BS EN 15199-4:2021

BSI Standards Publication

Petroleum products — Determination of boiling range distribution by gas chromatography method

Light fractions of crude oil

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National foreword

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The UK participation in its preparation was entrusted to Technical Committee PTI/13, Petroleum Testing and Terminology.

A list of organizations represented on this committee can be obtained on request to its committee manager.

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

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

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European foreword

This document (EN 15199-4:2021) 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of an identical text or by endorsement, at the latest by March 2022, and conflicting national standards shall be withdrawn at the latest by March 2022.

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 15199-4:2015.

In comparison with the previous edition, the following technical modification has been made.

The document is often used in combination with an analysis of boiling point distribution (Simdis) of crude oil. 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 normative Annex C

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*

Part 4 is harmonized with IP 601 [1] and ASTM D7900 [2].

Any feedback and questions on this document should be directed to the users' national standards body. A complete listing of these bodies can be found on the CEN website.

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.

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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 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].

Annex C specifies an algorithm for merging the boiling point distribution results obtained using this method with the results obtained with EN 15199-3. This will result in a boiling range distribution and recovery up to C120.

NOTE 1 There is no specific precision statement for the combined results obtained after merging the results of EN 15199-3 and EN 15199-4. For the precision of the boiling range distribution up to *n*-nonane, the precision statement of EN 15199-4 applies. For the precision of the boiling range distribution from *n*-nonane through C120, the precision of EN 15199-3 applies.

NOTE 2 For the purposes of this document, 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 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 document to take appropriate measures to ensure safety and health of personnel prior to application of the document and fulfil statutory and regulatory requirements for this purpose.

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:

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

3.1
recovery
combined mass percentages of all light hydrocarbon identified in the chromatogram(except the internal standard peak) of the sample up to and including n-nonane

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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-dimethyl-1-butene (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 disulfide (CS_2), purity 99,7 % (V/V) minimum.

WARNING — Extremely flammable and toxic by inhalation.

6 Apparatus

6.1 Analytical balance capable of weighing to the nearest 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 (see Annex B).

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 (see Annex B).

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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.

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	600 : 1
Injector temperature – °C	300	100		
Pre-column temperature – °C	200	100		
Injector program rate – °C/min		50		
Final injector temperature – °C		300		
Initial oven temperature – °C			35	35
Hold time – min			30	2,6
Oven program rate –°C/min			2	50 → 45 °C (hold time 3 min)
				5 → 60 °C (hold time 3 min)
				9,5 → 200 °C
Final oven temperature – °C			200 (hold time 20 min)	200 (hold time 1 min)
Flame Ionization Detector – °C			300	300

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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.

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).

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).

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

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.

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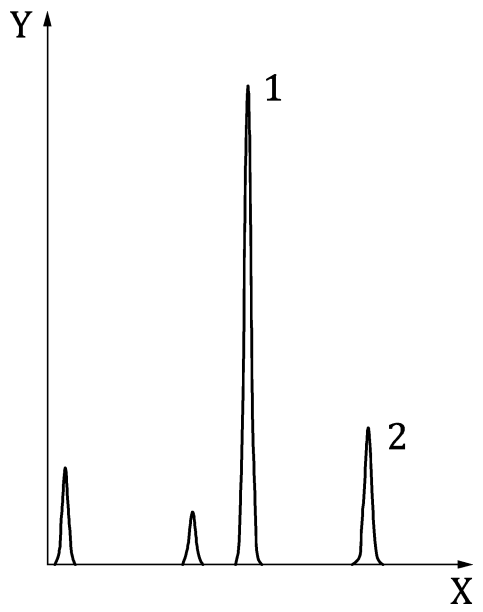

Figure 1 — Determination of resolution

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.

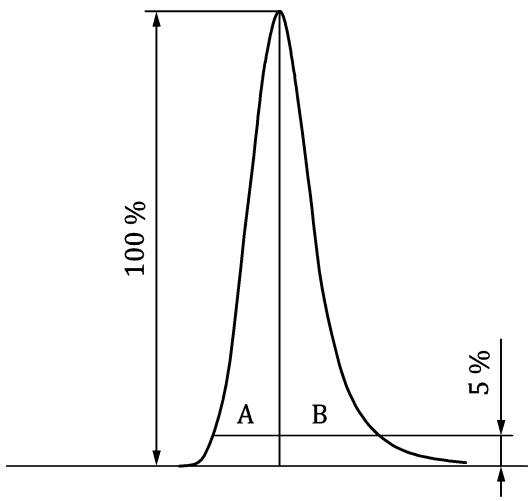

Figure 2 —Calculation of peak skewness

6.7 Data collection

A PC based chromatography data system or integrator with suitable software can 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.

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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).

$$RRf = \frac{\left[\left(C_{\text{aw}} \times C_n\right) + \left(H_{\text{aw}} \times H_n\right)\right] \times 0{,}748\,7}{\left(C_{\text{aw}} \times C_n\right)} \tag{2}$$

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

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