
**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 3.

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.

International Standard ISO 3924 prepared by Technical Committee ISO/TC 28, *Petroleum products and lubricants*.

This second edition cancels and replaces the first edition (ISO 3924:1977), of which it constitutes a technical revision.

Annex A of this International Standard is for information only.

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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.

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2 Normative references

The following normative documents contain provisions which, through reference in this text, constitute provisions of this International Standard. For dated references, subsequent amendments to or revisions of, any of these publications do not apply. However, parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the normative documents indicated below. For undated references, the latest edition of the normative document referred to applies. Members of ISO and IEC maintain registers of currently valid International Standards.

ISO 3170:1988, *Petroleum liquids — Manual sampling*.

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

ISO 4259:1992, *Petroleum products — Determination and application of precision data in relation to methods of test*.

3 Terms and definitions

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

3.1 initial boiling point

IBP

temperature corresponding to the point at which a cumulative area count equal to 0,5 % of the total area under the chromatogram is obtained

3.2 final boiling point

FBP

temperature corresponding to the point at which a cumulative area count equal to 99,5 % of the total area under the chromatogram is obtained

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.

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:

Silicone gum rubber UC-W98

Silicone gum rubber GE-SE-30

Silicone gum rubber OV-1

Silicone gum rubber OV-101

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, constituted 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 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.

NOTE 1 For packed columns, the final concentration should be approximately 10 parts of the hydrocarbon mixture to 100 parts of carbon disulfide. For capillary columns, the final concentration should be approximately 1 part of the hydrocarbon mixture to 100 parts of carbon disulfide.

NOTE 2 If the test sample contains significant quantities of *n*-alkanes which 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 be sure of peak identifications.

NOTE 3 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.

NOTE 4 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 A).

5.5 Reference material

The primary reference material used shall be the ASTM Reference Gas Oil No.1.

5.6 Carbon disulfide, reagent grade.

Table 1 — Boiling points of normal 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 These data were obtained from API Project 44, October 31, 1972.

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 % 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, 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 1 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.

NOTE 2 For the purposes of this International Standard, the term “%(m/m)” is used to represent the mass fraction of a material.

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 may 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 any 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 and the column resolution, R , is at least 3 but not more than 10 (see 8.3).

6.3 Recorder/plotter

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 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.

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 analyses to compensate for any baseline offset. Some integration systems also store and automatically subtract a blank analysis from subsequent sample analyses.

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 $\pm 1\%$ 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.

NOTE Sample injection may be either manual or automatic. Automatic sample injection is preferred because it gives better retention time precision.

7 Sampling

Obtain samples in accordance with ISO 3170 or ISO 3171.

8 Preparation of apparatus

8.1 Column preparation

Any satisfactory method that will produce 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.

8.1.1 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.

8.1.2 Capillary columns

Capillary columns may 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 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.

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 follows:

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

where

- R is the column resolution;
- t_1 is the retention time, in seconds, for C_{16} peak maximum;
- t_2 is the retention time, in seconds, for C_{18} peak maximum;
- y_1 is the width, in seconds, at half height of C_{16} peak;
- y_2 is the width, in seconds, at half height of C_{18} peak.

The resolution, R , obtained from the above equation, shall be at least 3 but not more than 10.

Table 2 — Typical operating conditions for packed columns

Packed columns	1	2
Column length, (m)	0,7	0,5
Column outside diameter, (mm)	3,2	3,2
Stationary phase	OV-101	UC-W98
Percent stationary phase	5	10
Support material	G ^a	P ^b
Support mesh size (µm)	80/100	80/100
Initial column temperature, (°C)	-40	-30
Final column temperature, (°C)	350	360
Programming rate, (°C/min)	10	10
Carrier gas	Helium	Nitrogen
Carrier gas flow, (ml/min)	30	25
Detector	FID	FID
Detector temperature, (°C)	370	360
Injection-port temperature, (°C)	370	350
Sample size, (µl)	0,5	1

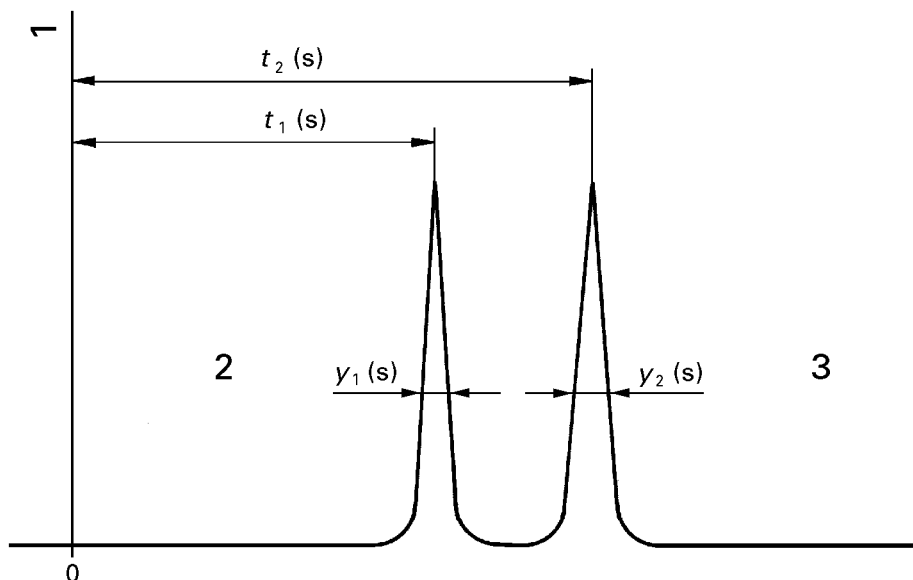
^a Chromosorb® G (AW-DMS).
^b Chromosorb® P (AW).

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Table 3 — Typical operating conditions for capillary columns

Capillary columns	3	4	5
Column length (m)	7,5	5	10
Column inner diameter (mm)	0,53	0,53	0,53
Stationary phase	DB-1	HP-1	HP-1
Stationary phase thickness (µm)	1,5	0,88	2,65
Carrier gas	Nitrogen	Helium	Helium
Carrier gas flow rate (ml/min)	30	12	20
Initial column temperature (°C)	40	35	40
Final column temperature (°C)	340	350	350
Programming rate (°C/min)	10	10	15
Detector	FID	FID	FID
Detector temperature (°C)	350	380	350
Injector temperature (°C)	340	Cool on-column type	Programmed temperature vaporization type
Sample size (µl)	0,5	1	0,2
Sample concentration [%(<i>m/m</i>)]	25	10	Neat

**Key**

- 1 Sample injection
- 2 Hexadecane
- 3 Octadecane

Figure 1 — Column resolution parameters
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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 for each alkane relative to decane using the following equation:

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

where

- F_n is the relative response factor;
- 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 $\pm 0,05$.

8.5 Peak skewness

Determine the peak skewness (the ratio A/B) of the largest peak in the calibration mixture as shown in Figure 2,

where

- A is the width of the leading part of the peak at 5 % of peak height;
- B is the width of the trailing part of the peak at 5 % of peak height.