



SLOVENSKI STANDARD

SIST EN 15199-2:2021

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Naftni proizvodi - Določanje porazdelitve območja vrelišč z metodo plinske kromatografije - 2. del: Težki destilati in goriva iz destilacijskih ostankov

Petroleum products - Determination of boiling range distribution by gas chromatography method - Part 2: Heavy distillates and residual fuels

Mineralölerzeugnisse - Gaschromatographische Bestimmung des Siedeverlaufes - Teil 2: Schweröle und Rückstandsöle

Produits pétroliers - Détermination de la répartition dans l'intervalle de distillation par méthode de chromatographie en phase gazeuse - Partie 2: Fiouls lourds et fiouls résiduels

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ICS:

75.080	Naftni proizvodi na splošno	Petroleum products in general
75.160.01	Goriva na splošno	Fuels in general

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EUROPEAN STANDARD
NORME EUROPÉENNE
EUROPÄISCHE NORM

EN 15199-2

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ICS 75.080

Supersedes EN 15199-2:2006

English Version

**Petroleum products - Determination of boiling range
distribution by gas chromatography method - Part 2:
Heavy distillates and residual fuels**

Produits pétroliers - Détermination de la répartition
dans l'intervalle de distillation par méthode de
chromatographie en phase gazeuse - Partie 2 : Fiouls
lourds et fiouls résiduels

Mineralölerzeugnisse - Gaschromatographische
Bestimmung des Siedeverlaufes - Teil 2: Schweröle und
Rückstandsöle

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

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 CEN-CENELEC Management Centre 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 CEN-CENELEC Management Centre has the same status as the official versions.

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European foreword

This document (EN 15199-2:2020) 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 15199-2:2006.

The main changes in this edition include:

- updated text to give better guidance to operators executing the test;
- additional clarification in the sample preparation section.

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 fractions of crude oil.*

This document specifies the determination of boiling range distribution of materials with initial boiling points (IBP) above 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 can 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 is applicable. Part 4 describes the determination of boiling range distribution of hydrocarbons up to n-nonane in crude oil.

This document is a joint development between the EI [5], ASTM [4] and CEN.

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

EN 15199-2:2020 (E)**1 Scope**

This document specifies 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 materials having a vapour pressure low enough to permit sampling at ambient temperature, and which have a boiling range of at least 100 °C. The standard is applicable to materials with initial boiling points (IBP) above 100 °C and final boiling points (FBP) above 750 °C, for example, heavy distillate fuels and residuals. The method is not applicable to bituminous samples.

The test method is not applicable for the analysis of petroleum or petroleum products containing low molecular weight components (for example naphthas, reformates, gasolines) or middle distillates like Diesel and Jet fuel.

Petroleum or petroleum products containing blending components, which contain hetero atoms (for example alcohols, ethers, acids, or esters) or residue, are not to be analysed by this test method.

NOTE For the purposes of this document, the terms “% (m/m)” and “% (V/V)” are used to represent respectively the mass fraction and the volume fraction.

WARNING — The 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 ISO 3170, *Petroleum liquids — Manual sampling (ISO 3170)* -9948-4d8d-bc0c-e056cdd0dc4c/sist-en-15199-2-2021

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:

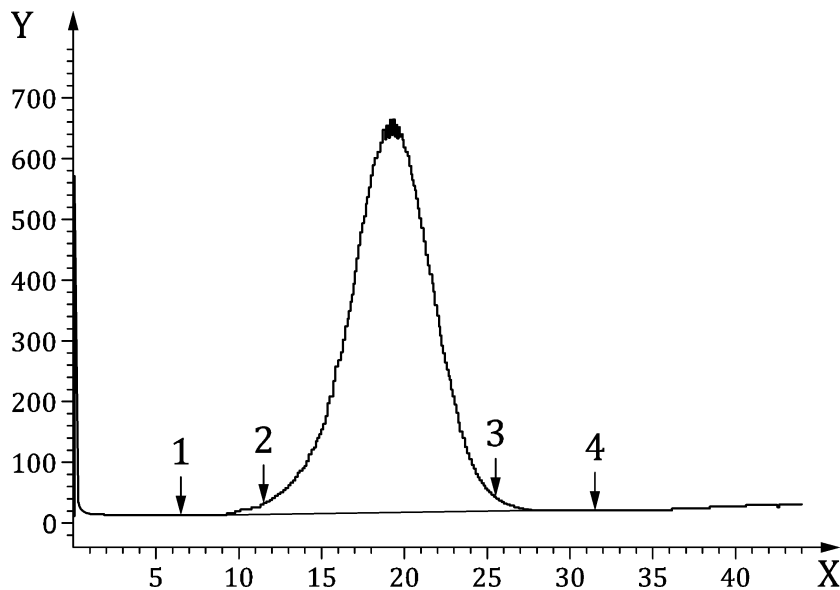
- ISO Online browsing platform: available at <https://www.iso.org/obp>
- IEC Electropedia: available at <http://www.electropedia.org/>

3.1**initial boiling point****IBP**

temperature corresponding to the retention time at which a net area (3.7) counts equal to 0,5 % of the total sample area (3.6) under the chromatogram is obtained (see Figure 1)

3.2**final boiling point****FBP**

temperature corresponding to the retention time at which a net area (3.7) counts equal to 99,5 % of the total sample area (3.6) under the chromatogram is obtained (see Figure 1)

**Key**

1	start of elution	4	end of elution
2	IBP (3.1)	X	retention time (minutes)
3	FBP (3.2)	Y	response (pA)

Figure 1 — Typical chromatogram
 (standards.iteh.ai)

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 (3.3) in a previously recorded blank (non-sample) analysis

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 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

3.7 net area

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

EN 15199-2:2020 (E)**3.8****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, which is obtained by running a mixture of known n-alkanes covering the test portion boiling range, under the same conditions. From these data, the boiling range distribution is obtained. The recovery (3.8) at a specified temperature is determined by comparing the area under the chromatogram with that of a reference standard which has been completely eluted. The temperature at which the recovery was measured is recorded. If the found recovery is less than 100 %, the final boiling point (3.2) is reported as 720 °C or 750 °C at that recovery.

Several SIMDIS methods are standardized test methods and each one is dedicated to a certain boiling point range or product.

EN ISO 3924 [2] is limited to products having an initial boiling point greater than 55 °C, a final boiling point lower than 538 °C and having a vapour pressure sufficiently low to permit sampling at ambient temperature.

EN 15199-1 [1] is applicable to materials having a boiling range of at least 100 °C, an initial boiling points (IBP) above 100 °C and final boiling points (FBP) below 750 °C, for example, middle distillates and lubricating base stocks.

EN 15199-3 is applicable to crude oils. The boiling range distribution and recovery up to C₁₀₀ or C₁₂₀ can be determined.

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5 Reagents and materials

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

5.1 Carrier gas, helium, 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.

5.2 Hydrogen, grade suitable for flame ionization detectors.

5.3 Compressed air, suitable for flame ionization detectors.

5.4 Alkanes, n-alkanes of at least 98 % (m/m) purity from C₅ to C₁₀, C₁₂, C₁₄, C₁₆, C₁₈, C₂₀, C₂₄ and C₂₈.

NOTE The calibration mixture from EN ISO 3924 [2] is also suitable.

5.5 Polywax 655 or 1000

5.6 Carbon disulfide (CS₂), with a minimum purity of 99,7 % (V/V).

WARNING — Extremely flammable and toxic.

CAUTION — It is recommended that all work with CS₂ is carried out in an explosion protected fume cupboard.

Cyclohexane (C₆H₁₂)—(>99 % pure) can be used in place of CS₂ for the preparation of the calibration mixture. However, the precision of this method is based on calibration mixtures, reference material and samples prepared with CS₂ only.

5.7 Calibration mixture

Dissolve 0,1 g of Polywax (5.5) in 7 ml CS₂(5.6), warming gently if necessary. Prepare an equal volume mixture of alkanes (5.4) 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 C₂₀ peak, and retention time versus boiling point calibration curve.

5.8 Reference materials

5.8.1 A reference material has two functions:

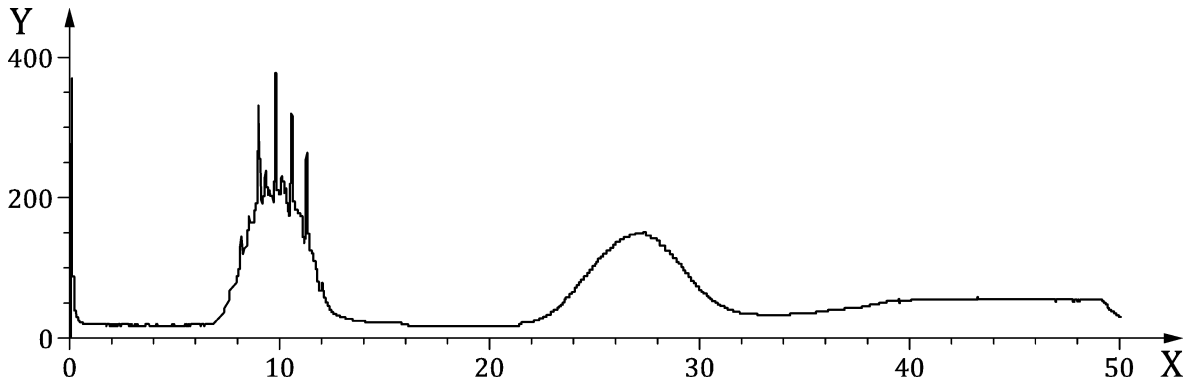
- External Standard: to determine the recovery (3.8) of samples by comparing the total sample area (3.6) of the reference material with the total sample area (3.6) of the unknown sample.
- Boiling Point Distribution Standard: to check the proper functioning of the system by comparing the results with a known boiling point distribution on a routine basis. Typical example is given in (5.8.2).

5.8.2 **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.

5.8.3 **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 2 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.

Table 1 — Reference Material 5010

% recovered	Accepted Reference value °C	Maximum allowable range 95,5 % Confidence Interval °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



Key
 Y response (pA)
 X retention time (minutes)

Figure 2 — 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.

(standards.iteh.ai)

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

<https://standards.iteh.ai/catalog/standards/sist/fa03bb9c-9948-4d8d-bc0c-056cd4974e61/sist-en-15199-2-2021>

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

6.2.1 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.

6.2.2 Use a metal column with 0,53 mm internal diameter and coated with methyl silicone. Commercially available columns with film thickness (d_f) = 0,09 μm (for analysis up to C₁₂₀) and (d_f) = 0,17 μm (for analysis up to C₁₀₀) 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).

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

Table 2 — Typical operating conditions for gas chromatograph

	Unit	Specification
Column length	m	5
Column internal diameter	mm	0,53
Column material	—	Ultimetall
Stationary phase	—	Methyl silicone
Film thickness	µm	0,09 or 0,17
Initial column temperature	°C	35
Final column temperature	°C	430
Program rate	°C/min	10
Injector initial temperature	°C	100
Injector final temperature	°C	430
Program rate	°C/min	15
Hold time	min	5
Detector temperature	°C	450
Detector hydrogen flow rate (5.2)	ml/min	35
Detector air flow rate (5.3)	ml/min	350
Carrier gas	—	Helium
Carrier gas flow rate	ml/min	19 ^a
Sample size	µl	1,0
Sample concentration	% (m/m)	2
Injector	—	PTV or COC
^a A carrier gas flow rate up to 25 ml/min can be used to ensure all material elutes before the end of the temperature program.		

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

6.5 Volumetric flask, 10 ml capacity.

6.6 Refrigerator, shall be of an explosion-protected design.

6.7 Analytical balance, capable of weighing to the nearest 0,1 mg.