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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

ICS: 75.080

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ISO/CEN PARALLEL PROCESSING

This draft has been developed within the European Committee for Standardization (CEN), and processed under the **CEN lead** mode of collaboration as defined in the Vienna Agreement.

This draft is hereby submitted to the ISO member bodies and to the CEN member bodies for a parallel five month enquiry.

Should this draft be accepted, a final draft, established on the basis of comments received, will be submitted to a parallel two-month approval vote in ISO and formal vote in CEN.

To expedite distribution, this document is circulated as received from the committee secretariat. ISO Central Secretariat work of editing and text composition will be undertaken at publication stage.

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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 jointed IP 406 [3] and ASTM D2887 [4] methods.

This fourth edition cancels and replaces the third edition (ISO 3924:2010). The third edition had several updates regarding the calculation of ISO 3405 equivalent data and, because ISO 3924 is extensively used, and referenced in many fuel specifications, a faster analysis had been included. These fuel specification (in any case those used in Europe) demand volume percentage recovered at 250 °C and 350 °C, but this volume percentage was not a result from the former text as described. This is updated with this edition (see Annex A), for which an assessment has been executed by CEN/TC 19/WG 9. Next several editorial updates have been made.

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 B10.

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

2 Normative references

The following 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, *Petroleum liquids — Manual sampling*

ISO 3171, *Petroleum liquids — Automatic pipeline sampling*

ISO 3405, *Petroleum products - Determination of distillation characteristics at atmospheric pressure*

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

3 Terms and definitions

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

3.1

initial boiling point

IBP

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

3.2
final boiling point
FBP

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

3.3
slice rate

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

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

4 Principle

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

Annex A presents a correlation model for the calculation of physical distillation (ISO 3405, IP 123 [6] or ASTM D86 [5]) equivalent data from boiling range distribution analysis by gas chromatography determined following this Standard.

Annex B describes an alternative, accelerated analysis that may be used

5 Reagents and materials

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

NOTE The following materials have been used successfully as liquid phases.

For packed columns:

- Silicone gum rubber UC-W98;
- Silicone gum rubber GE-SE-30;
- Silicone gum rubber OV-1;
- Silicone gum rubber OV-101;

For capillary columns:

- Polydimethylsiloxane.

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

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

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

5.3 Carrier gas, constituted of helium or hydrogen for use with thermal conductivity detectors, or nitrogen, helium or argon for use with flame ionization detectors.

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

The following mixture of alkanes has been found to be satisfactory for most samples: C₅, C₆, C₇, C₈, C₉, C₁₀, C₁₂, C₁₄, C₁₆, C₁₈, C₂₀, C₂₄, C₂₈, C₃₂, C₃₆, C₄₀, C₄₄. At least one component of the mixture shall have a boiling point lower than the initial boiling point of the sample and at least one component shall have a boiling point higher than the final boiling point of the sample. The boiling points of alkanes are listed in Table 1.

Table 1 — Boiling points of normal alkanes

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

NOTE API Project 44, October 31, 1972 [1], is believed to have provided the original normal paraffin boiling point data that were listed in former editions of this 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.

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

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

Propane and butane may be added non-quantitatively to the calibration mixture, if necessary, to comply with 5.4. 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 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).

5.5 Reference material

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

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

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

The programming rate shall be sufficiently reproducible to obtain retention time repeatability of 6 s for each component in the calibration mixture (5.4).

If the initial boiling point is less than approximately 93 °C, an initial column temperature below ambient may be required. However, excessively low initial column temperatures shall be avoided, to ensure that the stationary phase remains liquid. The initial temperature of the column shall be only low enough to obtain a calibration curve meeting the requirements of this International Standard.

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

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

6.2 Column

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

Table 2 — Typical operating conditions for packed columns

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

6.3 Recorder/plotter

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

6.4 Integrator/computer

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

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

6.5 Flow/pressure controllers

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

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

6.6 Micro-syringe

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

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

7 Sampling

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

8 Preparation of apparatus

8.1 Column preparation

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

8.1.1 Packed columns

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

8.1.2 Capillary columns

Capillary columns may be conditioned using the following procedure.

- a) Install the column following the manufacturer's instructions. Set the column and detector gas flows. Ensure that the system is leak free.
- b) Allow the system to purge with carrier gas at ambient temperature for at least 30 min. Then increase the oven temperature by approximately 5 °C/min to 10 °C/min to the final operating temperature and hold for approximately 30 min.
- c) Cycle the chromatograph through its temperature programme several times until a stable baseline is obtained.

NOTE 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.