



SLOVENSKI STANDARD

SIST EN 15199-4:2015

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Naftni proizvodi - Določevanje porazdelitve območja vrelišč z metodo plinske kromatografije - 4. del: Lahke frakcije surovega olja

Petroleum products - Determination of boiling range distribution by gas chromatography method - Part 4: Light fractions of crude oil

Mineralölerzeugnisse - Gaschromatographische Bestimmung des Siedeverlaufes - Teil 4: Leichte Fraktionen des Rohöls

Produits pétroliers - Détermination de la répartition dans l'intervalle de distillation par méthode de chromatographie en phase gazeuse - Partie 4 : Lumière fractions du pétrole brut

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EUROPEAN STANDARD

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Petroleum products - Determination of boiling range distribution by gas chromatography method - Part 4: Light fractions of crude oil

Produits pétroliers - Détermination de la répartition dans l'intervalle de distillation par méthode de chromatographie en phase gazeuse - Partie 4 : Lumière fractions du pétrole brut

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This European Standard was approved by CEN on 1 August 2015.

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European foreword

This document (EN 15199-4:2015) 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of an identical text or by endorsement, at the latest by March 2016, and conflicting national standards shall be withdrawn at the latest by March 2016.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. CEN [and/or CENELEC] 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 fractions of crude oil

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This part of the standard is based on IP 601 [1] and describes the determination of boiling range distribution of hydrocarbons up to n-nonane in crude oil. The results of this test method can be combined with those from EN 15199-3, to give a full boiling point distribution of crude oil.

Part 4 is harmonized with ASTM D7900 [2].

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

EN 15199-4:2015 (E)

1 Scope

This European Standard describes a method for the determination of the boiling range distribution of petroleum products by capillary gas chromatography using flame ionization detection. This European Standard is applicable to stabilized crude oils and for the boiling range distribution and the recovery up to and including *n*-nonane. A stabilized crude oil is defined as having a Reid Vapour Pressure equivalent to or less than 82,7 kPa as determined by IP 481 [3].

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

WARNING — The use of this European Standard can 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 take appropriate measures to ensure safety and health of personnel prior to application of the standard, and fulfil statutory and regulatory requirements for this purpose.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. 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)*

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3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

3.1

recovery

combined mass percentages of all light hydrocarbon peaks (except the internal standard peak) in the sample up to and including *n*-nonane

4 Principle

An amount of internal standard is quantitatively added to an aliquot of the stabilized crude oil. A portion of this mixture is injected into a pre-column in series via a splitter with a capillary analytical column. When the *n*-nonane has quantitatively passed to the analytical column, the pre-column is back-flushed to vent the higher boiling components. The individual components are identified by comparison with reference chromatograms and a database of hydrocarbon compounds (see Annex A). The boiling point distribution and recovery up to and including *n*-nonane (*n*-C9) is calculated.

5 Reagents and materials

5.1 Stationary phase for columns, with a bonded polydimethylsiloxane (PDMS) stationary phase for both the pre-column and the analytical capillary column.

5.2 Compressed gases

5.2.1 Carrier gas, helium or hydrogen of at least 99,995 % (V/V) purity or higher is required. Any oxygen present shall be removed by a suitable chemical filter.

CAUTION — If hydrogen is used as carrier gas, follow the safety instructions from the GC instrument manufacturer.

5.2.2 Combustion gases, hydrogen and clean air for the flame ionization detector, and suitable filters shall be used to ensure adequate gas cleanliness.

5.3 Internal standard, having a baseline resolution from any adjacent eluting peaks (Hexene-1 or 3,3-dimethylbutene-1 (99 % pure) have been found to be suitable).

5.4 Valve switching mixture, a qualitative mixture of approximately 1 % (m/m) of each normal alkane from pentane to decane.

5.5 Carbon disulphide (CS₂), purity 99,7 % (V/V) minimum.

WARNING — Extremely flammable and toxic by inhalation.

6 Apparatus

6.1 Analytical balance

Capable of weighing with an accuracy of 0,1 mg.

6.2 Gas chromatograph

The typical operational characteristics of the gas chromatograph are described in Table 1.

Two different pre-column configurations are possible:

The first configuration (A) employs a 1-metre column contained in a temperature controlled valve box, separately controlled. The valve box in this configuration is isothermal.

The second configuration (B) is a short pre-column (a packed injection port liner), that fits into the injection port. The injection port will be temperature programmed.

6.3 Detector

Flame Ionization Detector with sufficient sensitivity to detect 1 % mass n-heptane with a peak height of at least 10 % full-scale deflection under the conditions given in the method. When operating at this sensitivity level, detector stability shall be such that a baseline drift of not more than 1 % per hour is obtained. The detector shall be connected to the column carefully to avoid any cold spots. The detector shall be capable of operating at a temperature equivalent to the maximum column temperature used.

6.4 Pre-column configurations

6.4.1 Heated valve switching box (see Figure B.1)

For the isothermal 1 metre pre-column, a heated valve box is needed with its own temperature control. The box will contain an automated six-port valve which is used to back-flush the pre-column.

The six-port valve should be made out of material which will not be corroded by the sample (Some crude oils contain high amounts of sulfur components). The valve shall be situated in a heated isothermal oven and be attached to the injector, pre-column, splitter, analytical column and the detector without any cold spots.

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6.4.2 Injection port (see Figure B.2 and B.3)

A temperature programmable injection port capable of containing a 7,5 cm pre-column, and this injection port shall be equipped with a back-flush option. This injector can be connected directly to the capillary column (Figure B.2) or via a splitter (Figure B.3).

Table 1 — Typical chromatographic conditions

	Pre-column A	Pre-column B	Analytical	Accelerated Analytical
Column length – m	1,0	0,075	50 or 100	40
Column internal diameter – mm	2	2,5	0,25	0,10
Column material	polydimethylsiloxane			
Phase loading – %	5	10		
Film thickness – μm			0,5	
Injection volume – μL			0,1	0,1
Injector split ratio	100:1		100:1	600: 1
Injector temperature – $^{\circ}\text{C}$	300	100		
Pre-column temperature – $^{\circ}\text{C}$	200	100		
Injector program rate – $^{\circ}\text{C}/\text{min}$	50			
Final injector temperature – $^{\circ}\text{C}$		300		
Initial oven temperature – $^{\circ}\text{C}$			35	35
Hold time – min			30	2,6
Oven program rate – $^{\circ}\text{C}/\text{min}$			2	50 \rightarrow 45 $^{\circ}\text{C}$ (hold time 3 min)
				5 \rightarrow 60 $^{\circ}\text{C}$ (hold time 3 min)
				9,5 \rightarrow 200 $^{\circ}\text{C}$
Final oven temperature – $^{\circ}\text{C}$			200 (hold time 20 min)	200 (hold time 1 min)
Flame Ionization Detector – $^{\circ}\text{C}$			300	300

6.5 Analytical column

6.5.1 General

The column elutes hydrocarbons in a boiling point order. The eluate from the injector passes through the pre-column before eluting onto the analytical column.

6.5.2 Resolution

Determine the resolution between the internal standard and the nearest n-paraffin peak as per Formula (1).

$$P = \frac{2(t_2 - t_1)}{1,699(w_1 + w_2)} \quad (1)$$

Where

- P is the column resolution;
- t_1 is the retention time of the first peak (peak 1, see Figure 1);
- t_2 is the retention time of the second peak (peak 2, see Figure 1);
- w_1 is the peak width at half height of peak 1;
- w_2 is the peak width at half height of peak 2.

With Hexene-1 as I.S., the resolution is determined between the I.S. and n-hexane. The resolution shall be at least 2,0.

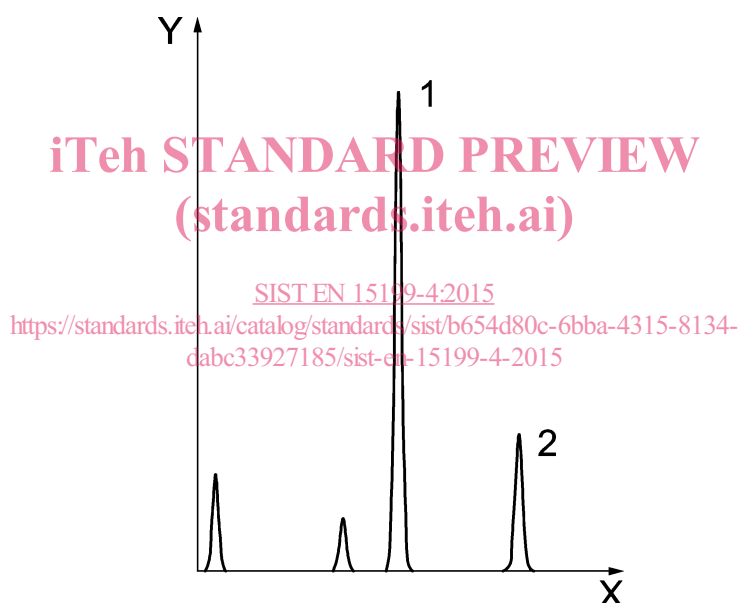


Figure 1 —Determination of resolution

6.6 Skewness

Determine the skew of the n-hexane peak by measuring the width of the leading part of the peak at 5 % peak height (A) and the width of the following part of the peak at 5 % peak height (B). The ratio (B)/(A) shall be not less than 1 or more than 4. See Figure 2 for further clarification.

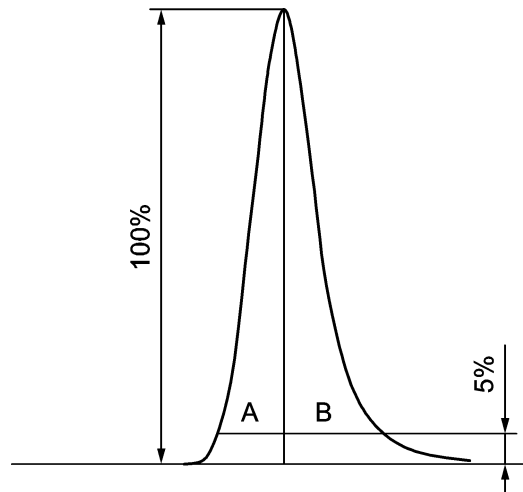


Figure 2 — Calculation of peak skewness

6.7 Data collection

A PC based chromatography data system or integrator with suitable software may be used. For systems using the analytical column, a data -sampling rate of 5 Hz is the recommended minimum.

For systems using the accelerated analytical column, a data-sampling rate of 20 Hz is required.

7 Sampling and sample handling

Take samples in accordance with either EN ISO 3170 or EN ISO 3171.

8 Calculation of response factors

Calculate the flame ionization detector response factor relative to methane, which is considered to have a response factor of unity (= 1), for each hydrocarbon group type of a particular carbon number using Formula (2).

$$RRf = \frac{[(C_{aw} \times C_n) + (H_{aw} \times H_n)] \times 0,7487}{(C_{aw} \times C_n)} \quad (2)$$

Where

- RRf is relative response factor for a hydrocarbon type group of a particular carbon number,
- C_{aw} is atomic mass of carbon, 12,011,
- C_n is number of carbon atoms in the hydrocarbon type group, of a particular carbon number,
- H_{aw} is atomic mass of hydrogen, 1,008,
- H_n is number of hydrogen atoms in the hydrocarbon type group of a particular carbon number, and 0,748 7 is factor to normalize the result to a methane response of unity (= 1).

Table 2 gives some response factors already calculated.

Table 2 — Calculated response factors for hydrocarbons

No. of Carbon atoms	Naphthenes	Paraffins	Cyclic olefins	Mono-olefins	Aromatics
3		0,916		0,874	
4		0,906		0,874	
5	0,874	0,899	0,849	0,874	
6	0,874	0,895	0,853	0,874	0,811
7	0,874	0,892	0,856	0,874	0,820
8	0,874	0,890	0,859	0,874	0,827
9	0,874	0,888	0,860	0,874	0,832

9 Procedure

9.1 Sample preparation

Weigh to the nearest 0,1 mg, approximately $5 \text{ g} \pm 0,2 \text{ g}$ of sample into a tared, screw-capped vial.

Add approximately $0,15 \text{ g} \pm 0,02 \text{ g}$ of internal standard and reweigh to the nearest 0,1 mg. Where the mass of available sample is less than 10 g, the internal standard shall be added to create the equivalent of a 3 % concentration.

Gently mix the two liquids without causing the sample to degas. Carbon disulphide (5.5) may be added to improve the viscosity of the sample.

Fill the sample into GC vials with a minimum amount of headspace. Store the vials in a sub ambient cupboard until use.

NOTE The amount of sample and internal standard taken can vary according to the level of light-end components in the sample and the amount of the sample available.

9.2 Determination of backflush time

9.2.1 Initial work

With the pre-column and analytical column in series, inject an aliquot of the pre-column switch test mixture (5.4) and determine the ratio of the alkanes.

9.2.2 Analytical column

Set the switching time to 1 min and repeat the analysis. Increase or decrease the valve time to ensure the complete recovery of the highest alkane required (e.g. nonane) and partly recovery of the next alkane (e.g. decane). (See 9.3.1 and the example chromatogram in Figure 3)

9.2.3 Accelerated analytical column

Set the switching time to 30 s and repeat the analysis. Increase or decrease the valve time to ensure the recovery of the highest alkane required (e.g. nonane) and partly recovery of the next alkane (e.g. decane). (For assistance in the identification of individual components see [1] and [2] and example chromatogram (Figure 3))