



SLOVENSKI STANDARD

oSIST prEN 15199-3:2019

01-november-2019

Naftni proizvodi - Določevanje destilacijskega območja z metodo plinske kromatografije - 3. del: Surova nafta

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

Mineralölerzeugnisse - Gaschromatographische Bestimmung des Siedeverlaufes - Teil 3: Rohöle

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

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ICS:

71.040.50	Fizikalnokemijske analitske metode	Physicochemical methods of analysis
75.040	Surova nafta	Crude petroleum

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EUROPEAN STANDARD
NORME EUROPÉENNE
EUROPÄISCHE NORM

DRAFT
prEN 15199-3

October 2019

ICS

Will supersede 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

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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

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European foreword

This document (prEN 15199-3:2019) 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.

This document will supersede EN 15199-3:2008.

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.

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 is harmonized with IP 545 [1] and ASTM D 7169 [2].

This second version replaces EN 15199-3:2008. The document is often used in combination with an analysis of the light end to improve the test method. Consensus has been reached about the algorithm for merging the results of the light end analysis and the Simdis analysis. This algorithm is added as an informative annex. Also, additional information on the determination of the IBP and FBP is added to help the user to improve the test results.

prEN 15199-3:2019 (E)**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 C₁₀₀ or C₁₂₀ 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 C₁₀₀ or C₁₂₀ in a single analysis

Procedure B (or Dual analysis mode) combines procedure A with the boiling point distribution from C₁ up to C₉ 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 European Standard, the terms “% (m/m)” and “% (V/V)” are used to represent the mass fraction, μ , and the volume fraction, φ , of a material respectively.

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.

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 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:

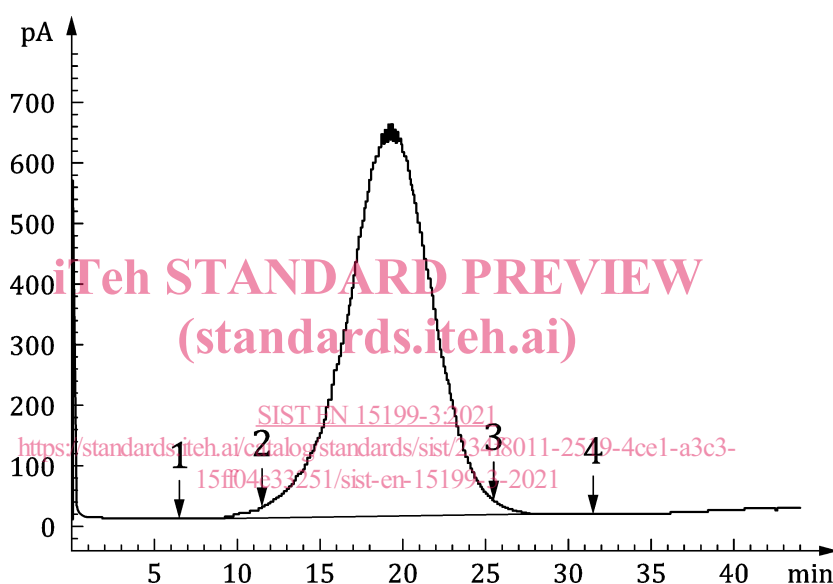
- IEC Electropedia: available at <http://www.electropedia.org/>
- ISO Online browsing platform: available at <http://www.iso.org/obp>

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 count equal to 0,5 % of the total sample area under the chromatogram is obtained



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 count equal to 99,5 % of the total sample area under the chromatogram is obtained

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.

prEN 15199-3:2019 (E)**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 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 1 to entry: 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 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, 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 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 (C₁₀₀) or 750 °C (C₁₂₀) is determined.

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

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 C₉ through C₁₀₀ or C₁₂₀. 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 C₁ up to C₉. 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 (C₁ to C₉) 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 C₅ to C₁₀, C₁₂, C₁₄, C₁₆, C₁₈, C₂₀, C₂₄ and C₂₈ 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).

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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).



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 of the C₂₀ 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.

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5.9 Reference materials (RM)

<https://standards.iteh.ai/catalog/standards/sist/234f8011-2519-4ce1-a3c3-15ff04e33251/sist-en-15199-3-2021>

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.

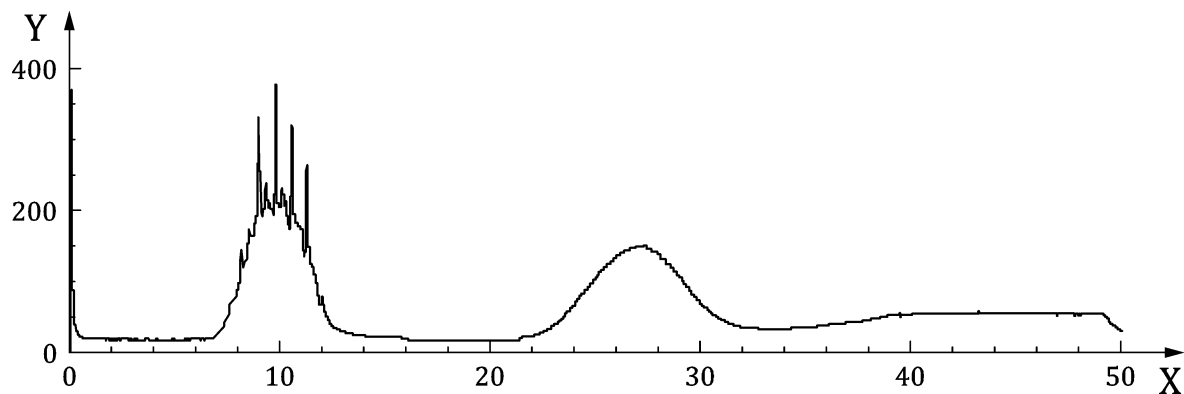
NOTE Consensus values of newer batches can differ from the ones in Table 1, for those we refer to the sample certificate.

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, (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 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 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 id coated with methyl silicone (5.1).

NOTE 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). 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.

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, $^{\circ}\text{C}$, Procedure A	-20	-20
Initial column temperature, $^{\circ}\text{C}$, Procedure B	40	40
Final column temperature, $^{\circ}\text{C}$	430	430
Programme rate, $^{\circ}\text{C}/\text{min}$	10	10
Hold time, min	5	5
Injector initial temperature, $^{\circ}\text{C}$	100	ambient
Injector final temperature, $^{\circ}\text{C}$	430	no setpoint
Programme rate, $^{\circ}\text{C}/\text{min}$	15	15
Detector temperature, $^{\circ}\text{C}$	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). 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.

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