BS EN 15199-3:2020

BSI Standards Publication

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

Part 3: Crude oil

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# National foreword

This British Standard is the UK implementation of EN 15199-3:2020. It supersedes BS EN 15199-3:2008, which is withdrawn.

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 committee manager.

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Published by BSI Standards Limited 2021

ISBN 978 0 539 05818 5

ICS 75.080

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This British Standard was published under the authority of the Standards Policy and Strategy Committee on 31 January 2021.

**Amendments/corrigenda issued since publication**

| Date | Text affected |
|---|---|

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EUROPEAN STANDARD

NORME EUROPÉENNE

EUROPÄISCHE NORM

# EN 15199-3

December 2020

ICS 75.080

Supersedes EN 15199-3:2008

English Version

# Petroleum products - Determination of boiling range distribution by gas chromatography method - Part 3: Crude oil

Produits pétroliers - Détermination de la répartition dans l'intervalle de distillation par méthode de chromatographie en phase gazeuse - Partie 3 : Pétrole brut

Mineralölerzeugnisse - Gaschromatographische Bestimmung des Siedeverlaufes - Teil 3: Rohöle

This European Standard was approved by CEN on 23 November 2020.

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# Contents

Page

European foreword ... 3
1 Scope ... 4
2 Normative references ... 4
3 Terms and definitions ... 4
4 Principle ... 6
5 Reagents and materials ... 7
6 Apparatus ... 10
7 Sampling ... 11
8 Preparation of the apparatus ... 12
8.1 Gas chromatograph preparation ... 12
8.2 System performance check ... 12
9 Corrected sample and reference material preparation ... 12
10 Calibration ... 13
11 Procedure ... 15
12 Visual inspection of the chromatograms ... 15
12.1 Blank run ... 15
12.2 Reference material ... 16
12.3 Sample run ... 16
13 Calculation ... 16
14 Expression of results ... 17
15 Precision ... 17
15.1 General ... 17
15.2 Repeatability ... 17
15.3 Reproducibility ... 17
16 Test report ... 19
Annex A (normative) Calculation procedure ... 20
Annex B (informative) Additional guidance for the calculation algorithm ... 23
Annex C (normative) System performance check ... 27
Annex D (normative) Algorithm for merging boiling point distribution results of EN 15199-3 and EN 15199-4 ... 29
Annex E (informative) Boiling points of normal alkanes ... 37
Bibliography ... 39



Documents
Document Sharing Hub
Full document details: BS EN 15199-3:2020

# European foreword

This document (EN 15199-3:2020) 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 June 2021, and conflicting national standards shall be withdrawn at the latest by June 2021.

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

This document supersedes EN 15199-3:2008.

The main changes in this edition are:

— the algorithm for merging the results of the light end analysis and the simulated distillation analysis has been added as an informative annex;

— additional information on the determination of the IBP and FBP is added to help the user to improve the test results.

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*

— *Part 4: Light fraction of crude oil*

This document 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. Part 4 is used for the determination of the boiling range distribution of hydrocarbons up to *n*-nonane in crude oil.

This document is harmonized with IP 545 [6] and ASTM D 7169 [4].

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

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# 1 Scope

This document describes a method for the determination of the boiling range distribution of petroleum products by capillary gas chromatography using flame ionization 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.

Procedure A (or Single analysis mode) determines the boiling range through $C_{100}$ or $C_{120}$ in a single analysis.

Procedure B (or Dual analysis mode) combines procedure A with the boiling point distribution from $C_1$ up to $C_9$ using the Detailed Hydrocarbon Analysis (DHA) according EN 15199-4. The results of both analyses are merged into one boiling point distribution.

NOTE 1 There is no specific precision statement for the combined results obtained by procedure B. For the precision of the boiling range distribution according to procedure B the precision statements of procedure A and EN 15199-4 apply. No precision has been determined for the results after merging.

NOTE 2 For the purpose of this document, the terms "% (*m/m*)" and "% (*V/V*)" are used to represent the mass fraction, $\mu$, and the volume fraction, $\varphi$, of a material respectively.

WARNING — Use of this document may involve hazardous materials, operations and equipment. This document 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 documents are referred to in the text in such a way that some or all of their content constitutes requirements 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 15199-4, *Petroleum products — Determination of boiling range distribution by gas chromatography method — Part 4: Light fractions of crude oil*

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

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

# 3 Terms and definitions

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

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— IEC Electropedia: available at http://www.electropedia.org/

— ISO Online browsing platform: available at https://www.iso.org/obp

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



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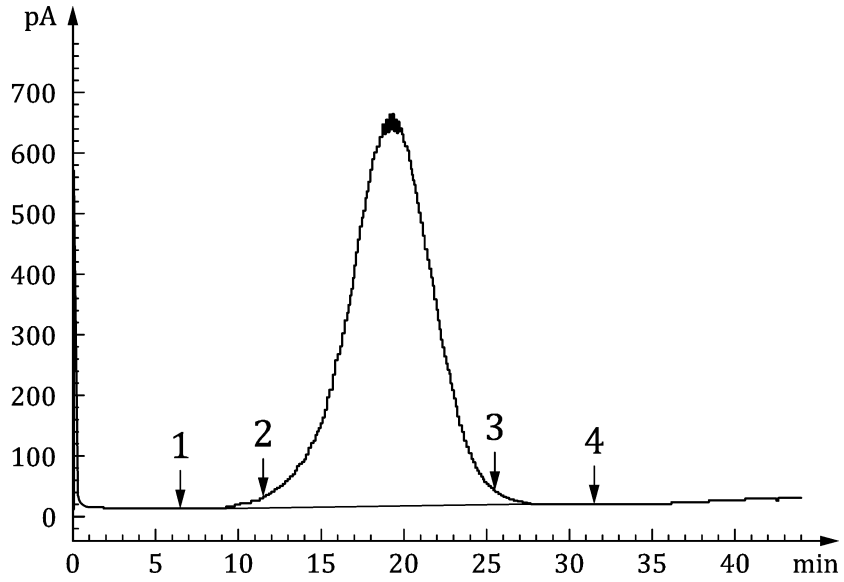
**3.1**
**initial boiling point**
**IBP**
temperature corresponding to the retention time at which a net area (3.9) count equal to 0,5 % of the total sample area (3.8) under the chromatogram is obtained (see Figure 1)




**Key**
1 start of elution
2 initial boiling point (IBP), 3.1
3 final boiling point (FBP), 3.2
4 end of elution

**Figure 1 — Typical chromatogram**

**3.2**
**final boiling point**
**FBP**
temperature corresponding to the retention time at which a net area (3.9) count equal to 99,5 % of the total sample area (3.8) under the chromatogram is obtained (see Figure 1)

Note 1 to entry: If the found recovery is less than 99,5 %, the final boiling point is reported as > 720 °C or > 750 °C at that recovery.

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

Note 1 to entry: 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.

**3.4**
**corrected area slice**
area slice (3.3) corrected for baseline offset by subtraction of the exactly corresponding area slice in a previously recorded blank (non-sample) analysis

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**3.5**
**cumulative corrected area**
accumulated sum of corrected area slices (3.4) from the beginning of the analysis through a given retention time, ignoring any non-sample area for example of solvent

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

Note 1 to entry: The slice rate is expressed in seconds.

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

Note 1 to entry: The slice time is the time at the end of each contiguous area slice.

**3.8**
**total sample area**
cumulative corrected area (3.5), 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 counts 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 (3.5) 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 (3.10) at 720 °C ($C_{100}$) or 750 °C ($C_{120}$) is determined.

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



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Two procedures are described in this document:

— 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 analyser as the low boiling components ($C_1$ to $C_9$) are analysed 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 ionization detectors.

**5.4 Compressed air**, regulated for flame ionization 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 ($CS_2$)**, with a purity of no less than 99,7 % ($V/V$).

WARNING — Extremely flammable and toxic by inhalation.

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



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**Figure 2 — Example of a good (A) and a bad (B) carbon disulfide solvent peak shape, obtained under cryogenic conditions**

## 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 (see C.4) of the $C_{20}$ peak, and retention time versus boiling point calibration curve.

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 analysed by laboratories participating in the test method cooperative study. Consensus values for the boiling range distribution of this sample are given in Table 1.

NOTE Consensus values of newer batches can differ from the ones in Table 1, for those we refer to the sample certificate.

**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.



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**Table 1 —Reference Material 5010**

| % OFF | Average<br>°C | Allowable deviation<br>± °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 |

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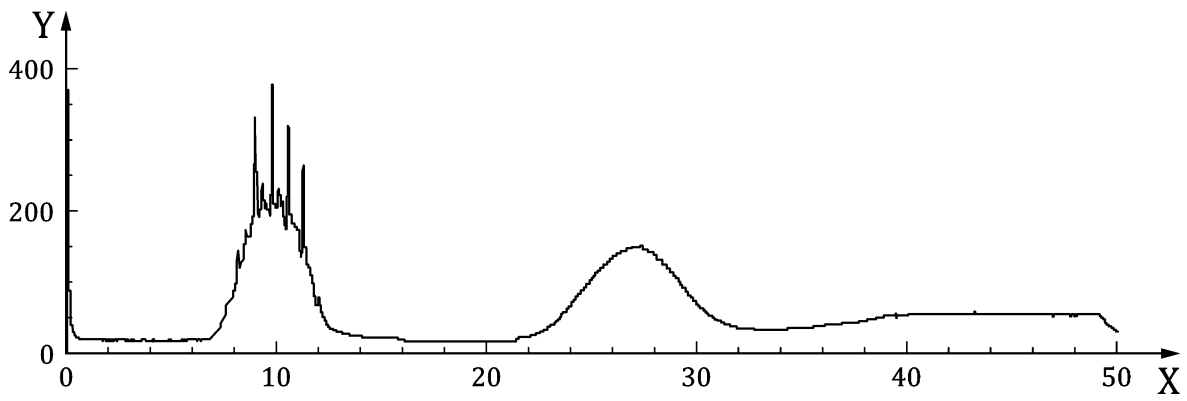


**Key**

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 ionization 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. 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 inner diameter coated with methyl silicone (5.1).

NOTE 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.

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. 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.

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

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



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**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,** recommended to 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 (see the requirements of national standards or regulations for the sampling of petroleum products for further information).

Store samples in either glass or metal containers. 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.

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