BRITISH STANDARD

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

Part 3: Crude oil

ICS 75.080

National foreword

This British Standard is the UK implementation of EN 15199-3:2008.

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

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.

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Foreword

This document (EN 15199-3:2008) 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of an identical text or by endorsement, at the latest by November 2008, and conflicting national standards shall be withdrawn at the latest by November 2008.

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.

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*

A fourth part on light fractions is under study.

This part of the standard describes the determination of boiling range distribution of materials with initial boiling points (IBP) below 100 °C and final boiling points (FBP) above 750 °C. For testing materials with initial boiling points (IBP) above 100 °C and final boiling point (FBP) below 750 °C, part 1 of the standard may be used. 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.

This part of the standard is harmonized with IP 545 [1] and ASTM D 7169 [2].

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, 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 the United Kingdom.

1 Scope

This European Standard describes 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 crude oils. The boiling range distribution and recovery to C_{100} or C_{120} can be determined.

Two procedures are described: single and dual analysis mode. The basis of each is the calculation procedure as described in Annex A.

NOTE 1 This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations.

NOTE 2 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 — 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.

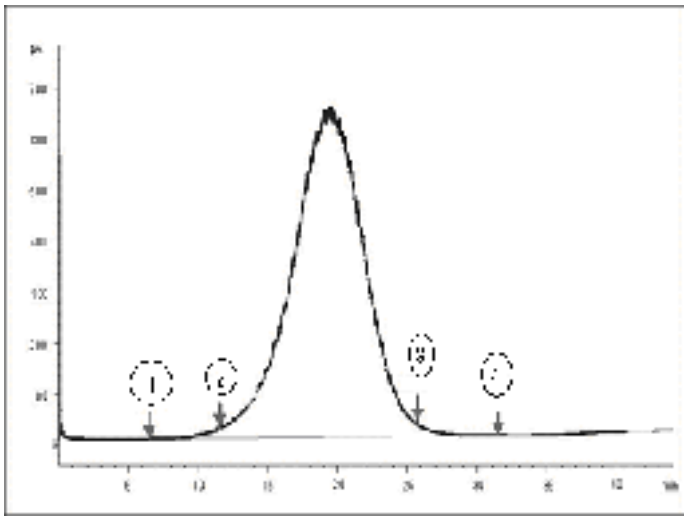
3.1
initial boiling point
IBP
temperature corresponding to the retention time at which a net area count equal to 0,5 % of the total sample area under the chromatogram is obtained

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

NOTE If the found recovery is less than 100 %, the final boiling point is reported as > 720 ºC or > 750 ºC at that recovery.

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.



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

Figure 1 — Typical chromatogram

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.

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

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

The boiling range distribution determination by distillation is simulated by the use of gas chromatography. A non-polar open tubular (capillary) gas chromatographic column is used to elute the hydrocarbon components of the sample in order of increasing boiling point.

A sample aliquot is diluted with a viscosity reducing solvent and introduced into the chromatographic system. Sample vaporization is provided by separately heating the point of injection or in conjunction with column oven heating.

The column oven temperature is raised at a specified linear rate to affect separation of the hydrocarbon components in order of increasing boiling point. The elution of sample components is quantitatively determined using a flame ionization detector. The detector signal is recorded as area slices for consecutive retention time intervals during the analysis.

Retention times of known normal paraffin hydrocarbons, spanning the scope of the test method, are determined and correlated to their boiling point temperatures. The normalized cumulative corrected sample areas for each consecutive recorded time interval are used to calculate the boiling range distribution. The boiling point temperature at each reported percent off increment is calculated from the retention time calibration following Annex A and the recovery at 720 °C (C_{100}) or 750 °C (C_{120}) is determined.

NOTE Further guidance on the algorithm used is given in Annex B.

Two procedures are described in this standard:

— Procedure A, Single analysis mode: The boiling range can be determined by a single analysis, but with a modified (quench corrected) detector response for those components that co-elute with the sample diluent. A quench compensation calculation procedure is described in C.5

— Procedure B, Dual analysis mode: This is an extension to the Procedure A method, where Procedure A is used to determine the boiling point distribution from C_9 through C_{100} or C_{120}. The extension to an analysis of the front end of the sample (including the quenched co-elution region) is achieved by a second analysis. This so-called Detailed Hydrocarbon Analysis (DHA) is used to determine the boiling point distribution from C_1 up to C_9. The results from Procedure A and DHA analysis are merged using the calculation procedure described in Annex D. Procedure B does not use the compensation calculation procedure given in C.5.

Procedure A (Single Analysis Mode): Cryogenic Initial Column Temperature (see Table 2) is preferred to improve resolution of low boiling components.

Procedure B (Dual Analysis Mode): Ambient Initial Column Temperature is used on the analyzer as the low boiling components (C_1 to C_9) are analyzed on the DHA system.

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, with a purity no less than 99,999 % (*V/V*), and any oxygen present 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 with a purity of at least 98 % (*m/m*) 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 (see 5.6).

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

5.6 Polywax 655 or 1000

5.7 Carbon disulfide, with a purity of no less than 99,7 % (*V/V*).

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).

Figure 2 — Example of a good (A) and a bad (B) carbon disulfide solvent peak shape[1)]

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 close to the temperature at which the recovery is measured.

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.

1) These peak shapes are applicable only under cryogenic conditions.

NOTE 3 For the DHA front end analysis, the calibration points are taken from the sample or a suitable calibration mixture.

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 (A.9.3).

— 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. Typical example is given in (5.9.2).

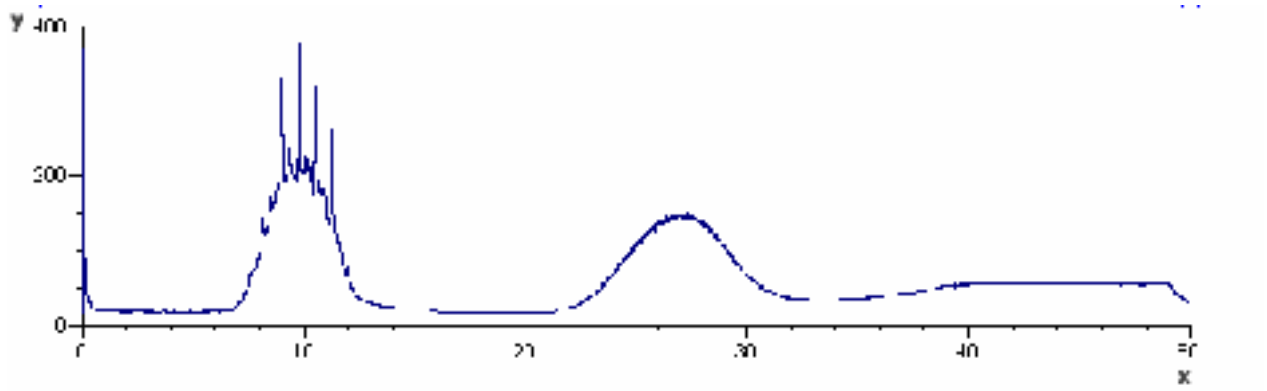
5.9.2 Reference Material 5010, a reference sample that has been analyzed by laboratories participating in the test method cooperative study. Consensus values for the boiling range distribution of this sample are given in Table 1.

Table 1 —Reference Material 5010

% OFF	**Average** °C	**Allowable deviation** ± °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

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 point ranges that gives a baseline at the start, a baseline between the two peaks and an 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.



Key

X retention time (min)

Y response

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 the range mentioned in Table 2.

6.2 Column

Use a metal column, 0,53 µm id 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.

6.3 Carrier gas control

The chromatograph shall be able to deliver a constant carrier gas flow over the whole temperature range of the analysis.

6.4 Micro-syringe, of appropriate volume, e.g. 10 µl, for introduction of 1 µl of the calibration mixture and test portions.

NOTE 1 The micro-syringe may be operated either manually or automatically.

NOTE 2 Plunger in needle syringes are not recommended due to excessive carry over of heavy ends to the following analysis.

Table 2 — Typical operating conditions for gas chromatograph

	PTV Injector	COC Injector
Column length, m	5	5
Column internal diameter, mm	0,53	0,53
Column material	Stainless steel	Stainless steel
Stationary phase	Methyl silicone	Methyl silicone
Film thickness, µm	0,09 or 0,17	0,09 or 0,17
Initial column temperature, °C, Procedure A	-20	-20
Initial column temperature, °C, Procedure B	40	40
Final column temperature, °C	430	430
Programme rate, °C/min	10	10
Hold time, min	5	5
Injector initial temperature, °C	100	ambient
Injector final temperature, °C	430	no setpoint
Programme rate, °C/min	15	15
Detector temperature, °C	430	430
Carrier gas	He	He
Carrier gas flow rate, ml/min	19	19
Sample size, µl	1,0	1,0
Sample concentration, %(*m/m*)	2% [a]	2% [a]
[a] see Clause 9		

6.5 Volumetric flask, 10 ml capacity.

6.6 Refrigerator

NOTE It is recommended that the refrigerator be of an explosion-protected design.

6.7 Analytical balance, able to weigh with a precision of 0,1 mg

7 Sampling

Samples shall be taken as described in EN ISO 3170 or EN ISO 3171 and/or in accordance with the requirements of national standards or regulations for the sampling of petroleum products. Plastic containers for sample storage shall not be used as prolonged contact with the sample can cause contamination of the sample due to possible leaching of the plasticizer.

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.

NOTE Typical operating conditions are shown in Table 2. For Procedure B, where the front end is determined by a second analysis, the initial column temperature is higher than for Procedure A where a lower initial column temperature is recommended to optimise the resolution of the front end and to minimise co-elution of sample components with the solvent.

8.1.2 Deposits can 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. However, if poor results are still obtained, the jet should be replaced.

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 oil. 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 C.

9 Corrected sample and reference material preparation

9.1 Mix the sample by shaking, warming prior to shaking where necessary.

9.2 Weigh approximately 0,1 g to 0,3 g, of the sample to the nearest 0,1 mg, into a clean 10 ml volumetric flask (6.5) and add 5 ml to 7 ml carbon disulfide.

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

Shake the mixture to completely dissolve the test portion and then add carbon disulfide to the mark. Immediately transfer the solution to auto test portion vials, seal, and store in a refrigerator until ready for use.

If the density of the sample is known, the test portion may be prepared on a mass/mass basis, and the following correction applied:

$$\%\left(m/V\right) = \frac{100 m_1}{\left(m_1/\sigma_1\right) + \left(m_2/\sigma_2\right)} \quad (1)$$

where

m_1 is the mass of the test portion in grams;

m_2 is the mass of carbon disulfide, in grams;

σ_1 is the density of the test portion at 20 °C, in kilograms per litre;

σ_2 is the density of carbon disulfide at 20 °C, in kilograms per litre (= 1,26).

NOTE The density is quoted at 20 °C as a temperature approximately ambient in most laboratories. If the laboratory temperature is outside 20 °C ± 5 °C, appropriate adjustments should be made.

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, reference standard (5.9) or test portion, but it may be the calibration mixture (5.8).

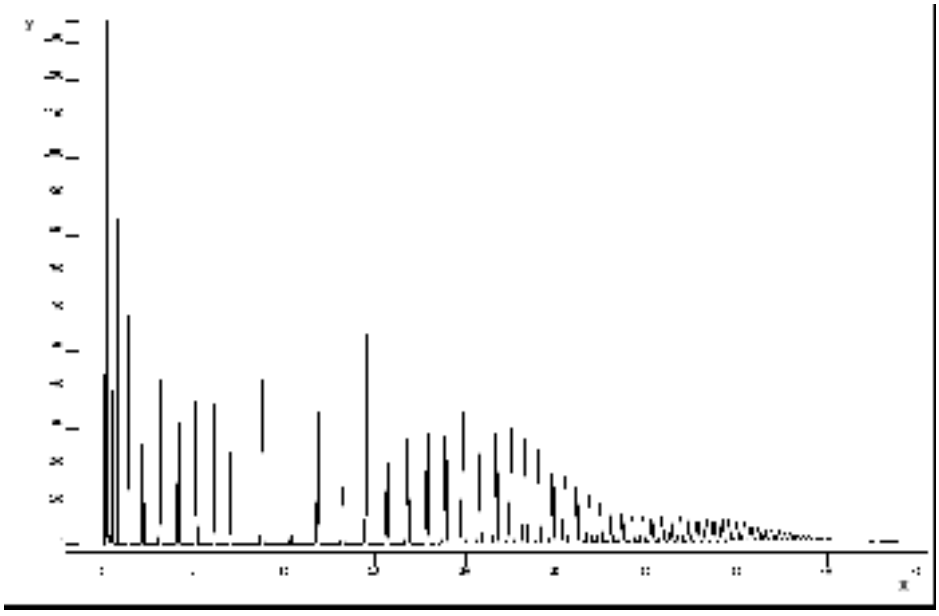
10.2 Run the calibration mixture (5.8) using the specified procedure described in Clause 11.

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, 0,1 µl to 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 E.

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

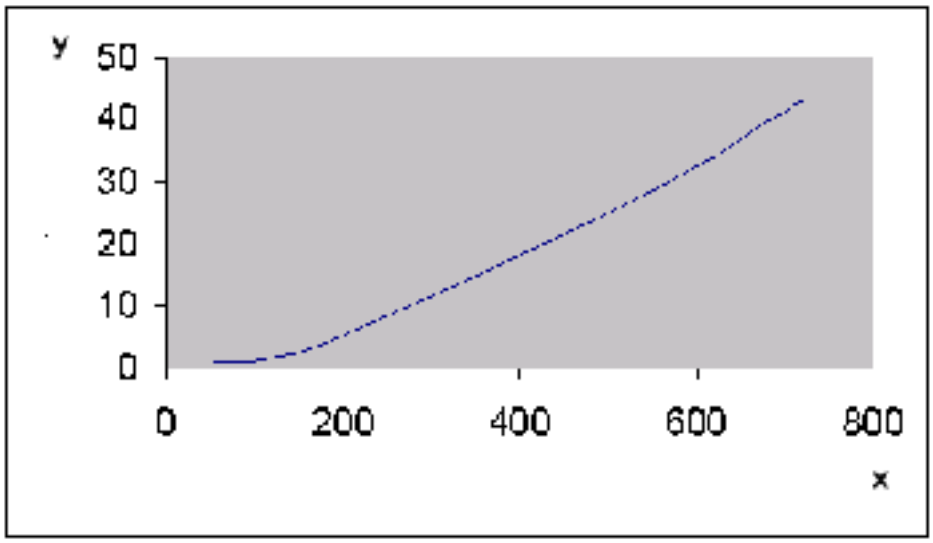


Key

X retention time
Y signal

Figure 4 — Typical chromatogram of calibration mixture

10.4 Run the reference material (5.9) 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.



Key

X temperature (°C)

Y retention time

Figure 5 — Typical calibration curve (retention time vs. temperature)

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).

NOTE 1 It is good practice to follow each test portion with a carbon disulfide blank to prevent carryover of heavy non-volatile material into the next analysis.

good baseline
merging

bad baseline
parallel
(high FBP)

bad baseline
crossing
(low FBP)

Figure 6 — Baselines

The identification of a constant baseline at the end of the run is critical to the analysis of the reference material. 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 (See Figure 6).

NOTE 2 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 upward at a rate that produces the separation specified in Annex C.

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

11.5 For Procedure B: Run the DHA front end analysis.

NOTE A typical procedure for the DHA analysis is described in IP 344 [4].

12 Visual inspection of the chromatograms

Using the data system, expand the chromatogram of the reference material, 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 reference material baselines are merged. This is taken before the start of the sample and after the end of the solvent.

— The end of the area of interest is taken at a point on the baseline where the blank and the reference material 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. For Procedure B: Merge these results with the data from the DHA front end analysis using Annex D.

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 [5] in a matrix of samples with properties in the range shown in Table 3.

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 3 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 3 only in one case in twenty.

Table 3 — Precision values

% *(m/m)* recovered	**Repeatability (*r*)** °C	**Reproducibility (*R*)** °C
IBP	0,2	1,1
5	1,3	4,8
10	1,9	5,2
20	3,3	8,8
30	6,1	10
40	6,8	12
50	8,3	12
60	10	14
70	14	20
80	20	26
90	12	31
95	7,5	
Fractions ° C	**Repeatability (*r*)** %	**Reproducibility (*R*)** %
150		
200	0,3	1,5
250	0,4	2,5
300	0,5	3,0
350	0,6	3,4
400	0,7	3,7
450	0,9	4,1
500	1,0	4,3
550	1,1	4,5
600	1,2	3,9
650	1,3	4,1
700	1,2	4,1
750	1,3	4,2

16 Test report

The test report shall specify:

a) reference to this European Standard, i.e. EN 15199-3;

b) type and complete identification of the material tested;

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

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

e) date of the test.

Annex A
(normative)

Calculation procedure

A.1 Application

The algorithm given in this annex only applies for a slice width of 0,1 s to 0,2 s (10 Hz to 5 Hz). The chromatogram for the reference material (5.9), the sample, and the baseline shall be zeroed. The baseline chromatogram is subtracted from the Reference Material 5010 (5.9.2) and from the sample chromatogram in order to obtain the net area.

NOTE An extended procedure is given as guidance on Annex B.

A.2 Starting conditions

The following data are required for the commencement of calculations:

i) sample data array (N data points);

ii) reference material data array (N data points);

iii) blank data array (N data points);

iv) processed data file from calibration run with retention times of normal alkanes;

v) boiling points of normal alkanes used in calibration run;

vi) start sample time;

vii) end sample time.

NOTE The data collection of the sample or reference should be identical to the data points used in the blank.

A.3 Zero sample or reference chromatogram

A.3.1 Subtract each blank slice area from the corresponding sample slice area.

A.3.2 Average the first twenty time slices from the subtracted slice areas.

A.3.3 Subtract the average slice area from each subtracted time slice to zero the chromatogram. Set negative numbers to zero.

A.4 Sample area

Calculate the total sample area by summing each of the corrected area slices.

A.5 Start of sample elution time

By inspection of the chromatogram, select a start time for the area of interest, after the elution of the solvent, where the baseline merges with the blank. The time slice, after this point, where the average rate of change first exceeds 0,000 01 %/s of the total area is defined as the start of sample. Report this time and/or indicate it on the chromatogram.

A.6 End of sample elution time

The end of the sample elution time is set by the user. It is the time equivalent to the temperature at which the recovery is to be determined. This time shall be before the end of the temperature programme.

A.7 End of reference material elution time

By inspection of the chromatogram, select an end time of the area of interest where the baseline merges with the blank. This shall be before the end of the temperature program. Calculate the average rate of change per second between two consecutive time slices beginning with the last time slice and working backwards in the manner given in A.5. Report this time and/or indicate it on the chromatogram. The end of sample time can be set.

NOTE 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.8 Corrected sample area

Calculate the total corrected sample area by summing the area slices from the start of sample to the end of sample.

A.9 Normalisation

A.9.1 Determine the area / weight factor for the reference material by summing all the area slices in the external standard and dividing by the weight of the external standard taken in 10 mL carbon disulphide.

A.9.2 Determine the area / weight of the sample by summing all the area slices and dividing by the weight of the sample taken in 10 mL carbon disulphide.

A.9.3 Determine the % recovery by:

$$\left(A_S / W_S\right) \times \left(A_{es} / W_{es}\right) \times 100 \qquad \text{(A.1)}$$

where

A_s is the sum of the area slices of the sample determined in A.8;

W_s is the weight of sample taken in 10 mL carbon disulphide in A.9.2;

A_{es} is the sum of the area slices of the reference material determined in A.8;

W_{es} is the weight of the reference material taken in 10 mL carbon disulphide in A.9.1.

A.9.4 To convert time slices to area percents, start with the time slice corresponding to the start of the sample and continue to the time slice corresponding to that set by the user and divide by the % recovery determined in A.9.3.

A.10 Conversion of retention time to percent off

A.10.1 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 %. Linearly interpolate to find the time corresponding to exactly 0,5 % of the total corrected sample area.

A.10.2 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. Use linear interpolation when the cumulative sum exceeds the percent being determined.

A.10.3 Final boiling point

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

If the recovery at 720 °C or 750 °C (depending on the method used) is lower than 99,5%, the FBP shall be given as > 720 °C or > 750 °C at that recovery.

A.11 Conversion of retention times to boiling points

A.11.1 For each retention time determined in A.10.1 to A.10.3, find the pair of calibration retention times that bracket the percent off time of interest.

A.11.2 Calculate each corresponding boiling point, B_i, in °C, from the following equation:

$$B_i = \left[\left(B_2 - B_1 \right) \Big/ \left(R_2 - R_1 \right) \right] * \left(R_i - R_1 \right) + B_1 \qquad \text{(A.2)}$$

where

R_i is the retention time for 1 percent off;

R_1 is the retention time of calibration point immediately below R_i;

R_2 is the retention time of calibration point immediately above R_i;

B_1 is the boiling point of compound at R_1;

B_2 is the boiling point of compound at R_2.

Report all results in accordance with Clause 14.

Annex B
(informative)

Additional guidance for the calculation algorithm

B.1 Zeroing of the reference material chromatogram

B.1.1 Examine the chromatogram obtained for Reference Material 5010 (5.9.2), and ensure, by visual inspection of the chromatogram in the data system, that the first 5 slices contain neither sample nor solvent elution.

B.1.2 Set up an array that contains slices obtained from the Reference Material 5010 chromatogram. Calculate the average of the first five area slices. Subtract the average slice area from each slice in the Reference Material 5010 chromatogram. Set negative numbers to zero.

B.1.3 Zero the blank baseline chromatogram by carrying out an analogous calculation as in B.1.2.

B.1.4 Subtract the blank baseline from the Reference Material 5010 chromatogram. Subtract each zeroed blank baseline slice from the corresponding zeroed Reference Material 5010 slice. If there are negative slices, set the slice values to zero.

B.1.5 Determine the end of elution time of Reference Material 5010.

NOTE Since it is a requirement that the sample chosen to obtain a response factor shall fully elute prior to the FEt time, the end of sample elution for this chromatogram should be determined as described in EN 15199-1 [6], using the algorithm to determine the time the signal of the completely eluted sample returns to baseline.

B.1.6 Determine the area of the chromatogram for Reference Material 5010. Determine the end time of solvent elution. Sum all of the slices from the end of solvent elution to the end of sample elution. This is the area of the standard, A_{STD}.

B.1.7 Calculate the boiling point distribution of Reference Material 5010. The resulting corrected slices obtained for Reference Material 5010 are submitted to a calculation for boiling point distribution as in EN 15199-1 [6]. A comparison of the values obtained with the consensus values listed in Table 1 is made and all the boiling point values should fall within the specified windows. If this requirement is not met, correct any chromatographic problems prior to proceeding with sample analysis.

Typical problems found in this step are: contaminated solvent; problems in sample preparation; sample residue in the inlet or column, or both; quality of the baseline used, a partially blocked detector jet, or a combination thereof.

B.2 Zeroing of sample chromatograms

B.2.1 In the case of crude oil analysis or samples in which the solvent peak is not resolved from the sample components, ensure, by visual inspection of the chromatogram in the data system, that the first 5 slices contain neither sample nor solvent elution. If there is sample elution, decrease the number of slices for the averaging to 3.

B.2.2 Zero the sample chromatogram. Proceed in a manner analogous to that described in B.1.2.

B.2.3 Zero the blank baseline chromatogram. Carry out an analogous calculation as in B.1.3.

B.3 Blank baseline subtraction from the sample chromatogram

Carry out an analogous calculation as in B.1.4.

B.4 Quenching correction

B.4.1 For crude oil samples, a quenching factor is used to correct for the diminished FID response when the CS_2 co-elutes with sample components. This factor is applied to the time segment corresponding to the elution of CS_2. In the interlaboratory study, the factor of 1,930 was applied. This value is determined from experiments made by dissolving butane, pentane, and hexane in toluene.

The solution is analyzed by injecting it under conditions identical to sample analysis. The areas for the components are compared to the areas obtained by gradually adding weighed aliquots of CS_2 to the original solution. Samples that do not have components that co-elute with solvent, for example, residues or the Reference Material 5010, do not require the quenching correction.

B.4.2 Determine the quenching interval. Select the time that the solvent peak starts to elute. Determine when the solvent peak has eluted. Note the times of this interval in minutes.

B.4.3 Locate the slices of the quenching interval. For samples in which the solvent component co-elutes with the sample chromatogram (that is, crude oils), determine the quenching interval, *QI*, as described in B.4.2. Find the closest slice corresponding to the beginning of elution of the solvent peak as well as the final slice corresponding to the end of elution of the solvent peak.

B.4.4 Correct the diminished response of the interval by multiplying each slice of this interval by the quenching factor, *QF*. Use the value as discussed in B.4.1.

B.5 Determination of the sample final elution time (*FEt*)

Determine the time at which the oven reaches the isothermal portion of the temperature program. This is usually recognized as an inflection point in the baseline. This point is called the final elution time (*FEt*). The conversion of this slice to temperature will yield the final elution temperature, *FET*. This conversion is carried out in B.9.4.

B.6 Determination of the sample area

The net sample area is obtained by adding all slices from time $t = 0$ to the final elution time, *FEt*. This net area is the A_{SMP}.

B.7 Response factor

Calculate the response factor, *RF*, as follows:

$$RF = \frac{(M_{STD})}{(M_{STD} + M_{SLSTD})} \times \frac{1}{A_{STD}} \qquad \text{(B.1)}$$

where:

A_{STD} = net area obtained for the Reference Material 5010 chromatogram after baseline subtraction and after excluding the solvent peak (see B.1.6),

M_{SLSTD} = solvent mass, in grams, used for reference material dissolution, and

M_{STD} = mass, in grams, of Reference Material 5010 used in preparing the response factor solution.

NOTE The mass term in (B.1) is expressed as a fraction of the mass of solute and solvent.

B.8 Calculation of the percentage recovery

The percentage recovery, *%RC*, is defined as:

$$\%RC = \frac{(ME)}{\left(\frac{M_{SMP}}{(M_{SMP} + M_{SLSMP})}\right)} \times 100 = \frac{ME \times (M_{SMP} + M_{SLSMP})}{M_{SMP}} \times 100 \quad \text{(B.2)}$$

where:

ME = mass, in grams, of the sample eluted,

M_{SMP} = sample mass, in grams, and

M_{SLSMP} = mass of solvent, in grams, used in the sample solution.

Since:

$$ME = (A_{SMP}) \times (RF) \quad \text{(B.3)}$$

where:

A_{SMP} = net sample area, and

RF = response factor of the Reference Material 5010.

Substituting Equation (B.3) for the value of *ME* in Equation (B.2) yields:

$$\%RC = \frac{A_{SMP} \times RF \times (M_{SMP} + M_{SLSMP})}{(M_{SMP})} \times 100 \quad \text{(B.4)}$$

Substituting Equation (B.1) in Equation (B.4) for the value of *RF* yields:

$$\%RC = \frac{(M_{STD})}{(M_{STD} + M_{SLSTD})} \times \frac{(M_{SMP} + M_{SLSMP})}{M_{SMP}} \times \frac{A_{SMP}}{A_{STD}} \times 100 \quad \text{(B.5)}$$

Determine whether the %recovery, (%*RC*) falls below the recovery threshold (*Rt*) limits set. If it is less than or equal to the recovery threshold (*Rt*), use the %recovery determined by Equation (B.5). If the %recovery is greater than the recovery threshold (*Rt*), then the recovery is set to 100 %. If the %recovery is larger than 102 % (1 standard deviation of the residue), repeat the analysis or determine the chromatographic problem.

B.9 Determination of the boiling point distribution:

B.9.1 Multiply each slice of the sample chromatogram by the %recovery as established in B.8. Divide each slice by the total area of the sample obtained in B.6. This will express the slices in a percent scale.

B.9.2 Add the slices that will yield 0,5 %, 1 %, 2 %, . . . %recovery. Determine, at 1 % intervals, the time of the slice yielding exactly 0,5 %, 1 %, 2 %, ...%recovery. Use an interpolation procedure to find the fractional slices required to yield exactly 0,5 %, 1 %, ...2 %, ...%recovery.

B.9.3 Stop the calculation carried out in B.9.2 when obtaining a slice summation equal to the nearest whole integer of the %recovery.

B.9.4 Convert the retention times to boiling points as outlined in the algorithm in A.11.2. Use the boiling point temperatures listed in Table E.1. For each retention time obtained in B.9.2, find the corresponding temperature from the boiling point vs. retention time function as shown in Figure 5. Calculate the corresponding boiling points as determined in A.10.

B.10 Calculation of cut point intervals

B.10.1 For the two temperatures that define the cut point interval, find the two corresponding slices.

B.10.2 Using the calibration curve, convert this temperature range to a time range.

B.10.3 Convert the time range to a slice number range by multiplying by 60 and dividing by the slice width in seconds.

B.10.4 Sum the normalized slices, starting with the initial slice of the cut and terminating with the last slice after the cut. This sum will be equal to the %mass of the cut.

B.10.5 The %recovery, *%RC*, determined at a temperature T_{RC} that is equal to or less than *FET*, can be determined at a new temperature T_N by using the following equation:

$$E_{RC} = \frac{(\%RC_{TRC} - \%R_{C-1\%})}{(T_{RC} - T_{RC-1\%})} \times (T - T_{RC-1\%}) + \%R_{C-1\%} \quad \text{(B.6)}$$

where:

E_{RC} = estimated recovery at temperature T;

$\%RC_{TRC}$ = %recovery determined at temperature T_{RC} in B.8.;

$\%R_{C\text{-}1\%}$ = %recovery determined at 1 % below the $\%RC_{TRC}$;

$T_{RC\text{-}1\%}$ = temperature corresponding to $\%R_{C\text{-}1\%}$.

The use of this equation for values $T_N > FET$ is not recommended.

Annex C
(normative)

System performance check

C.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 C.2 to C.4.

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

C.2 Column resolution

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

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

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.

C.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;

d) the ratio of the areas of the two distillates shall be constant and should have the following specifications for the gravimetric blend: (32,4 ± 0,6) % (*m/m*) at 400 °C.

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.

C.4 Skewing of peak

Determine the skewing of the peak as the ratio A/B as shown in Figure C.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.

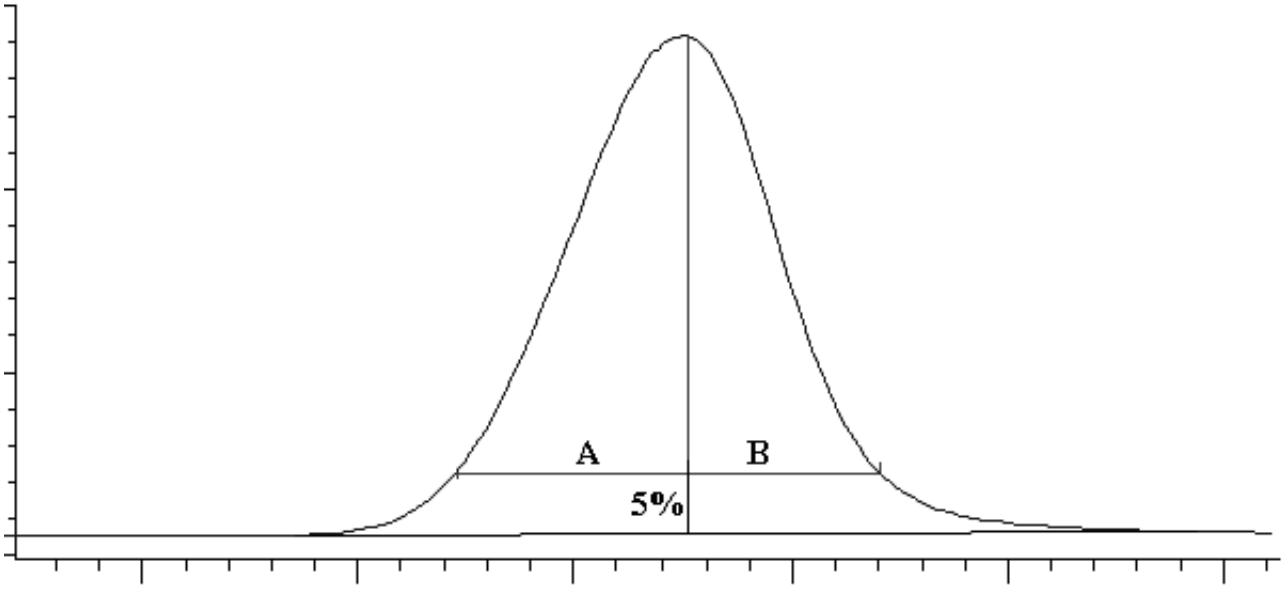


Figure C.1 — Peak skewness

C.5 Quench compensation

The quench compensation calculation is required to correct the detector response for components co-eluting with carbon disulfide.

A mixture of C_5, C_6 and C_8 in carbon disulfide is made at a concentration of the final sample. Determine the response factors for C_5 and C_6 with respect to C_8.

Use the ratio of the C_5 and C_6 response factors (quenching factor) to compensate for the loss of response in the calculation of the final sample.

Annex D
(informative)

Calculation method for amount recovered

Data for the region C_1 to C_9 may be determined with IP344 [4] with internal standard calibration.

The Procedure B method is used to determine the data from C_9 till C_{120} (and above), using external standard calibration.

Merge the two data sets and calculate the total amount recovered at 750 °C by:

$$\text{Amount recovered} = w_1 + w_2 \quad \text{(D.1)}$$

where

w_1=fraction up to C_9

w_2=fraction from C_9 till C_{120}.

Annex E
(informative)

Boiling points of normal alkanes

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

Table E.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 C_{60} are extrapolated.			

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[1] IP 545:2007, *Crude Petroleum and Petroleum products — Determination of boiling range distribution of crude oil - Gas chromatography method*

[2] ASTM D7169-05, *Standard test Method for Boiling Point Distribution of Samples with residues Such as Crude Oils and Atmospheric and Vacuum Residues by High Temperature Gas Chromatography*

[3] ISO 3924:1999, *Petroleum products — Determination of boiling range distribution — Gas chromatography method*

[4] IP 344, *Determination of light hydrocarbons in stabilized crude oils - Gas chromatography method*

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

[6] EN 15199-1, *Petroleum products — Determination of boiling range distribution by gas chromatography method — Part 1: Middle distillates and lubricating base oils*

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Tel +44 (0)20 8996 9001
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