SLOVENSKI STANDARD
oSIST prEN ISO 3924:2017

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Naftni proizvodi - Določevanje destilacijskega območja - Metoda plinske kromatografije (ISO/DIS 3924:2017)

Petroleum products - Determination of boiling range distribution - Gas chromatography method (ISO/DIS 3924:2017)

Mineralölerzeugnisse - Bestimmung des Siedeverlaufs - Gaschromatographisches Verfahren (ISO/DIS 3924:2017)

Produits pétroliers - Détermination de la répartition dans l'intervalle de distillation - Méthode par chromatographie en phase gazeuse (ISO/DIS 3924:2017)

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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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Foreword

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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).

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

ISO 3924 was prepared by the European Committee for Standardization (CEN) Technical Committee CEN/TC 19, *Gaseous and liquid fuels, lubricants and related products of petroleum, synthetic and biological origin*, in collaboration with ISO Technical Committee ISO/TC 28, *Petroleum products and related products of synthetic or biological origin*, in accordance with the Agreement on technical cooperation between ISO and CEN (Vienna Agreement).

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

This fifth edition cancels and replaces the fourth edition (ISO 3924:2016) which is updated with the following items. First, the accelerated procedure is 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 is added with the newly defined boiling points for normal Alkanes to keep the method technically equivalent with ASTM D2887 and IP406, In addition, several safety warnings and editorial updates have been made.

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

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

1 Scope

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

The document describes two procedures both have successfully been applied to samples containing fatty acid methyl esters (FAME) up to 10 % (*V*/*V*) and up to 20 % (*V*/*V*) for Procedure B.

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

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 3170, *Petroleum liquids — Manual sampling*

ISO 3171, *Petroleum liquids — Automatic pipeline sampling*

3 Terms and definitions

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

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

3.2
final boiling point
FBP
temperature corresponding to the retention time at which a net area count equal to 99,5 % of the total sample area under the chromatogram is obtained

3.3

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

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

4 Principle

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

Procedure A (Table 2 and 3) 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 (Table 1). Analysis times range from 14 to 60 minutes.

Procedure B (Table 4) is restricted to only three capillary columns and requires no sample dilution. In addition, Procedure B is used not only for the sample types described in Procedure A but also for the analysis of samples containing fatty acid methyl esters (FAME) up to 20 % (*V*/*V*). The analysis time, when using Procedure B, is reduced to about 8 min and therefore it is known as 'Accelerated ISO 3924'.

Annex A presents a correlation model for the calculation of physical distillation (see References [1], [5] and [6]) equivalent data from boiling range distribution analysis by gas chromatography determined following this International Standard.

5 Reagents and materials

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

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

For packed columns:

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

For capillary columns:

- polydimethylsiloxane.

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

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

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

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

a) helium or hydrogen for use with thermal conductivity detectors, or

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

CAUTION- Helium, Argon and Nitrogen are compressed gases under high pressure. Hydrogen is an extremely flammable gas under high pressure.

5.4 Hydrogen, grade suitable for flame ionization detectors.

CAUTION - Hydrogen is an extremely flammable gas under high pressure. **5.5 Compressed air**, free of oil and water, regulated for flame ionization detectors.**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 should be approximately 10 parts of the alkane mixture to 100 parts of carbon disulfide. For capillary columns, the final concentration should be approximately 1 part of the alkane mixture to 100 parts of carbon disulfide.

The following mixture of alkanes has been found to be satisfactory for most samples: C_5, C_6, C_7, C_8, C_9, C_{10}, C_{12}, C_{14}, C_{16}, C_{18}, C_{20}, C_{24}, C_{28}, C_{32}, C_{36}, C_{40}, C_{44}. At least one component of the mixture shall have a boiling point lower than the initial boiling point of the sample and at least one component shall have a boiling point higher than the final boiling point of the sample. The boiling points of alkanes are listed in Table 1.

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

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

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

5.7 Reference material, the primary reference material used shall be the ASTM Reference Gas Oil No.1 or 2. (See Annex B)

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

CAUTION - Carbon disulfide is extremely volatile flammable and toxic.

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

6 Apparatus

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

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

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

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

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

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

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

6.1.1 Sample inlet system,

Temperature programmable inlets (PTV) 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 may be used, provided that, under the conditions of the test, separations are in the order of boiling points as given in Table 1, and the column resolution, *CR*, is at least 3 (8.3). Typical column operating conditions are given in Table 2, 3 and 4.

Table 2 — Typical operating conditions for Procedure A 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) neat sample volume	0,5	1

[a] Chromosorb® G (AW-DMS).

[b] Chromosorb® P (AW).

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