
**Petroleum products — Determination
of boiling range distribution — Gas
chromatography method**

*Produits pétroliers — Détermination de la répartition dans l'intervalle
de distillation — Méthode par chromatographie en phase gazeuse*

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

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For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 28, *Petroleum and related products, fuels and lubricants from natural or synthetic sources*.

This method was originally based on the joined IP 406^[3] and ASTM D2887^[4] methods.

This fifth edition cancels and replaces the fourth edition (ISO 3924:2016), which has been technically revised. The main changes compared with the previous edition are as follows.

- The accelerated procedure has been moved from [Annex B](#) to the main body text. It is described as Procedure B and has a precision and bias calculation in relation to Procedure A (the original procedure).
- A new annex has been added with the newly defined boiling points for n-alkanes to keep the method technically equivalent with IP 406 and ASTM D2887.
- [Annexes E](#) and [F](#) have been added with information on the use of alternative carrier gases.
- Several safety warnings and editorial updates have been made.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Petroleum products — Determination of boiling range distribution — Gas chromatography method

WARNING — The use of this document can involve hazardous materials, operations and equipment. This document does not purport to address all the safety problems associated with its use. It is the responsibility of users of this document to take appropriate measures to ensure the safety and health of personnel prior to application of the document.

1 Scope

This document specifies a method for the determination of the boiling range distribution of petroleum products. The method is applicable to petroleum products and fractions with a final boiling point of 538 °C or lower at atmospheric pressure as determined by this document. This document does not apply to gasoline samples or gasoline components. The method is limited to products having a boiling range greater than 55 °C and having a vapour pressure sufficiently low to permit sampling at ambient temperature.

The document describes two procedures.

- a) Procedure A allows a larger selection of columns and analysis conditions, such as packed and capillary columns as well as a thermal conductivity detector in addition to the flame ionization detector. Analysis times range from 14 min to 60 min.
- b) Procedure B is restricted to only three capillary columns and requires no sample dilution. The analysis time is reduced to about 8 min.

Both procedures have been successfully applied to samples containing fatty acid methyl esters (FAME) up to 20 % (volume fraction).

NOTE For the purposes of this document, the terms “% (mass fraction)” and “% (volume fraction)” are used to represent the mass fraction (μ), the volume fraction (φ) of a material.

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.

ISO 3170, *Petroleum liquids — Manual sampling*

ISO 3171, *Petroleum liquids — Automatic pipeline sampling*

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

3.2
T10, T30, T50, T70, T90

temperature (T) corresponding to the retention time at which a net area count equal to the 10 %, 30 %, 50 %, 70 % or 90 % of the total sample area under the chromatogram is obtained

3.3
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

3.4
slice rate

number of data slices acquired per unit of time 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, slices per second).

4 Principle

A sample is introduced into a gas chromatographic column, which separates hydrocarbons in the order of increasing boiling point. The column temperature is raised at a reproducible rate and the area under the chromatogram is recorded throughout the analysis. Boiling temperatures are assigned to the time axis from a calibration curve, obtained under the same conditions by running a known mixture of hydrocarbons covering the boiling range expected in the sample. From these data, the boiling range distribution is obtained.

[Annex A](#) presents a correlation model for the calculation of physical distillation^{[1][5][6]} equivalent data from boiling range distribution analysis by gas chromatography determined following this document.

5 Reagents and materials

5.1 Stationary phase for columns, non-polar, that elutes hydrocarbons in boiling point order.

NOTE The following materials have been used successfully as liquid phases, other stationary phases can be used, see [6.2](#).

For packed columns:

- silicone gum rubber UC-W98;
- silicone gum rubber GE-SE-30;
- silicone gum rubber OV-1;
- silicone gum rubber OV-101.

For capillary columns:

- polydimethylsiloxane.

5.2 Solid support for packed columns, usually consisting of crushed fire brick or chromatographic diatomaceous earth.

The particle size and support loading shall be such as to give optimum resolution and analysis time.

NOTE In general, support loadings of 3 % to 10 % have been found most satisfactory.

5.3 Carrier gas, with a minimum purity of 99,995 %, constituted of:

- a) helium for use with flame ionization detectors (FIDs) or thermal conductivity detectors;
- b) for the use of nitrogen or hydrogen as a carrier gas, see [Annexes E](#) and [F](#).

CAUTION — Helium and nitrogen are compressed gases under high pressure. Hydrogen is an extremely flammable gas under high pressure.

5.4 Hydrogen, grade suitable for FIDs.

CAUTION — Hydrogen is an extremely flammable gas under high pressure.

5.5 Compressed air, free of oil and water, regulated for FIDs.

CAUTION — Compressed air is a gas under high pressure and supports combustion.

5.6 Calibration mixture, consisting of an accurately weighed mixture of n-alkanes covering the range from C₅ to C₄₄ and dissolved in carbon disulfide ([5.8](#)).

For packed columns, the final concentration in mass should be approximately 10 parts of the n-alkane mixture to 100 parts of carbon disulfide. For capillary columns, the final concentration in mass should be approximately 1 part of the n-alkane mixture to 100 parts of carbon disulfide.

The following mixture of n-alkanes has been found to be satisfactory for most samples: C₅, C₆, C₇, C₈, C₉, C₁₀, C₁₂, C₁₄, C₁₆, C₁₈, C₂₀, C₂₄, C₂₈, C₃₂, C₃₆, C₄₀, C₄₄. At least one component of the mixture shall have a boiling point lower than the initial boiling point (IBP) of the sample and at least one component shall have a boiling point higher than the final boiling point (FBP) of the sample. The boiling points of n-alkanes are listed in [Table 1](#).

If the test sample contains significant quantities of n-alkanes that can be identified on the chromatogram, these peaks can be used as internal boiling point calibration points. However, it is advisable to use the calibration mixture to be sure of peak identifications.

Propane and butane can be added non-quantitatively to the calibration mixture, if necessary, to conform to [5.6](#). This can be done by bubbling a small amount of the gaseous hydrocarbon into a septum-sealed vial of the calibration mixture using a gas syringe.

If stationary phases other than those listed in the note in [5.1](#) are used, the retention times of a few alkylbenzenes across the boiling range, such as *o*-xylene, *n*-butylbenzene, 1,3,5-tri-isopropylbenzene, *n*-decylbenzene and *n*-tetradecylbenzene, shall also be checked to make certain that the column is separating according to the boiling point order (see [Annex C](#)).

5.7 Reference material, the primary reference material used shall be ASTM reference gas oil no. 1 or no. 2 (as specified in [Annex B](#)).

5.8 Carbon disulfide, reagent grade or better (CAS RN 75-15-0).

CAUTION — Carbon disulfide is extremely volatile flammable and toxic.

Table 1 — Boiling points of normal n-alkanes

Carbon no.	Boiling point °C	Carbon no.	Boiling point °C
2	-89	24	391
3	-42	25	402
4	0	26	412
5	36	27	422
6	69	28	431
7	98	29	440
8	126	30	449
9	151	31	458
10	174	32	466
11	196	33	474
12	216	34	481
13	235	35	489
14	254	36	496
15	271	37	503
16	287	38	509
17	302	39	516
18	316	40	522
19	330	41	528
20	344	42	534
21	356	43	540
22	369	44	545
23	380		

NOTE API Project 44^[5] is believed to have provided the original normal paraffin boiling point data that were listed in former editions of this document. However, over the years, some of the data contained in both API Project 44 (Thermodynamics Research Center Hydrocarbon Project) and the test methods have changed, and they are no longer equivalent. This table represents the current normal paraffin boiling point values accepted by ISO, ASTM and the Energy Institute. [Annex D](#) contains information about revised boiling points.

6 Apparatus

6.1 Chromatograph, any gas chromatograph that has the following performance characteristics can be used.

6.1.1 Detector, of either the flame ionization or thermal conductivity type.

The detector shall have sufficient sensitivity to detect a mass fraction of 1,0 % of dodecane with a peak height of at least 10 % of full scale under the conditions specified in this document, and without loss of resolution as defined in 8.3. When operating at this sensitivity level, detector stability shall be such that a baseline drift of not more than 1 % of full scale per hour is obtained. The detector shall be capable of operating continuously at a temperature equivalent to the maximum column temperature employed. The detector shall be connected to the column in such a way that any cold spots between the detector and the column are avoided.

NOTE It is not desirable to operate thermal conductivity detectors at a temperature higher than the maximum column temperature employed. Operation at higher temperatures only serves to shorten the useful life of the detector, and generally contributes to higher noise levels and greater drift.

6.1.2 Column temperature programmer, capable of programmed temperature operation over a range sufficient to establish a retention time of at least 1 min for the IBP and to elute the entire sample within the temperature ramp.

The programming rate shall be sufficiently reproducible to obtain retention time repeatability of 6 s for each component in the calibration mixture (5.6).

6.1.3 Cryogenic column cooling. Column starting temperatures below ambient will be required if samples with IBPs of less than 93 are to be analysed. This is typically provided by adding a source of either liquid carbon dioxide or liquid nitrogen, controlled through the oven temperature circuitry.

However, excessively low initial column temperatures shall be avoided, to ensure that the stationary phase remains liquid. The initial temperature of the column shall be only low enough to obtain a calibration curve meeting the requirements of this document.

6.1.4 Sample inlet system. Programmed temperature vaporization (PTV) inlets or cool on-column inlets shall be used for this method.

The sample inlet system shall be connected to the chromatographic column in such a way that any cold spots between the inlet system and the column are avoided.

6.2 Column. Any column and conditions can be used, provided that, under the conditions of the test, separations are in the order of boiling points as given in Table 1, and the column resolution, R_c , is at least three (see 8.3). Typical column operating conditions are given in Tables 2, 3 and 4.

Table 2 — Typical operating conditions for packed columns — Procedure A

Parameter	Column 1
Column length (m)	0,7
Column outside diameter (mm)	3,2
Stationary phase	OV-101
Per cent stationary phase	5
Support material	G ^a
Support mesh size (µm)	80/100
Initial column temperature (°C)	-40
Final column temperature (°C)	350
Programming rate (°C/min)	10
Carrier gas	Helium
Carrier gas flow (ml/min)	30
Inlet	Packed inlet
Detector	FID
Detector temperature (°C)	370
Injection-port temperature (°C)	370
Sample size (µl), neat sample volume	0,5

^a Dioxosilane.

Table 3 — Typical operating conditions for capillary columns — Procedure A

Parameter	Column 2	Column 3
Column length (m)	5	10
Column inner diameter (mm)	0,53	0,53
Column	PDMS	PDMS
Stationary phase thickness (μm)	0,88	2,65
Carrier gas	Helium	Helium
Carrier gas flow rate (ml/min)	12	20
Initial column temperature ($^{\circ}\text{C}$)	35	40
Final column temperature ($^{\circ}\text{C}$)	350	350
Programming rate ($^{\circ}\text{C}/\text{min}$)	10	15
Final time at final column temperature (min)	4	4
Detector	FID	FID
Detector temperature ($^{\circ}\text{C}$)	380	350
Injector temperature ($^{\circ}\text{C}$)	Cool on-column type	Programmed temperature vaporization type
Sample size (μl)	1	0,2
Sample concentration [% (mass fraction)]	10	Neat
Key		
PDMS = polydimethylsiloxane.		

Table 4 — Typical operating conditions for accelerated analysis — Procedure B

Parameter	Column 1	Column 2	Column 3
Column length (m)	10	5	7,5
Column ID (mm)	0,53	0,53	0,53
Stationary phase	PDMS ^a	PDMS ^a	PDMS ^a
Stationary phase thickness (μm)	0,88	2,65	1,5
Carrier gas	Helium	Helium	Helium
Carrier gas flow rate (ml/min)	26	35	37
Initial column temperature ($^{\circ}\text{C}$)	60	40	40 (0,5 min)
Final column temperature ($^{\circ}\text{C}$)	360	350	360
Oven programming rate ($^{\circ}\text{C}/\text{min}$)	35	35	35
Final time at final column temperature (min)	4	4	4
Detector	FID	FID	FID
Detector temperature ($^{\circ}\text{C}$)	360	360	365
Injector	PTV	PTV	Cool on-column
Injector initial temperature ($^{\circ}\text{C}$)	100	100	100 (0,5 min)
Injector programming rate ($^{\circ}\text{C}/\text{min}$)	35	35	35
Injector final temperature ($^{\circ}\text{C}$)	360	350	350
Sample size (μl)	0,1	0,1	0,1
Dilution concentration	Neat	Neat	Neat
Analysis time (min)	8	7,8	8
Key			
PDMS = polydimethylsiloxane.			

6.3 Integrator/computer, used for determining the accumulated area under the chromatogram. This can be achieved by using a computer-based chromatography data system or an electronic integrator. The integrator/computer system shall have normal chromatographic software for measuring the retention times and areas of eluting peaks. In addition, the system shall be capable of converting the continuously integrated detector signal into area slices of fixed duration. These contiguous area slices, collected for the entire analysis, shall be stored for later processing. The electronic range of the integrator/computer (e.g. 1 V) shall be within the linear range of the detector/electrometer system used. The system shall be capable of subtracting the area slice of a blank run from the corresponding area slice of a sample run.

NOTE Some gas chromatographs have an algorithm built into their operating software that allows a mathematical model of the baseline profile to be stored in the memory. This profile can be automatically subtracted from the detector signal on subsequent sample analysis to compensate for any baseline offset. Some integration systems also store and automatically subtract a blank analysis from subsequent sample analysis.

6.4 Flow/pressure controllers.

6.4.1 If a packed column is used, the chromatograph shall be equipped with constant-flow controllers capable of maintaining the carrier gas flow constant over the full operating temperature range.

6.4.2 If a wide-bore capillary column is used, the chromatograph shall be equipped with a controller of carrier gas flow or pressure appropriate for the inlet used.

6.5 Micro-syringe, used to introduce the sample into the chromatograph. Sample injection can be either manual or automatic. Automatic sample injection is preferred because it gives better retention time precision.

7 Sampling

Unless otherwise specified, samples shall be taken by the procedures described in ISO 3170 or ISO 3171.

8 Preparation of apparatus

8.1 Column preparation

8.1.1 General

Any satisfactory method that will produce a column meeting the requirements of [6.2](#) can be used. The column shall be conditioned at the maximum operating temperature to reduce baseline shifts due to bleeding of the column substrate.

8.1.2 Packed columns

An acceptable method of column conditioning, which has been found effective for columns with an initial loading of 10 % liquid phase, consists of purging the column with carrier gas at the normal flow rate while holding the column at the maximum operating temperature for 12 h to 16 h.

8.1.3 Capillary columns

Capillary columns shall be conditioned using the following procedure.

- a) Install the column following the manufacturer's instructions. Set the column and detector gas flows. Ensure that the system is leak free.
- b) Allow the system to purge with carrier gas at ambient temperature for at least 30 min. Then increase the oven temperature by approximately 5 °C/min to 10 °C/min to the final operating temperature and hold for approximately 30 min.

c) Cycle the chromatograph through its temperature programme several times until a stable baseline is obtained.

NOTE 1 Capillary columns with cross-linked and bonded phases are available from many manufacturers and are usually preconditioned. These columns have much lower column bleed than packed columns.

NOTE 2 The column is not always connected to the FID when making a first conditioning of the column to overcome that initial column bleed affects the detector’s sensitivity.

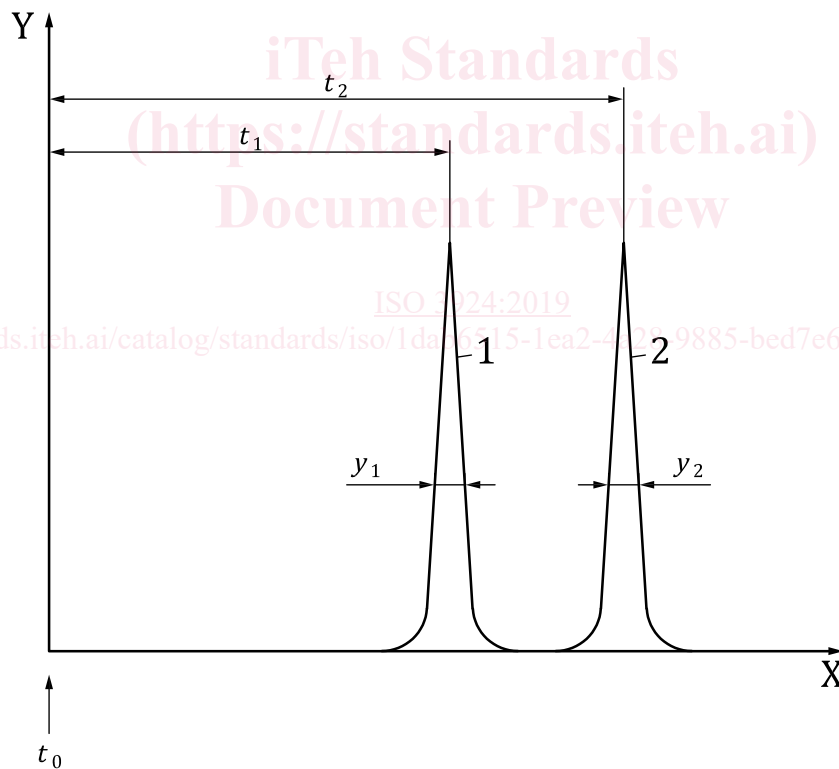
8.2 Chromatograph

Place the chromatograph in service in accordance with the manufacturer’s instructions. Typical operating conditions are shown in [Tables 2](#) and [3](#).

If a FID is used, the deposits formed in the detector from combustion of the silicone decomposition products shall be removed regularly, as they change the response characteristics of the detector.

8.3 Column resolution

Analyse the calibration mixture under the same conditions as those used for the samples. Using the procedure illustrated in [Figure 1](#), calculate the resolution, R_c , from the time between the hexadecane and octadecane peaks at the peak maxima t_1 and t_2 and the widths y_1 and y_2 of the peaks at half height, as given by [Formula \(1\)](#).



Key

X	time, in s	y_1	width of hexadecane peak at half height, in s
Y	detector signal	y_2	width of octadecane peak at half height, in s
t_0	start analysis time	1	hexadecane
t_1	retention time hexadecane, in s	2	octadecane
t_2	retention time octadecane, in s		

Figure 1 — Column resolution parameters