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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.

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

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

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

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

— The accelerated procedure has been moved from Annex B to the main body text. It is described as Procedure B and has a precision and bias calculation in relation to Procedure A (the original procedure).

— A new annex has been added with the newly defined boiling points for n-alkanes to keep the method technically equivalent with IP 406 and ASTM D2887.

— Annexes E and F have been added with information on the use of alternative carrier gases.

— Several safety warnings and editorial updates have been made.

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

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

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

1 Scope

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

The document describes two procedures.

a) Procedure A allows a larger selection of columns and analysis conditions, such as packed and capillary columns as well as a thermal conductivity detector in addition to the flame ionization detector. Analysis times range from 14 min to 60 min.

b) Procedure B is restricted to only three capillary columns and requires no sample dilution. The analysis time is reduced to about 8 min.

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

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

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 3170, *Petroleum liquids — Manual sampling*

ISO 3171, *Petroleum liquids — Automatic pipeline sampling*

3 Terms and definitions

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

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at http://www.electropedia.org/

3.1
initial boiling point
IBP
temperature corresponding to the retention time at which a net area count equal to 0,5 % of the total sample area under the chromatogram is obtained

3.2
T10, T30, T50, T70, T90
temperature (T) corresponding to the retention time at which a net area count equal to the 10 %, 30 %, 50 %, 70 % or 90 % of the total sample area under the chromatogram is obtained

3.3
final boiling point
FBP
temperature corresponding to the retention time at which a net area count equal to 99,5 % of the total sample area under the chromatogram is obtained

3.4
slice rate
number of data slices acquired per unit of time used to integrate the continuous (analogue) chromatographic detector response during an analysis

Note 1 to entry: The slice rate is expressed in Hz (for example, slices per second).

4 Principle

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

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

5 Reagents and materials

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

NOTE The following materials have been used successfully as liquid phases, other stationary phases can be used, see 6.2.

For packed columns:

— silicone gum rubber UC-W98;

— silicone gum rubber GE-SE-30;

— silicone gum rubber OV-1;

— silicone gum rubber OV-101.

For capillary columns:

— polydimethylsiloxane.

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

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

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

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

a) helium for use with flame ionization detectors (FIDs) or thermal conductivity detectors;

b) for the use of nitrogen or hydrogen as a carrier gas, see Annexes E and F.

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

5.4 Hydrogen, grade suitable for FIDs.

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

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

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

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

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

The following mixture of n-alkanes has been found to be satisfactory for most samples: 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 (IBP) of the sample and at least one component shall have a boiling point higher than the final boiling point (FBP) of the sample. The boiling points of n-alkanes are listed in Table 1.

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

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

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

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

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

CAUTION — Carbon disulfide is extremely volatile flammable and toxic.

Table 1 — Boiling points of normal n-alkanes

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

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

6 Apparatus

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

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

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

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

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

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

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

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

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

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

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

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

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

[a] Dioxosilane.

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

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

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

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

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

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

6.4 Flow/pressure controllers.

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

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

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

7 Sampling

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

8 Preparation of apparatus

8.1 Column preparation

8.1.1 General

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

8.1.2 Packed columns

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

8.1.3 Capillary columns

Capillary columns shall be conditioned using the following procedure.

a) Install the column following the manufacturer's instructions. Set the column and detector gas flows. Ensure that the system is leak free.

b) Allow the system to purge with carrier gas at ambient temperature for at least 30 min. Then increase the oven temperature by approximately 5 °C/min to 10 °C/min to the final operating temperature and hold for approximately 30 min.

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

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

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

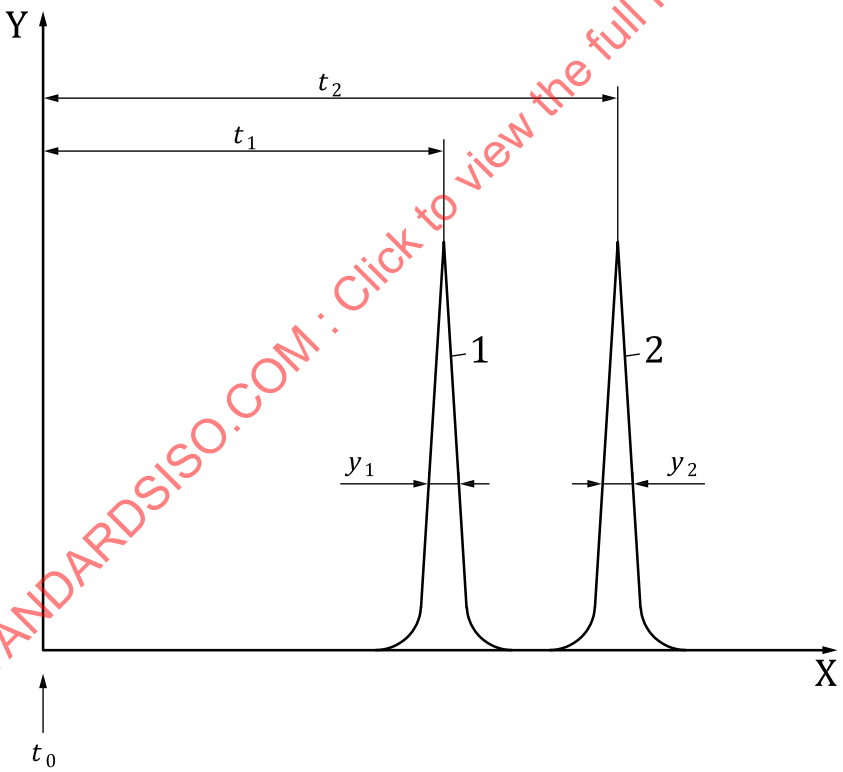
8.2 Chromatograph

Place the chromatograph in service in accordance with the manufacturer's instructions. Typical operating conditions are shown in Tables 2 and 3.

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

8.3 Column resolution

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



Key

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

Figure 1 — Column resolution parameters

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

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, R_c, obtained from 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 n-alkane relative to decane using Formula (2):

$$F_n = \frac{m_n / A_n}{m_{10} / A_{10}} \quad (2)$$

where

F_n is the relative response factor;

m_n is the mass of the n-alkane in the mixture;

A_n is the peak area of the n-alkane;

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

A_{10} is the peak area of decane.

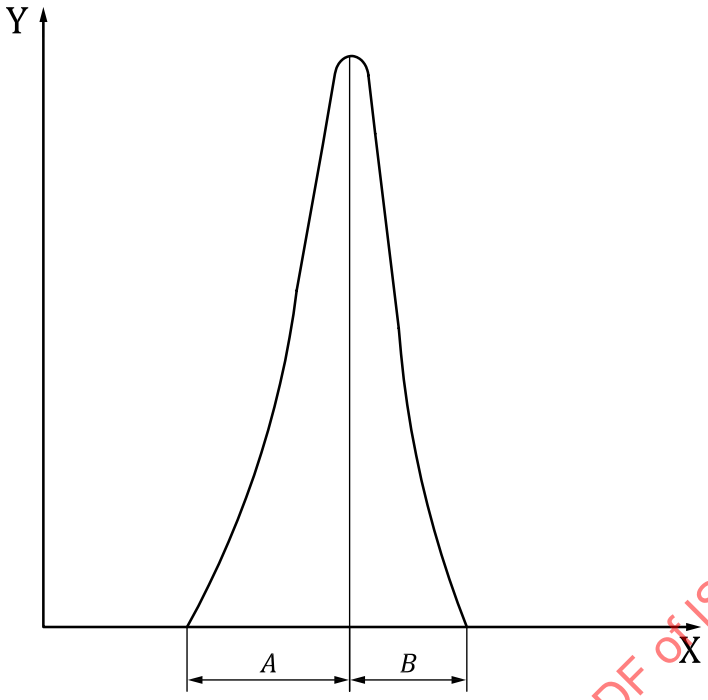
The relative response factor, F_n, of each n-alkane shall not deviate from 1,0 by more than ±0,1.

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.



Key

X time, in s

Y detector signal

A width of the leading part of the peak at 5 % of peak height, in s

B width of the trailing part of the peak at 5 % of peak height, in s

Figure 2 — Peak skewness

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, and 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 to be used and hold 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 (5.6) or sample into the chromatograph, or make no injection (baseline blank). At the time of injection and/or at the start of the baseline blank, start the chromatograph time cycle and the integrator/computer data acquisition. Follow this analysis sequence protocol for all subsequent analysis, blanks or calibrations.

9.2 Baseline compensation analysis

9.2.1 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 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.

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

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.

9.2.3 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 It is highly recommended to perform a retention time versus boiling point calibration (see Figure 3) 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 (5.6) into the chromatograph following the analysis sequence protocol.

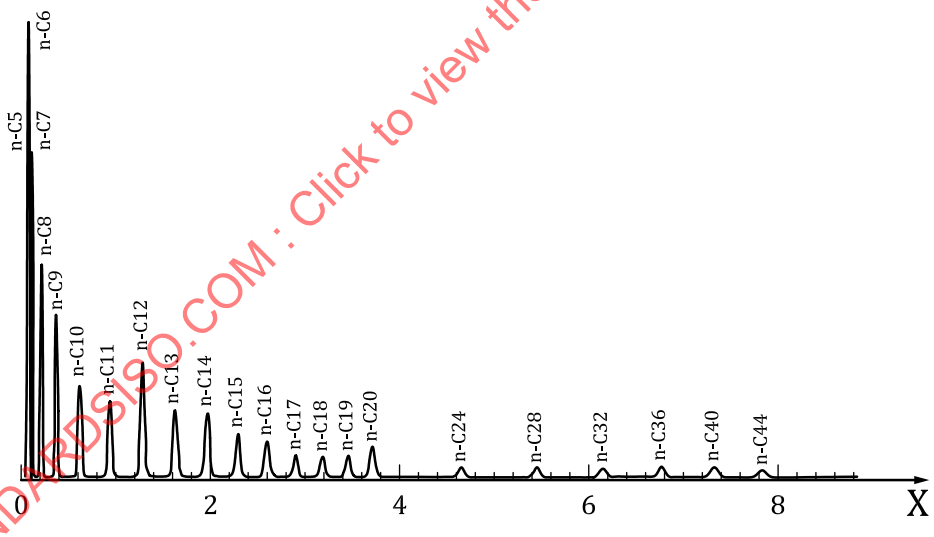


Figure 3 — Typical chromatogram of a retention time versus boiling point sample

9.3.2 Prepare a calibration table based on the results of the analysis of the calibration mixture (5.6) by recording the retention time and the boiling temperature for each component in the mixture. Boiling temperatures of n-alkanes are listed in Table 1.

9.3.3 Plot the retention time of each peak versus the corresponding boiling temperature for that component. A typical calibration curve is shown in Figure 4.

9.3.4 Ensure that 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 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 n-alkanes, which elute from the column relatively quickly and have the largest difference in boiling temperatures. In general, the lower the sample IBP, the lower the starting point of the analysis will be.

9.4 Analysis of reference material

9.4.1 The reference material (5.7) is used to verify both the chromatographic and calculation processes involved in this method.

A secondary reference material can be used, providing it satisfies the following criteria:

a) it is similar in nature and boiling range to the samples to be analysed;

b) the boiling range distribution values assigned to that 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 (5.7).

9.4.2 Analyse the primary reference material (5.7) 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. See Figure 4 for a typical chromatogram of reference material.

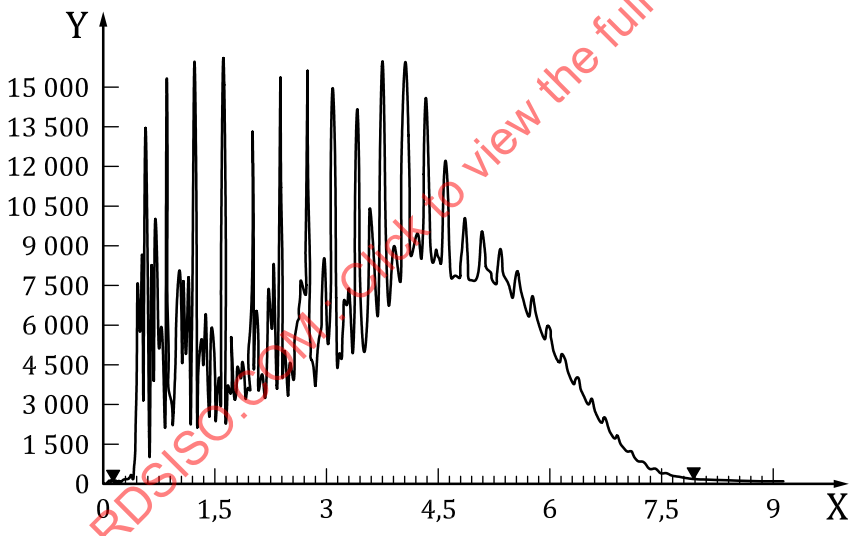
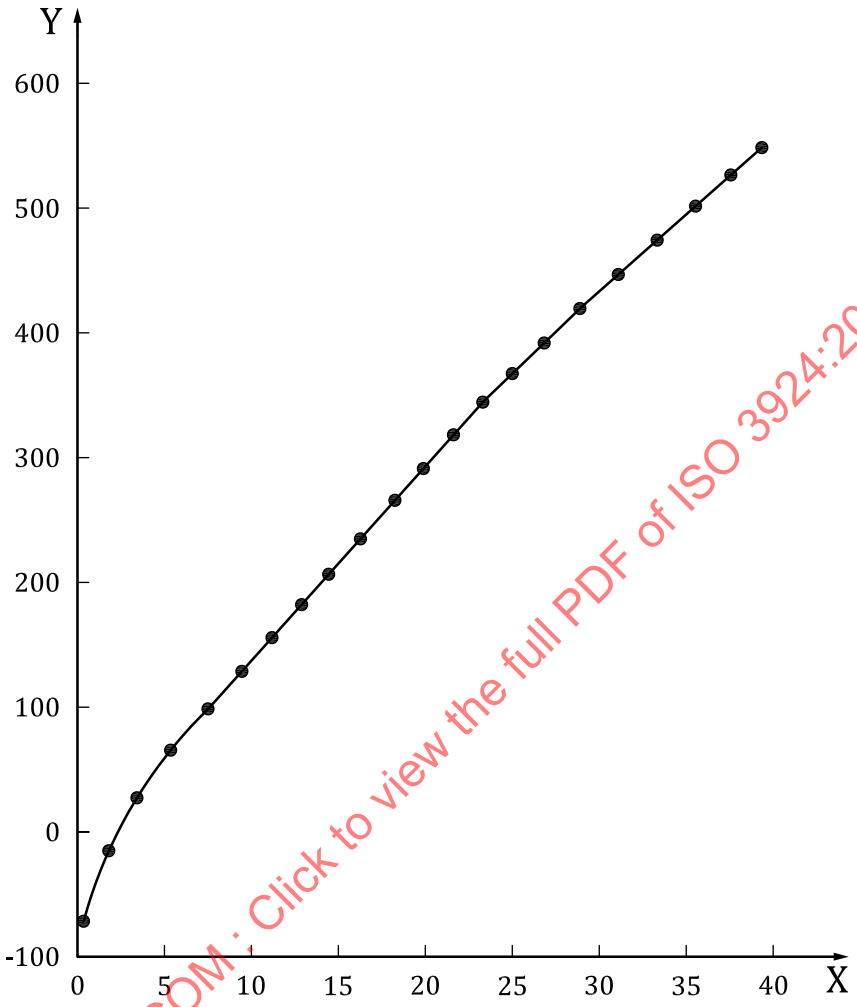


Figure 4 — Typical chromatogram of a reference material

9.4.3 The results of the analysis of the reference material (either batch 1 or batch 2 can be used) shall not deviate more from the values for that batch given in Annex B than the range specified by the reproducibility of this document (see 13.3 or 13.5). See Figure 5 for a typical calibration curve.



Key

X retention time, in min

Y boiling point, in °C

Figure 5 — Typical calibration curve

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 narrow boiling range sample will require the injection of a smaller amount than a wider boiling range sample.

10.1.2 The column stationary phase capacity can be estimated from the chromatogram of the calibration mixture (5.6). Different volumes of the calibration mixture (5.6) can be injected to find the maximum amount of a component that the stationary phase can tolerate without overloading (see 8.5, NOTE). Note

the peak height for this amount of sample. The maximum sample signal intensity shall not exceed this peak height.

10.1.3 Samples that are of low enough viscosity to be sampled with a syringe at ambient temperature shall be injected undiluted. Samples that are too viscous or waxy to be sampled with a syringe shall be diluted with carbon disulfide (5.8).

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 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 FBP.

NOTE Location of the FBP 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 column bleed 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 IBP 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 IBP 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 IBP and the FBP 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 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 IBP at 0 % and the FBP at 100 % recovered. Draw a smooth curve connecting the points.

13 Precision

13.1 General

The precision, as determined by a statistical examination in accordance with ISO 4259:2006[2] of the interlaboratory test results, is given in 13.2 and 13.3 for Procedure A (normal) and in 13.4 and 13.5 for Procedure B (accelerated).

NOTE Statistics is based on data obtained from ILS programmes for Procedure A[7] and Procedure B[8] organized by ASTM with participants from the Americas and Europe.

The precision values for Procedure B are to be used only in the temperature ranges of Table 5.

Table 5 — Range of results covered in the ILS study

Per cent recovered	Range °C
IBP	110 to 131
5	138 to 201
10	144 to 282
20	159 to 322
30	170 to 340
40	184 to 350
50	196 to 360
60	208 to 370
70	221 to 384
80	236 to 396
90	259 to 423
95	268 to 439
FBP	288 to 534

13.2 Repeatability Procedure A

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 6 in only one case in twenty.

13.3 Reproducibility Procedure A

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 6 in only one case in twenty.

Table 6 — Repeatability and reproducibility values — Procedure A

Per cent recovered	Repeatability °C	Reproducibility °C
IBP	0,011 X	0,066 X
5 %	0,003 2 (X + 100)	0,015 (X + 100)
10 % to 20 %	0,8	0,015 (X + 100)
30 %	0,8	0,013(X + 100)
NOTE X is the average of the two results, in °C.		

Table 6 *(continued)*

Per cent recovered	Repeatability °C	Reproducibility °C
40 %	0,8	4,3
50 % to 90 %	1,0	4,3
95 %	1,2	5,0
FBP	3,2	11,8
NOTE *X* is the average of the two results, in °C.		

13.4 Repeatability Procedure B

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 twenty.

13.5 Reproducibility Procedure B

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 7 in only one case in twenty.

Table 7 — Repeatability and reproducibility values — Procedure B

Per cent recovered	Repeatability °C	Reproducibility °C
IBP	2,94	7,97
5 % to 95 %	0,000 857 * (*X* + 500)	0,004 49 * (*X* + 500)
FBP	3,32	7,63
NOTE *X* is the average of the two results, in °C.		

13.6 Bias

An interlaboratory study was carried out to determine the between-procedure bias for Procedure A (normal) and Procedure B (accelerated)[9]. The data obtained are shown in Table 8.

Table 8 — Assessment outcome — Procedure A versus Procedure B

Per cent recovered	Can bias correction improve agreement?	Bias corrected B = predicted A °C	Sample specific bias	Practically equivalent after correction?	Range off sample averages in ILS study °C
IBP	N	= B	N	Y	103 to 329
10	Y	= B – 1,207	N	Y	161,3 to 369,4
30	Y	= B – 1,508	N	Y	185,2 to 390,6
50	Y	= 0,991 B + 0,671	N	Y	208,4 to 408,7
70	Y	= B – 1,99	N	Y	232,1 to 426,8
90	Y	= B – 1,732	N	Y	259,4 to 451,8
FBP	N	= B	N	Y	291,5 to 501,5

The following conclusions are drawn from Table 8.

For IBP, FBP: No bias-correction considered in practice D6708[6] can further improve the agreement between results from Procedure A and Procedure B for materials studied. For applications where

Procedure B is used as an alternative to Procedure A, results from Procedure B shall be considered to be practically equivalent to results from Procedure A, for sample types and property range studied. No sample specific bias, as defined in practice D6708, was observed for the materials studied.

For T10, T30, T50, T70 and T90: The degree of agreement between results from Procedure A and Procedure B can be further improved by applying correction equations as listed in Table 8. For applications where Procedure B is used as an alternative to Procedure A, bias-corrected results from Procedure B, as per correction equations in Table 8, shall be considered as practically equivalent to results from Procedure A, for sample types and property ranges studied. No sample-specific bias, as defined in practice D6708, was observed after the bias correction for the materials studied.

Between-procedure reproducibility (RXY): Differences between bias-corrected results from Procedure B and Procedure A, for the sample types and property ranges studied, are expected to exceed the following between-methods reproducibility (RXY), as defined in ASTM D6708[6], about 5 % of the time, as shown by Formula (3):

$$R_{XY} = \left[0{,}5\left(R_X\right)^2 + 0{,}5\left(R_Y\right)^2\right]^{\frac{1}{2}} \tag{3}$$

where

R_X reproducibility of Procedure B in ° C as shown in Table 7;

R_Y reproducibility of Procedure A in ° C as shown in Table 6.

14 Test report

The test report shall contain at least the following information:

a) reference to this document, i.e. ISO 3924:2019;

b) procedure used, i.e. Procedure A or Procedure B;

c) type and complete identification of the product tested;

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

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

f) 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[1] equivalent data from boiling range distribution analysis by gas chromatography (Procedure A) following the main part of this document.

The correlation model is only valid for diesel and jet fuels and should obey the sample specification given in Clause 1.

The correlation model is validated by an analysis of variance procedure in accordance with ASTM D6708[6].

Valid data for conversion to ISO 3405[1] equivalent data can be obtained using this annex.

A.4 describes the calculation of per cent volume recoveries at temperature cutpoint intervals from the data obtained through this correlation model.

A.2 Procedure

ISO 3405[1] equivalent data are calculated from this document's data using Formula (A.1) and the 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 n^{th} boiling temperature of ISO 3405[1] equivalent;

a_i i^{th} coefficient from Table A.1;

T_n n^{th} boiling temperature as calculated and reported in Clause 12.

A.3 Justification

The correlation model is based on data from 46 jet fuel samples and 39 diesel samples analysed using methods in accordance with ISO 3405[1] and this document. From these results, a correlation model is determined using regression, specifying coefficients per recovery. A model of the remaining bias is determined by use of the procedure as described in ASTM D6708[6], on a data set from the ASTM interlaboratory crosscheck programme containing 5 jet fuels and 6 diesels analysed by 38 laboratories using the method as described in this document and 201 laboratories using ISO 3405[1].

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 found sufficiently precise to distinguish among the samples.

Table A.1 — Correlation coefficients

t_n	a_0	a_1	a_2	a_3	T_n		
IBP	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}
FBP	19,444	−0,381 61	1,085 71	0,177 29	T_{90}	T_{95}	T_{FBP}

A.4 Calculating volume per cent recoveries at temperature cutpoint intervals

The % (volume fraction) recovery (x) at a certain temperature cutpoint is obtained through linear interpolation between two known recoveries, as shown by Formula (A.2):

$$x = x_1 + (y - y_1)\frac{(x_2 - x_1)}{(y_2 - y_1)} \tag{A.2}$$

where

y is the required temperature cutpoint;

x_1 is known recovery at the temperature below y;

x_2 is known recovery at the temperature above y;

y_1 is temperature cutpoint belonging to x_1;

y_2 is temperature cutpoint belonging to x_2.

A typical example is given in Tables A.2 and A.3.

Table A.2 — Example data of temperature versus per cent volume recovery

Volume recovered % (volume fraction)	**Temperature** °C
0,5	199,9
5,0	215,6
10,0	228,2
20,0	246,8
30,0	261,3
50,0	280,5
70,0	305,3
80,0	318,1
90,0	335,4
95,0	348,7
99,5	365,4

Table A.3 — Calculated recoveries in per cent volume from data in Table A.2

Cutpoint °C	Volume recovered % (volume fraction)
250	22,2
350	95,4

A.5 Precision and bias

The reproducibility of the converted chromatographic data into ISO 3405[1] equivalent data is in accordance with the reproducibility of the gas chromatographic data described in 13.3 and 13.5.

Cross-method reproducibility after conversion of chromatographic data into ISO 3405[1] equivalent data is specified in Table A.4.

Table A.4 — Cross-method reproducibility

t_n	IBP	5 %	10 %	20 %	30 %	50 %	70 %	80 %	90 %	95 %	FBP
R	13,71	11,80	10,73	8,83	7,39	6,96	7,03	7,62	8,85	17,32	12,94
NOTE R is the reproducibility in °C.											

The reproducibility of the calculated recoveries in % (volume fraction) at 250 °C and 350 °C can be estimated from Table 7 by linear interpolation between the nearest values below and above the calculated recovery.

EXAMPLE Reproducibility (R) calculation using the results from Table A.3:

R at 20 % is 5,2 °C and R at 30 % is 4,7 °C R at 22,2 % (volume fraction) = 5,1 °C

R at 95 % is 5,0 °C and R at 99,5 % is 11,8 °C R at 95,4 % (volume fraction) = 5,6 °C

Annex B
(normative)

Reference material specified values and deviation limits

B.1 Specified values

Table B.1 (Procedure A) and Table B.2 (Procedure B) give the specified temperature recovery values for ASTM reference gas oil no. 1 and no. 2, which are given as the primary reference material in 5.7. Two batches of lot no. 1 are currently in circulation. The figures given were obtained by multiple analyses carried out by an ASTM study group.

Table B.1 — Specified recovery temperatures for ASTM reference — Procedure A

Recovery % (mass fraction)	Specified recovery temperature °C		
	Lot no. 1 batch 1	Lot no. 1 batch 2	Lot no. 2
IBP	114	115	106
5	143	151	173
10	169	176	196
20	221	224	233
30	258	259	2 687
40	287	289	298
50	312	312	321
60	332	332	342
70	354	354	358
80	376	378	378
90	404	407	406
95	425	428	431
FBP	475	475	496

Table B.2 — Specified recovery temperatures for ASTM reference — Procedure B

Recovery % (mass fraction)	Specified recovery temperature °C
	Lot no. 1 batch 2
IBP	113
5	150
10	175
20	224
30	260
40	289
50	312
60	332
70	354
80	378

Table B.2 *(continued)*

Recovery % (mass fraction)	**Specified recovery temperature** °C
	Lot no. 1 batch 2
90	408
95	430
FBP	481

B.2 Deviation limits

Table B.3 gives allowable deviation limits for reference material analysis.

Table B.3 — Allowable deviation limits

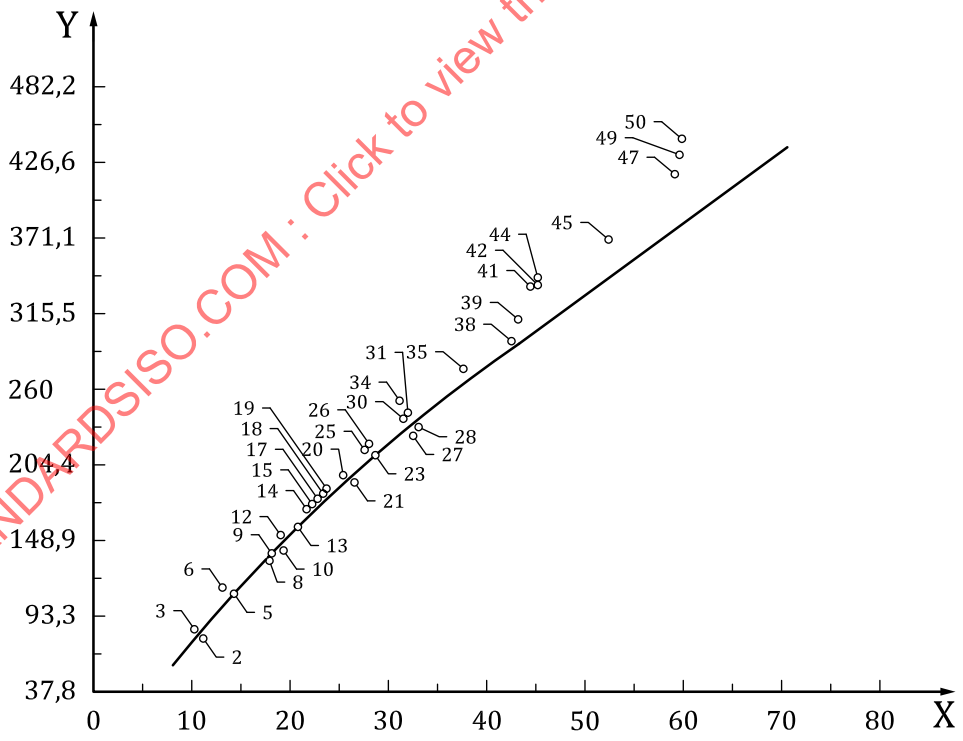
Recovered % (mass fraction)	**Allowable deviation** °C
IBP	±4
5 to 95	±3
FBP	±7

Annex C
(informative)

Boiling points of non-normal n-alkane hydrocarbons

C.1 There is an apparent discrepancy in the boiling point versus retention time 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 graph 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.

If columns containing different percentages of stationary phase or different temperature-programming rates were 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 would exist when n-alkane boiling points at atmospheric pressure were used.



Key

X retention time, in min

Y boiling point, in °C

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

Table C.1 — Compound identification corresponding to numbered dots from Figure C.1

No.	Boiling point °C	Compound
2	80	Benzene
3	84	Thiophene
5	111	Toluene
6	116	Pyridine
8	136	2,5-Dimethylthiophene
9	139	1,4-Xylene
10	143	Dipropylsulfide
12	152	Cumene
13	159	*trans*-Hexahydroindane
14	171	Dec-1-ene
15	173	*sec*-Butylbenzene
17	178	2,3-Dihydroindene
18	183	Butylbenzene
19	186	*trans*-Decalin
20	194	*cis*-Decalin
21	195	Dipropyldisulfide
23	213	Dodec-1-ene
25	218	Naphthalene
26	221	2,3-Benzothiophene
27	227	Diamylsulfide
28	234	1,3,5-Tri-isopropylbenzene
30	241	2-Methylnaphthalene
31	245	1-Methylnaphthalene
34	254	Indole
35	279	Acenaphthene
38	298	Decylbenzene
39	314	Octadec-1-ene
41	339	Phenanthrene
42	342	Anthracene
44	346	Acridine
45	395	Pyrene
47	424	Triphenylene
49	438	Naphthacene
50	447	Chrysene

Table C.2 — Deviations from true boiling points of boiling points obtained from this document

Compound	True boiling point	Deviations from true boiling point	
	°C at 101,325 kPa	°C at 101,325 kPa	°C at 1,333 kPa
Benzene	80	+4	−2
Thiophene	86	+4	+1
Toluene	111	+2	−1
[a] No data exists at 1,333 kPa for chrysene.			

Table C.2 *(continued)*

Compound	True boiling point	Deviations from true boiling point	
	°C at 101,325 kPa	°C at 101,325 kPa	°C at 1,333 kPa
1,4-Xylene	139	0	+2
Dodec-1-ene	213	0	0
Naphthalene	218	−12	−4
2,3-Benzothiophene	221	−13	0
2-Methylnaphthalene	241	−12	−2
1-Methylnaphthalene	245	−12	−5
Dibenzothiophene	332	−32	−6
Phenanthrene	339	−35	−8
Anthracene	342	−36	−8
Pyrene	395	−48	−16
Chrysene	447	−60	[a]

[a] No data exists at 1,333 kPa for chrysene.

C.2 However, this discrepancy does not introduce any significant error when compared with laboratory distillation, because the pressure is reduced in such procedures when overhead temperatures reach approximately 260 °C, to prevent cracking of the sample. Thus, distillation data are subject to the same deviations experienced in distillation by gas chromatography. A comparison of data obtained from true boiling point distillations with those obtained from simulated distillation by gas chromatography of three high-boiling petroleum fractions is shown in Table C.3. The true boiling point distillations were made on 100 theoretical plate-spinning band columns at 0,133 kPa.

C.3 The decanted oil is of particular interest because it contains a high percentage of polycyclic aromatic compounds and the high sulfur coker gas oil should contain ring-type sulfur compounds and complex olefinic types.

Table C.3 — Distillation of heavy gas oils

% (mass fraction)	Virgin gas oil		High sulfur coker gas oil		Decanted oil	
	TBP °C	GC °C	TBP °C	GC °C	TBP °C	GC °C
IB	230	215	223	209	190	176
10	269	265	274	259	318	302
20	304	294	296	284	341	338
30	328	321	316	312	357	358
40	343	348	336	344	377	375
50	367	373	356	364	390	391
60	394	409	377	386	410	409
70	417	424	399	410	425	425
80	447	451	421	434	445	443
90	—	488	462	467	—	469
95	—	511	482	494	—	492
100	—	543	—	542	—	542

Key

TBP: true boiling point.

GC: gas chromatography, i.e. boiling point determined in accordance with this document.

Annex D
(informative)

Boiling point revision

A joint effort was initiated among ASTM, API, AIChe and the Design Institute of Physical Properties (DIPPR) to address discrepancies in boiling points of the n-Paraffins. A revised set of boiling points are defined and added as information to this document in Table D.1.

Table D.1 — Boiling points

Carbon number	Boiling point °C	Carbon number	Boiling point °C
1	−161,48	23	380,99
2	−88,58	24	392,21
3	−42,11	25	402,98
4	−0,49	26	413,33
5	36,06	27	423,29
6	68,71	28	432,88
7	98,38	29	442,11
8	125,62	30	451,01
9	150,76	31	459,60
10	174,12	32	467,89
11	195,90	33	475,90
12	216,30	34	483,64
13	235,48	35	491,12
14	253,58	36	498,36
15	270,70	37	505,36
16	286,93	38	512,15
17	302,34	39	518,72
18	317,00	40	525,09
19	330,98	41	531,26
20	344,33	42	537,25
21	357,08	43	543,06
22	369,29	44	548,70

Annex E
(informative)

Alternative hydrogen and nitrogen carrier gases using Procedure B

WARNING — Use caution when hydrogen is used as the carrier gas. The use of a hydrogen sensor in the gas chromatography oven is strongly recommended to shut off the hydrogen source in case of a high concentration build-up of hydrogen that exceeds the explosive limit.

E.1 General

This annex lists the gas chromatography conditions for Procedure B using hydrogen and nitrogen as carrier. It is subdivided into hydrogen carrier (see E.2) and for nitrogen carrier (see E.3). In both subclauses, the operating conditions for Procedure B using H_2 and Procedure B using N_2 are given. The purity of the gases is given in 5.3 of this test method.

For each type of carrier, the calibration chromatograms and the ASTM reference gas oil chromatograms are shown. The boiling point distributions of the reference gas oil are also presented along with the accepted reference values. The conditions and chromatograms were obtained from the ILS[10].

E.2 Hydrogen carrier

E.2.1 General

The gas chromatography conditions for using H_2 are shown in Table E.1

A typical chromatogram obtained with hydrogen carrier for the calibration is shown in Figure E.1 obtained with Procedure B. Figure E.2 shows the chromatogram of ASTM reference gas oil no. 2 using hydrogen. The boiling point distribution values obtained are shown in Table E.2.

Table E.1 — Gas chromatography conditions using hydrogen carrier — Procedure B

Parameter	Procedure B hydrogen carrier
Column	10 m, 0,53 mm ID, 0,88 µm PDMS
Carrier gas	35 ml/min
Oven temperature programme	40 °C to 350 °C at 35 °C/min, hold 0 min
Inlet	PTV 100 °C to 350 °C at 30 °C/min
FID temperature	355 °C
Sample	0,1 µl, neat

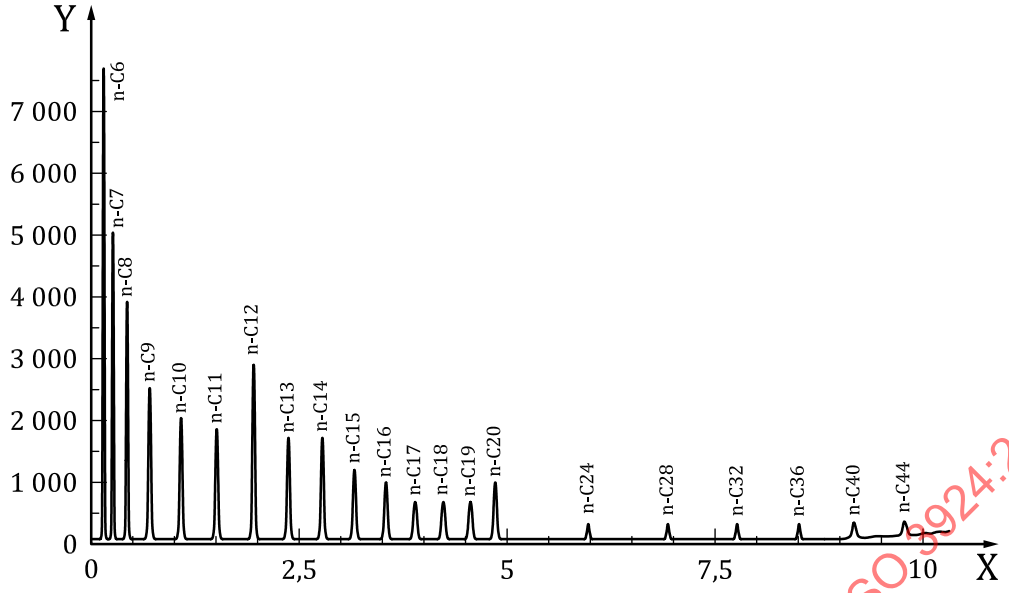


Figure E.1 — Calibration chromatogram for hydrogen carrier — Procedure B

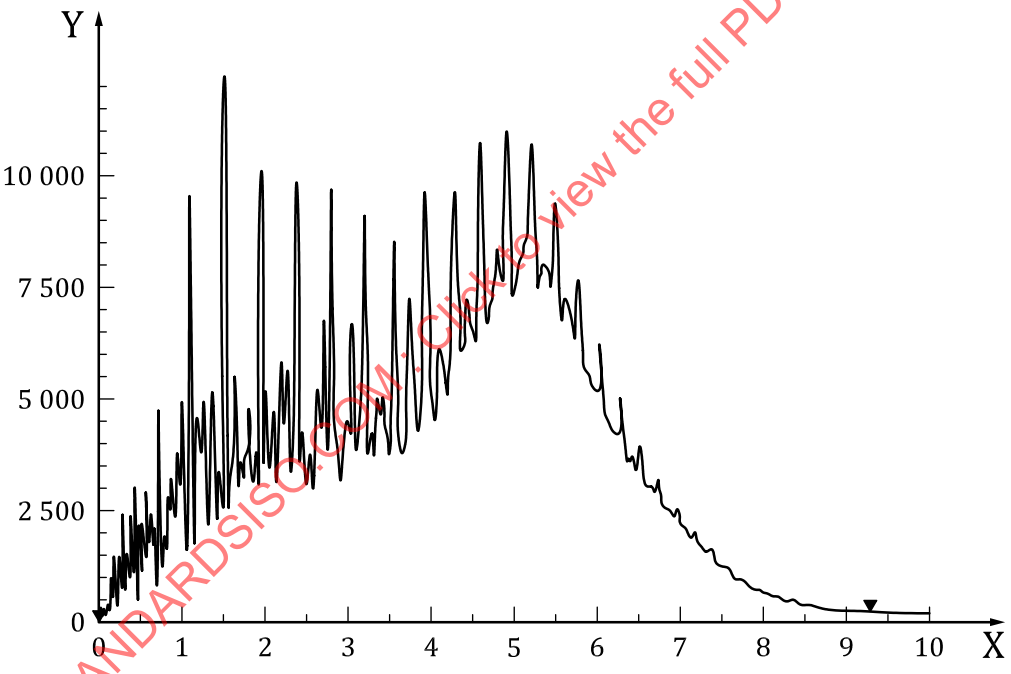


Figure E.2 — Chromatogram of ASTM reference gas oil no. 2 using hydrogen carrier — Procedure B

Table E.2 — ASTM D2887 reference gas oil no. 2 boiling point distribution values obtained with hydrogen carrier gas — Procedure B

Procedure B hydrogen carrier				
ASTM reference gas oil no. 2				
%Off	BP °C	QC °C	(–)	Limit
IBP	110,2	106,1	4,1	7
5	174,2	172,8	1,4	4,1

Table E.2 *(continued)*

Procedure B hydrogen carrier				
ASTM reference gas oil no. 2				
%Off	BP °C	QC °C	(–)	Limit
10	196,9	195,6	1,3	4,4
15	216,9	215,6	1,3	4,7
20	234,5	233,3	1,2	5
25	251,5			
30	267,8	266,7	1,1	4,8
35	283,6			
40	298,4	297,8	0,6	4,3
45	310,7			
50	321,5	321,1	0,4	4,3
55	332,1			
60	342,5	341,7	0,8	4,3
65	351,3	350	1,3	4,3
70	359,7	358,3	1,4	4,3
75	369,2	367,8	1,4	4,3
80	379,1	377,8	1,3	4,3
85	391,4	390	1,4	4,3
90	407,2	406,1	1,1	4,3
95	431,7	431,1	0,6	5
FBP	493,1	496,1	–3,1	11,8

E.2.2 Precision and bias for Procedure B using H_2 carrier

E.2.2.1 Repeatability

The difference between successive 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 following values by only one case in twenty. Values obtained from the precision study are shown in Table E.3.

Table E.3 — Repeatability (r) and reproducibility (R) for H_2 carrier — Procedure B

Procedure B hydrogen carrier				
	r °C	r °F	R °C	R °F
IBP	6,07	10,9	9,8	17,64
5 %	6,543E-3 (X + 500)	6,54E-3 (Y + 868)	6,543E-3 (X + 500)	6,543E-3 (Y + 868)
10 % to 90 %	1,12E-2 (X + 100)	1,12E-3 (Y + 868)	1,12E-2 (X + 100)	1,12E-3 (Y + 868)
95 %	1,23E-2 (X)	1,23E-2 (Y – 32)	1,56E-2 (X)	1,56E-2 (Y – 32)
FBP	11,1	19,98	15,34	27,6

E.2.2.2 Reproducibility

The difference between two single and independent 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 following values only one case in twenty. Results of the

precision study for reproducibility are shown in Table E.3. There were insufficient degrees of freedom for the reproducibility for the FBP (as per ISO 4259[2]). The minimum number of six laboratories was not met (as per ISO 4259[2]). Data was obtained from five laboratories.

E.2.2.3 Bias

An ILS study was carried out to determine the between-procedures bias for Procedure B – He (referee procedure) and Procedure B – H_2. The data obtained are described in RR:D02-1803[7]. The results of practice D6708 are shown in Table E.4. By applying the bias corrections to the experimental H_2 values, the predicted He carrier values can be obtained. No bias correction can statistically improve the agreement for the FBP. Bias correction can improve agreement statistically for the IBP, 10 %, 30 %, 50 %, 70 % and 90 %. This study is only valid for the temperature ranges listed in Table E.4.

Table E.4 — Practice D6708 assessment outcome — Procedure B – He (referee) versus Procedure B – H_2

	Can bias correction improve agreement?	Predicted He carrier = bias corrected H_2 carrier	Sample specific bias	Practically equivalent after correction?	Range of sample averages in ILS study °C	Range of sample averages in ILS study °F
IBP	Y	= H_2 + 1,486 °C	N	Y	104 to 331	217 to 631
IBP	Y	= H_2 + 2,674 8 °F				
10 %	Y	= 1,005 · H_2 – 0,242 °C	N	Y	162 to 368	323 to 694
10 %	Y	= 1,005 · H_2 – 0,435 6 °F				
30 %	Y	= H_2 + 1,026 °C	N	Y	186 to 390	366 to 734
30 %	Y	= H_2 + 1,846 8 °F				
50 %	Y	= H_2 + 1,102 °C	N	Y	209 to 408	408 to 766
50 %	Y	= H_2 + 1,983 6 °F				
70 %	Y	= H_2 + 1,054 °C	N	Y	233 to 426	451 to 799
70 %	Y	= H_2 + 1,897 °F				
90 %	Y	= H_2 – 0,737 °C	N	Y	271 to 451	520 to 844
90 %	Y	= H_2 – 1,327 °F				
FBP	N	= H_2 = HE °C or °F	N	Y	291 to 502	556 to 936

E.2.2.4 Between-carrier reproducibility

The between-carrier reproducibility can be expressed as: $(RHe\_H_2) = [0,5(RHe)^2 + 0,5(RH_2)^2]^{0,5}$.

E.3 Nitrogen carrier

E.3.1 General

The gas chromatography conditions for using N_2 are shown in Table E.5

A typical chromatogram obtained with nitrogen carrier for the calibration is shown in Figure E.3 obtained with Procedure B. Figure E.4 shows the chromatogram of ASTM reference gas oil no. 2 using nitrogen. The boiling point distribution values obtained are shown in Table E.6.

Table E.5 — Gas chromatography conditions using nitrogen carrier — Procedure B

Parameter	Procedure B nitrogen carrier
Column	7,5 m, 0,53 mm ID, 1,5 µm PDMS

Table E.5 *(continued)*

Parameter	Procedure B nitrogen carrier
Carrier gas	35 ml/min constant flow
Oven temperature programme	40 °C for 0,5 min, ramp to 360 °C at 35 °C/min, hold 0 min
Inlet	Cool on-column 100 °C to 350 °C at 35 °C/min
FID temperature	365 °C
Sample	0,1 µl, neat

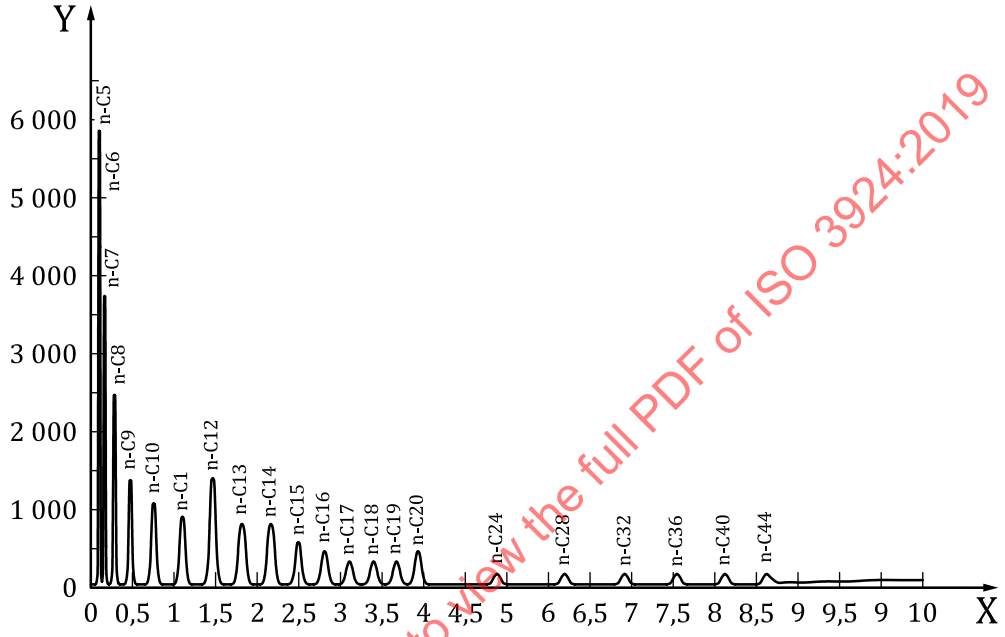


Figure E.3 — Calibration chromatogram for nitrogen carrier — Procedure B

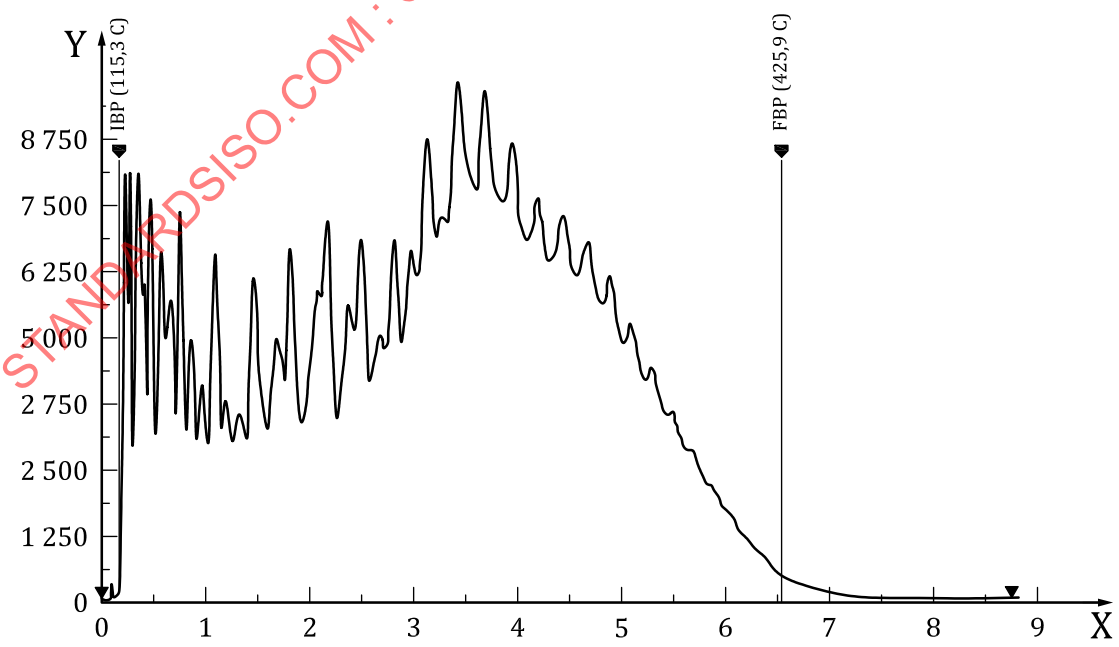


Figure E.4 — Chromatogram of ASTM reference gas oil no. 2 using nitrogen carrier — Procedure B