SLOVENSKI STANDARD
SIST EN 15199-1:2021

01-marec-2021

Nadomešča:
SIST EN 15199-1:2006

Naftni proizvodi - Določanje porazdelitve območja vrelišč z metodo plinske kromatografije - 1. del: Srednji destilati in mazalna olja

Petroleum products - Determination of boiling range distribution by gas chromatography method - Part 1: Middle distillates and lubricating base oils

Mineralölerzeugnisse - Gaschromatographische Bestimmung des Siedeverlaufes - Teil 1: Mitteldestillate und Grundöle

Produits pétroliers - Détermination de la répartition dans l'intervalle de distillation par méthode de chromatographie en phase gazeuse - Partie 1: Distillats moyens et huiles lubrifiantes

Ta slovenski standard je istoveten z: **EN 15199-1:2020**

ICS:

75.080	Naftni proizvodi na splošno	Petroleum products in general
75.100	Maziva	Lubricants, industrial oils and related products

SIST EN 15199-1:2021 **en,fr,de**

EUROPEAN STANDARD

NORME EUROPÉENNE

EUROPÄISCHE NORM

EN 15199-1

December 2020

ICS 75.080

Supersedes EN 15199-1:2006

English Version

Petroleum products - Determination of boiling range distribution by gas chromatography method - Part 1: Middle distillates and lubricating base oils

Produits pétroliers - Détermination de la répartition dans l'intervalle de distillation par méthode de chromatographie en phase gazeuse - Partie 1 : Distillats moyens et huiles lubrifiantes

Mineralölerzeugnisse - Gaschromatographische Bestimmung des Siedeverlaufes - Teil 1: Mitteldestillate und Grundöle

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.

CEN members are the national standards bodies of 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 United Kingdom.

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

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

Ref. No. EN 15199-1:2020 E

Contents

Page

European foreword

This document (EN 15199-1:2020) 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 15199-1:2006.

The main changes in this edition are:

— the precision is extended for the recovery points between 10 % and 50 %;

— the text has been updated editorially in order to give better guidance to operators executing the test.

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) below 750 °C. For testing materials with initial boiling points (IBP) above 100 °C and final boiling point (FBP) above 750 °C, Part 2 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 can be used. Part 4 describes the determination of boiling range distribution of hydrocarbons up to *n*-nonane in crude oil.

This document is based on IP Test Method IP 480 [4] and ASTM Test Method ASTM D6352 [3].

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.

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 a boiling range of at least 100 °C. The standard is applicable to distillates with initial boiling points (IBP) above 100 °C and final boiling points (FBP) below 750 °C, for example, middle distillates and lubricating base stocks.

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

Petroleum or petroleum products containing blending components which contain heteroatoms (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 can 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)*

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 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)

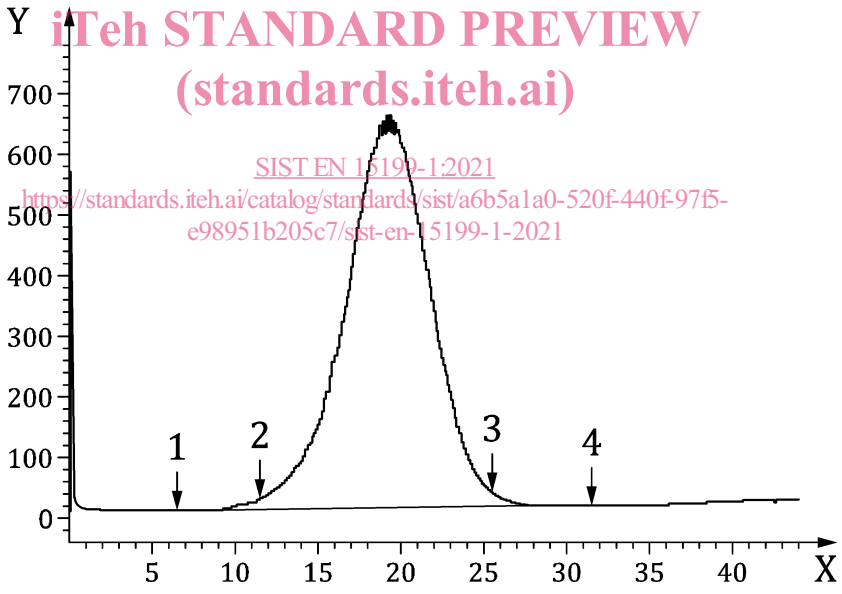
3.3
area slice
area resulting from the integration of the chromatographic detector signal within a specified retention time interval

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

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



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

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 obtained by running a mixture of known n-alkanes, covering the sample boiling range, under the same conditions. From these data, the boiling range distribution is obtained.

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

EN ISO 3924 [1] 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 15199-2 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.

EN 15199-3 is applicable to crude oils. The boiling range distribution and recovery (3.8) up to C_{100} or C_{120} can be determined.

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 C_5 to C_{10}, C_{12}, C_{14}, C_{16}, C_{18}, C_{20}, C_{24} and C_{28}.

NOTE The calibration mixture from EN ISO 3924 [1] is also suitable.

5.5 Polywax 655® or 1000®

5.6 Carbon disulfide, (CS_2) purity 99,7 % (V/V) minimum.

WARNING — Extremely flammable and toxic by inhalation.

CAUTION — It is recommended that all work with CS_2 is carried out in an explosion protected fume cupboard.

Cyclohexane (C_6H_{12})—(>99 % pure) can be used in place of CS_2 for the preparation of the calibration mixture. However, the precision of this method is based on calibration mixtures, reference material and samples prepared with CS_2 only.

5.7 Calibration mixture

Dissolve 0,1 g of Polywax (5.5) in 7 ml CS_2 (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 C_{20} 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 of samples by comparing the total sample area (3.6) of the reference material with the total sample area (3.5) of the unknown sample;

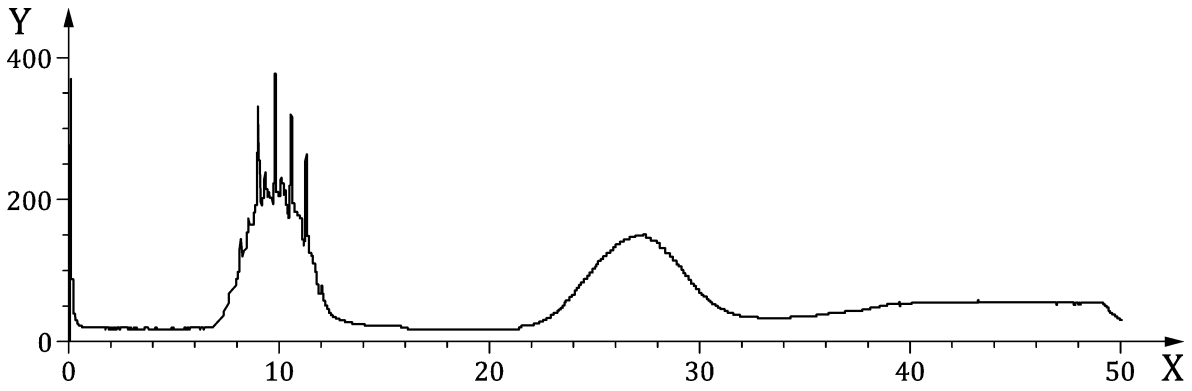
— Boiling Point Distribution Standard: to check the proper functioning of the system by comparing the results with a known boiling point distribution on a routine basis. A typical example is given in (5.8.2).

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

% Recovery	Accepted Reference value °C	Allowable difference 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 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.

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, 0,53 µm internal diameter coated with methyl silicone. 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).

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.