiling point, and the 99,5 % (*m/m*) point as the final boiling point;

d) report intermediate percentages as required, at intervals of not less than 1 % (*m/m*).

15 Precision

15.1 General

The precision was determined by statistical examination of inter-laboratory test results using EN ISO 4259 [4] in a matrix of samples with properties in the range shown in Table 3.

Table 3 — Range of results

Boiling range % *(m/m)*	**Range of results** °C
IBP	283 to 467
5	311 to 507
10	322 to 521
20	336 to 540
30	348 to 555
40	359 to 568
50	369 to 582
60	379 to 595
70	390 to 611
80	404 to 631
90	421 to 659
95	434 to 685
FBP	465 to 728

Licensed copy: Lee Shau Kee Library, HKUST, Version correct as of 03/01/2015, (c) The British Standards Institution 2013

15.2 Repeatability

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 given in Table 4 only in one case in twenty.

15.3 Reproducibility

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 given in Table 4 only in one case in twenty.

Table 4 — Precision values

% (*m/m*) recovered	Repeatability °C	Reproducibility °C
IBP	6	12
5	2	4
10	1	6
50 to 90	2	8
95	4	10
FBP	10	17

16 Test report

The test report shall specify:

a) a reference to this European Standard, i.e. EN 15199-1;

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

c) the result of the test (see Clause 14);

d) any deviation, by agreement or otherwise, from the standard procedures specified;

e) the date of the test.

Licensed copy: Lee Shau Kee Library, HKUST, Version correct as of 03/01/2015, (c) The British Standards Institution 2013

Annex A
(normative)

Calculation procedure

A.1 Starting conditions

A.1.1 Sample data array, *N* area slices

The data shall be collected at a minimum sampling frequency of 5 Hz to 10 Hz (slice width is 0,2 s to 0,1 s). In addition, the slice width shall be such that no sample or solvent elutes in the first 10 to 20 slices, respectively.

A.1.2 Blank data array, *N* area slices

The slice width for the blank and sample runs shall be identical.

NOTE A blank data array may not be necessary if electronic baseline compensation is used (see A.2).

The analysis conditions for blank and sample shall be identical through the point where sample analysis is terminated.

The number of slices in the blank array shall be equal to or greater than the number of slices in the sample chromatogram. If the number of slices in the blank array is greater than the number of slices in the sample array, then drop the extra slices in the blank array. This situation could occur if a blank run extended beyond the point where the sample analysis was terminated.

A.1.3 Retention times of *n*-paraffins

The retention time of each *n*-paraffin in the calibration mixture shall be obtained from a processed (peak) data file from the analysis of the calibration mixture, run under identical conditions as the samples and blank.

A.1.4 Boiling points of *n*-paraffins

The boiling point of each *n*-paraffin in the calibration mixture (to the nearest whole degree Celsius) can be obtained from Table C.1.

A.1.5 Solvent exclusion time

The solvent exclusion time is that time when the signal has returned to baseline after elution of the solvent. This parameter is used to exclude area due to the solvent used, if any. If a solvent is used, the detector signal has to return to baseline before any sample components start to elute.

A.2 Subtraction of the blank from the sample

Subtract each blank area slice from the exactly corresponding sample area slice. This corrects the sample area slice from the blank.

If the data was acquired on an instrument using automatic baseline compensation, this paragraph may be skipped. In this case, the zeroed sample data array contains the corrected area slices to be used in subsequent calculations.

Licensed copy: Lee Shau Kee Library, HKUST, Version correct as of 03/01/2015, (c) The British Standards Institution 2013

IMPORTANT — Automatic baseline compensation is available on many instruments and is allowed by this test method. However, automatic baseline compensation may not give the same results as slice-by-slice blank subtraction. On some instruments using automatic baseline compensation, the compensated baseline has been observed to exhibit an anomalous feature at or near the point in the chromatogram where the programmed oven temperature reaches maximum and is held for some period of time. The anomalous feature appears as a slow rise in baseline, followed by a relatively sharp decrease, followed by a level baseline. While the magnitudes of the anomalies observed have been very small (only a few picoamps), the slope of the sharp decrease may be sufficient to meet the criterion for determining the end of sample elution. In such an event, this false triggering of the end of sample criterion will result in erroneously high values for the FBP. If false triggering occurs and cannot be eliminated, the user should disable automatic baseline compensation and perform blank subtractions as described in this annex.

A.3 Zero data slices

A.3.1 Calculate the average of the first 10 to 20 (5 Hz to 10 Hz) area slices of the blank-subtracted data array.

A.3.2 Subtract the average slice area (A.3.1) from each area slice in the blank-subtracted data array. Set negative numbers to zero.

A.4 Total chromatogram area

A.4.1 Calculate the total sample area by starting at the first slice (or the solvent exclusion time if a solvent is used), sum all of the area slices through the last slice.

A.4.2 Designate this sum as the total chromatogram area (A_{tc}).

A.5 Start of sample elution time

A.5.1 Start at the slice corresponding to the solvent exclusion time (or the first slice if no solvent was used) and work towards the end of the data array, determine where the rate of change per second between two consecutive slices first exceeds 0,000 01 % of the total chromatogram area (see A.4.2).

A.5.1.1 For determining the start of sample elution, the rate of change is calculated by subtracting the area of a slice from the area of the immediately following slice and dividing by the slice width (ws) in seconds.

A.5.1.2 If the requirement in Equation (A.1) is valid, with S_N being the area of the Nth slice, take slice $N + 1$ as the start of sample slice (see A.2).

$$\frac{S_{N+1} - S_N}{ws} > 1\,E^{-7} \times A_{tc} \qquad \text{(A.1)}$$

A.5.2 Report this retention time corresponding to the start of sample elution.

NOTE This can be done by printing the retention time and/or indicating it on the chromatogram.

A.6 End of sample elution time

A.6.1 Start at the last slice in the data array and working toward the start of sample, determine where the rate of change per second between two consecutive slices first exceeds 0,000 01 % of the total chromatogram area (see A.4.2).

Licensed copy: Lee Shau Kee Library, HKUST, Version correct as of 03/01/2015, (c) The British Standards Institution 2013

A.6.1.1 For determining the end of sample elution, the rate of change is calculated by subtracting the area of a slice from the area of the immediately preceding slice and dividing by the slice width (ws) in seconds.

A.6.1.2 If the requirement in equation (A.2) is valid, take slice N – 1 as the end of sample slice.

$$\frac{s_{N-1} - s_N}{ws} > 1\mathrm{E}^{-7} \times A_{tc} \qquad \text{(A.2)}$$

A.6.2 Report this retention time corresponding to the end of sample elution.

NOTE 1 This can be done by printing the retention time and/or indicating it on the chromatogram.

NOTE 2 Determination of the start and end of sample elution time is done by slope detection. As the slope can differ according to sample properties, the sensitivity levels may require adjustment, but this should not be done during an analysis. Where possible, the use of set start and end of sample elution times is recommended.

A.7 Total corrected sample area

A.7.1 Sum the corrected area slices from the start of sample slice (A.5.1.2) to the end of sample slice (A.6.1.2).

A.7.2 Designate this sum as the total corrected sample area, and save it for subsequent calculations.

A.8 Normalisation to area percentage

A.8.1 Begin at the start of sample slice (A.5.1.2) and continue to the end of sample slice (A.6.1.2), divide each corrected area slice by the total corrected sample area (A.7.2) and multiply by 100.

A.8.2 Record these normalized area percentages in an array for subsequent calculations.

A.9 Retention time corresponding to percent off

A.9.1 Initial boiling point

Starting with the time slice corresponding to start of sample, add the normalised area percents until the total is equal to, or greater than, 0,5 % (see A.9.4). Linearly interpolate to find the time corresponding to exactly 0,5 % of the total corrected sample area.

A.9.2 Intermediate boiling points

For each percent off between 1 % and 99 %, find the retention time where the cumulative area percent is equal to or greater than the percent being determined (see A.9.4). Use linear interpolation when the cumulative sum exceeds the percent being determined.

A.9.3 Final boiling point

Find the retention time where the cumulative area percent is equal to, or greater than, 99,5 % (see A.9.4). Use linear interpolation to find the time corresponding to exactly 99,5 % of the total corrected sample area.

A.9.4 Overall procedure

A.9.4.1 For each X, where X = 0,5, 1, 2, ..., 98 and 99,5, find the retention time corresponding to X percent off.

Licensed copy: Lee Shau Kee Library, HKUST, Version correct as of 03/01/2015, (c) The British Standards Institution 2013

A.9.4.2 Begin with the start of sample slice and working toward the end of sample slice, determine the slice (designated $N + 1$ in the equations) at which the cumulative area percent first equals or exceeds X.

NOTE The cumulative area percent of a given slice is the sum of the normalized area percents from the start of sample slice through the given slice.

A.9.4.3 For the slice ($N + 1$) determined above, the following inequality should hold:

$$CA_N \leq X \leq CA_{N+1} \tag{A.3}$$

where

CA_N is the cumulative area percent from start of sample slice through slice N;

CA_{N+1} is the cumulative area percent through slice $N + 1$.

A.9.4.4 Calculate the fraction (f) of the (non cumulative) normalized area percent (A) in slice ($N + 1$) needed to give exactly X percent off as follows:

$$f = \left(X - CA_N\right) \Big/ A_{N+1} \tag{A.4}$$

A.9.4.5 The retention time corresponding to X percent off (RT_X) is the retention time of the fractional slice ($N + f$) and is calculated as follows:

$$RT_X = \left(N + f\right) \times ws \tag{A.5}$$

A.10 Conversion of retention times to boiling points

A.10.1 For each retention time determined in A.9.1 to A.9.4, calculate the boiling point equivalent to that retention time. Find the pair of calibration compound retention times that are closest to and bracket the percent off retention time of interest.

A.10.2 Calculate the boiling point corresponding to the percent off retention time, BP_i, in °C, from the following equation:

$$BP_i = \left[\left(BP_2 - BP_1\right) \Big/ \left(RT_2 - RT_1\right)\right] * \left(RT_i - RT_1\right) + BP_1 \tag{A.6}$$

where

RT_i is the retention time for 1 percent off;

RT_1 is the retention time of calibration point immediately below R_i;

RT_2 is the retention time of calibration point immediately above R_i;

BP_1 is the boiling point of compound at R_1;

BP_2 is the boiling point of compound at R_2.

NOTE A report giving percent off at selected boiling point intervals can be calculated in an analogous manner.

A.11 Reporting

Report all results in accordance with Clause 14.

Licensed copy: Lee Shau Kee Library, HKUST, Version correct as of 03/01/2015, (c) The British Standards Institution 2013

Annex B
(normative)

System performance check

B.1 Frequency

Carry out a run on the calibration mixture (5.8), using identical conditions and injection volumes to those used for the sample analysis, whenever:

a) the analytical system and conditions have been altered in any way since the last performance check was carried out, or

b) the results obtained for the secondary working standard fall outside the permitted limits.

Determine the characteristics described in B.2 to B.4.

NOTE This procedure may be carried out as part of the boiling range calibration (see Clause 10).

B.2 Column resolution

Determine the column resolution, R, using the C_{50} and C_{52} peaks and the following equation:

$$R = \frac{2\,(t_2 - t_1)}{1{,}699\ (W_1 + W_2)} \qquad \text{(B.1)}$$

where

t_1 is the retention time, in seconds, for the C_{50} peak;

t_2 is the retention time, in seconds, for the C_{52} peak;

W_1 is the width, in seconds, at half-height of C_{50} peak;

W_2 is the width, in seconds, at half-height of C_{52} peak.

Resolution as determined above shall be at least 2, but no greater than 4.

B.3 Detector response (gravimetric blend)

Use a binary gravimetric blend (5.9.4) distillate to determine the detector response. Since the most critical area of the chromatogram is where column bleeding occurs, the binary blend is also used as a recovery test. The binary blend shall have the following characteristics:

a) the lower boiling distillate shall not interfere with the solvent;

b) there shall be a baseline between distillates;

c) the higher boiling point distillate shall elute totally and as close to the end of the temperature programme as possible;

Licensed copy: Lee Shau Kee Library, HKUST, Version correct as of 03/01/2015, (c) The British Standards Institution 2013

d) the ratio of the areas of the two distillates shall be constant which can be checked by measuring the % recovered at 400 °C which shall be: (32,4 ± 0,6) % (*m/m*).

If one of these criteria is not met, it is advised to carefully follow the manufacturer's instructions regarding chromatographic problem solving and related diagnostics.

B.4 Skewing of peak

Determine the skewing of the peak as the ratio A/B as shown in Figure B.1, for the C_{20} peak, where;

A is the width of the leading part of the peak at 5 % of the peak height;

B is the width of the following part of the peak at 5 % of the peak height.

The ratio shall not be less than 1 nor greater than 3.

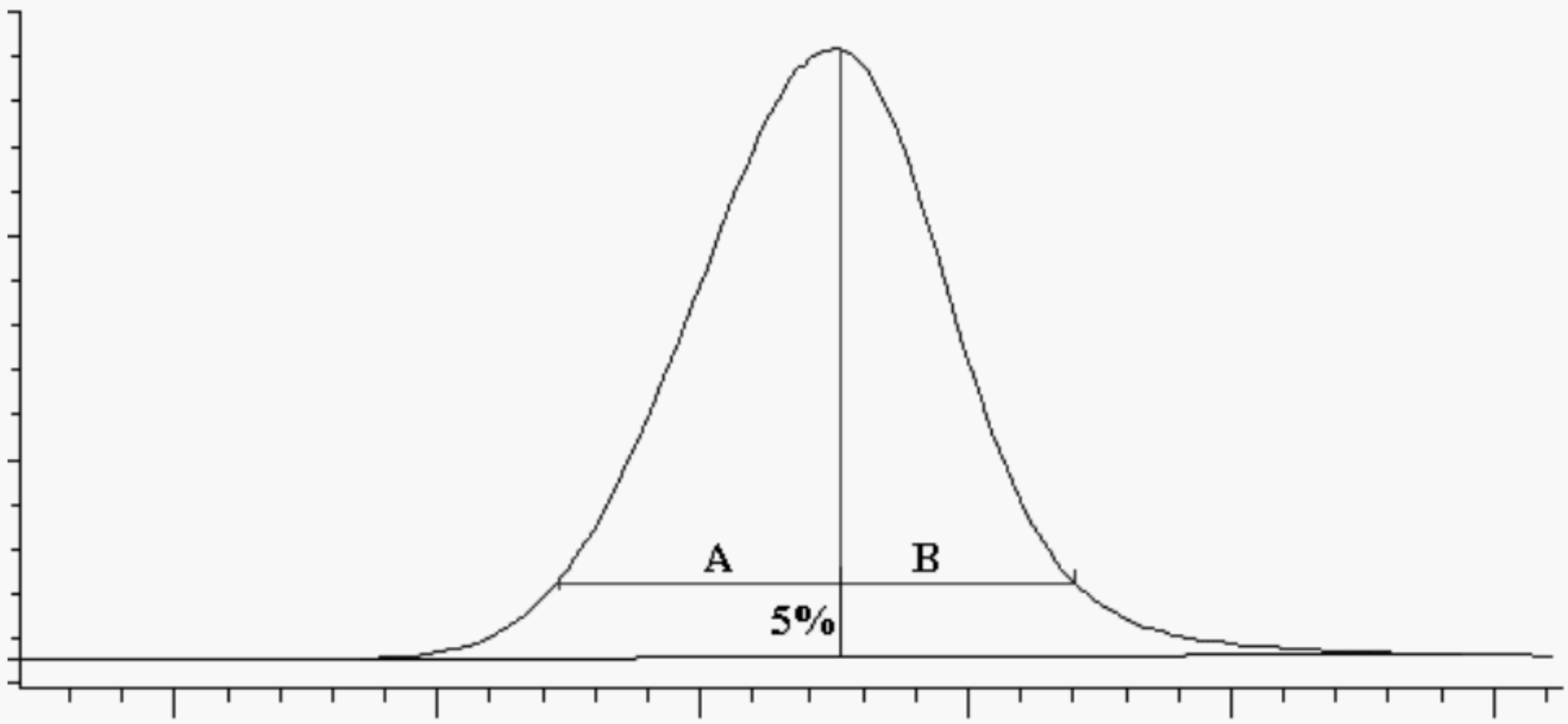


Figure B.1 — Peak skewness

Licensed copy: Lee Shau Kee Library, HKUST, Version correct as of 03/01/2015, (c) The British Standards Institution 2013

Annex C
(informative)

Boiling points of normal alkanes

The boiling points of normal alkanes used for construction of the calibration curve are given in Table C.1.

Table C.1 — Boiling points of normal alkanes

Carbon number	Boiling point °C	Carbon number	Boiling point °C
5	36	50	575
6	69	52	584
7	98	54	592
8	126	56	600
9	151	58	608
10	174	60	615
11	196	62	622
12	216	64	629
13	235	66	635
14	254	68	641
15	271	70	647
16	287	72	653
17	302	74	658
18	316	76	664
20	344	78	670
22	369	80	675
24	391	82	681
26	412	84	686
28	431	86	691
30	449	88	695
32	466	90	700
34	481	92	704
36	496	94	708
38	509	96	712
40	522	98	716
42	534	100	720
44	545	110	735
46	556	120	750
48	566	-	-
NOTE Boiling points for carbon numbers above C60 are extrapolated.			

Licensed copy: Lee Shau Kee Library, HKUST, Version correct as of 03/01/2015, (c) The British Standards Institution 2013

Bibliography

[1] IP 480/05, *Petroleum products — Determination of boiling range distribution by gas chromatography method — Part 1: Middle distillates and lubricating base oils*

[2] ASTM D 6352-04, *Standard test Method for Boiling Range Distribution of Petroleum Distillates in Boiling Range from 174 °C to 700 °C by Gas Chromatography*

[3] ISO 3924, *Petroleum products — Determination of boiling range distribution — Gas chromatography method*

[4] EN ISO 4259, *Petroleum products — Determination and application of precision data in relation to methods of test (ISO 4259:2006)*

Licensed copy: Lee Shau Kee Library, HKUST, Version correct as of 03/01/2015, (c) The British Standards Institution 2013

BS 2000 Series

Energy Institute

Buying Parts of BS 2000

Orders for BS 2000 publications should be addressed to either:

Energy Institute – Library and Information Service
61 New Cavendish Street
London
W1G 7AR

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

Order standards securely via:
www.energyinstpubs.org.uk

or:

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 exists 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 Energy Institute. Enquiries about copyright should be made to the Secretary of PTI/13 at the Energy Institute.