SLOVENSKI STANDARD
SIST EN 15199-1:2006

01-december-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 15199-1:2006

ICS:

75.100	Maziva	Lubricants, industrial oils and related products

SIST EN 15199-1:2006 **en**

EUROPEAN STANDARD

NORME EUROPÉENNE

EUROPÄISCHE NORM

EN 15199-1

October 2006

ICS 75.080

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 par 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 28 August 2006.

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 Central Secretariat 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 Central Secretariat has the same status as the official versions.

CEN members are the national standards bodies of Austria, Belgium, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Romania, Slovakia, Slovenia, Spain, Sweden, Switzerland and United Kingdom.

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Ref. No. EN 15199-1:2006: E

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Foreword

This document (EN 15199-1:2006) 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 April 2007, and conflicting national standards shall be withdrawn at the latest by April 2007..

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*

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) 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 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 may be used.

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

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

1 Scope

This European Standard specifies a method for the determination of the boiling range distribution of petroleum products by capillary gas chromatography using flame ionisation 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 naphthas, reformates, gasolines, diesel). Components containing hetero atoms (for example alcohols, ethers, acids, or esters) or residue are not to be analyzed by this test method.

NOTE For the purposes of this European Standard, the terms "% (*m/m*)" and "% (*V/V*)" are used to represent respectively the mass fraction and the volume fraction.

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 referenced documents are indispensable for the application 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.

NOTE 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

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

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

NOTE 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

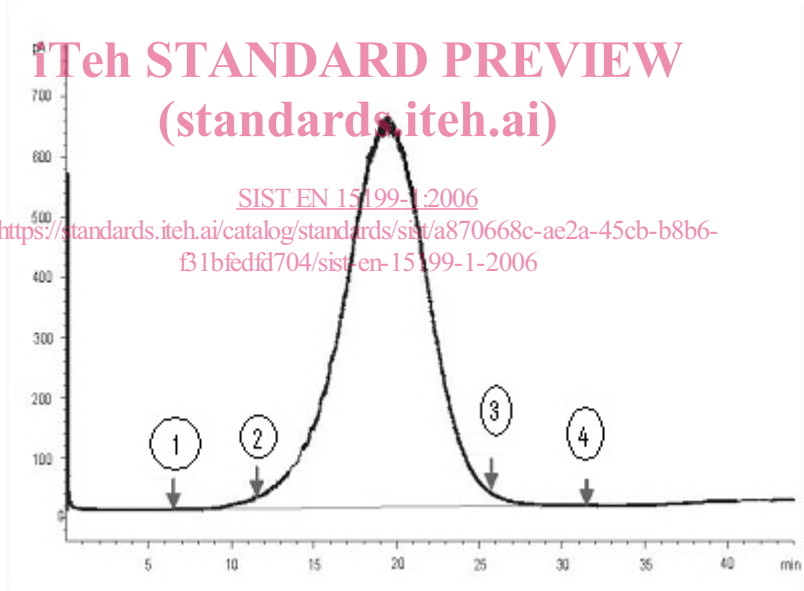
3.5
cumulative corrected area
accumulated sum of corrected area slices from the beginning of the analysis through a given retention time, ignoring any non-sample area for example of solvent

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

NOTE 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 The slice time is the time at the end of each contiguous area slice.



Key:

1 start of elution
2 initial boiling point (IBP)
3 final boiling point (FBP)
4 end of elution

Figure 1 — Typical chromatogram

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 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 normal alkanes, covering the sample boiling range, under the same conditions. From these data, the boiling range distribution is obtained.

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, 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 ionisation detectors

5.4 Compressed air, regulated for flame ionisation detectors.

5.5 Alkanes, normal 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} to be used with Polywax (5.6).

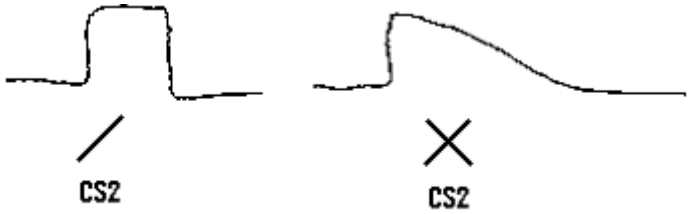
NOTE The calibration mixture from ISO 3924 [3] is also suitable.

5.6 Polywax 655 or 1000

5.7 Carbon disulfide, purity 99,7 % (*V/V*) minimum.

WARNING — Extremely flammable and toxic by inhalation.

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



Key:

/ good
X bad

Figure 2 — Solvent peak shape

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 higher than the FBP of the sample.

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 C_{20} 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 of samples by comparing the total sample area (3.8) of the reference material with the total sample area 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 (5.9.2).

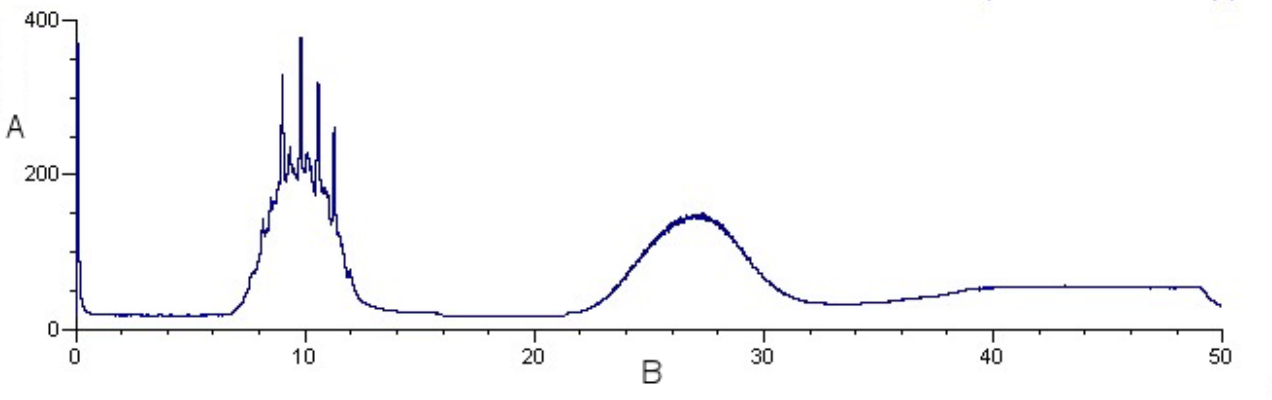
5.9.2 Reference Material 5010, a reference sample that has been analyzed by laboratories participating in the test method cooperative study. Consensus values for the boiling range distribution of this sample are given in Table 1.

5.9.3 Cyclohexane. (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 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.

Table 1 — Reference Material 5010

% recovered	Reference temperature °C	Maximum allowable range 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



Key:

A response
B retention time (min)

Figure 3 — Typical chromatogram of binary gravimetric blend distillate

6 Apparatus

6.1 Gas chromatograph, with the following performance characteristics.

6.1.1 Flame ionisation 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.

NOTE 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 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

Use a metal column with 0,53 mm internal diameter and coated with methyl silicone (5.1). 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.

NOTE 1 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.

NOTE 2 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.