INTERNATIONAL STANDARD

ISO 3924

Fourth edition
2016-09-15

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

Reference number
ISO 3924:2016(E)

ISO copyright office
Ch. de Blandonnet 8 • CP 401
CH-1214 Vernier, Geneva, Switzerland
Tel. +41 22 749 01 11
Fax +41 22 749 09 47
copyright@iso.org
www.iso.org

Contents

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).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the WTO principles in the Technical Barriers to Trade (TBT) see the following URL: Foreword - Supplementary information

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 ISO Technical Committee ISO/TC 28, *Petroleum products and related products of synthetic or biological origin*, in accordance with the Agreement on technical cooperation between ISO and CEN (Vienna Agreement).

This fourth edition cancels and replaces the third edition (ISO 3924:2010), which has been technically revised. The third edition had several updates regarding the calculation of ISO 3405[1] equivalent data. Because ISO 3924 is extensively used and referenced in many fuel specifications, a faster analysis procedure was included. Many fuel specifications concerned demand volume percentage recovered at 250°C and 350°C but this result was not part of the report of ISO 3924 in the former version as described. This is updated with this edition (see Annex A), for which an assessment has been executed by CEN/TC 19. In addition, several editorial updates have been made.

This method is originally based on the jointed IP 406[3] and ASTM D2887[4] methods.

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

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

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 fatty acid methyl esters (FAME) up to 10 % (*V*/*V*).

NOTE For the purposes of this International Standard, the terms "% (*m*/*m*)" and % (*V*/*V*) are used to represent the mass fraction (μ), respectively the volume fraction (φ) of a material.

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.

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.

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 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 (see References [1], [5] and [6]) equivalent data from boiling range distribution analysis by gas chromatography determined following this International Standard.

Annex B describes an alternative, accelerated analysis (see 8.2).

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.

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 or hydrogen for use with thermal conductivity detectors, or

b) nitrogen, helium, hydrogen or argon for use with flame ionization detectors.

5.4 Hydrogen, grade suitable for flame ionization detectors.

5.5 Compressed air, free of oil and water, regulated for flame ionization detectors.

5.6 Calibration mixture, consisting of an accurately weighed mixture of *n*-alkanes covering the range from C_5 to C_{44} and dissolved in carbon disulfide (5.8).

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

The following mixture of alkanes has been found to be satisfactory for most samples: C_5, C_6, C_7, C_8, C_9, C_{10}, C_{12}, C_{14}, C_{16}, C_{18}, C_{20}, C_{24}, C_{28}, C_{32}, C_{36}, C_{40}, C_{44}. 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 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, October 31, 1972[7], is believed to have provided the original normal paraffin boiling point data that were listed in former 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.

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.

Propane and butane may be added non-quantitatively to the calibration mixture, if necessary, to comply with 5.6. 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 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 the ASTM Reference Gas Oil No.1.

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

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 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 (5.6).

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 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 as given in Table 1, and the column resolution, *CR*, is at least 3 (8.3). Typical column operating conditions are given in Table 2 and 3.

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).

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
Column	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 [% (*m*/*m*)]	25	10	Neat

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

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 described in 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 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.

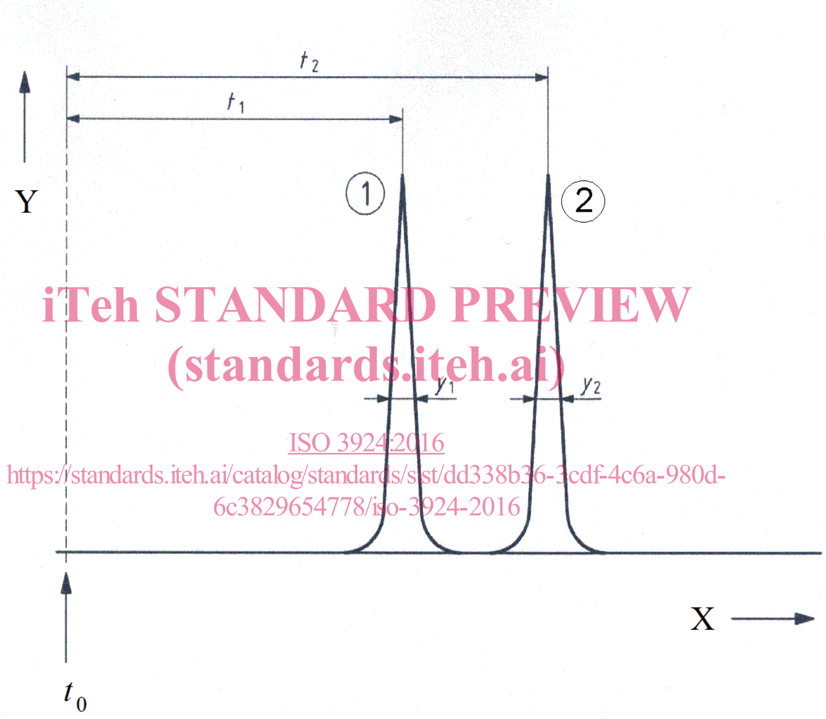
NOTE 2 The column is not always connected to the FID when making a first conditioning of the column to overcome that initial column bleed affects the detector's sensitivity.

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 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. Annex B describes such an accelerated analysis.

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

Figure 1 — Column resolution parameters

$$CR = \frac{2\left(t_2 - t_1\right)}{1{,}699\left(y_1 + y_2\right)} \tag{1}$$

where

t_1 is the retention time, in seconds, for hexadecane peak maximum;

t_2 is the retention time, in seconds, for octadecane peak maximum;

y_1 is the width, in seconds, at half height of hexadecane peak;

y_2 is the width, in seconds, at half height of octadecane peak.

The resolution, CR, obtained from the Formula (1), shall be at least three.

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 (5.6) using the same conditions as those used for the samples. Calculate the response factor, F_n, for each alkane relative to decane using Formula (2):

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

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 peak area of decane.

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

8.5 Peak skewness, determine the peak skewness (the ratio A/B) of the largest peak in the calibration mixture (5.6) as shown in Figure 2.

The peak skewness shall be not less than 0,5 and not more than 2,0. If peak skewness is outside these parameters, reanalyse the calibration mixture using a smaller sample size or a more dilute solution, if necessary, to avoid peak distortion.

NOTE Skewness is often an indication of overloading the column that results in displacement of the peak apex relative to non-overloaded peaks. Distortion in retention time measurement and hence errors in boiling point determination will be likely if column overloading occurs. The column liquid phase loading has a direct bearing on the acceptable sample size.