INTERNATIONAL STANDARD

ISO 3924

Third edition
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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.

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.

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:

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 C_5 to C_{44} and dissolved in carbon disulfide (5.6).

The following mixture of *n*-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 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.

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)].

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 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

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.

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.

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.

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

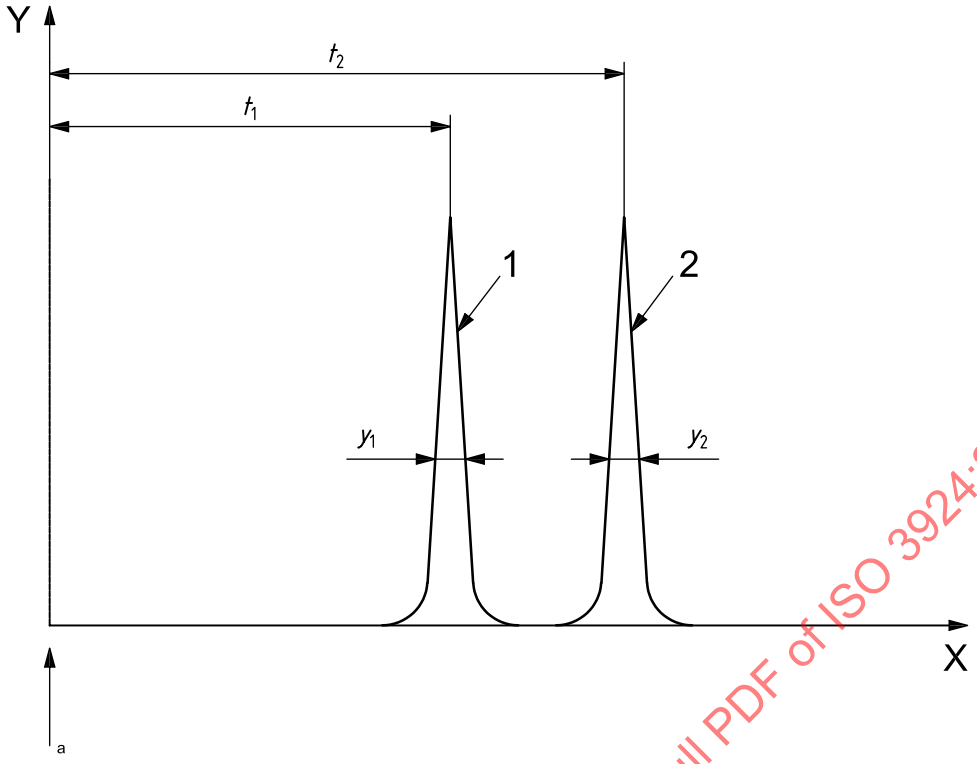
t_1 is the retention time, expressed in seconds, for the C_{16} peak maximum;

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.

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;

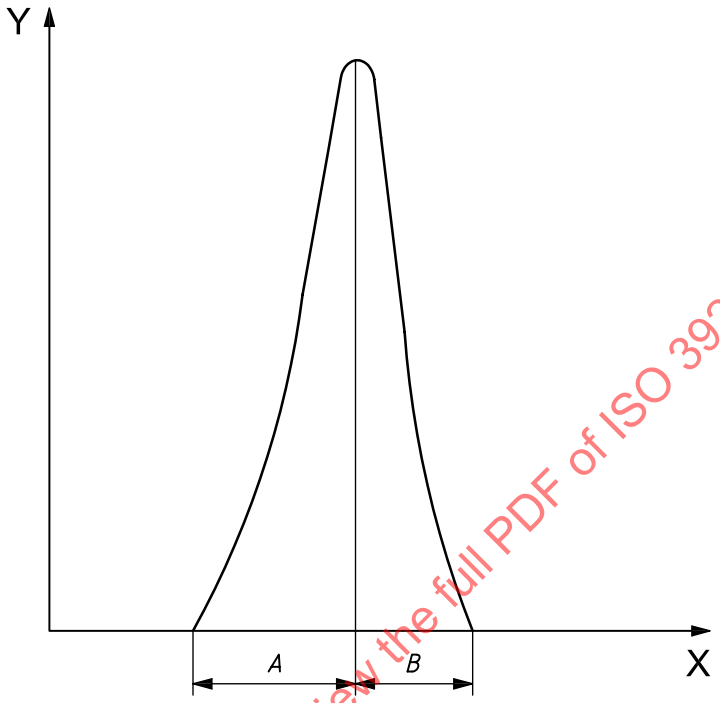
m_{10} is the mass of decane in the mixture;

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 ±0,1.

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.



Key

X time

Y recorder response

A width of the leading part of the peak at 5 % of peak height

B width of the trailing part of the peak at 5 % of peak height

Figure 2 — Peak skewness

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 sample capacity of the column, which results in a displacement of the peak apex relative to non-overloaded peaks. Distortion in retention-time measurement, and hence errors in boiling point determination, are likely if column overloading occurs. The column liquid-phase loading has a direct bearing on the acceptable sample size.

9 Calibration

9.1 Analysis sequence protocol

9.1.1 Define and use for all runs a predetermined schedule of analysis events to achieve maximum reproducibility. The schedule shall include cooling the oven to the initial starting temperature, equilibration time, sample injection and system start, analysis and final temperature hold time.

9.1.2 After the chromatographic conditions have been set to meet performance requirements, programme the column temperature upward to the maximum temperature being used and hold at that temperature for the selected time. Following the analysis sequence protocol, cool the column to the initial starting temperature.

9.1.3 During the cool-down and equilibration time, prepare the integrator/computer system for data acquisition. If a retention-time or detector-response calibration is being performed, use the peak detection mode. For samples and baseline-compensation determinations, use the area-slice mode of integration. The recommended slice rate for this method is 1 Hz (one slice per second).

9.1.4 At the exact time set by the schedule, inject either the calibration mixture or sample into the chromatograph; or make no injection (baseline blank). At the time of injection, start the chromatograph time cycle and the integrator/computer data acquisition. Follow this analysis sequence protocol for all subsequent analysis, blanks and calibrations.

9.2 Baseline compensation analysis

A baseline compensation analysis, or baseline blank, shall be performed at least once each day that the test is run, using the same technique for a sample analysis except that no injection is made.

NOTE 1 The blank analysis is necessary due to the normal occurrence of chromatographic baseline rise near the maximum column temperature. Factors that influence baseline stability are column bleed, septum bleed, detector temperature control, constancy of carrier and detector gas flows, leaks, instrument drift, etc.

Subtract the blank analysis from the sample analysis to remove any non-sample slice area from the chromatographic data.

NOTE 2 The blank analysis is typically performed prior to sample analysis, but can be useful if determined between samples or at the end of a sample sequence to provide additional data regarding instrument operation or residual sample carry-over from previous sample analysis.

Carry out periodic baseline blank analysis in accordance with the analysis sequence protocol to give an indication of baseline stability.

9.3 Retention time versus boiling point calibration

9.3.1 A retention-time versus boiling-point calibration shall be performed at least once each day that the test is run. Inject an appropriate aliquot (0,2 µl to 2,0 µl) of the calibration mixture into the chromatograph following the analysis sequence protocol.

9.3.2 Prepare a calibration table based on the results of the analysis of the calibration mixture by recording the retention time and the normal boiling point temperature for each component in the mixture. Boiling point temperatures of alkanes are listed in Table 1.

9.3.3 Plot the retention time of each peak versus the corresponding boiling point temperature for that component. A typical calibration curve is shown in Figure 3.

9.3.4 Ensure that the calibration points bracket the boiling range of the sample at both the low and high ends. Ideally, the calibration plot of retention-time versus boiling-point temperature should be linear, but it is impractical to operate the chromatograph such that curvature is eliminated completely.

NOTE The greatest potential for deviation from linearity is associated with the lower-boiling-point alkanes, which elute from the column relatively fast and have the largest difference in boiling point temperatures. In general, the lower the sample initial boiling point, the lower the starting point of the analysis.

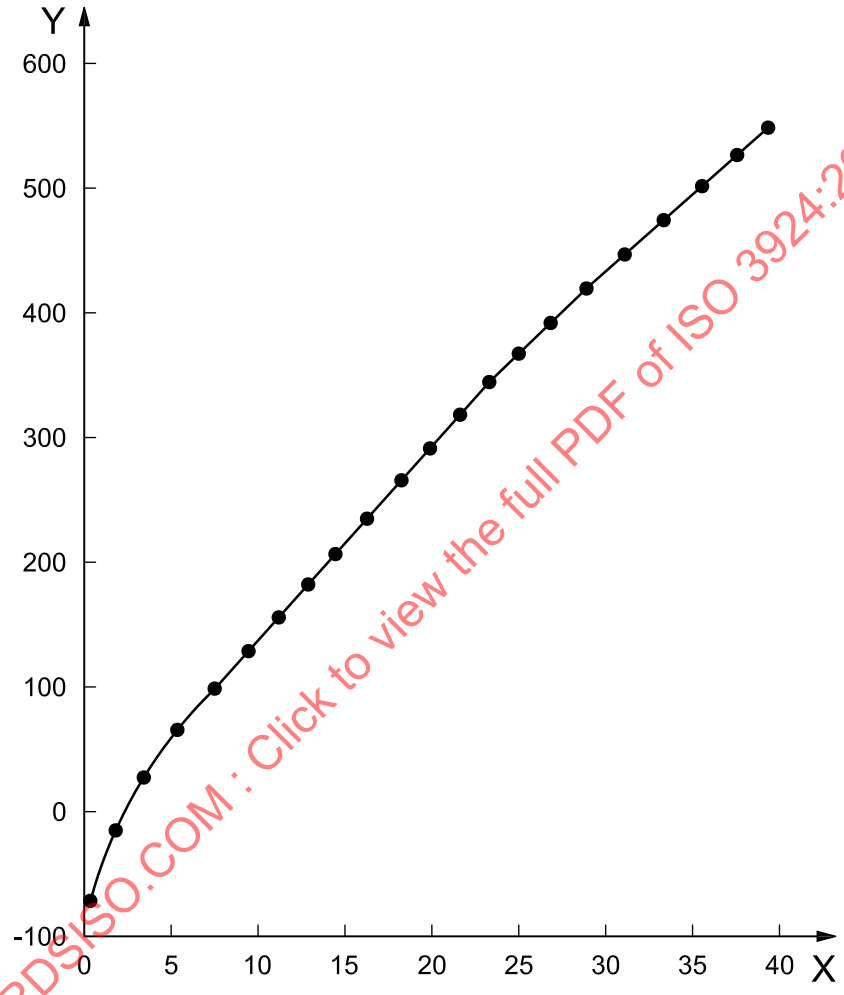
9.4 Analysis of reference material

9.4.1 The reference material (5.5) is used to verify both the chromatographic and calculation processes involved in this method.

A secondary reference material may be used, providing it satisfies the following criteria.

a) It is similar in nature and boiling range to the samples being analysed.

b) The boiling-range distribution values assigned to it are obtained by averaging multiple analysis of the secondary reference material on a system that is first shown to be operating properly with the primary reference material (5.5).



Key

X retention time, expressed in minutes

Y boiling point, expressed in degrees Celsius

Figure 3 — Typical calibration curve

9.4.2 Analyse the primary reference material (5.5) or a secondary reference material at least once each day that the test is run. Perform an analysis of the reference material following the analysis sequence protocol (see 9.1). Collect the area slice data and provide a boiling-point distribution report in accordance with 12.1.

9.4.3 The results of the analysis of the reference material (5.5) (either batch 1 or batch 2 may be used) shall not deviate from the values for that batch given in Table 4 by more than the range specified by the reproducibility given in 13.3.

Table 4 — Specified temperature-recovery values for ASTM gas-oil No. 1

Percent recovered	Temperature °C	
	Batch number 1	Batch number 2
[a]	114	115
5	143	151
10	169	176
15	196	201
20	221	224
30	258	259
40	287	289
50	312	312
60	332	332
70	354	354
80	376	378
90	404	407
95	425	428
[b]	475	475

[a] Initial boiling point.

[b] Final boiling point.

10 Procedure

10.1 Sample preparation

10.1.1 The amount of sample injected shall not overload the column stationary phase capacity nor exceed the detector linear range.

NOTE A sample with a narrow boiling range requires the injection of a smaller amount than that with a wider boiling range.

10.1.2 The column stationary phase capacity can be estimated from the chromatogram of the calibration mixture (5.4). Different volumes of the calibration mixture can be injected to find the maximum amount of a component that the stationary phase can tolerate without overloading (see 8.5, Note). Record the peak height for this amount of sample. The maximum sample signal intensity shall not exceed this peak height.

10.1.3 Samples with a viscosity low enough to be sampled with a syringe at ambient temperature shall be injected undiluted. Samples that are too viscous or waxy for sampling with a syringe may be diluted with carbon disulfide (5.6).

10.1.4 Typical sample injection volumes are shown in Tables 5 and 6.

Table 5 — Typical sample injection volumes for packed columns

Stationary phase loading %	Neat sample volume µl
10	1,0
5	0,5

Table 6 — Typical sample injection volumes for capillary columns

Film thickness µm	Neat sample volume µl
0,8 to 1,5	0,1 to 0,2
1,8 to 3,0	0,1 to 0,5
3,0 to 5,0	0,2 to 1,0

10.2 Sample analysis

Using the analysis sequence protocol (see 9.1), inject a sample aliquot into the gas chromatograph. At the time of injection, start the chromatograph time cycle and the integrator/computer data acquisition.

11 Calculation

11.1 Correct the sample area slices for the non-sample detector response by subtracting each blank analysis area slice from each sample area slice at the equivalent slice time. Sum the corrected area slices to obtain the cumulative corrected areas for each time interval during the run.

11.2 At the point on the chromatogram where the baseline at the end of the run first becomes steady, record the total cumulative area counts. Move back along the chromatogram until the cumulative area equals 99,5 % of the total area. Mark this point as the final boiling point.

NOTE Locating the final boiling point can be the most difficult step in this method. Some samples have extremely long tail-end portions due to gradually decreasing amounts of heavy material. This fact, coupled with the natural tendency of the chromatographic baseline to rise at the end of the run due to septum and/or column bleed and/or elution of traces of heavy components from previous samples, can preclude the possibility of the chromatogram returning precisely to the original baseline established prior to the initial boiling point of the sample. Thus, the most satisfactory procedure is to inspect the chromatogram and the area counts at each interval near the end of the run to determine the point at which the rate of change of the chromatographic signal has reached a constant low value of no greater than 0,000 01 % of the total area counts per second.

11.3 Observe the area counts at the start of the run until the point is reached where the cumulative area count is equal to 0,5 % of the total area. Mark this point as the initial boiling point of the sample. If carbon disulfide is used as the solvent, its response shall be ignored in the calculations.

11.4 Divide the cumulative area at each interval between the initial and final boiling points by the total area and multiply by 100 to give the percentage of the sample recovered at each time interval.

11.5 Tabulate the cumulative percentage recovered at each interval and the retention time at the end of the interval. Using linear interpolation where necessary, determine the retention time associated with each percentage between 1 % and 99 %.

11.6 For each percentage and its associated retention time, determine the corresponding boiling point temperature from the calibration table (see 9.3.2). Use linear interpolation between data points.

12 Expression of results

12.1 Report the temperature to the nearest 0,5 °C at 1 % intervals between 1 % and 99 % and at the IBP and the FBP.

12.2 If a plot of the boiling-point distribution curve is required, use graph paper with uniform subdivisions and plot each boiling temperature against its corresponding percentage recovered. Plot the initial boiling point at 0 % and the final boiling point at 100 % recovered. Draw a smooth curve connecting the points.

13 Precision

13.1 General

The precision, as determined by statistical examination in accordance with ISO 4259 of interlaboratory test results, is given in 13.2 and 13.3.

13.2 Repeatability

The difference between two test results, obtained by the same operator with the same apparatus under constant operating conditions on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the values given in Table 7 in only one case in 20.

Table 7 — Repeatability values

Percent recovered %	Repeatability °C
[b]	0,011 X[a]
5	0,003 2 $(X + 100)$
10 to 40	0,8
50 to 90	1,0
95	1,2
[c]	3,2

[a] X is the average of the two results, expressed in degrees Celsius.

[b] Initial boiling point.

[c] Final boiling point.

13.3 Reproducibility

The difference between two single and independent test results, obtained by different operators working in different laboratories on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the values given in Table 8 in only one case in 20.

Table 8 — Reproducibility values

Percent recovered %	Reproducibility °C
[b]	0,066 X[a]
5 to 20	0,015 $(X + 100)$
30	0,013 $(X + 100)$
40 to 90	4,3
95	5,0
[c]	11,8

[a] X is the average of the two results, expressed in degrees Celsius.

[b] Initial boiling point.

[c] Final boiling point.

14 Test report

The test report shall contain at least the following information:

a) reference to this International Standard;

b) type and complete identification of the product tested;

c) result of the test (see Clause 12);

d) any deviation, by agreement or otherwise, from the procedure specified;

e) date of the test.

Annex A
(informative)

Calculation of ISO 3405-equivalent data

A.1 General

A correlation model is presented for the calculation of ISO 3405-equivalent data from the boiling-range distribution analysis by gas chromatography described in the main part of this International Standard.

The correlation model is valid only for diesel and jet fuels, excluding biodiesel, and it is required to adhere to the sample specification given in Clause 7.

The correlation model is validated by an analysis of variance procedure in accordance with ISO 4259.

Valid data for conversion to ISO 3405-equivalent data can be obtained by the use of this annex.

A.2 Procedure

ISO 3405-equivalent data are calculated from values obtained by the method of this International Standard using Equation (A.1) and coefficients specified in Table A.1.

$$t_n = a_0 + a_1 \times T_{n-1} + a_2 \times T_n + a_3 \times T_{n+1} \quad \text{(A.1)}$$

where

t_n is the nth boiling-point temperature of the ISO 3405 equivalent;

a_i is the ith coefficient from Table A.1;

T_n is the nth boiling point temperature of this International Standard (ISO 3924).

A.3 Justification

The correlation model is based on data from 46 jet fuel samples and 39 diesel samples analyzed using methods in accordance with ISO 3405 and with this International Standard. From these results, a correlation model is determined using regression analysis, specifying the coefficients for the recovery. A model of the remaining bias is determined by use of the procedure as described in ISO 4259, on a dataset from the ASTM inter laboratory crosscheck program consisting of 5 jet fuels and 6 diesels that were analyzed by 38 labs using the method as described in this International Standard and 201 labs using the ISO 3405 method.

The bias-correction model has been used to correct the results from the correlation model, resulting in a new correlation matrix given in Table A.1.

Both methods are sufficiently precise to distinguish among the samples.

Table A.1 — Correlation coefficients

t_n %	a_0	a_1	a_2	a_3	T_n		
a	25,351	0,322 16	0,711 87	–0,042 21	T_{IBP}	T_5	T_{10}
5	18,822	0,066 02	0,158 03	0,778 98	T_{IBP}	T_5	T_{10}
10	15,173	0,201 49	0,306 06	0,482 27	T_5	T_{10}	T_{20}
20	13,141	0,226 77	0,290 42	0,460 23	T_{10}	T_{20}	T_{30}
30	5,776 6	0,372 18	0,303 13	0,311 18	T_{20}	T_{30}	T_{50}
50	6,375 3	0,077 63	0,689 84	0,183 02	T_{30}	T_{50}	T_{70}
70	–2,843 7	0,163 66	0,421 02	0,382 52	T_{50}	T_{70}	T_{80}
80	–0,215 36	0,256 14	0,409 25	0,279 95	T_{70}	T_{80}	T_{90}
90	0,099 66	0,243 35	0,320 51	0,373 57	T_{80}	T_{90}	T_{95}
95	0,898 80	–0,097 90	1,038 16	–0,008 94	T_{90}	T_{95}	T_{FBP}
b	19,444	–0,381 61	1,085 71	0,177 29	T_{90}	T_{95}	T_{FBP}

a Initial boiling point.

b Final boiling point.

A.4 Precision and bias

Based on the non-significant method distinction, it may be assumed that the reproducibility of converted chromatographic data into ISO 3405-equivalent data is equal to the reproducibility of the gas chromatographic data.

Cross-method reproducibility after the conversion of this International Standard (ISO 3924) data into ISO 3405-equivalent data is specified in Table A.2.

Table A.2 — Cross-method reproducibility

t_n	**IBP**	5 %	10 %	20 %	30 %	50 %	70 %	80 %	90 %	95 %	**FBP**
R[a]	13,71	11,80	10,73	8,83	7,39	6,96	7,03	7,62	8,85	17,32	12,94

a R is the reproducibility, expressed in degrees Celsius.

Annex B
(informative)

Accelerated analysis

B.1 General

Because the test method described in this International Standard is extensively used, there is a need for an analytical method that is faster. Without any instrumental adaptation, it is possible to decrease analysis time by a factor 5. This annex describes a set-up to reduce the original analysis time of 40 min to less than 10 minutes. Such a method is usually referred to as accelerated analysis.

Simulated distillation methods have been reported for which the analysis time is less than 2 min. These methods are referred to as fast analysis and are not described in this annex.

A research report with supporting data is available[2].

B.2 Procedure

B.2.1 Column dimensions as needed for an accelerated procedure fall within those described in 8.2, except for the programming rate, which is typically set at a value of 35 °C/min. Table B.1 gives the typical operating conditions.

Table B.1 — Typical column dimensions for accelerated analysis

Column length, metres	10
Column inner diameter, millimetres	0,53
Stationary phase	HP-1
Stationary phase thickness, micrometres	0,88
Carrier gas	Helium
Carrier gas flow rate, millilitres per minute	26
Initial column temperature, degrees Celsius	40
Final column temperature, degrees Celsius	360
Programming rate, degrees Celsius per minute	35
Detector	FID
Detector temperature, degrees Celsius	360
Injector temperature initial, degrees Celsius	100
Injector programming rate, degrees Celsius per minute	35
Injector temperature final, degrees Celsius	360
Sample size, microlitres	0,1
Sample concentration	Neat

B.2.2 Slice rate as given in 9.1 should be adjusted so that the total number of data points stays around 1 500.

B.2.3 The provision as defined in 6.1.2 will not be met, e.g. the retention time for the IBP will be less than 1 min. No negative impact could be found.

B.3 Justification

A comparison between the test method as defined in the main body of this International Standard (the standard procedure) and an accelerated procedure has been made based on 40 instruments and 26 instruments, respectively. No significant bias could be found[2].

B.4 Precision and bias.

Repeatability is determined in accordance with Table 7. See Reference [2].

Reproducibility is determined in accordance with Table 8. See Reference [2].

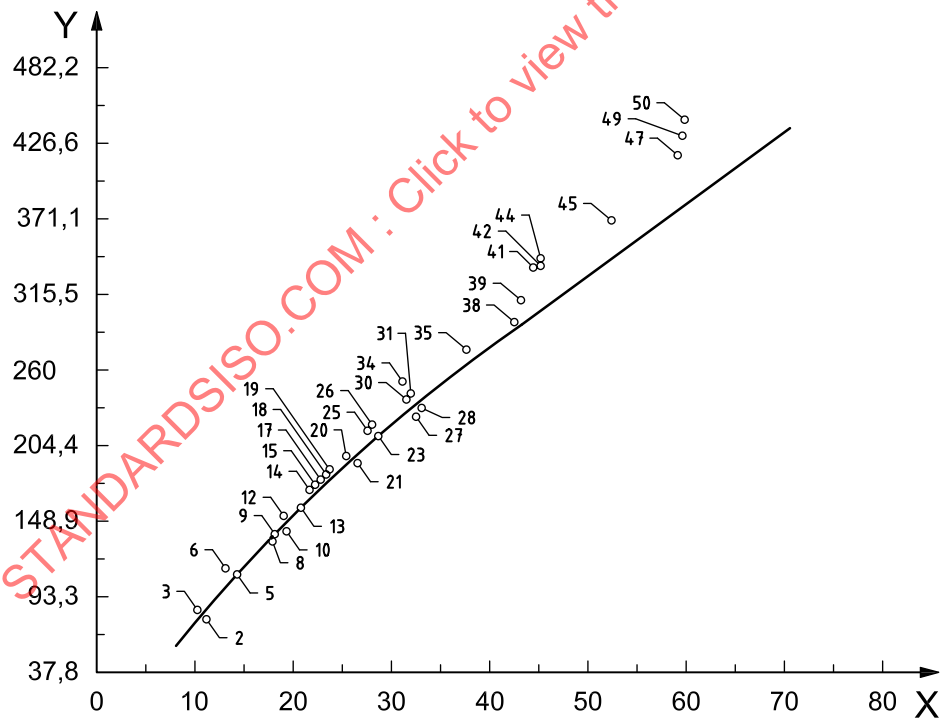
No significant bias between the standard procedure and the accelerated procedure could be found in comparison studies[2]. If an accelerated procedure is implemented, a primary reference material (5.5), should be analyzed, so that the bias can be verified.

Annex C
(informative)

Boiling points of non-normal alkane hydrocarbons

C.1 There is an apparent discrepancy in the boiling-point versus time relationship of certain high-boiling multiple-ring-type compounds. When the retention times of these compounds are compared with those of *n*-alkanes of equivalent atmospheric boiling point, these ring compounds appear to be eluted early from silicone rubber columns. A curve showing 36 compounds other than *n*-alkanes plotted along the calibration curve for *n*-alkanes alone is shown in Figure C.1. The numbered dots are identified in Table C.1. In Figure C.1, the atmospheric boiling points are plotted against the observed retention times.

When columns containing different percentages of stationary phase or different temperature-programming rates are used, the slope and curvature of the *n*-alkane curve (solid line) remains essentially the same. Deviations of distillation boiling points, as estimated from the curve, from true boiling points for a few compounds are shown in Table C.2. The deviations obtained by plotting boiling points at 1,333 kPa rather than 101,325 kPa are also tabulated. It is apparent that the deviation is much less at 1,333 kPa pressure. This indicates that the distillation data produced by gas chromatography closely approximate those obtained in reduced-pressure distillation. Since the vapour pressure versus temperature curves for multiple-ring-type compounds do not have the same slope or curvature as those for *n*-alkanes, an apparent discrepancy exists when *n*-alkane boiling points at atmospheric pressure are used.



Key

X retention time, expressed in minutes

Y boiling point, expressed in degrees Celsius

Figure C.1 — Boiling point-retention time relationship for several multiple-ring-type compounds with high boiling points