
**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.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

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.

ISO 3924 was prepared by the European Committee for Standardization (CEN) Technical Committee CEN/TC 19, *Gaseous and liquid fuels, lubricants and related products of petroleum, synthetic and biological origin*, in collaboration with Technical Committee ISO/TC 28, *Petroleum products and lubricants*, in accordance with the Agreement on technical cooperation between ISO and CEN (Vienna Agreement).

This method is harmonized with the analogous IP 406^[3] and ASTM D2887^[4] methods.

This third edition cancels and replaces the second edition (ISO 3924:1999), to which two additional informative annexes, Annexes A and B, have been added and some updating on definitions has been incorporated. (The Annex A in ISO 3924:1999 has become Annex C in this revised edition.) Annex A basically contains a table for a correlation of certain data with those obtained using the ISO 3405 method and some extra wording to the basic procedure, without changing the scope. With this information, the revised ISO 3924 becomes an updated document, describing the method actually in practice without changing the basic procedure. The data presented in Annex A allow a reference in modern, global specifications, such as for aviation fuels. This underlines the fact that availability of these chemical data in an ISO method supports their use in these specific fields.

Also, because ISO 3924 is extensively used and referenced in many fuel specifications and there is a requirement for a faster method, Annex B describes a method that, without any instrumental adaptation, reduces the analysis time by a factor 5.

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

WARNING — The use of this International Standard may involve hazardous materials, operations and equipment. This International Standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this International Standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

1 Scope

This International Standard 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 International Standard. This International Standard is not applicable 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 method has successfully been applied to samples containing biodiesel up to 10 %.

NOTE For the purposes of this International Standard, the term “% (m/m)” is used to represent the mass fraction of a material.

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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.

ISO 3170:2004, *Petroleum liquids — Manual sampling*

ISO 3171:1988, *Petroleum liquids — Automatic pipeline sampling*

ISO 3405:2000, *Petroleum products — Determination of distillation characteristics at atmospheric pressure*

ISO 4259:2006, *Petroleum products — Determination and application of precision data in relation to methods of test*

3 Terms and definitions

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

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

slice rate

number of data slices acquired per unit of time used to integrate the continuous (analogue) chromatographic detector response during an analysis

NOTE The slice rate is expressed in hertz (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 (ISO 3405-, IP 123^[6]- or ASTM D86^[5]-equivalent data) from boiling-range distribution analysis by gas chromatography determined following this International Standard.

Annex B describes an alternative, accelerated analysis.

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5 Reagents and materials

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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:

- a) for packed columns:
 - silicone gum rubber UC-W98,
 - silicone gum rubber GE-SE-30,
 - silicone gum rubber OV-1,
 - silicone gum rubber OV-101;
- b) 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, consisting of helium or hydrogen for use with thermal conductivity detectors, or nitrogen, helium or argon for use with flame ionization detectors.

5.4 Calibration mixture, consisting of an accurately weighed mixture of hydrocarbons covering the range from C₅ to C₄₄ and dissolved in carbon disulfide (5.6).

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 of the sample and at least one component shall have a boiling point higher than the final boiling point of the sample. The boiling points of alkanes are listed in Table 1.

Table 1 — Boiling points of normal alkanes

Carbon number	Boiling point °C	Carbon number	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 It is believed that API Project 44^[1] provided the original normal paraffin boiling point data that were listed in the first and second editions of this International Standard. 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.

NOTE It is recommended that the final concentration for packed columns be approximately 10 parts by volume of the hydrocarbon mixture to 100 parts by volume of carbon disulfide and for capillary columns, approximately 1 part by volume of the hydrocarbon mixture to 100 parts by volume of carbon disulfide.

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

Propane and butane can be added non-quantitatively to the calibration mixture, if necessary, to comply with 5.4. This may 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 5.1, Note, are used, the retention times of a few alkylbenzenes, such as *o*-xylene, *n*-butylbenzene, 1,3,5-tri-isopropylbenzene, *n*-decylbenzene and *n*-tetradecylbenzene, across the boiling range shall also be checked to confirm that the column is separating according to the boiling point order (see Annex C).

5.5 Primary reference material, which shall be the ASTM reference gas-oil No. 1.

5.6 Carbon disulfide, reagent grade.

6 Apparatus

6.1 Chromatograph

Any gas chromatograph that has the following performance characteristics may 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 % (*m/m*) of dodecane with a peak height of at least 10 % of full scale on the recorder under the conditions specified in this International Standard, and without loss of resolution as defined in 8.3. When operating at this sensitivity level, the 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 cold spots between the detector and the column are avoided.

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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 initial boiling point 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 (5.4).

If the initial boiling point is less than approximately 93 °C, an initial column temperature below ambient can be required. 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 International Standard.

6.1.3 Sample inlet system, either be capable of operating continuously at a temperature equivalent to the maximum column temperature employed or provide on-column injection with some means of programming the entire column, including the point of sample introduction, up to the maximum temperature required.

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

6.2 Column

Any column and conditions may be used, provided that, under the conditions of the test, separations are in the order of boiling points as given in Table 1, and that the column resolution, *R*, is at least 3. Typical column operating conditions are given in Tables 2 and 3.

Table 2 — Typical operating conditions for packed columns

Packed columns	1	2
Column length, metres	0,7	0,5
Column outside diameter, millimetres	3,2	3,2
Stationary phase	OV-101	UC-W98
Percent stationary phase	5	10
Support material	G ^a	P ^b
Support mesh size, micrometres	80/100	80/100
Initial column temperature, degrees Celsius	-40	-30
Final column temperature, degrees Celsius	350	360
Programming rate, degrees Celsius per minute	10	10
Carrier gas	Helium	Nitrogen
Carrier gas flow, millilitres per minute	30	25
Detector	FID	FID
Detector temperature, degrees Celsius	370	360
Injection-port temperature, degrees Celsius	370	350
Sample size, microlitres	0,5	1
^a Chromosorb® G (AW-DMS) ¹⁾ . ^b Chromosorb® P (AW) ¹⁾ .		

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6.3 Recorder/plotter

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This apparatus is used for plotting the chromatogram. This may be accomplished using a 0 mV to 1 mV recording potentiometer having a full-scale response time of 2 s or less and a minimum chart width of approximately 120 mm. Alternatively, a computer or other device may be used, provided it is capable of a graphics presentation of the same or better quality as a potentiometric recorder.

6.4 Integrator/computer

This apparatus is used for determining the accumulated area under the chromatogram. This may 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.

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

1) Chromosorb® G and Chromosorb® P are examples of suitable products available commercially. This information is given for the convenience of users of this International Standard and does not constitute an endorsement by ISO of this product.

6.5 Flow/pressure controllers

6.5.1 If a packed column is used, the chromatograph shall be equipped with constant-flow controllers capable of maintaining the carrier gas flow constant to ± 1 % over the full operating temperature range.

6.5.2 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.

6.6 Micro-syringe

This apparatus is used to introduce the sample into the chromatograph.

Sample injection may 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 in accordance with ISO 3170 or ISO 3171.

8 Preparation of apparatus

8.1 Column preparation

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8.1.1 General

Any satisfactory method that produces a column meeting the requirements of 6.2 may be used. The column shall be conditioned at the maximum operating temperature to reduce baseline shifts due to bleeding of the column substrate.

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8.1.2 Packed columns

An acceptable method of column conditioning that 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 may be conditioned using the following procedure.

- Install the column following the manufacturer's instructions. Set the column and detector gas flows. Ensure that the system is leak-free.
- 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.
- Cycle the chromatograph through its temperature programme several times until a stable baseline is obtained.

NOTE 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.

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 flame ionization detector 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.

NOTE Without any instrumental adaptation, it is possible to decrease analysis time, as described in Annex B.

Table 3 — Typical operating conditions for capillary columns

Capillary columns	3	4	5
Column length, metres	7,5	5	10
Column inner diameter, millimetres	0,53	0,53	0,53
Stationary phase	DB-1	HP-1	HP-1
Stationary phase thickness, micrometres	1,5	0,88	2,65
Carrier gas	Nitrogen	Helium	Helium
Carrier gas flow rate, millilitres per minute	30	12	20
Initial column temperature, degrees Celsius	40	35	40
Final column temperature, degrees Celsius	340	350	350
Programming rate, degrees Celsius per minute	10	10	15
Detector	FID	FID	FID
Detector temperature, degrees Celsius	350	380	350
Injector temperature, degrees Celsius	340	Cool on-column type	Programmed temperature vaporization type
Sample size, microlitres	0,5	1	0,2
Sample concentration, % (m/m)	25	10	Neat

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 , from the time between the C_{16} and C_{18} alkane 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 Equation (1):

$$R = \frac{2(t_2 - t_1)}{1,699(y_1 + y_2)} \quad (1)$$

where

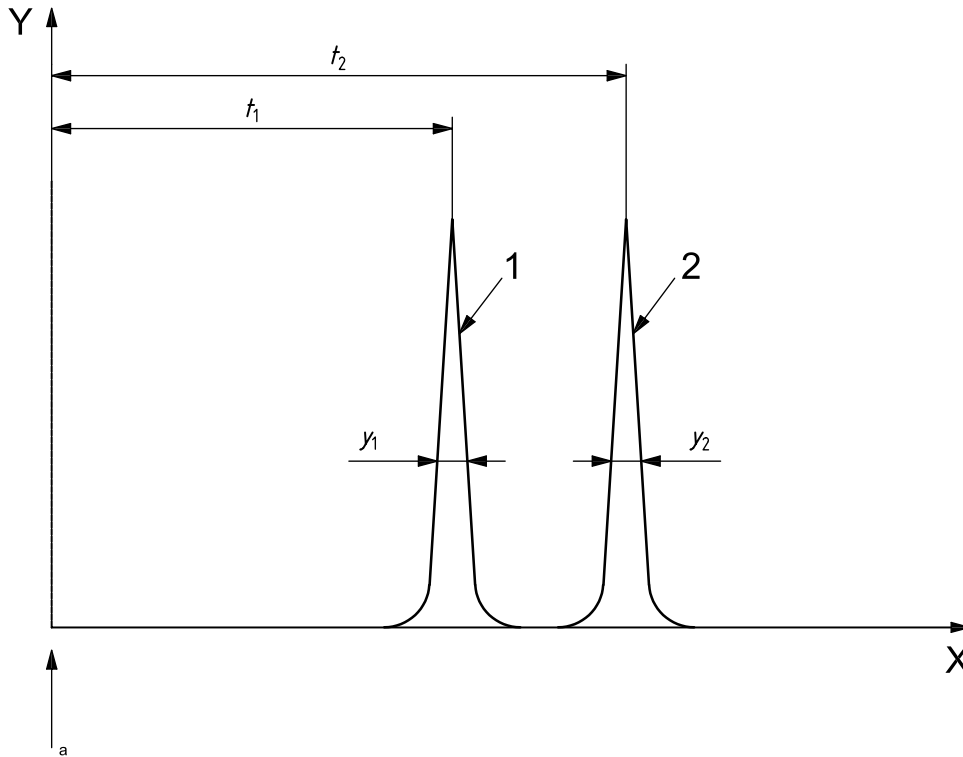
t_1 is the retention time, expressed in seconds, for the C_{16} peak maximum;

t_2 is the retention time, expressed in seconds, for the C_{18} peak maximum;

y_1 is the width, expressed in seconds, at half height of the C_{16} peak;

y_2 is the width, expressed in seconds, at half height of the C_{18} peak.

The resolution, R , obtained from Equation (1), shall be at least 3.



- Key**
- X time, expressed in seconds
 - Y recorder response
 - 1 hexadecane
 - 2 octadecane
 - a Sample injection.

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Figure 1 — Column resolution parameters

8.4 Detector response check

This method assumes that the detector response to petroleum hydrocarbons is proportional to the mass of individual components. This shall be verified when the system is put into service and whenever any changes are made to the system or operational parameters. Analyse the calibration mixture using the same conditions as those used for the samples. Calculate the response factor, F_n , for each alkane relative to decane using Equation (2):

$$F_n = \frac{m_n/A_n}{m_{10}/A_{10}} \tag{2}$$

where

- m_n is the mass of the alkane in the mixture;
- A_n is the peak area of the alkane;
- m_{10} is the mass of decane in the mixture;
- A_{10} is the area of decane.

The relative response factor, F_n , of each alkane shall not deviate from 1,0 by more than $\pm 0,1$.