



SLOVENSKI STANDARD

oSIST prEN 15199-2:2019

01-december-2019

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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ICS 75.080

Will supersede 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 draft European Standard is submitted to CEN members for enquiry. It has been drawn up by the Technical Committee CEN/TC 19.

If this draft becomes a European Standard, 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.

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Recipients of this draft are invited to submit, with their comments, notification of any relevant patent rights of which they are aware and to provide supporting documentation.

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

CEN-CENELEC Management Centre: Rue de la Science 23, B-1040 Brussels

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prEN 15199-2:2019 (E)**European foreword**

This document (prEN 15199-2:2019) 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 document is currently submitted to the CEN Enquiry.

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 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) 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) below 100 °C and final boiling points (FBP) above 750 °C, such as crude oils, Part 3 is applicable.

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

This second edition cancels and replaced the first edition (EN 15199-2:2006) which is updated editorially and contains additional clarification in the sample preparation section.

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. This document 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. This document 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, diesel). Components containing 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, μ , and the volume fraction, φ .

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 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 3170:2004)*

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.

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

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

Note 1 to entry: 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 (3.7) counts equal to 0,5% of the total sample area (3.6) under the chromatogram is obtained

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

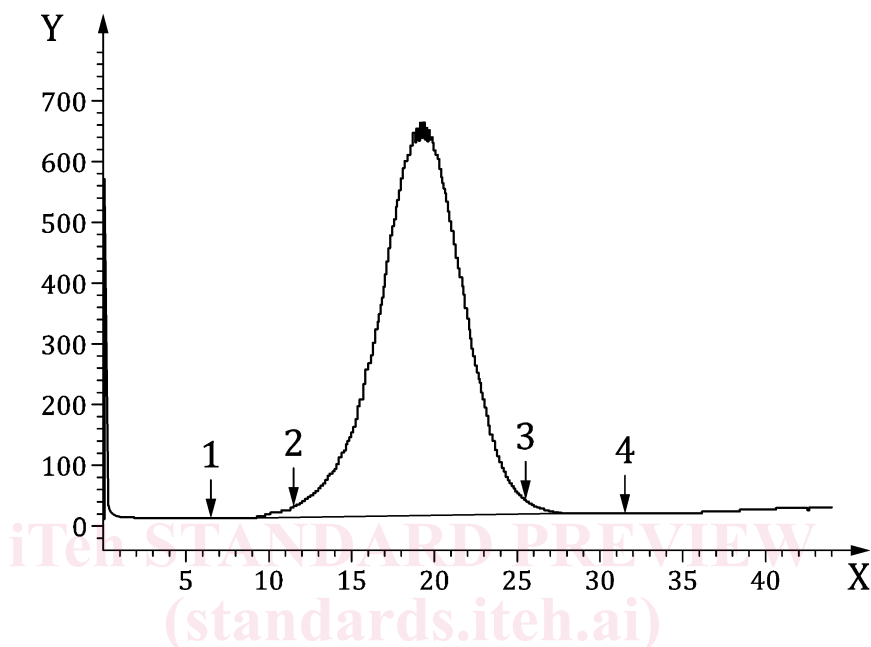
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3.3

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.

**Key**

1 start of elution

2 initial boiling point (IBP) (3.1)

3 final boiling point (FBP)

4 end of elution

X min

Y pA

Figure 1 — Typical chromatogram

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
- 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 normal 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 (3.8) was measured is recorded.

NOTE 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.

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 gas**, 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 ionization detectors.
- 5.4 Compressed air**, regulated for flame ionization detectors.
- 5.5 Alkanes**, normal alkanes of at least 98 % (m/m) purity from C₅ to C₁₀, C₁₂, C₁₄, C₁₆, C₁₈, C₂₀, C₂₄ and C₂₈ to be used with Polywax 655 or 1000 (5.6).

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

- 5.6 Polywax 655 or 1000**
- 5.7 Carbon disulphide**, with a minimum purity of 99,7 % (V/V).

WARNING — Extremely flammable and toxic.

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

To confirm the suitability of the carbon disulphide (5.7) as a solvent, it is recommended to check elution profiles (see Figure 2).

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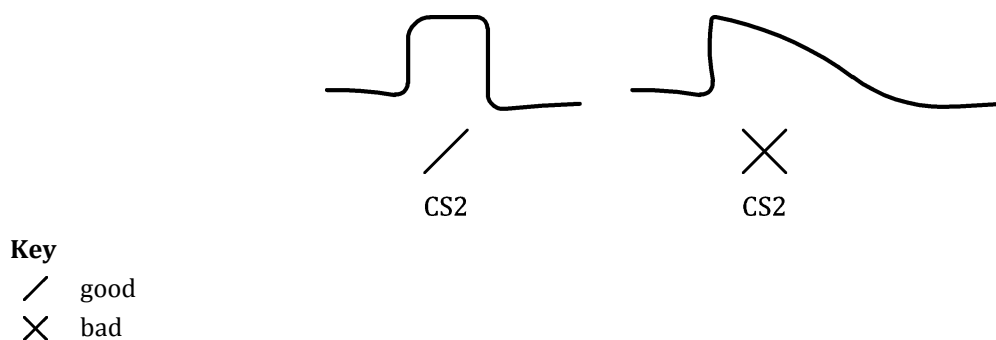


Figure 2 — Solvent peak shapes

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 (3.8) is measured.

Dissolve 0,1 g of Polywax (5.6) in 7 ml carbon disulphide (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 C₂₀ 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 (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 (5.9.2).

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.

5.9.3 Cyclohexane, (C₆H₁₂)—(99+ % pure) may be used in place of CS₂ 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.

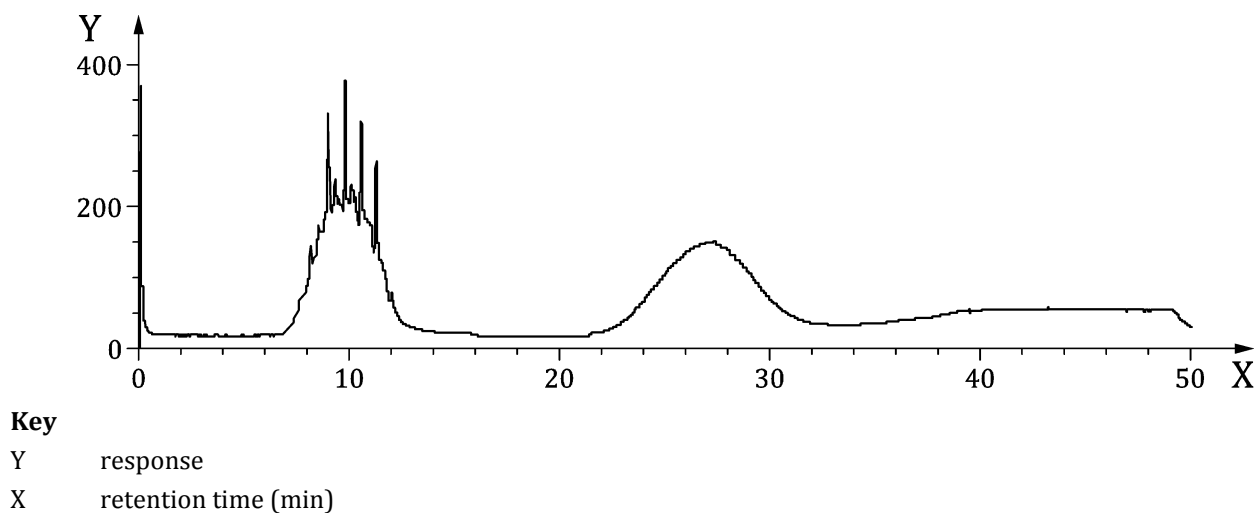


Figure 3 — Typical chromatogram of binary gravimetric blend distillate

Table 1 — Reference Material 5010

% recovered	Reference temperature	Maximum allowable range
	°C	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

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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.

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.

Table 2 — Typical operating conditions for gas chromatograph

	Unit	Specification
Column length	m	5
Column internal diameter	mm	0,53
Column material	—	Ultimetel
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 (5.3)	ml/min	35
Detector air flow (5.4)	ml/min	350
Carrier gas	—	He
Carrier gas flow rate	ml/min	19
Sample size	µl	1,0
Sample concentration	% (m/m)	2
Injector	—	PTV or COC